C: MOF HYBRIDS, NANOCOMPOSITES and ORGANIC NETWORKS

* Invited Speaker

SESSION CP1: Poster Session: MOF Hybrids, Nanocomposites and Organic Networks I
C: MOF Hybrids, Nanocomposites and Organic Networks
Sunday Afternoon, September 11, 2016
6:00 PM
International Ballroom IV/V

CP1.01 moved to Wednesday Poster Session
Hydrogen-Bonded Organic Frameworks—A New Class of Porous Crystalline Proton Conducting Materials Avishek Karmakar, Rajith Illathvalappil, Bihag Anothumakool, Arunabha Sen, Partha Samanta, Aamod V. Desai, Sreekumar Kurungot and Sujit K. Ghosh; Department of Chemistry, Indian Institute of Education and Research, Pune, India; Physical and Materials Chemistry Division, National Chemical Laboratory, Pune, India.

The conceivable design and development of solid-state ion conductors is currently a distinguished area of active research. In particular, the domain of porous crystalline solids has attracted considerable attention owing to the unambiguous insight into mechanistic details of conduction pathways. Also stability, long-range ordering and feasibility of designable architectures have propelled the advancement of such porous crystalline solid materials including metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs). In this regard, hydrogen-bonded organic frameworks (HOFs) which are built from organic motifs and held by cooperative non-covalent forces have started evolving as a promising material owing to seemingly similar potential applicability as MOFs & COFs. While HOFs have been explored for applicability in gas/solvent separation and storage applications, its function as a solid-state ion-conductor is yet to be realized. Two porous Hydrogen-Bonded Organic Frameworks (HOFs) based on arene sulfonates and guanidinium ions have been synthesized. As a result of the presence of ionic backbone appended with a Bronsted acid protonic source, the compounds exhibit ultra-high proton conduction values $\sigma \approx 0.75 \times 10^{-2}$ S cm$^{-1}$ and $1.8 \times 10^{-2}$ S cm$^{-1}$ under hydrous conditions. Very low activation energy values and highest proton conductivity at ambient conditions (low humidity and at room temperature) among all known porous materials like metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) are the hallmark features of these crystalline porous hydrogen bonded frameworks. These values are not only comparable to the conventionally used proton exchange membranes i.e. Nafion used in fuel cell technologies, but is also the highest value reported in organic based porous architectures. Notably, this report inaugurates the usage of crystalline hydrogen bonded porous organic frameworks as solid state proton conducting materials.

CP1.02
Synthesis of Conjugated Polymer Embedded Porous PEGMA Polymer Nanonetworks Mehmet Sahin Atas and Mustafa S. Yavuz; Advanced Technology Research and Application Center, Selcuk University, Konya, Turkey; Department of Metallurgy and Materials Engineering, Selcuk University, Konya, Turkey.

There has been a great interest on responsive polymeric micelles over the last decade. In general, porous smart materials show quick responses when there is a change in environmental factors such as temperature, pH, reduction capability, ionic strength and magnetic field[1]. Synthetic or biological macromolecules exhibiting a lower critical solution temperature (LCST) in water are structures of prime importance in applied polymer research. Recently, there has been a great interest on responsive porous polymeric micelles. Indeed, these water-soluble polymers precipitate over their LCST due to shrinking phenomena [2]. In case of thermo-responsive polymers, temperature can be used as a simple external trigger to change the conformation of the polymer. Poly(N-isopropylacylamide) (PNIPAM) and its copolymers are one of the most frequently used thermo-responsive systems. On the other hand, PNIPAM formulations show toxic behavior, especially at collapsed state while some certain cell types can tolerate PNIPAM containing colloids. In the recent studies, PEGMA polymers attract more attention because of its biocompatible and thermo-responsive nature[3]. In this study, new porous poly(ethylene glycol methyl ether metacrylate) (PEGMA) colloids having different LCST values ranging from 32 to 90 °C are successfully synthesized and characterized by using BET, DLS, UV, and FTIR. The conjugated polymers were fabricated inside the porous PEGMA colloids via the oxidation of embedded pyrrole monomers using iron oxidents. Controlled drug release mechanisms of these polypyrrole embeded PEGMA colloids are investigated under conventional heating or laser ablation (photothermal).Acknowledgements This work was supported by the Scientific and Technological Research Council of Turkey (TUBITAK Grant 214M232) and Selcuk University Scientific Research Fund (BAP). *Corresponding author: selmanyavuz@selcuk.edu.tr, selmanyavuz@gmail.com References[1]. Lutz, J.-F.; Hoth, A.; Schade, K., Designed Monomers & Polymers 2009,12 (4), 343-353.[2] Ulasan, M.; Yavuz, E.; Bagriacik, E. U.; Cengeloglu, Y.; Yavuz, M. S., Journal of biomedical materials research. Part A 2015,103 (1), 243-51.[3]. Yavuz, M. S.; Buyukserin, F.; Zengin, Z.; Camli, S. T., Journal of Polymer Science Part a-Polymer Chemistry 2011,49 (22), 4800-4808.

CP1.03
Highly Stable Sulfur-Bridged Nanoporous Covalent Organic Polymer Networks for CO$_2$ Capture Mehmet Sahin Atas and Mustafa S. Yavuz; Metallurgy and Materials Engineering, Selcuk University, Konya, Turkey; Advanced Technology Research and Application Center, Selcuk University, Konya, Turkey.

Carbon dioxide emissions resulting from the burning of fossil fuels in automobiles and power plants is a pressing global environmental problem. The conventional amine solutions absorb CO$_2$ effectively but it is energy-intensive and costly[1]. Porous materials deemed as attractive candidates of CO$_2$ adsorbents have been intensively investigated due to their large surface areas and suitable enthalpy of adsorption between pores and CO$_2$ molecules. Furthermore, the incorporation of accessible nitrogen-donor units (e.g., amine, triazine, etc.) into porous materials,
usually named as nitrogen-rich porous materials, can promote the CO2 uptake capacity and selectivity through dipole-quadrupole interactions between accessible nitrogen sites and polarizable CO2 molecules[2]. Several porous materials such as metal−organic frameworks (MOFs), covalent-organic frameworks (COFs), and porous covalent-organic polymers (PCOPs) with excellent CO2 adsorption capacities have been reported. This porous materials gained substantial attention due to their high surface area, ability to be functionalized, thermal stability, recyclability, and selectivity for CO2 over other gases[3]. Herein, this study focuses on the uptake performance of CO2 through adsorption process utilizing the highly stable sulfur-bridged PCOPs. The research results showed that this highly stable PCOPs as adsorbant has a relatively good adsorption capacity for CO2 system. Optimal CO2 adsorption capacities at 273 and 298 K were 2.69 cm3/g and 2.46 cm3/g. Acknowledgements This study was carried out as a Master thesis by Mehmet Sahin Atas at the Graduate School of Natural and Applied Science at Selcuk University, Konya, Turkey. Academic Staff Training Program (ÖYP) (Project Number 2015-ÖYP-128), which authors gratefully acknowledge. *Corresponding author: selmanyavuz@selcuk.edu.tr, selmanyavuz@gmail.com

References

CP1.04
Spectroscopic Characterization of Covalent Triazine Frameworks—On the Nature of Nitrogen Species for Metal Incorporation
Dmitrii Osadchii, Alma Olivos-Suarez, Anastasiya Bavykina, Freek Kapteijn and Jorge Gascon; Delft University of Technology, Delft, Netherlands.

Covalent triazine frameworks (CTFs) are a novel class of organic polymers that have recently brought much attention in the fields of catalysis and separation [1-3]. Remarkable properties of CTFs, such as high porosity, thermal stability and presence of nucleophilic nitrogen functionalities suitable for metal coordination, make these materials attractive as supports for heterogenization of homogeneous catalysts [1-2]. However, it has been observed that an increment of porosity will be enhanced only by the expenses of regularity of nitrogen functionalities. This has an important impact on characterization of catalysts and materials based on CTFs and often represents a challenge because increasing porosity will reflect low crystallinity and high degree of electronic density delocalization. These properties result in black materials with strong absorbance in the energy spectrum range of most common spectroscopic techniques. Additionally, the low regularity also results in the presence of different types of nitrogen functional groups within the framework and a combination of spectroscopic methods is required for its full characterization, making determination of the active sites challenging. Recently it was shown [4] that only a combination of methods such as XPS, EXAFS and NMR provides a more reliable and reasonable description of the active site structure and assignment of the different types of nitrogen functionalization present in CTF-based catalysts. In this work we make use of novel synthetic routes in order to improve the CTF properties and to seek for a more regular material. We applied various spectroscopic techniques as approach to investigate different metal functionalized CTF catalysts. Original procedure for synthesis of CTFs [5] involves ZnCl2, as a Lewis acid catalyst, but, as a result, additional step of ZnCl2 removal is necessary. Use of other Lewis acids (CuCl2, SnCl2, etc) allows the CTF synthesis as well as the direct introduction of the desired metal into the catalyst during the step of CTF synthesis. For comparison we prepared series of CTFs with ZnCl2 and other Lewis acids as catalysts and studied spectroscopically the coordination of metals to nitrogen functional groups. Precise XPS and EXAFS characterization of obtained polymers in combination with additional spectroscopic techniques give new insights in determination of different types of nitrogen functionality in CTFs and understanding of the actual active site structure in the catalyst. References: [1] Palkovits, R. et al. (2009). Angew. Chem. Int. Ed., 48, 6909 –6912.[2] Bavykina, A. V. et al. (2015). ChemSusChem, 8, 809-812.[3] Zha, X. et al. (2012). J. Am. Chem. Soc., 134, 25, 10478-10484.[4] Soorholtz, M. et al. (2016). ACS Catal., 6, 2332–2340.[5] Kuhn, P. et al. (2008). Angew. Chem. Int. Ed., 47, 3450 –3453.

CP1.05
In-Situ Reduction of HAuCl4 for Generation of Catalytic AuNPs Supported Porous Covalent Polymer Networks
Sami Dursun1,2, Halit Cavusoglu1,2 and Mustafa S. Yavuz1,2; 1Department of Metallurgical and Materials Engineering, Selcuk University, Konya, Turkey; 2Advanced Technology Research and Application Center, Selcuk University, Konya, Turkey.

Over the last decades, functionalized porous covalent organic polymers (PCOPs) have been intensively investigated due to their remarkable high BET surface area and a broad versatility of framework compositions [1]. These materials are lightweight and porous which are well known for their applications in gas storage, catalytic supports, semiconductive and photoconductive devices [2]. The utilization of porous materials as heterogeneous catalysts intrigues since these materials offer great advantages compared to traditional heterogeneous catalysts with larger accessibility of active sites. Despite their high porosity and great tunability, the usage of PCOPs in catalysis remains widely unexplored pertaining to other classes of porous materials [3]. Gold (Au) nanoparticles supported on suitable supports for heterogeneous catalysts hold unique advantages [4]. Even though a set of studies about host supported Au catalysts showed high catalytic activity for oxidations, hydrogenation, and C–C coupling reactions, the unstable supports holding these nanoparticles impose restrictions to their uses [5]. The weak interactions between supports and nanoparticles usually result in the sintering and leaching of the nanoparticles. PCOPs as the host material has been used for the immobilization of gold nanoparticles, prepared by using strong reductants (e.g. NaBH4) after the gold ions entrapped to the PCOP materials via diffusion. The resulting material shows high activity in the reduction of 4-nitrophenol to 4-aminophenol [6]. Herein, we present a simple synthetic route to generate a highly stable Au nanoparticle embedded PCOP hybrids (AuNP@PCOP) without using an extra reducing agent. The robust and stable AuNP@PCOP catalyst was fabricated via in-situ reduction of Au ions with alcohol functionality of PCOP material. High catalytic activities of these synthesized catalyst material towards the reduction of 4-nitrophenol (4-NP) to 4-aminophenol were illustrated. The catalytic reduction of 4-NP was clearly observed by UV-Vis spectroscopy analysis, even with a relatively small amount of the AuNP@PCOP catalyst. The supported gold catalysts show great potential as catalyst for a variety of organic reactions. Acknowledgements This study was carried out as a Master thesis by Sami Dursun at the Graduate School of Natural and Applied Science at Selcuk University, Konya, Turkey. The authors gratefully acknowledge Academic Staff Training Program (ÖYP).
for the financial support.*Corresponding author: selmanyavuz@gmail.com

References

Ethylene Oligomerization Using Porous Aromatic Frameworks Based Molecular Catalyst
Elena Rozhko, Anastasiya Bavkina, Freek Kapteijn and Jorge Gascon; Delft University of Technology, Delft, Netherlands.

α-Olefins in the C₂–C₂₀ range are of utmost importance as they are valuable and versatile feedstocks and building blocks for a variety of products, i.e., detergents, plasticizers, low-density polyethylene. Currently oligomerization of inexpensive ethylene is used as the prevalent method for the synthesis of such olefins. Existing commercial processes usually utilise transition metal based homogeneous catalysts in the presence of an alkyl aluminum co-catalyst. Though homogeneous catalysts in general show better performance, employment of a heterogeneous catalyst instead can be better from the practical point of view, as it would ease the catalyst handling and recycling. A possible way to achieve a heterogeneous catalyst that has a performance similar to the homogeneous systems is by supporting the complex on the surface of a porous solid, i.e. metal-organic frameworks (MOFs) or porous silica. Herein we report the synthesis, characterization and catalytic performance of new active molecular heterogeneous catalyst for ethylene oligomerization based on porous aromatic framework. Different types of organic polymers were used: covalent triazine frameworks (CTFs) with different BET surface areas, and a lamellar structured imine-linked polymer network (IL-PON). Ni²⁺ was coordinated to nitrogen atoms of the networks, resulting in an active and fully recyclable molecular heterogeneous catalyst (CTF*Ni and IL-PON*Ni respectively). Employing both CTF*Ni and IL-PON*Ni catalysts, ethylene oligomerization yields an entire range of even-numbered carbon chain-length olefins (up to C₂₀) rather than a single product. A thorough catalyst evaluation study, including long term and recycling in combination with in-depth characterization will be presented.[1] Finiels, A.; Fajula, F.; Hulea, V.; Catal. Sci. Technol. 4 (2014) 2412.[2] Canivet, J.; Aguado, S.; Schuurman, Y.; Farrusseng, D.; J. Am. Chem. Soc. 135 (2013) 4195.[3] Zheng, Z.; Liu, J.; Li, Y.; J. Catalysis 234 (2005) 101.

PolyMOFs—Exploring Polymer Structure Effects on Metal-Organic Frameworks
Sergio Ayala¹, Zhenjie Zhang¹, Ha T. Hoang Nguyen¹, Stephen A. Miller² and Seth M. Cohen¹; ¹Chemistry and Biochemistry, University of California, San Diego, San Diego, California, United States; ²Chemistry, University of Florida, Gainesville, Florida, United States.

Incorporating metal ions into organic polymers has gained attention as metals can be used for the fine-tuning of the macromolecular structure and properties of polymers, including molecular sensing, self-healing, and catalysis. We recently reported a new class of polymer MOF hybrid materials (polyMOFs) that use organic polymers containing metal-binding

Synthesis of New Triazine-Based Porous Covalent Organic Polymers for CO₂ Capture
Huseyin Sakalak¹,² and Mustafa S. Yavuz¹,²; ¹Metallurgical and Materials Engineering, Graduate School of Natural Sciences, Konya, Turkey; ²Advanced Technology Research and Application Center, Konya, Turkey.

Porous polymers with rising to 5000 m²/g surface area and having porous channels in the structure have been a new area on which researchers focused. These porous structures which have uniform repeating units including covalent bonds are described as porous covalent organic polymers (PCOP) or covalent organic frameworks (COF). Global warming is still a great problem today. CO₂ emission from burning fossil fuels is the major factor which contributes greatly habitat change. When we consider this problem, CO₂ capture and storage has a great importance. PCOPs are used as selective CO₂, H₂, and CH₄ capture materials depending on tri-dimensional orientation of units in the network structure, pore size, functional groups such as –N, –S, –O, and hydrogen bond formation. It is possible to capture CO₂ selectively from the gas mixture produced by many industrial plants such as thermoelectricity plant by PCOPs with their CO₂-phlic and N⁺-phobic nature. In this work, different novel triazine-based PCOPs with high N-content were synthesized as a new porous adsorbant. These materials were characterized by using FTIR, solid-state CNMR, Elemental analysis and TGA. BET surface area, pore volume and CO₂ capture capacities of these new materials were measured.

CP1.07 Withdrawn
groups to create crystalline, porous, three-dimensional structures by coordination chemistry. Previously, we demonstrated that polyMOFs with an IRMOF-1 architecture could be prepared. However, little is known about how the topology of polymer ligands affects the development of polyMOFs, as well as our accessibility to different types of MOF structures. In particular, UiO-66 is an attractive MOF for many applications due to its high stability under ambient conditions and proven promise in catalysis. Preparing a polyMOF with a UiO-66 architecture would be deemed more challenging than IRMOF-1, as it is more limited in pore volume and contains a more complex structure. However, its ability to withstand defects makes UiO-66 a promising scaffold for polyMOF formation. Herein we expand our knowledge of polyMOFs by exploring different topologies of the polymer ligands on a UiO-66 MOF architecture, and determining the extent to which they produce highly-ordered, porous materials. Using step-growth polymerization techniques, polymers with different organic spacers (alkyl or glycol) were prepared. It was determined that polymers with appropriate organic spacer length produce polyMOFs, regardless of the spacer type. Furthermore, it was noted that spacer length has a substantial affect on the morphology of the UiO-66 polyMOFs. Investigating the topology of polymers that form polyMOFs increases our understanding of the compatibility between polymer and MOF structures.1. Zhang, Z. J.; Nguyen, H. T. H.; Miller, S. A.; Cohen, S. M., polyMOFs: A Class of Interconvertible Polymer-Metal-Organic-Framework Hybrid Materials. Angew Chem Int Ed 2015, 54 (21), 6152-6157.

CP1.10
Towards Functional Devices via MOF-Polymer Fiber Nanocomposites

Many Metal Organic Frameworks, such as Zif-8 and HKUST-1, have potential high-impact applications such as in separation processes, sensing, and catalysis. However, MOFs are not easily shaped into devices due to their brittle structure. Therefore, combining MOF functionality with the ductility of polymer nanofibers opens the way towards robust functional devices. Zif-8/Polyvinylidene fluoride (PVDF) fiber (~1-2 microns diameter) mats were produced via electrospinning. Zif-8 (~200 nm) crystals were mixed into the initial polymer solution for electrospinning, and additional crystals were then grown onto these ‘anchors’ by immersing in a rapid room temperature synthesis solution mixture of Zn(NO$_3$)$_2$. $\cdot$ 6H$_2$O in Methanol (MeOH) and 2-methylimidazole in MeOH. High loading of Zif-8 crystals in the fiber mats was thus achieved largely without sacrificing the mechanical performance of the polymer fibers. HKUST-1 (~100 nm) crystals were grown on the surface of electrospun PVDF fibers (~700 nm diameter). Copper(II) nitrate was added to the precursor polymer solution and the resulting fibers were then immersed at room temperature in an HKUST-1 growth solution mixture of copper(II) nitrate in MeOH and trimesic acid with triethylamine in MeOH. The resulting fiber mat consisted of PVDF fibers with a uniform overgrowth of HKUST-1 crystals on individual fiber surfaces. This combines the functionality of HKUST-1 with the mechanical toughness of PVDF nanofibers. These two approaches to making MOF-polymer fiber composites are readily scalable and thus pave the way for developing functional nanocomposite devices on an industrial scale.

CP1.11
Withdrawn

CP1.12 moved to C8.01
Progress toward Covalently Integrated MOF-Polymer Materials
Michael S. Denny and Seth M. Cohen; Chemistry and Biochemistry, University of California, San Diego, San Diego, California, United States.

In efforts to integrate MOFs into real-world applications, difficulty in processing and handling of MOFs as crystalline powders has been a limiting factor in their utility. Integration of MOFs into engineered hybrid structures, such as mixed matrix membranes, is proving to be an exciting route toward improving the processability and handling of MOFs by embedding these microcrystalline powders in a polymeric matrix. A significant challenge in this process, however, is achieving good adhesion between the MOF and polymer components. The next step in improvement of these membranes is to employ postsynthetic methods to improve MOF-polymer adhesion. This includes surface modification of the MOF and covalent bonding between the MOF crystallites and the interstitial polymer to ensure tight MOF-polymer. We describe efforts toward covalent modification of MOF particles to create strong interactions with the polymer, seeking to covalently integrate MOF particles within a polyamide matrix. The properties of the hybrid material, including porosity, thermal stability, and mechanical strength, are explored with an eye toward integration of these materials into functional textiles.

CP1.13
MOF Fabrics for Chemical Protection
Annie Xi Lu, Gregory W. Peterson, Jared B. Decoste, Monica McEntee and Wesley O. Gordon; Edgewood Chemical Biological Center, Edgewood, Maryland, United States.

Several Metal Organic Frameworks (MOFs) have shown remarkable capabilities of degrading chemical warfare agents (CWAs) and their simulants. However, the exploration of MOFs in textiles and clothing for chemical protection has not been prominently explored. It is envisioned that the next generation of chemical protective clothing will integrate reactive materials, such as MOFs, into the fabric, where in addition to providing a physical
barrier, the protective clothing can also undergo self-decontamination. Toward that end, we have engineered a nonwoven fiber composite containing reactive Zr-based MOFs that show the ability to degrade G- and V-type nerve agents. Our approach allows us to load a high weight content of MOFs on the fabric and offers access to reactive sites on the MOFs. We demonstrate through simulant and chemical agent reactions that MOFs in the fabric matrix remain highly reactive and mimic reactions of native MOF powders. These newly developed textiles are further evaluated for breathability, moisture vapor transport, and toxic gas permeation rates across the composite. This approach will serve as a platform for engineering MOFs into usable textiles without compromising MOF reactivity and performance. Approved for public release; distribution unlimited.

**CP1.14 Capture and Immobilisation of Iodine (I) Utilising Polymer-Based ZIF-8 Nanocomposite Membranes**


Polymer nanocomposites made up of nanoporous metal-organic frameworks (MOFs) is fast becoming a staple of next generation hybrid composites, and are currently being intensely developed for gaseous capture and separations. We report the first attempt of capture and retention of iodine (I) using polymer-MOF (ZIF-8) nanocomposites. Membranes of ZIF-8-based nanocomposites (comprising either a glassy Matrimid or a rubbery polyurethane (PU) matrix) were prepared via the colloidal-mixing approach, and its viability for I capture and retention effects were determined through absorption experiments, nanoindentation mechanical measurements, and thermogravimetric (TGA) analysis. The absorption experiments demonstrated that I capture and retention is possible in all of the nanocomposite membranes, although some classes of membranes demonstrated higher affinities for this than others. We propose that the affinity of the organic ligands in ZIF-8 and the formation of free volume in the nanocomposites from the presence of ZIF-8 attracted I, and the formation of secondary bonds between these constituents (H-bonds) act to strengthen not only the nanocomposite, but keeping I from being released despite the larger pore size and gate-opening dynamics of ZIF-8. It was therefore concluded that a combination of nanoparticles of porous MOFs and rubbery polymer is promising for further development to enable I capture and retention applications. References[1] Mahdi, E. M.; Tan, J.-C. Journal of Membrane Science 2016, 498, 276-290[2] Jeazet, H. B. T., Staudt, C., Janiak, C. Dalton Transactions 2012, 41, 14003-14027[3] D. F. Sava, T. J. Garino and T. M. Nenoff, Industrial Engineering Chemical Research, 2012, 51, 614-620

**CP1.15 MOF Coatings with Low Binder Content on Macroporous Cellular Supports**

Jakob G. Eggebrecht, Lena Friedrichs and Alexandra E. Lieb; Chemistry, Otto-von-Guericke University, Magdeburg, Germany.

Metal Organic Frameworks with high hydrothermal stability showing an isotherm with a steep uptick of water vapor between 5 and 40 % relative humidity are promising candidates for thermochemical heat storage or sorption-based cooling processes. Usually, MOF materials occur as fine powders resulting in high pressure loss in packed beds, exhibiting insufficient heat and mass transfer properties. In order to exploit the full potential of functional MOF materials for heat transformation processes, immobilization and improvement of thermal conductivity and mass flow is necessary. When using an immobilization route with binder-based suspensions, a low binder content is necessary in order to avoid pore blockage and the presence of nonfunctional material in the device. Besides the active material, commercially available granules or extrudates consist of approximately 20 wt% oxides, such as colloidal silica or aluminum oxide.[1,2] Furthermore, acceptable heat transfer is only achieved with a thin layer of coating, but not with granules or extrudates. Layers could be produced via a customized direct crystallization [3,4] or via a widely applicable slurry-based coating procedure. Here we present a procedure to form cellulose-based MOF coatings on macroporous cellular supports. In the resulting MOF-composite materials the support provides good thermal conductivity during the ad- and desorption of water, as well as mechanical protection of the active material. The macroporosity of the support material allows a high mass flow. Different MOFs (e.g. HKUST-1, MIL-100(Fe), Aluminum fumarate) are used to show the versatility of our procedure. The derived samples were characterized by sorption experiments, XRD, thermogravimetric analysis and microscopic methods.[1] M. Gaab, M. Kostur, U. Müller, Stable spherical, porous metal-organic framework shaped bodies for gas storage and gas separation, WO 2014118054 A1[2] M. Gaab, C. Eichholz, M. Kostur, U. Müller, S. Maurer, Metal-organic framework extrudates with high packing density and tunable pore volume, WO 2014118074 A1[3] F. Jermias, S. K. Henninger, C. Janiak, High performance metal–organic-framework coatings obtained via thermal gradient synthesis, Chem. Commun. 2012, 48 (78), 9708.[4] U. Bette, S. Proemmel, J. G. Eggebrecht, S. Rannabauer, A. Lieb, M. Scheffler, F. Scheffler, Micro-Macroporous Composite Materials: SiC Ceramic Foams Functionalized With the Metal Organic Framework HKUST-1, Chemie Ingenieur Technik 2016, 88 (3), 264.

**CP1.16 High Throughput Computational Predictions of Gas Separation Properties of Mixed Matrix Membranes**

Samir Budhathoki1, Jan Steckel1 and Christopher E. Wilmer2; 1Department of Energy, National Energy Technology Laboratory, Pittsburgh, Pennsylvania, United States; 2Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

Molecular organic framework (MOF) materials distributed in a polymer matrix can enhance the gas separation performance of the composite material beyond the intrinsic properties of the polymer. Mixed matrix membranes (MMMs) combine the high selectivity of porous materials with the attractive mechanical and economical properties of polymer membranes. While MMMs show great promise for gas separation applications, the large number of choices for filler fraction, polymer material and especially possible MOF filler particles presents researchers with a large number of hypothetical MMM combinations. Moreover, synthesis and characterization of MMMs are time-consuming and costly procedures. Thus, a method in which the gas separation properties of hypothetical MMMs could be predicted would be useful. In this work, high-throughput screening calculations have been used to estimate selectivity and permeation properties for mixed matrix membranes for use in a membrane-based carbon capture process. Our work makes use of an existing database (Wilmer et al.[1]) containing over 137,000 hypothetical porous MOF structures. With the use of Maxwell’s equation and experimentally obtained properties for a range of polymers, it is possible to create gas separation predictions for a very large number of hypothetical mixed matrix membranes. Results are analyzed for structure-
functional relationships such as dependencies on MOF chemistry, pore limiting diameter (PLD) and the largest cavity diameter (LCD). MMMs showing desirable properties help inform the creation of a new database of hypothetical MOF structures that is targeted for CO₂ separation in the context of MMMs. Finally, a major goal of this project is to connect atomistic-level simulations with the toolset of the Carbon Capture Simulation Initiative (CCSI), making it possible to screen new or hypothetical carbon capture materials within the context of an optimized carbon capture process[1] C. E. Wilmert, M. Leaf, C. Y. Lee, O. K. Farha, J. T. Hupp, B. G. Hauser, R. Q. Snurr, Nature. Chem. 4 (2012), 83.

**CP1.17**
**Attachment of MOFs to Nylon and Cotton Fabrics** T. Grant Glover, Kevin N. West and Meagan A. Bunge; Chemical and Biomolecular Engineering, University of South Alabama, Mobile, Alabama, United States.

Chemistry conventionally used to bind chromophores to fabrics has been used to develop a platform technology that can modify commercially available fibers with nanoscale structures. Based on reactive dye chemistry, the method was used to attach Cu-BTC to both cotton and nylon. The Cu-BTC modified fabrics have surface areas of approximately 700 m²/g, X-ray diffraction patterns consistent with Cu-BTC, and FESEM images that show crystals decorating the fabric surfaces. To demonstrate the ability of the fibers to perform separations, ethane and ethylene single component gas adsorption isotherms were measured and ammonia breakthrough experiments were conducted. The results show that the attachment of the MOF to the fiber does not alter the gas separation properties of the MOF. In addition to MOFs, the attachment technique has also been used to attach quantum dots and gold nanoparticles to fibers. The results illustrate how the reactive dye method provides a platform to modify fibers with MOF structures. In addition to Cu-BTC, this presentation will also discuss recent results detailing the attachment of UiO-66 to fabric swatches.

**CP1.18**
**Investigation of Polymer Ligand Architecture in polyMOF Growth** Joseph M. Palomba, Sergio Ayala and Seth M. Cohen; Chemistry, University of California, San Diego, San Diego, California, United States.

Metal-organic frameworks (MOFs) have intrinsic properties such as high surface area, regular crystallinity, and tunable functional components, but exist primarily as powders. As MOFs become more application driven, many research groups have investigated the interactions of MOFs with soft materials like polymers. By combining properties of polymers and MOFs, a new class of hybrid materials can be explored for a wider range of applications. Our approach to MOF-polymer hybrids has been to synthesize materials in which the MOF linkers are themselves polymerized¹. Using a bottom-up approach in this study, we are investigating the formation and properties of polymer-metal-organic frameworks (polyMOFs). By altering the polymer construction with copolymers, chain structure, or chemical functionality, we are able to affect the macroscopic properties of the MOF while maintaining its intrinsic microscopic properties. In order to probe the formation of the polyMOF, the architecture of the polymer was altered systematically. By exploring types of polymer ligands that can and cannot result in MOF formation, a greater library of polyMOF materials can be generated. Access to this information about polymer-MOF interactions opens the door to a wide variety of interesting material properties.¹. Zhang, Z. J.; Nguyen, H. T. H.; Miller, S. A.; Cohen, S. M., polyMOFs: A Class of Interconvertible Polymer-Metal-Organic-Framework Hybrid Materials. Angew Chem Int Ed 2015, 54 (21), 6152-6157.

**CP1.19 Withdrawn**

**CP1.20**
**Preparation and Comparative Study of MIL-53-Based Mixed-Matrix Membranes Involving Different Casting Solvents** Yi-Wei Chang and Bor Kae Chang; Chemical and Materials Engineering, National Central University, Taoyuan City, Taiwan.

Membranes for gas separation have already become a promising field of technology. It offers a continuous and relatively simple process for industry and is also an economical, environmentally friendly and efficient separation method. Additionally, organic polymer membranes are one of the feasible options for separating natural gas from other components as an alternative energy source. In this research, we prepared pure polysulfone (PSF) membranes with four kinds of solvents – chloroform, tetrahydrofuran (THF), diethylene glycol dimethyl ether (DEG), and N-methyl-2-pyrrolidone (NMP). Due to differences in interactions between the polymer and solvents, we observed varying structures during the pure PSF membrane formation process using several drying techniques. The addition of metal-organic frameworks (MOFs) to form mixed-matrix membranes (MMM) opens the door to enhanced separation performances over pure polymer systems as a result of the combined polymeric phase dispersed with hybrid fillers. MOFs interact well with the polymer due to its organic linkers, and in this work we focus on MIL-53 as a candidate filler because of several advantageous properties including structural stability in water, flexible pore openings, and outstanding selectivity for specific gases. He aim of this research was to fabricate mixed-matrix membranes with four different solvents to investigate their potential in gas separation applications. The synthesis of MMM was divided into two parts: the synthesis of MIL-53 crystals and preparation of the polymer in different solvents, and the combination of both to form the final product. The morphology of as-synthesized MIL-53 and MMMs were characterized by scanning electron microscopy (SEM), while
the results of X-ray diffraction (XRD) confirmed the crystal structures. MMMs prepared through different solvents and drying processes demonstrated varied results that are predicted to impact gas separation performance, thus highlighting the influence of different solvents in forming membranes.

**CP1.21**
**Investigating MOF Mixed-Matrix Membranes with Styrene-Based Polymers** Jessica Moreton, Michael Denny and Seth Cohen; Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, United States.

The high surface area and tunable porosity of MOF materials have prompted many studies exploring their use in a range of applications, including separations, gas storage, and catalysis, among others. By combining MOF microcrystalline powders with a polymer phase in mixed-matrix membrane (MMM) form, the industrial promise of MOFs can be more easily realized. Research in MOF MMMs thus far has mainly utilized only a small subset of polymers with intrinsic gas separation abilities, leaving a huge range of potentially useful polymers unexplored. Given our group’s interest in other MOF applications such as liquid separations and chemical warfare agent sequestration, our exploration of under-utilized polymers continues to yield interesting new insights. In this report, we employ styrene-based polymers spanning a range of physical properties to form MOF MMMs of more than 60 wt% MOF. As our results show, visibly uniform, flexible MMMs can be obtained via either a drop-cast or drawdown method. The accessibility and porosity of the MOFs, as well as their chemical reactivity within the membrane, have been assessed.1 Zornoza, B.; Tellez, C.; Coronas, J.; Gascon, J.; Kapteijn, F. Microporous Mesoporous Mater. 2013, 166, 67. (2) Denny, M. S., Jr.; Cohen, S. M. Angew. Chem. Int. Ed. 2015, 54, 9029. (3) DeCoste, J. B.; Denny, M. S., Jr.; Peterson, G. W.; Mahle, J. J.; Cohen, S. M. Chem. Sci. 2016, 7, 2711.

**CP1.22**
**A Comparative Study on Photoluminescence and Color Properties between Crystalline and Amorphous Organic-Inorganic Hybrid Materials for White-Light Emission** Gongyi Guo1 and Yuli Chen2;1Shanghai Jiao Tong University, Shanghai, China; 2Shanghai University, Shanghai, China.

Direct white-light emission from a single-phased and single-doped phosphor is both an excellent option and a challenging task for the development of fluorescent materials, and hence can only been found from sparse references. In assessing the merit of fluorescent materials for actual LEDs application, one will inevitably consider the ease and environmental friendliness of a synthesis method and ultimately also the cost of the material. We report the broad-band direct white-light emission originating from a single-phased and single-doped phosphor, i.e., a luminescent zirconium oxy-hydroxyl acetate-per sulfate complex and the complex doped by Eu3+. The amorphous complexes exhibit the photoluminescence and color properties comparable to or better than those of the crystalline MOFs or organic-inorganic hybrid semiconductors for white-light emission. The pristine complex is totally free of rare-earth metals and can realize near white-light emission with CIE chromaticity coordinates (0.282, 0.339), color rendering index 79.6, and correlated color temperature 8054K. The complex doped by Eu3+ under UV excitation at 365nm exhibits a white-light emission with CIE chromaticity coordinates (0.3405, 0.3562), color rendering index 94.5, and correlated color temperature 5192K. The fluorescence quantum yield of the Eu3+–doped complex is 14.13% when excited by 392nm light. The attracting feature of this route to white-light emission comes from the single-phased and single-doped phosphors that can be prepared through a low-cost chemical synthesis approach without incurring the burden of intrinsic toxicity and without the need for stringent, tricate, tedious, or costly preparation steps.

**CP1.23 Withdrawn**

**CP1.24**
**Alternative Preparation of Metal Organic Framework-Polyelectrolyte Composites for Anion Exchange Application** Joseph F. Olorunyomi1, Kwong-Yu Chan1, Liang Gao2 and Chi-Ying V. Li2;1Department of Chemistry, University of Hong Kong, Hong Kong, Hong Kong; 2Guangdong University of Technology, Guangdong Province, China.

Metal organic frameworks (MOFs) have continued to receive attention because of flexibility in their designs leading to a large number of uniformly ordered structures which possess high surface area and high porosities. They have shown significant performance in many separation applications including ion-exchange. Therefore, in a bid to exploit the versatility of MOFs and harness their advantages with those of polyelectrolytes for ion-exchange processes, we have prepared MOF-polyelectrolyte composites for ion-exchange applications. The functionalities of the polyelectrolyte guests in the host MOFs are freely exposed to the solution consequently allowing a more efficient ion exchange than in the conventional resins where the ion-exchange functionalities are hidden within the polymeric beads. In an earlier work, [1], an anion exchange MOF-polymer composite was prepared and functionalized under conditions of high pH and involving lengthy steps. This procedure disfavors MOFs that are unstable in strong alkaline medium. In the present study, we have prepared another anion exchange MOF-polymer composite under mild conditions by using a simpler approach. The preliminary results from the HNMR, FTIR, thermal degradation and nitrogen gas sorption tests indicate successful insertion of the polyelectrolyte within the cavities of the MOF. The XRD also confirms that the crystalline structure of MOF is retained after the polymerization. References [1] J. Am. Chem. Soc., 2014, 136 (20), 7209-12. [2] Chem. Mater., 2015, 27 (10), 3601–3608
SESSION C2: MOF Hybrids, Nanocomposites and Organic Networks—Covalent Organic Frameworks I
C: MOF Hybrids, Nanocomposites and Organic Networks
Chair: Thomas Bein
Monday Morning, September 12, 2016
Pacific Room

9:45 AM *C2.01
Structural Diversity and Functional Exploration of Covalent Organic Frameworks Donglin Jiang; Field of Energy and Environment, Japan Advanced Institute of Science and Technology, Nomi, Japan.

Covalent organic frameworks are a class of crystalline polymers that enable the incorporation of organic building blocks into well-defined primary and high-order structures. In recent years, we have explored the design principle, synthetic reactions, structural diversity, functional design, and potential applications. One significant feature of COFs is that the merge of covalent bonds and noncovalent interactions enables the precise control over the primary and high-order structures. The geometry-directed covalent bonding enables the growth of polymer layers in which the primary-order structures are precisely controlled. The noncovalent π−π interactions guided by the total crystal stacking energy encode the ordered primary-order structure into high-order structures to constitute periodically aligned polymer skeletons and nanometer sized unidirectional channels. These structural features make COFs as an attractive platform for designing functional materials and exploring various functions, including gas adsorption, catalysis, semiconductors, energy conversion and storage. In this talk, I will discuss our recent work on structural diversity and functional explorations of COFs.

10:05 AM C2.02
Weaving As a Strategy to Make Covalent Organic Frameworks Yuzhong Liu1, Omar M. Yaghi1, Yanhang Ma2 and Osamu Terasaki2; 1University of California, Berkeley, Berkeley, California, United States; 2Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden.

Weaving of long threads is one of the oldest and most enduring methods of making fabric that are soft that can be wore, but also robust so it cannot be torn easily. The equivalent of this important design concept can be adopted in extended chemical structures by linking molecular building units by strong bonds through reticular synthesis into weaving forms with exceptional mechanical properties and dynamics. In order to successfully design weaving of chains into two- and three-dimensional chemical structures, long threads of covalently linked molecules must be able to cross at regular intervals. It would also be desirable if such crossings serve as points-of-registry so that the threads can have a high number of degrees of freedom to move away and back to such points without collapsing the overall structure. A general strategy has been demonstrated to achieve such weaving frameworks. Copper(I) ions were used as templates upon coordination with aldehyde-functionalized phenanthroline ligands to direct the formation of the first crystalline weaving structure of covalent organic framework (COF-505) with atomically accurate precision. The synthesis of COF-505 was carried out by imine condensation reactions of aldehyde functionalized copper(I)-bisphenanthroline tetrafluoroborate, Cu(PDB), as building units and linked by benzidine (BZ), with a crystal structure of the basic topology of dia. The copper centers are independent of the weaving within the COF structure and serve as templates for bringing the helical threads into a weaving pattern rather than the more commonly observed parallel arrangement. The copper(I) ions can be reversibly removed and added as a switch without loss of the COF structure. A ten-fold increase in elasticity accompanies its demetalation, and this demetalated material displays polymer-like properties. Upon remetalating, the crystallinity and overall structure can be fully restored. The threads in COF-505 have many degrees of freedom for enormous deviations to take place without undoing the weaving of the overall structure, facilitated by the unique structure of weaving threads that easily ‘zip’ and ‘unzip’ at their points-of-registry. This strategy for weaving organic threads and its successful implementation is the first step in the development of a large area of synthetic chemistry based on making weaving forms with tunable mechanical properties.

10:25 AM C2.03
Enhanced CO2 Capture by Porous Aromatic Framework Bearing Ionic Liquid Functionality Obtained via Click-chemistry Approach Alessandro Danil1,2; Valentina Crocella1; Jiayin Yuan1 and Silvia Bordiga1,2; 1Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany; 2Department of Chemistry, NIS, INSTM Reference Centre, University of Torino, Torino, Italy; 3Department of Chemistry, University of Oslo, Oslo, Norway.

In this work we developed a facile strategy direct to create porous aromatic framework functionalized with ionic liquid in form of imidazolium moiety (named by us PAF-PILs), bearing different counter-anions and with the possibility to introduce NHC carbene along the PAF framework. Our new synthetic approach follows the main principles of the click-chemistry, and allows to obtain the PAF-PILs in one pot reaction, making the synthetic ways of functionalized PAFs even more green and sustainable. The reaction that we used for closing the imidazolium ring and forming the PAF in one step is a modified version of Debus-Radziszewski imidazole synthesis. This reaction allows to form an imidazole ring between two amino groups. Since the amino groups belong to tetrakis(4-aminophenyl)methane - a tetra-functional, sterically hindered, homo-condensation monomer - the resulting material is a Poly(Ionic Liquid)s (PILs) shaped as a PAF. Our synthetic route for PAF-PILs follows the principles of click-chemistry: nearly 100% yield, only water as sub-product, stable reaction products, not-reversible reaction, 85% efficiency in atomic economy, mild reaction conditions, water as solvent, solid final product easy to purify. PAF-PILs were obtained with a set of different counter-anions like: acetate, BF4−, PF6−, trifluoromethanesulfonate and bis(trifluoromethane)sulfonimid. All the PAF-PILs were extensively characterized in order to prove their porosity and their chemical structure, taking advantage of a large range of characterization techniques like: IR-ATR, N, adsorption at 77K, SEM, SS-NMR, TGA and HR-MS spectroscopy. Carbon dioxide adsorption at different temperature was tested on all PAF-PILs, and at 298K the maximum loading is between 1 and 1.2 mmol/g for all the PAF-PILs with different counter-anions. These values are nowadays among the highest ever recorded for the field of imidazolium PILs. Most of all because of the high porosity of the materials (BET specific surface area around 400 m2/g) mainly in the microporous range, furthermore because of the high ratio between imidazolium and phenyl ring, which makes the PAF-PILs materials with a high degree of functionalization. Furthermore, NHC carbene was...
introduced on the PAF-PILs, in order to study the different behaviour towards carbon dioxide adsorption. Interestingly, the loading of carbon dioxide for NHC carbene PAF-PIL is almost the same of the starting PIL with acetate as counter-anion (1.2 mmol/g). However, a deep physico-chemical study involving in-situ FTIR and CO$_2$ adsorption micro-calorimetry allows to evidence the difference in the interaction between CO$_2$ and the two adsorption sites. In fact, CO$_2$ adsorbed on NHC carbene shows higher heat of adsorption, mainly due to the formation of a covalent bond and new vibrational features arising from the carbonyl symmetric and antisymmetric stretching of the adduct between CO$_2$ and imidazolium NHC carbene.

10:45 AM C2.04
 Oriented Thin Films of Covalent Organic Frameworks Comprising Cobalt Porphyrins for Catalytic CO$_2$ Reduction in Water Christian S. Diercks, Song Lin, Yue-Biao Zhang, Christopher J. Chang and Omar M. Yaghi; Chemistry, University of California, Berkeley, Berkeley, California, United States.

Oriented thin films of covalent organic frameworks comprising cobalt porphyrins for catalytic CO$_2$ reduction in water: C. S. Diercks, S. Lin, Y-B Zhang, N. Kornienko, C. J. Chang, O. M. Yaghi* Global energy demands and climate change underpin broad interest in the sustainable reductive transformation of carbon dioxide (CO$_2$) to value-added carbon products like carbon monoxide (CO). In this context, molecular catalysts for electrochemical CO$_2$ conversions can be systematically tuned to achieve high activity and selectivity over proton reduction but typically require organic media to function. In contrast, heterogeneous catalysts are often stable in water, but optimizing their activity through structural changes at a molecular level remains a substantial challenge. Against these backdrops we decided to use Covalent Organic Frameworks (COFs) as CO$_2$ reduction catalysts in an attempt to combine the advantages of both molecular homogeneous and heterogeneous catalytic systems. For this project we synthesized a COF, in which one of the building blocks is a cobalt porphyrin catalysts that is linked by organic struts through imine bonds. The synthesized bulk material shows great promise as a CO$_2$ reduction catalyst however the morphology of the sample has yet to be optimized to achieve a truly functional catalyst. Based on the cyclic voltammetry measurements of the synthesized COF materials deposited on porous carbon fabric only 6-9% of the cobalt centers are actually electrochemically accessible. We reasoned that this problem could potentially be overcome by growing oriented thin films of COF-366-Co directly on the electrode material. Oriented thin films of COFs have been shown to expedite redox processes within the material. Films of COF-366-Co were grown on highly ordered pyrolytic graphite (HOPG). Grazing incidence wide angle X-ray scattering shows the preferred orientation of the COF layers to be perpendicular to the electrode surface. Scanning electron microscopy reveals the uniform film growth of the COF which results in a thickness of approximately 200nm for the film. The microscopy reveals the uniform film growth of the COF which is parallel to the electrode surface. Scanning electron microscopy reveals the uniform film growth of the COF which results in a thickness of approximately 200nm for the film. The microscopy reveals the uniform film growth of the COF which is parallel to the electrode surface.

11:25 AM C2.06
 Anionic Silicate Organic Frameworks Constructed From Hexacoordinated Silicon Centers—Towards Organic Zeolites Jerome Roesser1, Caren Goebel1, Michael J. Bojdys2, Abbie Trewin1 and Arne Thomas1; 1Technical University Berlin, Berlin, Germany; 2Charles University in Prague, Prague, Czech Republic; 1Lancaster University, Lancaster, United Kingdom.

It has been illustrated that predetermined crystalline frameworks, with extended 2D or 3D structures, can be rationally built using the design principles of reticular chemistry by a judicious choice of building blocks and reaction conditions where the criteria for rigidity, directionality and reversibility are simultaneously met. [1] For purely organic covalent organic frameworks (COFs), [2] those crystalline structures are so far obtained by condensation reactions based on the reversible formation of B-O, C-N or B-N bonds into either planar heterocycles (boroxine, boronate, triazine borazine, squaraine, succinimide) or planar unsaturated functional groups (imine, hydrazone, azine). [3] Here we demonstrate a strategy to elaborate negatively charged COFs formed entirely through covalent bonds. This could be achieved by the successful implementation of Si-O reversible chemistry for the synthesis of such crystalline frameworks, which we believe has great potential to extend the range of structures and properties in the field of COFs. [4] [1] O. M. Yaghi, M. O’Keeffe, N. W. Ockwig, H. K. Chae, M. Edaoudi, J. Kim, Nature 2003, 423, 705-714,[2] A. P. Côté, A. I. Benin, N. W. Ockwig, M. O’Keeffe, A. J. Matzger, O. M. Yaghi, Science 2005, 310, 1166-1170.[3] X. Feng, X. Ding, D. Jiang, Chem. Soc. Rev. 2012, 41, 6010-6022.[4] J. Roesser, C. Goebel, M. J. Bojdys, A. Trewin, A. Thomas, submitted.

References
1:15 PM C3.01

Enhancing Pore Performance of Cobalt-Catalyzed Oxygen Reduction by Molecular Tuning of Covalent Triazine Frameworks

Chair: Donglin Jiang

Monday Afternoon, September 12, 2016

Pacific Room

We set out to correlate the properties of frameworks, more specifically surface area and porous structure, with electrochemical behaviors of ORR. In this work we synthesize three cobalt-containing CTFs varying mainly in pore size and study their electrochemical differences. Each contains analogous cobalt catalysts, which are immobilized on the porous CTFs. We reveal that ligand expansions of CTFs improve the utilization rate of oxygen in the pores, and decreases the over-potential energies required to carry out ORR. Our largest pore structure contains a BET surface area of 1425 m$^2$/g, with total pore volume of 0.72 cc/g, all while containing very active cobalt species. The resultant framework exhibits excellent ORR and stability, surpassing commercial Pt/C by a outstanding 40 mV in overpotential. This work provides a valuable strategy and information for future framework design to maximize electrocatalyst performance.

1:35 PM C3.02

Covalent Organic Materials Made from Polycyclic Aromatic Hydrocarbons

Chair: Ronald A. Smaldone

Monday Afternoon, September 12, 2016

Pacific Room

Organic materials hold much promise to address the growing need for new solutions in energy storage, sensing and computing. As such, the development of new paradigms in materials chemistry remains as relevant as ever. The research described here lies at the interface of organic synthesis and materials science. One of the fundamental challenges in synthetic chemistry involves the precise placement of atoms, bonds, and functional components within a molecule or material. Over the past several years, the interest in exploiting the unique properties of highly conjugated polycyclic aromatic materials, namely graphene and carbon nanotubes, has skyrocketed leading to novel chemical methods to modify these compounds using both covalent, and non-covalent approaches. Tunable graphitic materials are likely to be paramount in the fabrication of the next generation of electrical, solar and hydrocarbon-based energy storage materials. This presentation will discuss the challenges and benefits presented by the use of large conjugated monomers such as hexabenzocoronene and hexaphenylbenzene in the synthesis of porous polymers and covalent organic frameworks. Control over the interlayer stacking interactions is key to developing new COFs with well-defined structures. The use of large PAH-monomers provides a platform to study the limits of COF assembly through systematic structural modification. The effects that the monomer substituents, aromatic ring electronics and conjugation and have on the structure, crystallinity and porosity of the COFs will be discussed along with their bulk properties such as gas and organic vapor adsorption capability.

1:55 PM C4.01

Surface Functionality Independent Conjugation of Biomolecules to Colloidal Metal-Organic Frameworks and Their Exemplified Application in Immuno-Assays

Chair: Francesco Paesani

Monday Afternoon, September 12, 2016

Pacific Room

Metal-organic framework (MOF) colloids hold great potential for bioanalytical and biomedical applications due to their unique features. These include responsive luminescent properties and exceptionally high loading capacities for small molecular drugs. However, currently the lack of a surface functionality independent method for biomolecule conjugation is strongly limiting the advancement of colloidal MOFs in bioanalytical or biomedical applications. Bioanalytical methods, especially for environmental analysis, would benefit dramatically when responsive luminescent properties of MOFs could be coupled with a specific antibody interaction. Targeted drug delivery in biomedical applications often requires specificity towards tissues of interest in addition to a high drug loading capacity. Thus, both envisioned applications require biomolecules and in particular antibodies to be conjugated to colloidal MOFs. Here, we propose a robust and easy to handle method that is suitable for a wide range of MOF templates and that allows reliable conjugation of biomolecules. Colloidal ZIF-67 MOFs with particle size between 300nm and 5µm were used as templates to adsorb polymeric multilayer through a Layer-by-Layer self-assembly process. Multilayer build up was confirmed by the change in zeta-potential of particles upon polyelectrolyte adsorption as well as dynamic light scattering experiments and SEM/TEM microscopy. Subsequent biomolecule conjugation to functional groups of the polymeric multilayer on the surface of colloidal MOFs was achieved by established carbodiimide/succinimide conjugation chemistry. Successful and stable conjugation was confirmed by employing fluorescent labeled biomolecules. Subsequently, colloidal MOF-antibody (IgG) conjugates were utilized in a solid-phase immuno assay using antibodies against carbamazepine and lithocholic acid, two interesting markers in environmental analysis. In brief, mouse anti-CBZ (Carbamazepine) and rabbit anti-lithocholic acid were separately and covalently immobilized on 2D polystyrene surfaces to form a small micro spot array. Two separate populations of colloidal MOF particles were conjugated with goat anti mouse IgG and goat anti rabbit IgG, respectively. The different fluorescent labels of the two MOF colloid populations allowed the determination of binding selectivity and strength of the colloidal MOF-antibody conjugates to the immobilized binding partners. The ability to coat MOFs in solution independent of their surface charge with polymers and subsequently to conjugate biomolecules to their surface makes this method a powerful tool to foster bioanalytical, biomedical as well as other applications.
Synthesis, Functionalization and Application of Metal-Organic Framework Based Biomaterials
Manuel Tsotsalas, Sophia Schmitt, Peter Krolla-Sidenstein and Christof Woell; Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, Germany.

The development of materials for biological and medical applications is a highly active area of research. The biological response to the final fabricated material will ultimately govern its success or failure. Their behaviour of cells towards synthetic materials is collectively determined by the combination of chemical cues on the surface or released to the cellular microenvironment and material properties, such as modulus or 3D morphology. We will describe the synthesis of MOF-based biomaterials, their bio-functionalization and application as culture substrate for eukaryotic and prokaryotic cells. The conversion of MOFs into polymer gels is performed by covalently cross-linking the organic linkers using click-chemistry, followed by removal of the metal centres.[1] This strategy creates biomaterials with high stability in physiological media and biocompatibility, while preserving the precise MOF morphology and network topology. The network composition can be varied in a wide range by choosing different molecular components and structures. The surface of the materials provide several chemical moieties, which can be chemically functionalized to tune the hydrophobicity and to attach recognition sites for cells (e.g. RGD). Furthermore, the pores of the gel networks can be loaded with bioactive molecules and released in a diffusion controlled mechanism or triggered via external stimuli.[2] In cell experiments we will show (a) the biocompatibility of the MOF based gels materials and (b) that the response of adhering cells and bacteria to the materials can be controlled via the (locally confined) release of bioactive molecules and or via (patterned) surface functionalization.[1] (a) T. Ishiwata et al. J. Am. Chem. Soc. 2013, 135, 5427. (b) M. Tsotsalas et al. J. Am. Chem. Soc. 2013, 136, 8.[2] (a) S. Schmitt et al. ACS Nano, 2015, 9, 4219. (b) V. Mugnaini et al. Chem. Commun., 2014,50, 11129.[3] P. Lindemann et al. J. Mater. Chem. A, 2016, Advance Artical

Graphene/Graphene Oxide-templated Growth of MOFs to Form Continuous Thin Films and Hierarchical Structures
Daeok Kim and Ali Coskun; School of Energy, Environment, Water and Sustainability, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Graphene oxide (GO) as a two-dimensional macromolecule offers unique advantages such as rich surface chemistry through oxygen functionalities. The highly functionalized 2 dimensional carbon surface can be used for the seeding and growing of metal organic framework (MOF) crystals through the interaction between MOF and surface functionalities to form MOF/GO nanocomposites. Importantly, these nanocomposites have been shown to inherit some of the unique properties of graphene, thus leading to materials with enhanced electrical, optical and adsorption properties, which have been utilized for various applications such as sensors, supercapacitors, batteries, gas storage and catalysis. To expand the application of this area, we introduce a new strategy to fabricate defect-free continuous MOF films using GO as an interfacial template on solid substrates. The unprecedented formation of a one-dimensional nanorod-shaped crystalline intermediate phase on the GO surface enabled the preferential growth of HKUST-1 films in the <220> direction.[1] Also, we report the preparation of graphene/ZIF-8 nanocomposites with tunable hierarchical porosity and surface areas, wherein the distribution of micro- and mesopores along with the particle size of ZIF-8 crystals was controlled by simply varying the annealing temperature of GO sheets.[2] These nanocomposites showed superior CO$_2$ uptake capacities up to 17 mmol g$^{-1}$ at 303 K, 35 bar to ZIF-8 as well as electrical conductivity up to 64 S m$^{-1}$ with graphene loading of 20 wt% due to the synergistic effect of the graphitic surface and ZIF-8 crystals. Our results offer new directions to develop MOF/GO composites with controlling their structure and properties.1 CrystEngComm, 2016, Advance Article DOI: 10.1039/C5CE02188J 2 J. Mater. Chem. A, 2016, Advance Article DOI: 10.1039/C6TA01899H

MOF Composites with Nano-CuS—Syntheses, Electrical Properties, and Applications
Keumnam Cho, Sungwan Han and Myunghyun Paik Suh; Department of Chemistry, Hanyang University, Seoul, Korea (the Republic of).

Development of efficient electrocatalysts for the oxygen reduction reaction (ORR) in fuel cells, which can replace platinum, is an important issue. We have synthesized composite materials, nano-CuS(x wt%)/Cu-BTC, which contain various amounts of nanostructured CuS in a Cu-MOF by a simple infiltration method using Cu-MOF as a sacrificial template. By controlling the reaction conditions, the amount and the size of nanostructured CuS fabricated in/on the Cu-MOF were varied. The electrical conductivity and porosity of the materials depend on the amount of CuS loaded in the MOF. As the amount of CuS increases, electrical conductivity increases up to ca. 10’ times and the porosity decreases to almost 1%, compared to those of the Cu-
MOF. The electrocatalytic activities significantly depend on the amount of nanostructured CuS in the composites. In particular, a material exhibits excellent electrocatalytic activity in the ORR, much better than those of Cu-MOF or nanostructured CuS alone, showing significantly higher onset potential and the quasi 4 electron transfer number, due to the synergistic effect of two different materials.

3:35 PM C4.06
Metal Nanoparticles@Porous Carbon Composites from Metal-Organic Frameworks for Li-Ion Battery and Biosensors

Metal-organic frameworks (MOFs) have used as a template for the synthesis of porous carbon materials. Furthermore, MOFs can act as a self-sacrificial carbon source for the synthesis of porous carbon materials without any carbon source. Interestingly, MOFs can serve as not only a carbon source, but also a metal source, which thus allows a facile synthesis of metal (oxide) nanoparticles and porous carbon composite materials. Herein, we will introduce the synthesis of a series of metal (oxide)@porous carbon composites using a MOF. A simple pyrolysis of MIL-100 and HKUST-1 results in porous carbon composites, FeO@C and Cu@C, respectively. By controlling pyrolysis conditions, the carbon composites show different oxidation state of metal (oxide) nanoparticles and different porosity (sorption properties). Due to the redox activity of FeO nanoparticles, FeO@C can be applied to an electrode material for a Li-ion battery. In addition, Cu@C shows redox catalytic activity in water. By combining mild catalytic reaction condition and hierarchical porosity of the Cu@C, the composite was applied to glucose oxidase based biosensor for glucose sensing. The Cu@C shows high sensitivity and selectivity compared to the other reported materials. It should be noted that the unique electrode performance and the high sensing capability. Coordination networks or MOFs present high porosity and may be promising for environmental applications. In this work we synthesized MOFs from dipicolinic acid (C7H4NO3), europium oxide (Eu2O3), and nanoparticles of iron oxide (NPs of Fe3O4), using hydrothermal conditions. The samples were characterized by emission and excitation spectroscopy, x-ray diffraction (XRD), and infrared spectroscopy (FT-IR). The excitation spectrum of the Eu/H,DPA compound indicates that the ligand acts as a sensitizer for the ion, even though direct excitation on the lanthanide ion is more efficient. The emission spectral profile suggests that the Eu3+ is in a low symmetry environment. The excitation spectrum of the composite Eu/H,DPA/NP shows that Eu3+ sensitization through the ligand is more efficient than the direct excitation on the ion. Furthermore, the ion has no inversion center. Both samples respond to UV excitation by the characteristic europium red emission. The Eu/H,DPA, however, showed more intense luminescence, compared to the material with the NPs. On the other hand, only the Eu/H,DPA/NP responds to the magnetic field due to the Fe3O4. The IR modes of pure H,DPA, with systematic peak shift, can be seen in Eu/H,DPA/NP, suggesting that the complex and the NPs interact. The characteristic peaks belonging to the tetragonal maghemite phase of Fe3O4 were seen by XRD. In addition, the XRD data suggests that the crystal structure of Eu/H,DPA differs from the structure of Eu/H,DPA/NP supporting the luminescence results. Porosimetry experiments, which will allow us to estimate surface areas are in progress, as well as dye adsorption experiments in aqueous media.

SESSION CP5: Poster Session: MOF Hybrids, Nanocomposites and Organic Networks II
C: MOF Hybrids, Nanocomposites and Organic Networks
Monday Afternoon, September 12, 2016
6:00 PM
International Ballroom IV/V

CP5.01
Synthesis and Characterization of Porous Coordination Networks (MOF’s) for Adsorption of Dyes Used in the Textile Industry

The continuous growth of industrial activity has been causing several environmental problems. In the textile industry, for example, dyeing and washing of jeans and other fabrics produce significant amounts of residues, which can sometimes contaminate water streams and reservoirs. Textile dyes are stable chemicals that withstand repeated washings and adverse conditions, such as wear and body sweat. Strategies to remove these chemicals from liquid media may involve materials with high adsorption capability. Coordination networks or MOFs present high porosity and may be promising for environmental applications. In this work we synthesized MOFs from dipicolinic acid (C7H4NO3), europium oxide (Eu2O3), and nanoparticles of iron oxide (NPs of Fe3O4), using hydrothermal conditions. The samples were characterized by emission and excitation spectroscopy, x-ray diffraction (XRD), and infrared spectroscopy (FT-IR). The excitation spectrum of the Eu/H,DPA compound indicates that the ligand acts as a sensitizer for the ion, even though direct excitation on the lanthanide ion is more efficient. The emission spectral profile suggests that the Eu3+ is in a low symmetry environment. The excitation spectrum of the composite Eu/H,DPA/NP shows that Eu3+ sensitization through the ligand is more efficient than the direct excitation on the ion. Furthermore, the ion has no inversion center. Both samples respond to UV excitation by the characteristic europium red emission. The Eu/H,DPA, however, showed more intense luminescence, compared to the material with the NPs. On the other hand, only the Eu/H,DPA/NP responds to the magnetic field due to the Fe3O4. The IR modes of pure H,DPA, with systematic peak shift, can be seen in Eu/H,DPA/NP, suggesting that the complex and the NPs interact. The characteristic peaks belonging to the tetragonal maghemite phase of Fe3O4 were seen by XRD. In addition, the XRD data suggests that the crystal structure of Eu/H,DPA differs from the structure of Eu/H,DPA/NP supporting the luminescence results. Porosimetry experiments, which will allow us to estimate surface areas are in progress, as well as dye adsorption experiments in aqueous media.

CP5.02

For years, surface-assisted laser desorption/ionization mass spectrometry (SALDI-MS) has been introduced as an alternative technique to overcome the serious background interference in matrix-assisted laser desorption/ionization (MALDI) of small molecule (< 500 DA). Herein, we present a novel platform for SALDI-MS analyses of organic compounds, such as polyaromatic hydrocarbons (PAHs), phthalate esters (PAEs), carbohydrates, phenolic acids (PAs) and amino acids (AAs), using metal-organic framework (MOF) and its derivatives, carbonized-MOF (cMOF). Based on the results, the MOFs and cMOFs demonstrated higher signal-to-noise intensities than the traditional or other nanoparticle matrices. Their good absorption capacities at 355 nm are deemed responsible for their high ionization efficiencies of organic compounds. The cMOFs also presented excellent dispersibility in aqueous solution than other nanoporous carbons. This could be associated to the presence of carboxylic acid moieties in the cMOFs, which were developed via direct carbonization of MOFs at different pyrolysis temperature. Therefore, the MOFs and cMOFs can be useful as new matrices for SALDI-MS analyses of small molecules. Furthermore, this study provides a new approach in developing a nanoporous carbon without conducting any surface modification in order to improve its dispersibility in aqueous solution.
The nature of metal-organic frameworks (MOFs) allows the implementation of desired properties by filling the framework cavities with various guest molecules and clusters molecule. The encapsulated metal nanoparticles in MOFs (MNPs@MOFs) is interesting in many application especially for heterogeneous catalyst application of MOFs. There are several reported that metal nanoparticles such as Cu, Ru, Au, Pt and Pd etc. loading on MOFs. Palladium (Pd) is one of the metal which have been use for catalyst for wild reaction e.g. hydrogenation, oxidation homocross coupling etc. Herein, the in situ fabrication of palladium nanoparticles at zeolitic imidazolate frameworks (ZIF-8) has been prepared via facile spray-dry technique. Crystal structure and morphologies of the Pd@ZIF-8 samples were investigated by powder XRD-ray, TEM, SAED, STEM, and EDX techniques. The investigation via high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) analysis strongly confirmed the presence of palladium nanoparticles inside the ZIF-8 structure. The porosity and surface area, including, the gas adsorption properties on materials were evaluate at several Pd content. Furthermore, Pd@ZIF-8 samples effectively have been applied as heterogeneous catalysts in alkenes hydrogenation. This straightforward method is able to speed up the synthesis of encapsulation of metal nanoparticles at metal organic frameworks.

**CP5.04**

**Controllable Assembly of Modular 3D Hierarchically-Structured Biscuit-Like Core/Satellite MOF-on-MOF Nanoclusters Yi-fan Gu, Yi-nan Wu, Ying Wang and Fengting Li; Tongji University, Shanghai, China.**

Functionalization of Metal-organic Frameworks (MOFs) is a great challenge for the broadening of their application. Design of MOF-on-MOF heterogeneous structure witnesses growing interests in recent years, which remains relatively unexplored but is promising for developing multifunctional MOF-based materials. In most reported cases, lattice matching is usually compulsorily required for MOF-on-MOF heteroepitaxial growth; that is, only those MOFs with similar crystallographic parameters are available candidates, which becomes the major limitation of this synthetic strategy on most kinds of MOFs with diverse crystal structures. In this work, a facile “Inside-Out-Growth” strategy is developed to prepare heterogeneous MOF-on-MOF composites. This modification strategy of MOFs endows the functional combination of each MOF component without the changing the pristine features to produce multifunctional MOFs composites. A series of MOFs, [NH₂-Uio-66(Zr), NH₂-MIL-125(Ti) and MIL-101(Cr)] with disparate crystallographic parameters, are successfully assembled with controllable morphology fashion of MOF interspersed on MOF crystals. Unlike conventional core-shell structured MOF-on-MOF hybrid materials, based on “Inside-Out-Growth” strategy, MOF nanocrystals are interspersed on matrix MOF nanotabiet forming modular 3D biscuit-like core/satellite hybridization system. Both the particle size of matrix MOF nanotabiet and the loadings of coated “satellite” MOF nanoparticle could be controlled by the amount of matrix MOF and capping agent added. The composites structure and growth mechanism are detailed analysed and discussed. It is expected that the biscuit-like MOF-on-MOF nanocomposites would be beneficial for wide applications of MOFs due to their versatile structure and properties.

**CP5.05**

**Multi-Shelled MOF-INP Composites Synthesized by a Sequential Etching/Re-Growth Approach Inhar Imaz1, Civan Avci1, Amirali Yazdi1, Javier Arinez-Soriano1, Arnau Carne-Sanchez1,2, Vincent Guillerm3, Carlos Carbonell1,4 and Daniel Maspoch1,4; 1Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Bellaterra, Spain; 2Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Kyoto, Japan; 3Department of Chemistry, University of Miami, Miami, Florida, United States; 4Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain.**

Modelling the shape of metal–organic framework (MOF) crystals is important for understanding their crystallization and useful for myriad applications. Well studied for inorganic particles, the controlled shaping of materials has been one of the key challenges in the advent of all technologies. Up to date, two main strategies namely top-down (e.g. etching, lithography, etc...) and bottom-up (e.g. use of surfactants, controlled self-assembly, etc...) have been employed to design materials with specific shapes. However, despite the many advances in shaping of inorganic nanoparticles (INPs), post-synthetic shape control of MOFs and, in general of molecular crystals, remains embryonic. Herein, we will firstly show a simple wet-chemistry process to control the anisotropic etching of colloidal ZIF-8 and ZIF-67 crystals. Our work enables uniform reshaping of these porous materials into unprecedented morphologies, including cubic and tetrahedral crystals, and even hollow boxes, by an acid–base reaction and subsequent sequestration of leached metal ions. Then, we will show how ZIF-8/-67 crystals can be re-grown on top of the cubic, tetrahedral and hollow etched crystals. This etching/re-growth method allows the creation of ZIF-8-on-ZIF-67 (and viceversa) composites in which the shape of both, the internal and external ZIF crystals, is controlled. Finally, we will demonstrate that a collection of multi-shelled MOF-INP composites can be created by attaching INPs on the ZIF crystal surface before the re-growth step. Following this approach, the synthesized multi-shelled MOF-INP composites can be made controlling the nature of the INPs (e.g. Au, Pd, and Pt), the INP shape (e.g. spherical, cubic, etc.), the INP size (from 8 to 50 nm), and the ZIF crystal shape and thickness. We anticipate that, by controlling the positioning of at least two types of INPs, these multi-shelled MOF-INP composites can be used as catalysts for cascade reactions.References:1. C. Avci, J. Ariñez-Soriano, A. Carné-Sánchez, V. Guillerm, C. Carbonell, I. Imaz, D. Maspoch Angew. Chem. Int. Ed. 2015, 54, 14417.

**CP5.06**

**Magnetic Metal-Organic Frameworks for Highly Efficient CO₂ Capture and Remote Trigger Release Haiqing Li1, Muhammad M. Sadiq1, Kiyonori Suzuki2, Christian Doblin1, Seng Lim1, Paolo Falcaro3 and Matthew Hill1; 1CSIRO, Clayton, Victoria, Australia; 2Monash University, Clayton, Victoria, Australia; 3Institute of Physical and Theoretical Chemistry, Graz, Austria.**

A number of metal-organic frameworks (MOFs) have been extensively explored for post-combustion CO₂ capture due to their ultrahigh specific surface area [1]. However, the significant energy penalty for the regeneration of MOF adsorbents greatly limits their widespread application. Large quantities of electrical energy (as much as 40% of the plant’s capacity) are required to deliver the pressure or temperature changes required for vacuum or temperature swing adsorption processes [1,2]. To address this issue, recent research demonstrated that UV and visible light
could act as alternatives which are not parasitic to the energy of the power plant [3]. However, the ability to scale these concepts could be challenging given the opaque nature of solid adsorbents. A more penetrating form of radiation could have a greater effect on triggering the release of adsorbed CO₂ from large quantities of adsorbent. In this regard, we present a set of magnetic framework composites (MFCs) which incorporate different amounts of Fe₃O₄ magnetic nanoparticles (MNPs) within Mg-MOF-74 frameworks [4]. When exposed to an alternating magnetic field, the MNPs within the MFCs acted as ‘nanoheaters’ to generate localised heat, triggering the release of the large majority of adsorbed CO₂ from the MFCs. The distributed nature of these nanoheaters proved crucial to overcoming the thermally insulating nature of MOFs, which is a key barrier to their use at scale in temperature swing settings. In addition, as the MNP content increased in the range tested, the specific surface area and hence the CO₂ adsorption capacity of the corresponding MFC was significantly enhanced. This is the first successful exploration in the development of MOF composites which, not only, can be effectively regenerated in a remote manner, but also maintain a substantially high CO₂ adsorption capacity. References[1] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herrn, T.-H. Bae, J. R. Long, Chem. Rev., 2012, 112, 724.[2] D. M. D’Alessandro, B. Smit, J. R. Long, Angew. Chem. Int. Ed., 2010, 49, 6058.[3] R. Lyndon, K. Konstas, B. P. Ladewig, P. D. Southon, C. J. Kepert, M. R. Hill, Angew. Chem. Int. Ed., 2013, 52, 3695.[4] H. Li, M. M. Sadiq, K. Suzuki, R. Ricco, C. Doblin, A. J. Hill, S. Lim, P. Falcaro, M. R. Hill, Adv. Mater., 2016, 28, 1839.

**CP5.07**

**Incorporation of a Ru and an Ir Complex Metallolinkers into UiO-67 for the Product-Selective Photocatalytic CO₂ reduction**

Shuhei Mine, Takashi Kajiwara, Masakazu Higuchi and Susumu Kitagawa; Kyoto University, Kyoto, Japan.

Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) have attracted much attention as a new heterogeneous catalyst because of their designability and large surface areas. The transformation of gaseous molecules catalyzed by PCPs is of particular interest due to their gas adsorption properties. Although several research groups reported PCP catalysts for CO₂ reduction with a characteristic focus upon the stability of catalysts or their recyclability, almost all of these research used PCPs as just a solid heterogeneous catalyst. Recently we have reported that a PCP catalyst has high catalytic activity for CO₂ reduction under low CO₂ concentrations, resulting from the synergy of its gas adsorption and catalytic properties. The result shows that PCPs are promising catalysts with multi-functions, which are difficult to achieve with common heterogeneous catalysts. In this study, a new ternary PCP composite, comprising a Ru complex as a CO₂ reduction catalyst, an Ir complex as a photosensitizer, and UiO-67 as a PCP, was successfully synthesized. The hybrid material was characterized by X-ray powder diffraction, thermogravimetric analysis, gas adsorption measurement, STEM-EDX and ¹H NMR digested by HF aq. The photochemical CO₂ reduction was carried out by utilizing this PCP composite in the presence of a sacrificial electron donor and solvent, producing predominantly HCOOH, a two-electron reduction product of CO₂. In stark contrast, the reaction utilizing the PCP composite with only Ru catalyst together with homogeneous Ir photosensitizer afforded CO, another two-electron reduction product of CO₂, mainly. In the presentation, this product selectivity (CO/HCOOH) in the CO₂ reduction will also be described. 1. C. Su et al., Chem. Soc. Rev., 2014, 43, 60112. Chong-Chen Wang et al., J. Mol. Struct. 2015, 1083, 1273. T. Kajiwara et al., Angew. Chem. Int. Ed. 2016, 55, 26974. Karl Petter Lillerud et al., J. Am. Chem. Soc., 2008, 130, 13850.

**CP5.08**

**Assembly of Ruthenium-Based Complex into Metal-Organic Framework for Area-Selected Luminescence and Enhanced Photon-to-Electron Conversion Efficiency**

Yanqun Tang, Wanhong He, Dongpeng Yan and Xu Xiang; Beijing University of Chemical Technology, Beijing, China.

Host-guest photofunctional materials have received enormous attention in the last decades due to their potential and broad applications in photonic and optoelectronic aspects. Studies on the assembly of guest chromophores into host MOFs have gradually increased, although the examples were still limited to date. These guest@MOF systems can result in new functionalities (such as tunable emission and enhanced photo/thermal stabilization) relative to their individual components due to the host-guest interaction and the isolating effect of the MOF on the guest molecules. During the construction of such an MOF-based host-guest system, how to rationally select the matching guest species and host porous topologies remains a major challenge. Here, a photoactive ruthenium-based complex was encapsulated into the biphenyl-based metal-organic framework (MOF) as a new host-guest material. The assembly (named as Ru@MOF) presented interesting two-color blue/red luminescence at the crystal interior and exterior regions. In addition, we observed up-conversion emission and an enhanced photoluminescence lifetime associated with the pristine Ru complex. Furthermore, the Ru@MOF was attached onto the rutile TiO₂ nanoarray electrode, which exhibited 5.5 times higher anode photocurrent and higher photon-to-electron conversion efficiency compared to that just modified by the Ru complex itself. The photocurrent showed the dependence on the loading amount of guest molecules in the MOF. The determination on the energy levels among semiconductor TiO₂, Ru complex and MOF confirmed the favorable photo-generated electron transfer pathway, which accounts for the photocurrent enhancement. It could be expected that, by the suitable choices of MOF and photoactive molecules with matching energy levels and desirable emissive wavelengths, the host-guest assemblies may be extended to other systems which have considerable flexibility and potential applications for designing a variety of luminescent and optoelectronic materials.

**CP5.09**

**Design of MOF Composites for Expanding Their Application Opportunities**

Matijaz Mazaj¹, Tomaz Cendak¹, Gianpiero Buscarino¹, Sebastijan Kovacic² and Natasa Zabukovec Logar²; 'National Institute of Chemistry, Ljubljana, Slovenia; 'Department of Physics and Chemistry, University of Palermo, Palermo, Italy.

MOFs with high external surface areas, void accessibilities and high density of open-metal sites enable wide range of application possibilities. However, MOF’s implementation in industrial scale is still rather limited. The main reasons lie in some cases in their chemical instability in solvothermal and hydrothermal conditions and in the shaping processes challenges. Various post-synthesis modification approaches have been already used in order to overcome these issues. The preparation of different MOF-containing composites is one of the possible paths. In this contribution the examples of MOF crystallization within mesoporous silica and nanoporous polymer matrices are described.
along with structural and sorption characterization investigations in order to address the above described challenges. MOF nanocomposites were prepared using two different paths. (1) MOF/mesoporous silica. Confined-space formation of HKUST-1 within the N₂-functionalized mesoporous FDU-12 silica matrix possessing ultra-large spherical mesopores was achieved by Cu²⁺ impregnation within the mesopores in the first step and solvothermal treatment with the 1,3,5-benzenetricarboxylic acid in the second step. In this way, HKUST-1(Cu) crystallized within the silica cavities. TEM, NMR and EPR methods proved that the crystalline MOF phase is anchored within the pores of silica matrix. Composite showed significant improvement of structural stability upon exposure to humid environment and comparable sorption properties for CO₂ and H₂ if compared to the parent MOF material. (2) MOF/polyHIPE. Different approaches of MOFs incorporation of into the high internal phase emulsion polymer homogenous were used to achieve homogenous immobilization of MOF phases within the polymer walls. With the first approach, MIL-100(Fe) was directly mixed within the monomeric solution. Second approach included post-synthesis crystallization of MOF phase from metal-oxide/polyHIPE nanocomposite. The latter approach which enabled high loadings of MOF phase was used to synthesize HKUST1/polyHIPE and MOF-5/polyHIPE composites. The procedure enables the design of heterostructures with different shaping possibilities retaining the accessibility of sorption and catalytic sites of MOFs.

CP5.10 Immobilization of Protein on Nanoporous Metal-Organic Framework Materials Chia-Her Lin and Hsi-Ya Huang; Department of Chemistry, Chung Yuan Christian University, Taoyuan City, Taiwan.


CP5.11 Nanoreactors Based on Metal-Organic Frameworks—Synthesis and Their Application Dawei Wang; School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou, China.

Nanoreactors have been extensively studied for their applications in advanced catalysis, controlled delivery, enzyme chemistry, and biological imaging. Typical nanoreactors possess core-shell or yolk-shell structures, which consist of active cores/yolks (for example, catalytic nanoparticles or enzymes) and permeable shells (porous silica, carbon, metal oxide, polymer, virus capsid, etc). The permeable shells are essential for nanoreactors, since they can provide sufficient space for reactions to take place in the nanoreactor, allow selective/controlled mass transfer of reactants, and keep all the yolks active by encapsulating every yolk in the permeable shells and stabilizing every yolk against aggregation or sintering. Metal-organic frameworks (MOFs), which feature porous crystalline structure, angstrom-level tunable pore apertures and exceptionally diverse structures/functionalities, are an ideal candidate for the nanoreactor shell. Here, we will present our work on the controlled synthesis of MOF-based nanoreactor and their application in catalysts and sensors.

CP5.13 A Mass-Based Method for Measuring the Solvent-Dependent Density of MOF Nanoparticles Thomas P. Burg1; Mario M. Modena; Patrick Hirschle; and Stefan Wuttke; ‘Max Planck Institute for Biophysical Chemistry, Göttingen, Germany; ‘Department of Chemistry, Ludwig-Maximilians Universität München, Munich, Germany.

MOF nanoparticles (MOF NPs) combine the richness of bulk MOF chemistry to the surface- and size-dependent properties of the nanoworld. After synthesizing MOF NP suspensions, the careful investigation of those cannot be underestimated. In this respect, density is unique in providing insights into the composition of the particles and, for porous materials, variation of particle density when these are dispersed in different solutions is symptomatic of permeability of the particles to the suspending fluid. However, current methods for measuring the density of NPs are limited to dry samples or they rely on the detection of hydrodynamic properties, which are often complex to interpret for non-spherical or porous objects. Here, we present a novel method for the direct characterization of the density of MOF NPs in solution by using micromechanical resonators with embedded microfluidic channels. Particle situated in the solution flowing through the embedded channel cause fluctuations of the resonance frequency of the resonators, and the amplitude of this fluctuations is directly proportional to the buoyant mass of the particles. By use of an autocorrelation analysis of the time-domain mass trace to separate the contribution of the particles with respect to the uncorrelated acquisition noise, variations of fluctuation amplitudes as a function of the suspending solution can be detected with high precision. By using this method, we were able to measure the density and permeability of MIL-101(Cr) MOF NPs in different solvents. Our measurements show that the buoyant mass of the particles remains almost constant when measuring in mixtures of ethanol and water, as both solvents can permeate the pores of the MOF nanoparticles: the buoyant mass of the particles corresponds to the excess mass of the metal clusters with respect to the excluded solution. However, when the particles are dispersed in mixtures of partially fluorinated liquids and ethanol, their buoyant mass show a clear dependence on the density of the solution. This is caused by the selective permeation of ethanol in the accessible regions of the particles and the exclusion of the larger partially-fluorinated molecules: the particles present a lower effective density, caused by the presence of ethanol inside. It is therefore evident how density measurements of particles in solution can provide unique information on the interaction between particles and fluids, and on the effective composition of the particles in solution. We expect that the method presented here can be of great help in the synthesis of MOF NPs whose targeted applications require operation in liquids.1 Modena MM, Wang Y, Riedel D, Burg TP, Lab on a Chip, vol. 14, pp. 342-350, 2014
There has been a rapid development in metal-organic frameworks (MOFs), especially porous MOFs, due to their high potential for diverse applications in the past decade. Recently, we have successfully synthesized a number of metal nanoparticle@metal-organic framework (MNP@MOF) composites and used them as high-performance catalysts. Metal nanoparticles (NPs) have been immobilized to MOFs by the solid-grinding method, impregnation method and double-solvents approach in combination with the H2 reduction, liquid-phase concentration-controlled reduction and the CO-directed reduction at the solid-gas interface, which exhibit excellent catalytic performances for various reactions, including hydrogen generation from chemical hydrides. MNP@MOF composites have also been used as templates/precursors for synthesis of metal@carbon composites, which are highly active for catalytic reactions such as oxygen reduction reaction (ORR). This talk will discuss the synthesis of metal nanoparticle@metal-organic framework composites and their application to catalysis. The author acknowledges coworkers for collaborations and AIST, METI and JSPS for financial support.

References

10:05 AM C6.02
Hard and Soft Templating of Hollow MOF and MOF-Core-Composite Architectures Darren Bradshaw; Chemistry, University of Southampton, Southampton, United Kingdom.

The preparation of metal-organic frameworks (MOFs) into application-specific configurations such as superstructure assemblies and hollow architectures is increasingly important as a way to enhance MOF properties and increase their relevance across diverse applications. This can often be achieved using appropriate templating strategies, where particles, supramolecular assemblies or emulsion droplets having the desired shape act as a template around which the MOF can form. If the template is itself active then this can be left in place to form MOF-composites with enhanced properties, or the template can be removed if hollow or hierarchically porous materials are the target. In this presentation I will discuss both hard and soft templating routes to hollow MOF structures and composite architectures. Building on our previous work using Pickering emulsions, we have developed a one-pot method to access MOF-based microcapsules using a surfactant-free oil-in-water emulsion where the MOF shell is formed in-situ during the reaction. The MOF capsules can be subsequently etched in the presence of nitrogen-heterocycles to generate hollow cage-like structures which resemble the architectures found in biomineralised tissue and provide a potential release mechanism for encapsulated cargo. As a route to shaped MOF composites, capsules and yolk-shell structures, we have also used metal oxides (MO) as both metal source and hard-etchable template. The success of our strategy relies on a surfactant-assisted oxide surface passivation mechanism which allows the rate of MOF conversion to be carefully controlled, permitting the template shape to be fully maintained in the resulting composites. This provides ready access to a range of MO@MOF core-shell composite architectures of well-defined morphology including microspheres, star-shapes and nanowires. By selective etching of the oxide core hollow MOF replicas of these structures can be obtained, as well as providing access to yolk-shell structures of complex shape.

Metal-organic frameworks (MOFs) have received much interest because of the highly versatile nature of the material, which are constructed from organic ligands connecting metal ions into a crystalline framework structure. A recent progress in the field of MOFs has been made to develop multifunctional composite materials by including metal nanoparticles to synergize with the MOF for new applications. This is an important development because the MOF can serve many functions around the metal nanoparticles. Here we report Pd@coated@(H)2,3,5-benzenetricarboxylate (HKUST-1) as a novel hydrogen storage material. The HKUST-1 coating on Pd nanocrystals results in a remarkably enhanced hydrogen-storage capacity and speed in the Pd nanocrystals, originating from the charge transfer from Pd nanocrystals to HKUST-1. Another material, Cu@[Zr6O4(OH)4(4-BDC)]6 (BDC = benzenedicarboxylate) (UiO-66) demonstrated higher activity for methanol synthesis from CO2 and H2, compared to Cu@Al2O3. We will also present novel one-pot synthetic methods to produce composite materials including Ni@Ni2(dphp) (H4dhp=2,5-dihydroxyterephthalic acid) (MOF-74). References [1] G. Li, H. Kobayashi, J. M. Taylor, R. Ikeda, Y. Kubota, K. Mato, K. Takata, T. Yamamoto, S. Matsumura, H. Kitagawa, Nature Materials, 13 (2014) 802. [2] M. Mukoyoshi, H. Kobayashi, K. Kusada, M. Hayashi, T. Yamada, M. Maesato, Jared M. Taylor, Y. Kubota, K. Mato, T. Yamamoto, S. Matsumura, H. Kitagawa, Chem. Commun., 51 (2015) 12463.

10:45 AM C6.04
Design of MOFs-Salts Based Composites for Heat Transfer Applications Anastasia Permiakova1, Emilie Courbon2, Sujing Wang1, Farid Nouar1, Perine Normand2, Pierre Billemont2, Guy De Weireld2, Nathalie Steunou1, Marc Freire3 and Christian Serre1; 1UVSQ, Institut Lavoisier de Versailles, Versailles, France; 2Laboratoire de Thermodynamique et de Physique mathématique, Université de Mons, Mons, Belgium.

The efficient storage of renewable energies is very important for their development and thermochemical energy storage is a very promising technology. Energy storage materials are inorganic salts or adsorbents (i.e. zeolite, silica gel, activated carbon) or...
composite materials containing a matrix and an inorganic salt. The energy storage application relies on the release of heat energy as a result of an adsorption (adsorbent) or/and hydration process (salt). In comparison with other classes of porous solids, MOFs display a higher degree of chemical versatility and their structural properties (pore size and shape), functionality and physico-chemical properties (hydrophilicity, water stability) may be modulated. [1] Therefore, one advantage for MOFs lies in the possibility to tune their sorption behavior in terms of sorption capacity as well as position of the adsorption step (p/p0) together with a relatively low energetic regeneration cost. All these features make them relatively interesting candidates for heat storage based on adsorption method. In this work, we have studied a series of MOFs-salts composites prepared by combining inorganic salts (CaCl₂, SrBr₂, ...) and water stable porous metal (Cr³⁺, Fe³⁺, Al³⁺, Ti⁴⁺, Zr⁴⁺) polycarboxylates (i.e. MIL-100 (Fe), MIL-101 (Cr), MIL-127 (Fe), MIL-125-NH₂(Ti), UIO-66-NH₂(Zr), MIL-160). [2-4] The microstructural properties of these composites and their evolution upon ageing were fully characterized by combining multiple techniques (XRD, TGA, elemental analysis, SEM, EDX, N₂ sorption) showing the possibility to encapsulate a high rate of salt (30-60 wt.%) in the porosity of MOFs while preserving their structure. The study of their water sorption capacity suggests that composites with the highest CaCl₂ content present both a high energy storage and a good stability under adsorption-desorption cycles. 

References:

11:05 AM C6.05
In-Situ Growth of Porphyrinic Metal-Organic Framework Nanocrystals on Graphene Nanoribbons for Electrocatalytic Oxidation of Nitrite
Chung-Wei Kung¹, Yan-Sheng Li², Wei-Hung Chiang³ and Kuo-Chuan Ho¹
¹Department of Chemical Engineering, National Taiwan University, New Taipei City, Taiwan; ²Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan.

Porphyrins and metalloporphyrins have been proposed for various applications such as solar cells, catalytic systems, and electrocatalysis. Given several advantages of metal-organic frameworks (MOFs) including regular porosity and ultrathin surface area, various MOFs constructed from porphyrin-based linkers have been widely reported. Taking advantage of the high-surface-area characteristics of MOFs, a few recent studies have utilized the thin films of such porphyrinic MOFs for electrocatalytic applications [1-3], but it has been found that the performance is restricted by the sluggish linker-to-linker charge hopping process inside the MOF thin films. To improve the charge transport inside the porphyrinic MOF, in this study, graphene nanoribbons (GNRs) are incorporated with the nanocrystals of a water-stable porphyrinic MOF, MOF-525, by solvothermally growing MOF-525 in the suspension of well-dispersed GNRs. The nanocomposite, which is composed of the MOF-525 nanocrystals with the size of about 100 nm interconnected by numerous one-dimensional GNRs, is successfully synthesized. The functional groups on the edges of GNRs can initiate the nucleation of MOF nanocrystals, which prevents the aggregation of GNRs during the growth of MOF. Thus, a uniform nanocomposite of GNRs and MOF-525 nanocrystals without conspicuous phase separation is obtained. To the best of our knowledge, this is the first report to incorporate GNRs with MOFs. Due to the excellent dispersity, uniform thin films of the MOF-525/GNRs nanocomposite can be simply deposited on conducting glass substrates by using drop casting. The obtained thin film of MOF-525/GNRs nanocomposite is applied for electrocatalytic nitrite oxidation. The MOF-525 nanocrystals are served as a high-surface-area electrocatalyst toward nitrite and the interconnected GNRs act as conductive bridges to render facile charge transport. The thin film of MOF-525/GNRs nanocomposite thus exhibits a much better electrocatalytic activity for the oxidation of nitrite compared to both the thin films of pristine MOF-525 and GNRs. This study provides a rational strategy to improve the slow-charge-transport issue of MOF by incorporating a highly functionalized carbon material into an electroactive MOF, which results in a better performance in electrocatalysis; similar approaches may be generalized to other electroactive MOFs for various electrochemical applications. 

References:

11:25 AM C6.06
From Smart Optical Films to Superparamagnetic Composites for Sensing—Perspectives of Luminescent LnMOFs
Klaus Muller-Buschbaum¹, Larissa V. Meyer¹, Tobias Wehner¹, Karl Mandel³, Dieter Fischer¹ and Martin Jansen¹
¹Institute of Inorganic Chemistry, University of Würzburg, Würzburg, Germany; ³Fraunhofer ISC, Würzburg, Germany; ²MPI FKF, Stuttgart, Germany.

Luminescent MOFs have attracted a lot of attention in the recent years due to fine tuning options of chromaticity and efficacies, and according to their use as chemical sensors for various chemical species such as VOCs (volatile organic molecules), inorganic gas molecules and ions [1]. The lanthanides are the most prominent metals used to generate luminescent MOFs as they have an intrinsic luminescence mainly from 4f-states. Linkers can be broadly chosen from a large variety of carboxylates and aromatic amides that can function as suitable sensitizer for the metal centers or participate with their intrinsic fluorescence and phosphorescence. In the current presentation, we show the development of smart optical films of LnMOFs that can be switched from transparent for daylight to non-transparent for UV-light by the MOF luminescence [2]. Film thickness proves a crucial parameter for this kind of optical switch. Films with controlled thickness and optical properties are created by PVD with ultra short laser pulses in the femtosecond region (femto PLD), which marks a novel approach to transport MOFs via the gas phase without the use of thermal energy. Furthermore, the sensing capabilities of luminescent LnMOFs is presented for a novel, signal augmented sensing with composite particles [3]. The sensing of molecules such as water can thereby be carried out in large volumes of liquid phases with only small amount of the sensing device. The sensors are composites that have core/shell structures of the MOF on superparamagnetic Fe₃O₄ particles maintaining the properties of both parts: luminescence and superparamagnetism. The MOF luminescence is used for the sensing process itself by a luminescence change upon analyte interaction, whereas the superparamagnetism allows for collecting the composite particles subsequent to sensing. It is thereby responsible for the strong signal augmentation, because it renders...

SESSION C7: MOF Hybrids, Nanocomposites and Organic Networks—Molecular Cage Compounds

C: MOF Hybrids, Nanocomposites and Organic Networks
Chair: Qiang Xu
Tuesday Afternoon, September 13, 2016
Pacific Room

1:15 PM C7.01
Cavity-Mediated Catalysis in Metal-Organic Supercontainers Z. R. Wang and Yupu Qiao; Department of Chemistry, University of South Dakota, Vermillion, South Dakota, United States.

Chemists have long endeavored to emulate the elegance of enzymatic catalysis in synthetic systems. However, designing enzyme-like, cavity-mediated supramolecular catalysis remains a significant challenge due in part to product inhibition. We recently reported a new class of container molecules, namely, metal-organic supercontainers (MOSCs), which can be constructed from the assembly of divalent metal ions, carboxylate linkers, and sulfonatedcalix[4]arene-based container precursors. These MOSCs possess a number of attractive features, including their modular structure, multiple binding cavities, and tunable chemical functionalities. We demonstrate that these important characteristics have allowed the MOSCs to serve as promising enzyme mimics and that their catalytic efficacy can be switched on through both cavity mediation and small-molecule regulation.

1:35 PM C7.02

The modular assembly of intrinsically porous organic cages is an alternative to forming porous materials through extended networks that are chemically bonded in 3-dimensions. These materials have shown promise in separations, catalysis, encapsulation, sensing, and, more recently, as porous liquids. We have been developing an evolutionary algorithm targeted upon the discovery of optimal structures and properties for porous molecular materials. These molecules are typically synthesised from organic precursors through dynamic covalent chemistry (DCC). If we consider cages synthesised from imine condensation reactions alone, there are approximately 500,000 possible aldehyde and amine precursors, combining these in all the different possible topologies results in over 830 million possible porous organic cages. Therefore, either from a computational or synthetic perspective, it is not possible for us to screen all these possible assemblies. Our evolutionary algorithm automates the assembly of hypothetical molecules from a library of precursors. The software belongs to the class of approaches inspired by Darwin’s theory of evolution and the premise of “survival of the fittest”. Each generation of candidates is tested with simple calculations that predict their performance and these properties are then used as a measure of their fitness. The fittest candidates are most likely to survive to the next generation, but also random mutations of their features will occur, for example exchange or modification of their precursor components, and pairs of candidates will parent new offspring with mixtures of their features. We continue to evolve the molecules over many generations, until we have a final set of candidates for a specific application. We then carry out in depth assessment of these molecules, including of their formation energies, which we have previously found to be indicative of their relative ease of synthetic realisation. Our approach has already suggested promising targets, with preliminary evidence of their synthetic realisation. We are now focusing on predicting optimal organic cage targets for a range of applications such as encapsulation and separation.

Further, we are addressing questions such as which topologies or DCC reactions maximise void size or whether specific chemical functionalities promote targeted applications.

1:55 PM C7.03
Porous Molecular Crystals Ognjen Miljanic; Department of Chemistry, University of Houston, Houston, Texas, United States.

Porous materials have numerous applications, most of which are related to energy and fuels. The field of porous materials has grown rapidly during the past two decades by the development metal-organic (MOFs) and covalent organic frameworks (COFs). These modularly synthesized materials offer essentially infinite possibilities for structural variation, and therefore allow the preparation of materials with tailored thermal and chemical stabilities, pore sizes, shapes, and internal functionalities. However, COFs and MOFs are not perfect: as insoluble solid-state structures, they have essentially no solution processability, and many of MOFs and COFs are also hydrolytically sensitive. Work in my group aims to address these challenges by creating porous molecular crystals, in which individual building blocks are held together only by noncovalent interactions: hydrogen bonding and [π—π] stacking. These structures are fundamentally interesting, as they are quite rare: molecules prefer to closely pack in the solid state. At the same time, these materials promise to be practical, since they are soluble, easily characterized, and highly thermally, hydrolytically, and chemically stable. In addition, their noncovalent connections can expand or shrink in response to adsorbed analytes, thus constituting a piezochromic sensing mechanism. These structures have been used as adsorbents for fluorinated pollutants, hydrocarbons, and inhalation anesthetics. In this presentation, I will survey our research results in this area, and also describe two other classes of porous materials prepared by my group: fluorinated MOFs and the emergent class of porous macrocycles known as cyclobenzoins, which can be synthesized in a single step from commercially available starting materials.

2:15 PM C7.04
Coordination Star Polymers with a Metal-Organic Polyhedral Core—Towards Processable Porous Materials Nobuhiro Hosono[1] and Susumu Kitagawa[1]; Institute for Integrated Cell-Material Sciences, Kyoto University, Kyoto, Japan; Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan.
Star polymers, which are a class of branched macromolecules possessing more than three “arm chains” connected at an identical center, have attracted significant interest due to not only their topological architecture but also their unique physical properties originating from the compact macromolecular shape. Here we report a new class of star polymers, termed coordination star polymer (CSP), which have a metal-organic polyhedral core at the branch center. Porous coordination polymers (PCPs) and metal-organic frameworks (MOFs) have received considerable attention as a new class of synthetic porous materials that are constructed through self-assembly of organic ligand and metal ions. Metal-organic polyhedra (MOPs) are discrete cage-like analogue of PCP/MOFs. The CSPs are synthesized through both divergent and convergent route. The divergent route entails conventional living graft polymerization initiated from the periphery of MOP. On the other hand, the convergent route simply undergoes one-step solution mixing of linear polymers and metal ions, resulting in the identical CSPs with MOP core. This powerful method allows instant access to a wide variety of multi-component star polymers that conventionally have required highly skilled and multistep syntheses. In addition, the MOP-core CSPs can offer a novel design strategy for highly processable porous soft materials by using the coordination nanocages as a building component.

Reference


2:35 PM C7.05

Porous Organic Cages for Drug Delivery Sophie Miller1, Shan Jiang2, Andrew Cooper1 and David Fairen-Jimenez1; 1Department of Chemical Engineering and Biotechnology, University of Cambridge, Greenwich, Connecticut, United States; 2Department of Chemistry, University of Liverpool, Liverpool, United Kingdom.

Porous materials have shown significant promise in drug delivery applications due to their high surface areas for adsorption, tunable pore size and chemistry, and regular, well-defined porosity. While several inorganic or hybrid organic-inorganic porous materials have been studied as drug carriers, concerns exist regarding the potential toxic effects of metals present in these systems. Porous organic cages are individual organic molecules with intrinsic porosity that, under specific conditions, self-assemble window-to-window with close packing to yield all-organic crystals with continuous, interconnected channels. In this work, we present the first-ever evaluation of these porous organic cages, specifically CC3 and CC5, for their drug delivery properties and biocompatibility. Crystalline particles of CC3 and CC5 have been loaded with cancer therapeutics (dichloroacetate and α-cyano-4-hydroxycinnamic acid), caffeine (useful for medicinal and cosmetic applications), and calcein (a model fluorescent molecule), with loadings of up to 25% by mass achieved, as determined by thermogravimetric analysis. Drug release from loaded CC3 and CC5 over several days was tested under simulated biological conditions in phosphate buffered saline (PBS), and drug release curves were obtained via UV-vis spectrometry to determine the kinetics and efficiency of drug delivery. The materials have also been shown to be stable in both water and PBS for at least one week, with no loss in crystallinity observed in powder x-ray diffraction patterns. Finally, two cytotoxicity assays have been conducted using HeLa cells to determine the effect of these materials both on cell membrane permeability and on metabolic activity. Neither CC3 nor CC5 compromised cell membrane integrity up to a concentration of 3 mg/mL. While cells incubated with CC3 showed no reduction in metabolic activity, cells incubated with low concentrations of CC5 had 34% reduction in activity after 24 hours, and the effects of particle size and potential breakdown products on cytotoxicity are being examined.

3:15 PM C7.07

The Solvent-Dependent Continuous Breathing Behaviour of a Diamondoid MOF Elliot J. Carrington1, Ashleigh Fletcher2 and Lee Brammer1; 1Chemistry, University of Sheffield, Sheffield, United Kingdom; 2Chemical and Process Engineering, University of Strathclyde, Glasgow, United Kingdom.

Metal-organic frameworks displaying large structural responses to a range of external stimuli provide the potential to design highly responsive and tunable materials for a wide variety of industrial applications. Unfortunately these flexible MOFs represent only a small fraction of all currently known porous materials and despite the interesting behaviour and associated application potential, such phenomena remain poorly understood, often due to challenges in experimental characterisation. Our work aims to use detailed structural studies to improve the current knowledge in the field and has included the discovery of the novel continuous flexibility exhibited by the indium-based diamondoid MOF (NH2Me2)4[In(ABDC)]. The flexibility of the MOF results in large structural changes affecting both the pore shape and size, but occurs without the defined phase transitions observed in almost all MOFs.
flexible materials. This unusual behaviour allows access to a potentially infinite number of different of pore states, depending on the amount of guest contained within the pore, rather than a small number of distinct phases. The framework has been characterised by extensive in situ crystallographic analysis using both single crystal and powder X-ray diffraction. The magnitude of the flexible behaviour is highly dependent on the nature of the guests being adsorbed or removed, and can be seen to strongly affect the overall gas sorption properties. This behaviour is of particular relevance due to the very high CO vs. CH selectivity previously reported for the MOF in which the flexibility was not recognized. This presentation will explain the solvent-dependence in the continuous breathing mechanism, using the behaviour of (NH4Me)[In(ABDC)] during removal of both DMF and CHCl3, guest molecules as a case study. It will then relate the observed structural changes to the differences seen in the frameworks gas adsorption after removal of the two differing guests. I. G. Férey and C. Serre, Chem. Soc. Rev., 2009, 38, 1380–1399. New. A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel, and R. A. Fischer, Chem. Soc. Rev., 2014, 43, 6062–6096. B. Yuan, D. Ma, X. Wang, Z. Li, Y. Li, H. Liu, and D. He, Chem. Commun., 2012, 48, 1135–1137.

SESSION C8: MOF Hybrids, Nanocomposites and Organic Networks—MOF Composites II
C: MOF Hybrids, Nanocomposites and Organic Networks
Chair: Guangshan Zhu
Wednesday Morning, September 14, 2016
Pacific Room

9:45 AM *C8.01 moved to C7.05
Controlled Encapsulation of Catalysts into Metal-Organic Frameworks Chia-Kuang Tsung: Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts, United States.

Towards our long-term vision of precisely controlling active sites, our group focuses on incorporating catalysts into crystalline nanoporous materials, metal-organic frameworks (MOFs). The precise molecularly-defined pores intrinsic to the MOFs provide a new tool to control the catalytic transformations on the catalysts. We have developed methods to combine organometallic catalysts, enzymes, and nanoparticle catalysts with MOFs of precisely tuned pore structures to manipulate the reactions. Shi, F.-K.; Wang, S.-C.; Yen, C.-I.; Wu, C.-C.; Dutta, S.; Chou, L.-Y.; Morabito, J. V.; Hu, P.; Hsu, M.-H.; Wu, K. C. W.; Tsung, C.-K. Imparting Functionalities to Biocatalysts via Embedding Enzymes into MOF Nanocarriers with Feed-Through Porosity and Molecular Sieving. J. Am. Chem. Soc. 2015, 137, 10986-10994. Yuen, B.; Ma, D.; Wang, Z.; Li, Y.; Li, H.; Liu, D.; He, P.; and Tsung, C.-K. Metal-organic frameworks (MOFs) as protective coatings for long-term protection and preservation strategies are often required. The study of isolated living cells is essential to understanding complex biological functions, and has led to their application in cell therapy, diagnostics, drug screening and the dairy and beverage industries. Cells are typically encased by a lipid bilayer membrane that offers limited protection ex vivo, thus long-term protection and preservation strategies are often required. Here, we report for the first time the biomimetic mineralization of Metal-organic Framework (MOF) material as protective coatings for long-term protection and preservation strategies are often required. The study of isolated living cells is essential to understanding complex biological functions, and has led to their application in cell therapy, diagnostics, drug screening and the dairy and beverage industries. Cells are typically encased by a lipid bilayer membrane that offers limited protection ex vivo, thus long-term protection and preservation strategies are often required.
for living cells. Based on our previous work,\cite{4–6} we postulate that the formation of a robust MOF exo-skeleton under physiological conditions is triggered by the biomolecule rich surface of living cells. We posit that living cell surface can locally concentrate MOF precursors, leading to the formation of a MOF coating. We demonstrate that MOFs can be crystallized on living cell surface as an exoskeleton that offers protection from toxic compounds such as enzymes and antifungal drugs while still allowing transport of essential nutrients from the extracellular environment, thus maintaining cells alive. More importantly, we found that the MOF shell prevents cell division, leading to an artificially induced pseudo-hibernation state. Upon removal of the MOF coating, cellular functions, including division, are fully restored.\cite{4–6} We note that such precise control over cellular behaviour is analogous to that observed in some unicellular organisms, which construct and dissolve exterior coatings as a protective mechanism. Accordingly, employing MOFs as a strategy to mimic natural protective mechanisms provides a new promising tool for the further progress of single cell in medicine and biotechnology.\cite{1} E. Shapiro, T. Biezuner, S. Limannsson, \textit{Nat. Rev. Genet.} 2013, 14, 618–30.\cite{2} N. de Souza, \textit{Nat. Methods} 2011, 8, S1–S1.\cite{3} J. El-Ali, P. K. Sorger, K. F. Jensen, \textit{Nature} 2006, 442, 403–11.\cite{4} K. Liang, R. Ricco, C. M. Doherty, M. J. Styles, S. Bell, N. Kirby, S. Mudie, D. Haylock, A. J. Hill, C. J. Doonan, et al., \textit{Nat. Commun.} 2015, 6, 7240.\cite{5} K. Liang, C. Carbonell, M. J. Styles, R. Ricco, J. Cui, J. J. Richardson, D. Maspoch, F. Caruso, P. Falcaro, \textit{Adv. Mater.} 2015, 27, 7293–8.\cite{6} K. Liang, R. Ricco, C. M. Doherty, M. J. Styles, P. Falcaro, \textit{CrystEngComm} 2016, DOI: 10.1039/C5CE02549D.\cite{7} K. Liang, J. J. Richardson, J. Cui, F. Caruso, C. J. Doonan, P. Falcaro, \textit{Submitted}.

10:45 AM C8.04

Encapsulation of Bio-Inspired Ni and Ni/Fe Complexes into a Mesoporous MOF \textit{Lucciano Marchiol}1, Davide Balestri2, Deborah Brazzolotto2, Paolo Pelagatti3, Alessia Bacchi3, Vincent Arteo4, Carole Duboc5 and Marcello Gennari2; 1Chemistry, University of the Studi di Parma, Parma, Italy; 2CNRS UMR, Univ. Grenoble Alpes, Grenoble, France; 3CEA, Laboratoire de Chimie et Biologie des Métaux, Univ. Grenoble Alpes, Grenoble, France.

The permanent porosity, high surface area, high thermal and chemical stability and low crystal density make MOFs attractive for a myriad of applications \cite{1}. MOFs offer congenial conditions for incorporating guest systems that can be as diverse as gases, inorganic nanoparticles, small molecular complexes, or bioactive molecules \cite{2}. In the present work, we wished to incorporate into the cavities of mesoporous MOFs two bio-inspired metal complexes, the mononuclear NiL, and the heterobiometallic NiLFeCpCO complexes \cite{3}, where L is a tetradentate ligand exhibiting a N2S2 coordination mode. NiLFeCpCO is a structural and functional model of [NiFe] hydrogenases, which are enzymes catalyzing the reversible reduction of protons into dihydrogen at high rates and close to the thermodynamic equilibrium. Like NiLFeCpCO, NiL can act as an electrocatalyst for H2 production in organic solvents, even if it is slightly less active. The aim of this work was to build a composite material in which a MOF framework would serve as a robust and regular host for the inclusion of NiL and NiLFeCpCO complexes, in order to evaluate the influence of the confinement on the functional properties of the guests. Ideally, the MOF’s cavities should act as the second coordination sphere of a protein backbone in the enzymes. We choose PCN6’ as a host, according to the presence of mesoporous cavities (30x30 Å) capable of hosting relatively large metal complexes \cite{4}. Another important factor is the usual formation of large single crystals of PCN6’, which allows for the investigation of the host-guest assembly by means of single crystal

11:05 AM C8.05

Bio-Macromolecule Based MOF Composites \textit{Paolo Falcaro}1,2,3; 1Graz University of Technology, Graz, Austria; 2Commonwealth Scientific and Industrial Research Organisation, Melbourne, Victoria, Australia; 3University of Adelaide, Adelaide, South Australia, Australia.

Among the different classes of Metal-Organic Framework (MOF) composites prepared during recent years using ceramic, metallic and polymeric nanoparticles, a new emerging type of MOF composite has been recently obtained encapsulating biomacromolecules within MOFs.\cite{5,6,7} Thanks to different water-based synthetic approaches such as co-precipitation and biomimetic mineralization methods, different types of MOFs have been self-assembled around bio-active compounds (e.g. enzymes). This new bio-composites have shown unprecedented properties for the protection and release of proteins. This strategy enables the fast encapsulation of guests larger than micropores of MOFs. Remarkably, this novel approach overcomes the need for MOFs with pores larger than the hosted biomolecules, and enable one-pot syntheses as an alternative preparation route to post infiltration methods.\cite{8} Thus, MOFs are now considered promising materials for biotechnological applications as the encapsulation technique is inexpensive, effective and fast. In this presentation, an overview ranging from the exploitation of simple proteins and their constituents (amino acids) to complex biological systems for the formation of MOFs will be provided. The functional properties of these composites will be disclosed providing examples of other methods used for the encapsulation of proteins within MOFs, including the preparation of hollow MOF capsules.\cite{9,10} Comparison of the protective properties will be illustrated and the applications of proteins for the controlled localization of MOFs discussed.\cite{11} The exciting challenges and promising applications of these new MOF composites will be presented. References(1) Falcaro, Ricco, Yazdi, Imaz, Furukawa, Maspoch, Ameloot, Evans, Doonan \textit{Coord. Chem. Rev.} 2016.(2) Zhu, \textit{Xu Chem Soc Rev} 2014.(3) Doherty, Buso, Hill, Furukawa, Kitagawa, Falcaro, \textit{Acc. Chem. Res.} 2014.(4) Li, Kobayashi, Taylor, Ikeda, Kubota, Kato, Takata, Yamamoto, Toh, Matsumura, Kitagawa \textit{Nat. Mater.} 2014.(5) Lyu, Zhang, Zare, Ge, Liu, \textit{Nano Lett.} 2014.(6) Liang, Ricco, Doherty, Styles, Bell, Kirby, Mudie, Haylock, Hill, Doonan, Falcaro \textit{Nat. Commun.} 2015.(7) Shieh,
Molecules. Both (ii) and (iii) act to weaken the shear strength of the epoxy resin becomes more plastic by incorporating H2O rather than an OH resides in close proximately to the bond. (iii) group forming such an Al-O bond is enhanced when an H2O the epoxy resin contributes substantially to the strength of the interface and largeness of the epoxy molecule. In this explanation exists. Microscopic understanding of the mechanisms is essential to propose an innovative method to solve the problem. The first-principles simulation of such a system is difficult because it requires a large system size due to the inhomogeneity of the interface and largeness of the epoxy molecule. In this research we use the hybrid quantum (QM)-classical (CL) simulation method to treat such systems directly, which is analogous to QM/MM method for polymeric materials, but applicable to inorganic-organic interfacial materials. The water molecules are placed at the interface of the partly oxidized Al and epoxy sub-systems. The QM region composed of about 1,000 atoms is set at the interface region, which is described by the electronic density-functional theory (DFT) using our original real-space grid code. During a simulation run, the Al sub-system is displaced parallel to the interface at a constant speed of to monitor the force experienced by the epoxy resin sub-system. It is thereby found that the adhesion strength reduces more significantly as the degree of the moisture content increases, in accordance with the experimental observations. Microscopic analyses find the following key features; (i) The inter-atomic Al-O bond between the Al atom of the oxide and the O atom of the epoxide group in the epoxy resin contributes substantially to the strength of the interfacial adhesion. (ii) Dissociation of the O atom of the epoxide group forming such an Al-O bond is enhanced when an H2O rather than an OH resides in close proximately to the bond. (iii) The epoxy resin becomes more plastic by incorporating H2O molecules. Both (ii) and (iii) act to weaken the shear strength of the interfacial adhesion.

In this presentation, we will explore the opportunities offered by spatially integrating photoactive molecular building blocks into a crystalline lattice based on the paradigm of covalent organic frameworks (COFs), thus creating models for organic bulk heterojunctions. We will address means of controlling the morphology and packing order of COFs through additives, (1) in thin films, (2) and with spatially locked-in building blocks. (3) We will discuss different strategies aimed at creating electroactive networks capable of light-induced charge transfer. For example, we have developed a COF containing stacked thiophene-based building blocks acting as electron donors with a 3 nm open pore system, which showed light-induced charge transfer to an intercalated fullerene acceptor phase. (4) Contrasting this approach, we have recently designed a COF integrated heterojunction consisting of alternating columns of stacked donor and acceptor molecules, promoting the photo-induced generation of mobile charge carriers inside the COF network. (5) Due to the great structural diversity and the large degree of morphological precision that can be achieved with COFs, these materials are viewed as intriguing model systems for organic heterojunctions.

11:25 AM C8.06
Moisture-Induced Reduction of Adhesion Strength Between Surface Oxidized Al and Epoxy Resin—Dynamics Simulation with Electronic Structure Calculation

Shuji Ogata; Nagoya Institute of Technology, Nagoya, Japan.

The adhesive bonding is a key issue for advanced packaging and construction of electronic devices and systems. The bisphenol-A epoxy resin has been used widely as the bonding glue. One of the fundamental unsolved problems in the adhesion between metal and epoxy resin is that the adhesion strength reduces significantly in a moist environment. Although various possible mechanisms due to water have been suggested, such as the increased plasticity of resin, swelling of resin, corrosion of metal, and screened interatomic interaction between metal and resin, no detailed explanation exists. Microscopic understanding of the mechanisms is essential to propose an innovative method to solve the problem. The first-principles simulation of such a system is difficult because it requires a large system size due to the inhomogeneity of the interface and largeness of the epoxy molecule. In this research we use the hybrid quantum (QM)-classical (CL) simulation method to treat such systems directly, which is analogous to QM/MM method for polymeric materials, but applicable to inorganic-organic interfacial materials. The water molecules are placed at the interface of the partly oxidized Al and epoxy sub-systems. The QM region composed of about 1,000 atoms is set at the interface region, which is described by the electronic density-functional theory (DFT) using our original real-space grid code. During a simulation run, the Al sub-system is displaced parallel to the interface at a constant speed of to monitor the force experienced by the epoxy resin sub-system. It is thereby found that the adhesion strength reduces more significantly as the degree of the moisture content increases, in accordance with the experimental observations. Microscopic analyses find the following key features; (i) The inter-atomic Al-O bond between the Al atom of the oxide and the O atom of the epoxide group in the epoxy resin contributes substantially to the strength of the interfacial adhesion. (ii) Dissociation of the O atom of the epoxide group forming such an Al-O bond is enhanced when an H2O rather than an OH resides in close proximately to the bond. (iii) The epoxy resin becomes more plastic by incorporating H2O molecules. Both (ii) and (iii) act to weaken the shear strength of the interfacial adhesion.

1:35 PM C9.02
Microporous Graphene Frameworks For Gas and Energy Storage Applications

Ali Coskun; Department of Chemistry and Graduate School of Energy, Environment, Water, and Sustainability, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Microporous polymers attracted significant deal of attention in recent years due to their permanent porosity, chemical tunability, physicochemical stability and exceptional gas sorption properties. Incorporation of graphene nanoribbons (GNRs) or graphene sheets into microporous polymers, however, has been a significant challenge mainly due to their low solubility and high affinity to restack to form graphic layers. Graphene is composed of single-atom-thick, sp² hybridized carbon atoms that are bonded together in a two-dimensional hexagonal honeycomb lattice, and presents high π-surface area, excellent chemical, thermal, mechanical stability along with superior thermal and electrical conductivity. Importantly, microporous polymers incorporating either graphene or GNRs are expected to inherit some of their unique properties.
In an effort to prevent restacking and to take full advantage of high n-surface area of graphene, we introduced a permanent ‘spacer’ such as porosity between GNRs and graphene layers within the microporous polymers. We utilized both noncovalent and covalent approaches to form three-dimensional graphene frameworks. Recently, we also utilized bottom-up approach to introduce graphene nanoribbons up to 2 nm in length and 1.1 nm in width into graphene nanoribbon frameworks (GNFs) via catalyst-free Diels-Alder cycloaddition polymerization and subsequent FeCl₃-catalyzed intramolecular cyclodehydrogenation reaction. GNFs showed high thermal stability up to 400°C in air and exhibited BET surface areas up to 700 m² g⁻¹ along with promising gas separation properties. More recently, we have also shown elemental sulfur-mediated synthesis of a graphitic covalent triazine framework under catalyst- and solvent-free reaction conditions using 1,4-dicyanobenzene and elemental sulfur. This material was used as a robust cathode for high-performance lithium–sulfur batteries with very good cycling stabilities. [1] Patel, H. A.; Je, S. H.; Park, J.; Chen, D. P.; Jung, Y.; Yavuz, C. T.; Coskun, A., Nature Commun., 2013, 4, 1357.[2] Srinivasan, S.; Je, S. H.; Back, S.; Barin, G.; Buyukcakir, O.; Gulyey, R.; Jung, Y.; Coskun, A., Adv. Mater., 2014, 26, 2725–2729.[3] Song, K. S.; Coskun, A., ChemPlusChem, 2015, 80, 1127–1132.[4] Byun, Y.; Coskun, A., Chem. Mater., 2015, 27, 2576–2583.[5] Talapaneni, S. N.; Hwang, T. H.; Je, S. H.; Buyukcakir, O.; Choi, J. W.; Coskun, A., Angew. Chem. Int. Ed., 2016, DOI: 10.1002/anie.201511553.

1:55 PM C9.03
Covalent Triazine Frameworks as Platform for Heterogeneous Molecular Catalyst Development—From Powders to Shaped Spheres

Anastasiya Bavykina, Michiel Makkee, Freek Kapteijn and Jorge Gascon; Delft University of Technology, Delft, Netherlands.

There exists large interest in the use of multifunctional catalysts that can convert, selectively and reversibly, small molecules into fuels. In this scenario, formic acid (HCOOH) is particularly attractive as hydrogen storage chemical. Recovery of H₂ from formic acid becomes efficient in the presence of a catalyst. Hitherto, the most active catalysts for the transformation of formic acid into H₂ and CO₂ are homogeneous and transition-metal based. Some of these complexes can also – under different conditions – promote the reverse reaction: the hydrogenation of CO₂ into formic acid. This flexibility allows for the possibility of a storage-release cycle with hydrogen, the industrial realization of which remains a main challenge. From the perspective of practical application, immobilization of a molecular catalyst would facilitate matters, as a heterogeneous system provides ease in handling and recycling. We herein report a highly active, selective and air-stable molecular heterogeneous catalyst based on a Covalent Triazine framework (CTF), a porous organic polymer. In our system, Ir⁶⁺Cp⁺ (Cp⁺=pentamethylcyclopentadienyl) is coordinated to bipyridinic moieties in a mesoporous CTF. This CTF is built from a 1:2 ratio of 2,6-pyridinedicarbonitrile and 4,4'-biphenyldicarbonitrile.Upon dispersion in a 3M formic acid solution, instantaneously gas production started, which was determined by GC analysis to be a CO-free CO₂/H₂ (1:1) mixture. The catalyst could be recycled for at least four times under standard reaction conditions without any loss of activity. At a catalyst loading of 0.2 wt.% and at 80°C, the catalyst reached an initial TOF of 27000 h⁻¹, by far the highest reported for any heterogeneous catalytic system to date for this reaction.¹ In basic conditions, the same catalyst works for the direct hydrogenation of CO₂ to formic acid. In order to further explore the catalyst’s application potential we developed a one-step method for the fabrication of porous, highly stable and mechanically rigid CTF-based spheres. This was done using a phase inversion method with the polyimide Matrimid® as a binder. Coordination of Ir⁶⁺Cp⁺ proceeds analogously to that in CTF powder, but the CTF spheres display greatly enhanced handling and recycling properties.² This is notable, for CTF-based catalysts are generally tested in slurry operation as a powder, leaving the aspect of catalyst formulation or shaping ill-investigated. This presents a number of drawbacks, such as partial loss upon sampling, or recovery in catalyst recycling. With the performance of a highly efficient molecular catalyst, and the handling properties of well-defined and large spheres, we expect this type of CTF-based materials to play an important role in the development of new-generation H₂ storage-release catalysts. The potential for fuel cell application is appealing.[1] Bavykina et. al. ChemSusChem 2015, 8, p. 809[2] Bavykina et. al. ChemCatChem 2016, accepted

2:15 PM C9.04
Chemistry in the Confined Spaces of Porous Polymers and the Rough Road for Porous Diamond

Jeehye Byun¹, Nesibe A. Dogan², Hasmukh A. Patel³, Damien Thiron⁴, Ercan Ozdemir⁵, Saravanan Subramanian⁶, Mustafa S. Yavuz⁷, Mert Atilha⁶ and Cafer T. Yavuz⁶, ⁶; ¹School of Energy, Environment, Water and Sustainability, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ²Chemistry, Northwestern University, Evanston, Illinois, United States; ³Institute of Nanotechnology, Gebze Technical University, Kocaeli, Turkey; ⁴Metallurgy and Materials Engineering, Selcuk University, Konya, Turkey; ⁵Chemical Engineering, Qatar University, Doha, Qatar; ⁶Chemistry, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Porous polymers with rigid organic structures through a covalent backbone feature permanent voids that can be used for chemical activities. We have developed a family of nanoporous (pore size < 100 nm) covalent organic polymers (COPs), which show significant capacities and selectivities for gases (e.g. CO₂), and water contamination (e.g. heavy metals). We’ve shown that azo (N=N) bearing COP-68 show lack of N₂-phobicity by increasing temperature, in other words N₂-phobicity, leading to very high CO₂/N₂ selectivities. Under high pressures COP-1 shows a record high capacity of 5.6 g/g CO₂ uptake at high pressures. COP-83 has a capacity of 5 mmol/g at 298 K and 1 bar, and COP-97 shows an uptake of 8 % (w/w) CO₂ in 2 minutes from a simulated flue gas mixture. More recently, we introduced ethylene diamines on the walls of COP-115 through bromination intermediates, providing tunability in binding energy. In COP-122, we controlled spherical morphology and converted nitrile pendant groups to amines for further grafting chemistry. COP-150 is scalable into kg and provides a hydrocarbon backbone for post-modification. Order in porous polymers can be achieved through dynamic covalent chemistry, a source of instability. We’ve sought to use irreversible binding through charged substituent guiding for systems like porous diamond. After numerous failed attempts, our approach is now to lock directional growth in order to achieve ordered assembly.
The light-harvesting complex (LHC) in natural systems uses antenna pigments for light-harvesting. Each pigment contains porphyrin units in a well-ordered J-aggregation, leading to a coherent migration of excitons to the photosynthetic reaction centre via excitonic coupling among porphyrin units. To mimic this strategy of nature, a synthetic light-harvesting unit should be stacked in an ordered J-aggregate giving the lower excitonic state than that of its single unit, and permitting excitons to funnel through the ordered aggregate. Through a combination of experiments and molecular dynamics (MD) simulations, we demonstrated that two-dimensional porphyrin organic network (PON) has ordered J-stacking of the porphyrin units, thus enable broadband light absorption and long-range exciton transfer to the reaction centre. The power X-ray diffraction experiment and MD simulation demonstrate that this J-stacking is composed mainly of two J/H and J/J configurations. The UV-visible absorption spectrum further proves that J-stacking gives broadband light absorption via strong excitonic coupling between each porphyrin sheet. Also, amplified fluorescence quenching experiments show that J-stacking enables long-range exciton migration to the reaction centre with an approximately 20-fold enhancement in collection of photons, in a similar manner to the LHC of a natural system. Our theoretical investigation supports that two dimensional J-stacks of J/H and J/J configurations can facilitate efficient exciton transfer.

Fabrication of Thin Porphyrin-Based Polymers via Conversion of SURMOFs

Porous Organic Cages (POCs) are wholly organic molecules that contain an intrinsic, shape persistent cavity that can be accessed via windows within the cage structure. As a consequence of their discrete nature they are soluble in common organic solvents and can be readily processed in solution to obtain polymorphic crystalline or amorphous phases, co-crystals, or composite materials. In order to be considered porous the intrinsic cage cavities must be connected in the solid state by a 1, 2, or 3-dimensional pore network. POCs have similarities with both metal-organic frameworks (MOFs) and porous coordination polymers (PCPs) in that they can pack together in an ordered (crystalline) or amorphous manner. However, unlike these network materials POCs are synthesised first, then separately assembled in the solid state. Starting with our simplest imine-based cage, CC1, self-assembled from 6 molecules of ethylenediamine and 4 molecules of 1,3,5-triformylbenzene, we have been able to extensively modify both the outer surface and the windows of the cage, while maintaining the same core structure. Analysis of these isostructural cages has allowed us to study the effect of these modifications on the porous properties of the organic cages. We have found that even subtle changes to the outer surface of the cage can drastically effect how the cages pack together, and hence pore connectivity in the solid state. Using crystal structure prediction (CSP) we were able to understand the interaction between single or multi-component cage mixtures and predict the effect of the surface modification on the crystal packing of cages. Guided by CSP we were able to select co-formers in order to synthesise co-crystals using a ‘mix and match’ strategy. This has led to the formation of molecule alloys with tunable properties. Randomisation of the surface functionality has allowed the development of amorphous cage mixtures that can be used as porous additives when combined with non-porous molecules. By further frustrating the packing of the amorphous cages we were able to increase the solubility of the cages to such an extent that when combined with a bulky solvent we were able to form a porous liquid. Finally, the introduction of a blocking group into the cage windows has allowed the formation of a series of pore constricted organic cages, which can be directed to pack in an isoreticular manner via prudent crystallisation solvent choice or co-crystallisation with a directing co-former — a non-trivial achievement for POCs.
The discovery and tailoring of materials towards energy applications is an important goal of current research. Carbon capture and storage as well as photocatalytic generation of solar fuels stand out as they are promising tools to fight the effects of global warming and provide a basis for sustainable and clean energy. Covalent organic frameworks (COFs) are light-weight materials and do not contain problematic elements such as heavy and toxic metals, which makes them suitable candidates for a new generation of energy materials. In 2014, we discovered the first photocatalytically active COF - hydrazone-linked TFPT-COF – which continuously produces hydrogen from water under visible light irradiation in the presence of Pt as a proton reduction catalyst (PRC) and a sacrificial electron donor.[1] We have further shown that photocatalytic activity can also be found in azine-linked COFs and that the gradual change in optoelectronic properties across a series of azine-COFs with different nitrogen content directly translates into varying levels of hydrogen evolution.[2] Furthermore, we have demonstrated that the sorption properties of COFs can be precisely tuned by polarity engineering of the pore surface in isosstructural azine COFs.[3] This knowledge is now being combined to establish new COF-based photocatalysts which at the same time are efficient at capturing CO\textsubscript{2}. We demonstrate how we can rationally tune photocatalytic activity, CO\textsubscript{2} capacity and CO\textsubscript{2} over N\textsubscript{2} sorption selectivity and present an in-depth characterization by solid-state NMR spectroscopy, FT-IR, X-ray diffraction and sorption analysis.[1] L. Stegbauer, K. Schwinghammer, B. V. Lotsch, Chemical Science 2014, 5, 2789-2793.[2] V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld, B. V. Lotsch, Nat Commun 2015, 6.[3] L. Stegbauer, M. W. Hahn, A. Jentys, G. Savasci, C. Ochsenfeld, J. A. Lercher, B. V. Lotsch, Chemistry of Materials 2015, 27, 7874-7881.

**CP10.02**

**Covalent Organic Frameworks as Platforms for Carbon Capture and Light-Driven Hydrogen Evolution**

Kerstin Gottschling\textsuperscript{1,2}, Linus Stegbauer\textsuperscript{1,2} and Bettina Lotsch\textsuperscript{1,2}; \textsuperscript{1}Max Planck Institute for Solid State Research, Stuttgart, Germany; \textsuperscript{2}Ludwig-Maximilians-Universität München, Munich, Germany.

The field of gold nanocatalysts has been thoroughly studied and has rapidly become a promising system for hydrogenation and epoxidation of alcohols and aldehydes as well as oxidation and even aerobic oxidation of alkanes.[1] Covalent organic frameworks (COFs) are lightweight and porous materials well-known for their applications in gas storage, catalytic supports, semiconductive and photoconductive devices. In addition to other porous materials such as charcoal, dendrimers, polymers, mesoporous silica, zeolites, and MOFs, metal doped COFs have also been applied as catalysts for various organic reactions[2]. Although nanoparticle decorated COFs have been used as catalyst for a few organic reactions, including selective oxidation and hydrogenation, cross-coupling reactions, C–H activation, nitro reduction, glycerol oxidation, and electron transfer reactions, the surface area of the COF was remarkably decreased after
nanoparticle formation inside the pores of COFs [3]. In order to overcome this issue, we believe that the synthesis of new porous materials having nanoparticles embedded on the polymer network is desperately needed[4]. In this study, Au nanoparticles were stabilized with tri-armed molecule having thiol ends (3SH) by means of gold-thiol linkage. Then, the disulfide-linked porous network was synthesized by oxidative coupling reaction of 3SH and 3SH-covered Au nanoparticles in order to generate robust nanogold polymer networks. This novel material was characterized by using UV, TEM, SEM, solid-state NMR and FTIR. The catalytic efficiencies of these nanogold networks were further investigated for organic coupling reactions.

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CP10.04 Reversible Nitroxide Exchange Reaction for the Synthesis of Covalent Organic Frameworks Qi An1,2, Isabelle Wessely2, Peter Weidler1, Peter Krolla-Sidenstein1, Hartmut Gliemann1, Christof Woell1, Stefan Brase1,2 and Manuel Tsotsalas1; 1IFG, KIT, Eggenstein-Leopoldshafen, Germany; 2IOC, KIT, Karlsruhe, Germany; 1ITG, KIT, Karlsruhe, Germany.

Covalent Organic Frameworks (COF) are materials of exceptionally low densities, which are particularly attractive for application in catalysis, gas storage, separation and sensing as well as applications in biology and medicine.[1] Thermal radical nitroxide exchange reactions have been successfully used for synthesis and functionalization of polymers. In these processes, thermal C-O bond homolysis in alkoxyamines leads to transient carbon-centered radicals and persistent nitroxide radicals. If homolysis of an alkoxyamine is performed in presence of an additional nitroxide radical, the thermodynamic product will be obtained. [2] Here we present the approaches to use nitroxide exchange reaction for the synthesis of COFs. The advantage of this reaction is the reversibility of the thermodynamic bonds, which allows for self-healing of the obtained COF. The progress of the COF formation can be easily followed by EPR spectroscopy or even be self-reporting, if profluorescent nitroxide molecules are used for the synthesis. [3] The high side-group tolerance of the nitroxide exchange reaction allows the incorporation of multiple functional groups and can be performed in almost any solvent, even water.[1] (a) J.-X. Jiang et al. Top. Curr. Chem. 2010, 293, 1; (b) R. Dawson et al. Progress in Polym. Sci. 2012, 37, 530; (c) J. R. Holst et al. Macromolecules 2010, 43, 8531.[2] (a) B. Schulte, M. Tsotsalas, M. Becker, A. Studer, L. De Cola. Angewante Chemie 2010, 49, 6881-6884. (b) L. Tebben, A. Studer. Angewante Chemie 2011, 50, 22, 5034-5068.[3] J.P. Blinksco, K.E. Fairfull-Smith, B.J. Morrow, S.E. Bottle Aust. J. Chem. 2011, 64, 373-389.

CP10.05 Molecular Docking Sites Designed for the Generation of Highly Crystalline Covalent Organic Frameworks Laura Ascherl1, Torben Sick1, Johannes T. Margraf1, Saul H. Lapidus2, Mona Cali1, Christina Hettstedt1, Konstantin Karaghiosoff3, Markus Doblinger1, Timothy Clerk1, Karen W. Chapman3, Florian Auras4 and Thomas Bein1; 1Department of Chemistry and Center for NanoScience, University of Munich, Munich, Germany; 2X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois, United States; 3Computer-Chemie-Centrum, Friedrich-Alexander-University Erlangen-Nürnberg, Erlangen, Germany.

Covalent organic frameworks (COFs), formed by connecting multideterminate organic building blocks through covalent bonds, provide a platform for designing multifunctional porous materials with atomic precision. Potential applications in optoelectronics would benefit from a maximum degree of long-range order within the framework. This has, however, remained a major challenge. We have now developed a synthetic concept for allowing consecutive COF sheets to lock in position during crystal growth, thus minimising the occurrence of stacking faults and dislocations. Hereby, the screw-like 3D conformation of the molecular building units is utilized to generate well-defined periodic docking sites, guiding the attachment of successive building blocks and promoting long-range order during COF formation. This way, we were able to realize COFs featuring an unmatched degree of crystallinity and well-defined crystal facets. Studying a series of COFs enabled us to gain insights into the conveyance of configurational information during COF formation, highlighting the importance of controlling and designing intra- and interlayer interactions. Having demonstrated the generality of this approach for a number of combinations of different building blocks and bridging units, we expect this concept to be applicable to a broad variety of functional building blocks and to promote the establishment of COFs in organic electronics. Reference Ascherl, L., Sick, T., Margraf, J. T., Lapidus, S. H., Cali, M., Hettstedt, C., Karaghiosoff, K., Döblinger, M., Clark, T., Chapman, K. W., Auras, F., Bein, T. Molecular docking sites designed for the generation of highly crystalline covalent organic frameworks, Nature Chem. 8, 310-316 (2016).

CP10.06 From Highly Crystalline to Outer Surface-Functionalized Covalent Organic Frameworks—A Modulation Approach Mona Cali1, Torben Sick, Mirjam Dogru, Markus Doblinger, Stefan Datz, Harald Budde, Achim Hartschuh, Florian Auras and Thomas Bein; Department of Chemistry and Center for NanoScience, University of Munich, Munich, Germany.

Covalent organic frameworks (COFs) represent an emerging class of crystalline, porous materials exhibiting unique structural and functional diversity. By combining multideterminate building blocks via covalent bonds, two- or three-dimensional frameworks with defined pore size and high specific surface area can be constructed.[1] Crystallinity and porosity are of central importance for many properties of COFs, including electronic transport. [2] Here, we present a new method for strongly enhancing both aspects through the introduction of a modulating agent in the synthesis. The competition between the bridging COF building block and the terminating modulation agent influences the dynamic equilibrium during framework formation, slowing down the COF growth and supporting the self-healing of crystal defects. Under optimized conditions, the crystal domains of COF-5 reach several hundreds of nanometers. The obtained materials feature

CP10.08 Modeling the Formation of COF-5 Michael Gruenwald and Hoang Vu Nguyen; Chemistry, University of Utah, Salt Lake City, Utah, United States.

Two-dimensional covalent organic frameworks (2D-COFs) are a promising family of porous materials but are extraordinarily difficult to synthesize with high-quality crystals. In an effort to reveal the kinetic bottlenecks and prevalent defects that plague 2D-COF formation, we are developing a coarse-grained model for the molecular constituents of the prototypical COF-5. In this model, covalent bond formation is treated only schematically, but the energetics of polymerization and stacking in solution, as well as fluctuations in bond geometry, as gauged against ab-initio calculations, are well represented. Preliminary molecular dynamics simulations of our model reveal a rich aggregation behavior that strongly depends on synthetic conditions. We discuss the implications of our simulations for the synthesis of highly crystalline 2d-COFs.


Covalent Organic Frameworks (COFs) have become of great interest in materials chemistry due to their potential application in photovoltaic and electrochemical devices, and in gas storage and separation systems. The light elements that compose these frameworks (C, H, O, B, N), their high porosity (BET surface areas > 1000 m$^2$ g$^{-1}$), and strong covalent bonding holding the framework gives way for their potential use in the mentioned applications. COFs usually crystallize as insoluble powders and their processing as materials for devices has been limited. This study is centered on a new processing strategy in which powder samples of isotropic bulk 2-dimensional COFs become highly anisotropic. Crystallographic studies of the processed COFs indicate the preferred orientation features between the h00 and the 00l planes. COFs of different functionality (boronate, boroxine, imine, triazine) and symmetry (hexagonal and tetragonal) were studied, as well as their stability and application to devices indicating the generality of our approach.


Two dimensional layered covalent organic frameworks (COFs) are promising candidates for light weight high density gas storage applications. The structure of layered COFs were reported in the slipped stacking where the neighboring π-π stacked COF layers are not exactly on top of each other. The interlayer π-π interaction and slipping can be tuned by using appropriate organic building units to minimize the interaction energy. Such slipped structures can enhance the gas adsorption and separation properties of COFs. To explore the effect of slipping, we have studied the CO$\text{2}$ and N$\text{2}$ adsorption characteristics of TpPa1, TpBD and polyimide (PI) COFs in the slipped structures with varied slipping direction and distance from eclipsed AA to AB stacking. The simulated CO$\text{2}$ adsorption isotherm in slipped TpPa1 COF was in good agreement with experiments, compared to the eclipsed AA stacked structure. This shows that the slipped structures are correct representation of COFs for simulation studies. Further we found that the oxygen atoms of a COF with nearby hydrogen atoms are most promising sites for CO$\text{2}$ adsorption. The adsorption mostly take place adjacent to the interlayer region in AA stacked COFs, and adjacent to the COF layer in the slipped COFs. References 1. S. Chandra, T. Kundu, S. Kandambeth, R. Babarao, Y. Marathe, S. Kunjir, and R. Banerjee, Journal of the American Chemical Society, 2014, 136, 6570 - 6573. IF: 11.444. 2. S. Chandra, B.P. Biswal, S. Kandambeth, B. Lukose, M. Kunjir, M. Chaudhary, R. Babarao, T. Heine, and R. Banerjee, Journal of the American Chemical Society, 2013, 135, 17853-17861.

CP10.11 Metal-Organic Polyhedra as a Platform for Porous Materials Zachary Perry and Hong-Cai Zhou; Chemistry, Texas A&M University, College Station, Texas, United States.

Porous materials composed of discrete molecular coordination entities represent a relatively small class of metal-organic coordination compounds. This is in part due to the difficulty in achieving stability in these structures during solvent removal processes. We have identified three features which must align to allow for porosity to be observed after removal of solvent. First the metal-ligand coordination bonds must be stable with respect to desolvation, second cage orientation must be aligned such that the oxygen atoms of a COF with nearby hydrogen atoms are >1000 m$^2$, and strong covalent bonding holding the framework gives way for their potential use in the mentioned applications. COFs usually crystallize as insoluble powders and their processing as materials for devices has been limited. This study is centered on a new processing strategy in which powder samples of isotropic bulk 2-dimensional COFs become highly anisotropic. Crystallographic studies of the processed COFs indicate the preferred orientation features between the h00 and the 00l planes. COFs of different functionality (boronate, boroxine, imine, triazine) and symmetry (hexagonal and tetragonal) were studied, as well as their stability and application to devices indicating the generality of our approach.
cages must have strong enough inter-cage interactions that they are orientationally static such that after activation they remain accessible to sorbates. This is shown through a series of isostructural and isoreticular metal-organic polyhedra with porosity dependence on ligand functionality and metal identity. The best materials can yield surface areas in excess of 1000 m$^2$/g. The intercage interactions and packing play a key role and will also be discussed.

**CP10.12**

**Engineering Multivariate Porous Organic Cage with Increased Acid Gas Stability**

Guanghui Zhu$^1$, Yang Liu$^1$, Uma Tumuluri$^2$, Zili Wu$^1$, David S. Sholl$^1$, Christopher W. Jones$^1$ and Ryan P. Lively$^1$; Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; $^2$Chemical Sciences Division and Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

In this work, we describe a new porous organic cage (POC) crystal, and deduce the acid degradation mechanism of this new crystal as well as other state-of-the-art POC materials. The degradation of imine-bond based porous organic cages under SO$_2$ conditions was studied with in situ IR experiments and DFT calculations. The synthesis of CC3 variants with mixed linkers at the molecular level is reported. The linkers with different chirality increased the stability of the resulting cages packed into the solid state. This is shown from decreased solubility in common solvents and increased SO$_2$ stability, as observed through electron microscopy, textural, spectral, and crystallographic analysis. Samples of CC3-R and CC3-S in both humid vapor and aqueous SO$_2$ exposure conditions showed severe decomposition while CC3-mix and CC3-trans showed only mild surface changes and no bulk property changes. The morphological differences in the two sample types and their acid-induced degradation was probed by fluorescent confocal microscopy; mesoporous grain boundaries in CC3-R and CC3-S (but not CC3-mix and CC3-trans) were observed. These mesoporous grain boundaries in CC3-R and CC3-S accelerated the corrosion due to reaction with SO$_2$ and water, as the acid can access surfaces small crystal grains throughout the CC3-R crystals. The good stability and preserved CO$_2$ uptake reveals CC3-mix as a potential candidate for enhancing membrane separations in aggressive industrial conditions. We also note that the self-synthesized 1,3,5-benzenetricarbaldehyde and racemic dianisocyclohexane used in CC3-trans and CC3-mix reduced the cost to one tenth of the original expected cost, which makes this material more cost-effective for use in large scale applications.

**CP10.13**

**Water-Mediated Structural Transformation from a Chain Polymer to a Metallocage Induced by Anion Templation**

Yu-Jui Tseng and Jing-Yun Wu; National Chi Nan University, Nantou, Taiwan.

Assembly of di(3-pyridylmethyl)amine (dpma) with NiSO$_4$/H$_2$SO$_4$ and Ni(BF$_4$)$_2$/HBF$_4$ affords anion-directed molecular architectures of Ni(II)-complexes involving a coordination chain polymer, [Ni(dpma)(H$_2$O)$_2$]SO$_4$)$_2$•4H$_2$O•4CH$_3$OH ($\{\text{1}\}$), and a tetragonal metallocage, [SiF$_6$]$^{2-}$·[Ni(dpma)(H$_2$O)], respectively. Their structures have been determined by single-crystal X-ray diffraction analysis and further characterized by infrared (IR) spectra, thermogravimetric (TG) analysis, and powder X-ray diffraction. The Ni(II) center in $\{\text{1}\}$ is a six-coordination octahedral geometry, made up of two trans-positioned pyridyl groups of the Hdpma$^+$ ligands and four H$_2$O molecules, while it in $\{\text{2}\}$ is coordinated by four pyridyl groups of the Hdpma$^+$ ligands at the equatorial plane and one H$_2$O molecule and one SiF$_6$$^{2-}$ dianion at the axial positions. Importantly, this work acquires unambiguous proof of a water-mediated anion-induced structural transformation from infinite SO$_4$$^{2-}$-containing chain structure 1 to discrete SiF$_6$$^{2-}$-containing metallocage 2 through a dissolution/reorganization process. This result suggests an interesting case of 1D-to-3D structural transformation through a solvent-mediated mechanism involving dissolution, exchange, formation, and recrystallization processes, in compare to that through a solid-state process.

**CP10.14**

**MOF Single Precursor-Derived Nanostructured Metal Phosphide and Porous Carbon Composites for Bifunctional Electro catalyst**

Sungeum Jeung; Chemistry, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Developing highly active, cost-effective and stable electrocatalysts are still an ongoing challenge. Metal phosphides and porous carbon composites, in particular, have been actively pursued as advanced electrocatalysts. Herein, we synthesized the nanostructured transition metal phosphide and porous carbon composites derived from metal and phosphorous-containing ligand coordination complexes in one step. The Ni-P and Co-P coordination act as the generation of similar nm-sized nickel and cobalt phosphides and carbon porosity. The composites, which have large surface area, high porosity providing catalytic active sites, and show excellent electrocatalytic activities for both HER and OER.

**CP10.15 moved to C4.06**

**CP10.16**

**A Metal-Free ORR/OER Bifunctional Electrocatalyst Derived from Metal-Organic Frameworks for Rechargeable Zn-Air Batteries**

Yuhong Qian, Zhigang Hu and Dan Zhao; Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore.

Rechargeable Zn-air batteries are under intensive studies because of their high-energy density, low cost, and safety. However, their wide application is prevented by several remaining technical issues, one of which is the lack of suitable bifunctional cathodic catalysts for oxygen reduction reaction (ORR) during discharging and oxygen evolution reaction (OER) during charging. Due to low material cost and wide raw material distribution, carbon-based materials may serve as promising electrocatalysts, while doping heteroatoms such as nitrogen or boron can effectively enhance their catalytic activity. Herein, we pyrolyze a metal-organic framework (MOF) containing Zn, N, and B as the precursor to synthesize dual-doped and metal-free porous carbon materials as efficient ORR/OER bifunctional electrocatalysts. The surface area of obtained carbon materials can be greatly enhanced by pyrolysis under H$_2$-containing atmosphere. In addition, N and B are evenly distributed within the carbon materials due to the crystalline MOF precursor. The resultant carbon materials exhibit high ORR and OER catalytic activities, as well as satisfying robustness in both half-cell and single-cell battery measurements. It shows an onset potential of 0.89 V and a number of electrons transferred > 3.6. Meanwhile for the OER catalysis, it has an onset potential around 1.40 V and can achieve a current density of 10 mA cm$^{-2}$ at 1.55 V in 6 M KOH solution. After an 100-hour cycling test in a two-
electric rechargeable Zn-air battery, the battery assembly exhibits negligible performance deterioration (about 3% loss in columbic efficiency and discharging voltage), suggesting its stable performance contributed by the cathodic electrocatalysts. Our study has demonstrated for the first time that MOFs can be used as precursors to synthesize metal-free ORR/OER bifunctional cathodic electrocatalysts with great potential in rechargeable Zn-air batteries.

**CP10.17**

A Generalized Recyclable Redox-Metallothermic Reaction Route to Hierarchically Porous Carbon/Metal Composites

Kyung Joo Lee\(^1\), Sinho Choi\(^2\), Soojin Park\(^2\) and Hoi Ri Moon\(^1\); \(^1\)Department of Chemistry, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); \(^2\)Department of Energy Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Herein, we develop a generalized synthetic route to obtain composites of porous carbon and electrochemically active metal particles such as Ge, In, Bi, and Sn. The thermolysis of a Zn-based metal-organic framework (MOF) produces hierarchically porous carbon (HPC) and metallic Zn at high temperatures, which can act as a reducing agent of metal oxides. In the reaction system of a Zn-based MOF with GeO\(_2\), in situ evolved Zn reduce GeO\(_2\), producing Ge and ZnO. Interestingly, ZnO is automatically reduced to Zn via a carbothermic reduction during the conversion process, which returns reducing agent to the reaction. Thus, the repeated occurrence of the zincothermic and carbothermic reduction reactions promotes a recyclable redox-metallothermic reaction. After complete reduction of GeO\(_2\), Zn metal is spontaneously vaporized to yield Ge/HPC composites. This facile method can be successfully extended to other metal oxides including In\(_2\)O\(_3\), Bi\(_2\)O\(_3\), and SnO. The as-synthesized Ge/HPC is tested as a rechargeable battery anode material, which exhibits a reversible capacity as high as ~600 mAh g\(^{-1}\) after 300 cycles at a rate of 0.5 C and a low electrode volume expansion (less than 30%).

**CP1.01**

Presenting Wednesday Poster Session

SESSION C11: MOF Hybrids, Nanocomposites and Organic Networks—MOF Polymer Hybrids/Membranes

C: MOF Hybrids, Nanocomposites and Organic Networks

Chair: Thomas Bennett

Thursday Morning, September 15, 2016

Pacific Room

**8:35 AM *C11.01**

Materials Science and Processing Issues in Polymer-MOF Hybrid Separation Membranes

William J. Koros\(^1\), Gongping Liu\(^1\), Kuang Zhang\(^1\), Chen Zhang\(^2\), Mohamed Eddaoudi\(^2\), Youssef Belmabhout\(^2\), Valeriya Chernikova\(^2\), Osama Shekhah\(^2\) and Amandine Cadiau\(^2\); \(^1\)Georgia Institute of Technology, Atlanta, Georgia, United States; \(^2\)King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Conventional high molecular weight amorphous polymers and highly crystalline metal-organic frameworks lie at opposite ends on the large family of materials with applications in molecular separations, especially those involving challenging gas mixtures. In fact, both conventional solution-processable polymers and MOFs each have limitations affecting their use across the full spectrum of membrane-based gas separation applications. Fortunately, when combined properly, these two different types of materials provide attractive vehicles for realistic next generation membranes and sorbents. Indeed, for amorphous polymers, penetrant size- and shape-discriminating ability is often lower than desired; however, for pure MOFs, brittleness and manufacturing cost are drawbacks. Ideally, hybrid materials comprising blends of amorphous polymers and MOFs can be formulated to combine the best characteristics of each of the components. Besides offering technical advantages, such hybrids are compatible with existing economical processes for membrane formation. The combination of technical and economic advantages makes such hybrids an exciting new area with a potential to expand significantly the range of application of membrane-based gas separations. Material science and processing technology will be shown to be critically important to overcoming the challenges to introducing this next generation of membranes. Specifically, the coupling between transport properties and other physical properties of these complex advanced materials must be understood and controlled better. These advanced membrane materials and structures push the state of the art in terms of theory and characterization techniques in the materials science and engineering fields. Control of the complex nanoscale interfaces between the two major phases must be achieved, and this adds an additional feature to the materials science and engineering challenges. The current state of development of typical examples of these types of materials will be discussed to illustrate the above points.

**8:55 AM C11.02**

UiO-66-NH\(_2\) Assembly on ALD-Modified Fiber Surfaces for Catalytic Degradation of Chemical Warfare Agents

Dennis T. Lee\(^1\), Junjie Zhao\(^1\), Gregory Peterson\(^2\) and Gregory Parsons\(^2\); \(^1\)Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States; \(^2\)Edgewood Chemical Biological Center, Aberdeen, Maryland, United States.

Metal-organic frameworks (MOFs) have garnered tremendous attention over the last two decades since they have demonstrated exceptionally high porosity with large surface area. A wide range of MOFs have been synthesized from a variety of organic linkers and metal clusters through isoreticular synthesis. These novel porous materials are promising for applications in gas storage, catalysis, separation, and gas sensing. However, handling and positioning MOFs are challenging due to the powder form obtained from conventional solvothermal synthesis. Integration of MOFs onto fibrous scaffolds can simply the deployment and enable new applications for MOFs. Here we introduce a facile route to assemble UiO-66-NH\(_2\) onto polypropylene fibrous scaffolds at ambient temperature. UiO-66-NH\(_2\) has been demonstrated with high thermal and chemical stability, and phenomenal catalytic activity for degrading chemical warfare agents (CWAs). In this work, ZnO thin films (20 nm thickness) were deposited onto polypropylene fibers using atomic layer deposition (ALD). As-synthesized UiO-66-NH\(_2\) nanocrystals were then assembled onto the ALD ZnO surface using cetyltrimethylammonium Bromide (CTAB) and β-cyclodextrin (β-CD) acting as gluing agents. Dense MOF coatings with high mass loadings were obtained on the ALD-pretreated fiber substrates. X-ray diffraction confirms good crystallinity of the UiO-66-NH\(_2\) coatings. SEM images show UiO-66-NH\(_2\)agglomerates even fill the void space inside the MOF-coated fiber mesh. Moreover, N\(_2\) adsorption analysis shows that the BET surface area of the MOF-functionalized fiber mats exceeds 200 m\(^2\) g\(^{-1}\). Due to the high overall surface area of MOF assembly on fibers, the composite structure enables fast catalytic
Matrix membranes with enhanced structural features and the filler in the polymer matrix. This understanding represents an FIB-SEM and Raman spectroscopy to assess the distribution of microstructure. In particular, we use different techniques such as issues in the field of MMMs: the evaluation of the membrane of membranes. Finally, in our work, we also tackle one of the main selectivity, showing the great potential of COFs in the preparation of bare polymer up to 120%, together with a slight increase of its wt% of an azine-linked COF improved the permeability of the MMMs comprising a commercial polyimide (Matrimid) and 16 CHCO dispersion of NH4 on the permeation properties of MMMs so that their performance hydrophobicity, etc. In this spirit, in our work, we address the particle morphology, functionalities, surface defects, the influence of different parameters, such as MOF structure, screening of different MOF/polymer systems, we gain insight into the preparation of MOF-based MMMs in which, through the investigated during the last decade with very promising results. Technology is a viable commercial alternative compared to traditional separation processes such as cryogenic distillation, adsorption, condensation or absorption processes. The majority of the membrane-based gas separation industrial processes use polymeric membranes because of their easy processability and low cost. However, in case of polymers, there is a trade-off between permeability and selectivity (known as Robeson limit). In this sense, mixed-matrix membranes (MMMs) have been proposed to overcome this limitation. MMMs consist of a composite comprising two phases: a polymer matrix and a dispersed phase, also named filler, and aim to combine the better processability of polymers with the superior gas transport properties of the filler. MOFs-based MMMs have been intensively investigated during the last decade with very promising results. However, a more systematic approach is needed for the preparation of MOF-based MMMs in which, through the screening of different MOF/polymer systems, we gain insight into the influence of different parameters, such as MOF structure, particle morphology, functionalities, surface defects, hydrophobicity, etc. In this spirit, in our work, we address the influence of different MOF particle morphologies and polymers on the permeation properties of MMMs so that their performance can be improved beyond the Robeson limit. Particularly, upon dispersion of NH2-MIL-53(Al) in 6FDA-DAM, CO2 permeabilities of up to 660 Barrer together with CO2/CH4 separation factors of 28 can be obtained when the separation of an equimolar mixture of CO2 and CH4 is considered. Moreover, the use of COF as fillers in MMMs remains unexplored despite their potential. In this work, we show that the preparation of MMMs comprising a commercial polyimide (Matrimid) and 16 wt% of an azine-linked COF improved the permeability of the bare polymer up to 120%, together with a slight increase of its selectivity, showing the great potential of COFs in the preparation of membranes. Finally, in our work, we also tackle one of the main issues in the field of MMMs: the evaluation of the membrane microstructure. In particular, we use different techniques such as FIB-SEM and Raman spectroscopy to assess the distribution of the filler in the polymer matrix. This understanding represents an important advancement towards the rational design of mixed matrix membranes with enhanced structural features and separation performance.

9:15 AM C11.03
MOF and COF-Based Mixed-Matrix Membranes for Gas Separation Beatriz Seoane de la Cuesta1, Anaheid Sabetghadam2, Meixia Shan2, Alexey Pustovarenko2, Freek Kapteijn1 and Jorge Gascon1,2. Department of Chemistry, Utrecht University, Utrecht, Netherlands; 3Chemical Engineering Department, Delft University of Technology, Delft, Netherlands.

Membrane-based separation processes have received significant attention as a promising technology due to their low energy consumption, operation flexibility and simplicity. Particularly, when gas separation is taken under consideration, membrane technology is a viable commercial alternative compared to traditional separation processes such as cryogenic distillation, adsorption, condensation or absorption processes. The majority of the membrane-based gas separation industrial processes use polymeric membranes because of their easy processability and low cost. However, in case of polymers, there is a trade-off between permeability and selectivity (known as Robeson limit). In this sense, mixed-matrix membranes (MMMs) have been proposed to overcome this limitation. MMMs consist of a composite comprising two phases: a polymer matrix and a dispersed phase, also named filler, and aim to combine the better processability of polymers with the superior gas transport properties of the filler. MOFs-based MMMs have been intensively investigated during the last decade with very promising results. However, a more systematic approach is needed for the preparation of MOF-based MMMs in which, through the screening of different MOF/polymer systems, we gain insight into the influence of different parameters, such as MOF structure, particle morphology, functionalities, surface defects, hydrophobicity, etc. In this spirit, in our work, we address the influence of different MOF particle morphologies and polymers on the permeation properties of MMMs so that their performance can be improved beyond the Robeson limit. Particularly, upon dispersion of NH2-MIL-53(Al) in 6FDA-DAM, CO2 permeabilities of up to 660 Barrer together with CO2/CH4 separation factors of 28 can be obtained when the separation of an equimolar mixture of CO2 and CH4 is considered. Moreover, the use of COF as fillers in MMMs remains unexplored despite their potential. In this work, we show that the preparation of MMMs comprising a commercial polyimide (Matrimid) and 16 wt% of an azine-linked COF improved the permeability of the bare polymer up to 120%, together with a slight increase of its selectivity, showing the great potential of COFs in the preparation of membranes. Finally, in our work, we also tackle one of the main issues in the field of MMMs: the evaluation of the membrane microstructure. In particular, we use different techniques such as FIB-SEM and Raman spectroscopy to assess the distribution of the filler in the polymer matrix. This understanding represents an important advancement towards the rational design of mixed matrix membranes with enhanced structural features and separation performance.

9:35 AM C11.04
Advanced Composite Membranes with Layered Fillers for Gas Separation Dan Zhao. Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore.

Gas separation technologies, especially for CO2 separation, have attracted increased attention recently because of their important applications in clean energy and environmental sustainability. Compared to other CO2 separation technologies, membrane-based CO2 separation has been greatly developed in recent years. In order to combine the merits of both polymeric and inorganic membranes, mixed matrix membranes (MMMs) were invented by dispersing porous fillers into continuous polymeric matrices hoping to increase the permeability and selectivity of the resulting membranes while preserving the properties of good mechanical strength and processability of the polymeric matrices. In this talk, I will introduce our work in preparing MMMs containing lamellar MOF or COF fillers with high-aspect-ratio, which exhibit good gas separation performance because of the increased tortuosity of gas permeation paths imposed by lamellar fillers. In addition, I will also discuss the direct fabrication of ultrathin membranes composed of 2D nanosheets. Because of their ultra-small thickness and precisely tunable pore size and functionality, these novel membranes may demonstrate unprecedented gas separation performance. References: I. Kang, Z. X.; Peng, Y. W.; Qian, Y. H.; Yuan, D. Q.; Addicoat, M. A.; Heine, T.; Hu, Z. G.; Tee, L.; Guo, Z. G.; Zhao, D.* Mixed matrix membranes (MMMs) comprising exfoliated 2D covalent organic frameworks (COFs) for efficient CO2 separation. Chem. Mater. 2016, 28, 1277-1285. 2. Kang, Z. X.; Peng, Y. W.; Hu, Z. G.; Qian, Y. H.; Chi, C. L.; Yeo, L. Y.; Tee, L.; Zhan, D.* Mixed matrix membranes comprising two-dimensional metal-organic framework nanosheets for pre-combustion CO2 capture: a relationship study of filler morphology versus membrane performance. J. Mater. Chem. A 2015, 3, 20801-20810.

9:55 AM BREAK

10:25 AM C11.05

Mixed matrix membranes (MMMs) are a relatively new hybrid system that combine the low cost and ease of processing of polymers with the excellent transport performance of molecular sieves (fillers). As such, MMMs have the potential to overcome the traditional limitations of polymeric membranes by improving the permeability and selectivity performance. MMMs studied for post combustion carbon capture from flue gas must demonstrate excellent permeability and selectivity for CO2 at low concentrations while operating slightly above ambient pressure. Therefore, Metal Organic Frameworks (MOFs) are of interest as fillers in MMMs as they can be designed to crystallize with well-defined pores, high surface areas, and other desired functionalities to physiosorb CO2 at low pressures. However, the fabrication of MOF based MMMs can be a challenge due to non-selective void formation at the interface of the MOF and polymer, MOF particle agglomeration, and or poor blockage. As such to accommodate these fabrication challenges, we have been focusing research efforts on the development of stable CO2 selective MOF materials that have good interaction with selected polymeric systems, as
as well as novel fabrication strategies to obtain extra thin MMms. Specific MOF materials employed in this study for MMms are literature developed SIFSIX and UiO66 (Zr) materials as well as in house synthesized new MOFs with engineered polymers, of which their gas separation performance will be discussed.

10:45 AM C11.06
Strategies for the Fabrication of MOF Films and Coatings Bo Wang*; Chemistry, Beijing Institute of Technology, Beijing, China.

Metal–organic frameworks (MOFs), with their well-defined pores and rich structural diversity and functionality, have drawn a great deal of attention from across the scientific community. However, industrial applications are hampered by their intrinsic fragility and poor processability. Stable and resilient MOF devices with tunable flexibility are highly desirable. We proposed a photo-induced post-synthetic polymerization (PSP) strategy to covalently assemble MOF crystals by flexible polymer chains, and thus endow the MOF powder with processibility and flexibility further. Further we presented a solvent- and binder-free approach for producing stable MOF coatings by a unique hot-processing (HoP) method, in which temperature and pressure are applied simultaneously to facilitate the rapid growth of MOF nanocrystals onto desired substrates. This strategy was proven to be applicable to carboxylate-based, imidazolate-based, and mixed-metal MOFs. We further successfully obtained superhydrophobic and “Janus” MOF films through layer-by-layer pressing. These methods can be scaled up in the form of roll-to-roll production and may push MOFs into unexplored industrial applications. References: [1] B. Wang, A. P. Côté, H. Furukawa, M. O’Keeffe and O. M. Yaghi,*Colossal Cages in Zeolitic Imidazolate Frameworks as Selective Carbon Dioxide Reservoirs, Nature, 2008, 453, 207–211.[2] Y. Zhang, X. Feng,* H. Li, Y. Chen, J. Zhao, S. Wang, L. Wang and B. Wang*Photoinduced Post-synthetic Polymerization of a Metal–Organic Framework toward a Flexible Stand-Alone Membrane, Angew. Chem. Int. Ed., 2015, 54, 4259–4263.[3] (a) Y. Chen, S. Li, X. Pei, J. Zhou, X. Feng, S. Zhang, Y. Cheng, H. Li, R. Han and B. Wang* A Solvent-Free Hot-Pressing Method to Prepare Metal-Organic Framework Coatings, Angew. Chem. Int. Ed., (b) Y. Zhang, S. Yuan, X. Feng, H. Li, J. Zhou, B. Wang* Preparation of Nanofibrous Metal-Organic Framework Filters for Efficient Air Pollution Control, J. Am. Chem. Soc., 2016, in press, DOI:10.1021/jacs.6b02553.

11:05 AM C11.07
Microscopic Insight into the MOF/Polymer Interface—A First Step toward Understanding the Compatibility in Mixed Matrix Membranes Rocio Semino¹, Naseem A. Ramasahye¹, Aziz Ghous², Marvin Benzaqui¹, Tanay Kundu¹, Nathalie Steunou¹, Christian Serre¹, Seth M. Cohen¹ and Guillaume Maurin¹; ¹Institut Charles Gerhardt Montpellier, Montpellier, France; ²Institut de Physique de Rennes, Rennes, France; ³Institut Lavoisier Versailles, Versailles, France; ⁴University of California San Diego, San Diego, California, United States.

MOF/polymer Mixed Matrix Membranes (MMMs) have attracted great interest in the last few years as a promising alternative to the polymer membranes currently used for gas separations. Although a number of experimental studies have been published on the elaboration of such MMMs, and on their efficacy for specific gas separations, both the interfacial structure of these composites, and their mechanism of action are far to be understood so far. In this contribution, we report a computational study that sheds light on the microscopic picture of MOF/polymer interfaces, by the application of an innovative multiscale simulation methodology based on the use of advanced forcefield- and quantum-based simulation tools. We present results on (1) ZIF-8/PIM-1 and ZIF-8/PIM-EA-TB, two composites that are of great interest for H2/CO2 separation, (2) MIL-69/6FDA-DAM, with potential applications for N2/CO2 separation, and (3) UiO66/PVPD, a system that exhibits very good MOF/polymer compatibility. Our simulations provide insight into the interactions and the coverage of the polymer at the MOF surface, explaining thus the compatibility for each system at the microscopic level. For ZIF-8/PIM-1, we found that the composites are stabilized by the presence of a preferential interaction between the CN group of the polymer and the NH of the organic linker at the surface. Changing the polymer to PIM-EA-TB, the interactions between the two species were found to be more uniform, and this shields a better surface coverage. In both cases, there are well defined “microvoids” at the interface. In contrast, for the MIL-69/6FDA-DAM system, a “percolated” void can be found at the interface, that could provide an additional path for CO2 diffusion. Our predictions are further complemented by experimental evidences issued from TEM, EXAFS, XPS, IR and NMR data.[1] B. Seoane, J. Coronas, I. Gasçon, M. E. Benavides, O. Karvan, J. Caro, F. Kapteijn, J. Gascón, Chem. Soc. Rev. 44, 2421 (2015).[2] R. Semino, N. Ramasahye, A. Ghoufi, G. Maurin, ACS Appl. Mater. Interfaces 8, 809 (2016).[3] M. Benzaqui et al, submitted.[4] M. S. Denny, Jr., S. M. Cohen, Angew. Chem. Int. Ed. 54, 9029 (2015).

11:25 AM C11.08
Assemble Face Metal Organic Framework Crystal in Direct Write, Self-Aligned Polymer Membrane by Electrospinning Xining Zang¹,², Duven Tran¹, Kwok Siong Teh³, Norman Su², Jeff Urban² and Liwei Lin¹; ¹University of California, Berkeley, Berkeley, California, United States; ²Molecular Foundry, Lawrence Berkeley National Laboratories, Berkeley, California, United States; ³Engineering, San Francisco State University, San Francisco, California, United States.

While great achievements in the design and synthesis of MOF have been accomplished, there exist still two major issues related to the practical application of MOF crystals. First, the orientation and alignment of the facets of MOF are not ordered. Such misalignment of porous structures will greatly decrease the efficiency of gas transportation and absorption and even reduce the number of gas pathways in some channel-structured MOF. In previous work, electric field has been used to control the ligand surface chemistry and to tune the orientation of MOF over a short range. ZIF-8 crystals has been aligned to certain orientation in PEO solution, however, the short assembly distance reveal a lack of long range order. Second, large-scale fabrication of MOF is still challenging due to their brittleness and fragility. Polymer have been used as a carrier media for MOF crystals to make flexible large-area membranes, yet the structure uniformity and functionality of embedded MOF still need improvement. In this project, we developed a novel method to synthesize large-scale direct-write polymer membrane containing orientated and assembled MOF by electrospinning. Electrospinning is a uniaxial polymer fiber drawing process which can produce ordered structure via DC electric field as high as 2,000,000V/m. The working electric field is one order of magnitude higher than that reported in literature in which ZIF-8 faceted crystals are aligned in polymer, which resulted in longer range order of MOF in fiber. ZIF-8 alignment is observed in different polymer system, and the polymer to PIM-EA-TB, the interactions between the two species were found to be more uniform, and this shields a better surface coverage. In both cases, there are well defined “microvoids” at the interface. In contrast, for the MIL-69/6FDA-DAM system, a “percolated” void can be found at the interface, that could provide an additional path for CO2 diffusion. Our predictions are further complemented by experimental evidences issued from TEM, EXAFS, XPS, IR and NMR data.[1] B. Seoane, J. Coronas, I. Gasçon, M. E. Benavides, O. Karvan, J. Caro, F. Kapteijn, J. Gascón, Chem. Soc. Rev. 44, 2421 (2015).[2] R. Semino, N. Ramasahye, A. Ghoufi, G. Maurin, ACS Appl. Mater. Interfaces 8, 809 (2016).[3] M. Benzaqui et al, submitted.[4] M. S. Denny, Jr., S. M. Cohen, Angew. Chem. Int. Ed. 54, 9029 (2015).
of PVP fiber (~300nm), we directly wrote a “necklace” structure of ZIF-8 distributed uniformly in fiber with tuned orientation. By increasing the electrospinning working distance from 2 mm to 10cm, we demonstrated a larger scale weaving of PVP-ZIF membrane that can be applied in gas absorption application. Further study of the effects of polymer permeability and ZIF-8 orientation on gas absorption is still on the go, and so is the optimization of ZIF-8 orientation control.

SESSION C12: MOF Hybrids, Nanocomposites and Organic Networks—MOF Composites III
C: MOF Hybrids, Nanocomposites and Organic Networks
Chair: William Koros
Thursday Afternoon, September 15, 2016
Pacific Room

1:15 PM C12.01
MOFs as Synthetic Fossils for the Protection of Nucleic Acid
Joseph J. Richardson¹, Kang Liang², Levente Bodrossy², Christian Doonan¹ and Paolo Falcaro¹; ¹Manufacturing, CSIRO, Clayton, Victoria, Australia; ²Oceans and Atmosphere, CSIRO, Hobart, Tasmania, Australia; ³University of Adelaide, Adelaide, South Australia, Australia; ⁴Graz University of Technology, Graz, Austria.

Nucleic acids act as the blueprint for all organisms and only small fragments are required to distinguish between organisms of the same species.(1) Therefore, DNA preservation is important for genomic research and development, and crucial for bio-banking, species identification, and forensics. Although DNA encode the history of life, it is relatively fragile and prone to degradation due to water through chemical (hydrolysis, oxidation and alklylation) or biological (enzymolysis) pathways.(2) In specific conditions of desiccation fossilization, DNA can be naturally preserved for thousands of years under cool ambient conditions. (3) This occurs due to the exclusion of water from the DNA backbone and because of the crystallization of inorganic materials around the DNA, thereby sealing it off from harmful external agents. Current synthetic methods attempt to mimic this by reducing the amount of water in the vicinity of the DNA utilizing agents that bind to the DNA backbone or sol gel chemistry. (4) Therefore they generally require complex and lengthy encapsulation and release procedures such as hydrofluoric acid, dialysis, etc., which makes them expensive and requires technical expertise. Here we utilize a recently introduced biomimetic MOF crystallization strategy(5) to encapsulate and preserve DNA against accelerated ageing (heat and UV). We found that the DNA backbone concentrates zinc ions by ~40 fold, thereby allowing for an accelerated crystallization process. Encapsulation takes place in under 60min using the inexpensive, benign reagents zinc and methyl imidazole to form ZIF-8. The DNA can be stored in water or dried, and then released instantaneously with the addition of acid (EDTA). Remarkably, purification is not necessary before qPCR amplification, making this method amenable to both laboratory and field settings. Overall, the MOFs protected the DNA significantly better than commercially available preservation matrices under accelerated ageing conditions and also cost roughly 1,000,000 less. (1) Woese, C.R. & Fox, G.E. Phylogenetic structure of the prokaryotic domain: the primary kingdoms. Proceedings of the National Academy of Sciences 74, 5088-5090 (1977). (2) Hofreiter, M., Serre, D., Poinar, H.N., Kuch, M. & Pääbo, S. Ancient DNA. Nature Reviews Genetics 2, 353-359 (2001). (3) Allentoft, M.E. et al. The half-life of DNA in bone: measuring decay kinetics in 158 dated fossils. Proceedings of the Royal Society of London B: Biological Sciences 279, 4724-4733 (2012). (4) Paunescu, D., Puddu, M., Soellner, J.O., Stoessel, P.R. & Grass, R.N. Reversible DNA encapsulation in silica to produce ROS-resistant and heat-resistant synthetic DNA fossils. Nature protocols 8, 2440-2448 (2013). (5) Liang, K. et al. Biomimetic mineralization of metal-organic frameworks as protective coatings for biomacromolecules. Nature communications 6 (2015).

1:35 PM C12.02
 Emerging Applications of Magnetic Metal-Organic Framework Composites Raffaele Ricco and Paolo Falcaro;
Institute of Physical and Theoretical Chemistry, Graz University of Technology, Graz, Austria.

Interfacial Synthesis of Task-Specific MOF-Based Composites through Pickering Emulsion  

**Jun Hu and Honglai Liu; Chemistry, East China University of Science and Technology, Shanghai, China.**

We proposed a novel and convenient method for fabricating MOF-based composites based on Pickering emulsion. MOFs, with precursors of oil-soluble organic ligands and water-soluble metal ions, can be produced at the interfacial layer of oil/water phases; while Pickering emulsion, stabilized by nanoparticles, can provide a large interface for MOFs’ interfacial growth. Thus, combining stabilizer and as-synthesized MOF nanoparticles, novel MOF-based composites can be easily obtained. Based on this approach, we selected GO sheet as the stabilizer to produce an n-octanol / water Pickering emulsion. With organic ligands dissolved in n-octanol and metal ions in water, the nucleation and growth of MOFs nanocrystals, such as ZIF-8, MOF-5 and Cu(BTC)₂, were observed at the interface of GO Pickering emulsion droplets, repetitively. It was shown that GO sheets were well exfoliated and dense MOFs nanocrystals covered or dispersed on the surface. Among various MOF/GO composites, Cu(BTC)₂/GO composite was successfully applied as the adsorbent for CO₂ capture. From the simulated flue gas (15 v/v % CO₂) with the humidity of 50% at 298K and normal pressure, the CO₂ adsorption capacity was as high as 3.30 mmol/g. Moreover, this approach was also verified by the fabrication of magnetic MOF hollow sphere. By using Fe₃O₄ nanoparticle as the stabilizer, magnetic PMMA@Fe₃O₄/Cu(BTC)₂ hollow microspheres were produced in a one-pot Pickering emulsion through two-step in-situ interfacial reactions, i.e. the growth of Cu(BTC)₂ nanocrystals and further interfacial polymerization of methyl-methacrylate (PMMA). The hollow PMMA@Fe₃O₄/Cu(BTC)₂ hybrid microspheres showed synergetic multi-functions, including the magnetic property caused by Fe₃O₄, the reversible thermal expansion by PMMA, and the adsorption enhanced permeation by porous Cu(BTC)₂, which ensured its promising applications, such as the drug carrier. The type of the nanoparticle stabilizer or the as-synthesized nanoparticle can be alternatively changed depending on the specific tasks, therefore, this strategy would have great inspiration for the fabrication of hybrids/composites with various structures and morphologies, such as Pickering emulsions, nanoparticles composites, as well as the hollow composites, and would have promising applications in many areas.

SESSION C13: MOF Hybrids, Nanocomposites and Organic Networks—MOF Nanoparticles/Nanostructures  
C: MOF Hybrids, Nanocomposites and Organic Networks  
Chair: Smaranda Marinescu  
Thursday Afternoon, September 15, 2016  
Pacific Room

2:15 PM C13.01  
**Biological Templates in Core-Shell MOF Composites**  
*Jeremiah J. Gassensmith; Chemistry and Biochemistry, University of Texas at Dallas, Richardson, Texas, United States.*

The objective of our research is to broaden the capability of a promising bionanomaterial, the tobacco mosaic virus (TMV), via surface mineralization with metal organic frameworks (MOF). Tobacco mosaic virus is the first purified and observed plant virus and has been intensively studied for decades. However, its high aspect ratio, rod-shaped morphology, various reactive sites for bio-conjugation and excellent stability in relatively broad range of conditions make it never out of fashion as robust building blocks in materials fabrication and medical applications. MOF is a type of coordinated polymer that contain highly ordered, 3-dimensional micropores and high surface area. Recent studies have demonstrated preparation of MOF under biocompatible conditions. These advanced synthetic strategies allowed MOF-coated biomaterials such as enzymes and proteins to obtain enhanced selectivity, catalytic efficiency and stability. In our project, we have successfully prepared MOF-coated TMV, which retains its rod-shape morphology and intact surface reactive tyrosine groups. More interestingly, the rod-shaped TMV@MOF composites can self-assemble into polyhedral microcrystals via modifying synthetic conditions. Both MOF-functionalized TMV and TMV@MOF self-assembly are novel in the field of nanotechnologies based on virus particles. With this encouraging discovery, a new type of bio-nanocomposite is emerging that will enable more robust, sophisticated and comprehensive integration of biological, inorganic and organic functional materials on the tens of nanometers scale.

2:35 PM C13.02  
**Multifunctional MOF Nanoparticles via Self-Assembly**  
*Ulrich Lachelt, Ruth Roder, Patrick Hirschle, Tobias Preiss, Andreas Zimpel, Joachim Raedler, Ernst Wagner, Thomas Bein and Stefan Wuttke; Chemistry, Ludwig Maximilian University of Munich, München, Germany; 1Pharmacy, Ludwig Maximilian University of Munich, Munich, Germany; 1Physics, Ludwig Maximilian University of Munich, Munich, Germany.*

The controlled manipulation of the external surface of nanoparticles (NPs) is of paramount importance as it defines the interface between the NP and its surroundings and strongly determines the overall performance of the NP especially in terms of biomedical applications. In this respect, self-assembly of functional units on the NPs’ surface appears as a powerful approach as it would ensure a defined arrangement of these units without any guidance from an outside source. In addition it would provide the possibility for the fabrication of complex functional nanosystems from individual molecules that can be designed and precisely generated by chemistry. In this regard, we have recently established a novel functionalization approach[1] that uses the coordinatively unsaturated sites present on the MOF NPs’ external surface to self-assemble functional units bearing Lewis bases, such as oligohistidine tags, which are routinely used for the purification of recombinant proteins.[2] The talk will be divided into two parts; first, the detailed study of the interaction of MOF NPs with the functional units and second, the biological application of these functionalized MOF NPs. The binding of different oligohistidine containing units (e.g. dyes, artificial peptides or recombinant green fluorescent protein (GFP)) to MOF NPs (e.g. MIL-88(Fe) or ZrF₄-mum MOF) by simple mixing in aqueous medium has been studied by different techniques such as HPLC quantification assay, fluorescence correlation spectroscopy and fluorescence release experiments. Furthermore, the cellular uptake of fluorescent functional units assembled on the MOF surface into tumor cells has been demonstrated by FACs analysis and confocal laser scanning microscopy. Additionally MOF NPs modified with apoptosis inducing peptides or CytC lead to enhanced cell killing. The authors believe that the novel MOF NP platform and functionalization concept will have numerous applications in the biomedical sciences and other research fields requiring multifunctionality at the nanoscale. References: [1] S. Wuttke et al., in preparation. [2] E. Hochuli et. Nature Biotechnology 6, 1321 - 1325 (1988).
Conformal and oriented metal-organic frameworks thin film enclosing arbitrary nanostructures (substrates, nanowires, nanocrystals) are fabricated with precisely controlled thickness and pristine interface. This is achieved by atomic layer deposition of aluminum oxide on the substrates and addition of a tetra-topic porphyrin based linker, 4,4′,4″,4‴-(porphyrin-5,10,15,20-tetrayl)tetrabenzoic acid (H₂TCPP), to react with alumina and make MOF [Al₂(OH),TCPP] enclosures. Alumina thickness is precisely controlled from 0.1 to 3 nm, thus allowing control of the MOF thickness from 10 to 50 nm. Electron microscopy and grazing angle X-ray diffraction confirm the order and orientation of the MOF by virtue of the porphyrin units being perpendicular to the substrate surface. These features of the MOF enclosure enable us to use surface-enhanced Raman spectroscopy to directly track the porphyrin metalation process of the MOF enclosing octahedral silver nanocrystals. When metalated with cobalt, the Al₂(OH),TCPP-Co thin film functions as catalyst for the selective and efficient reduction of carbon dioxide to carbon monoxide (CO) in aqueous electrolytes with a selectivity for CO beyond 76% and stability over 7 h with a per-site turnover number (TON) of 1400. This electrochemical catalytic activity is unique to the thin film form of the MOF (below 100 nm) and depends strongly on the film thickness. This research presents a generalizable method to produce structurally well-defined nano-MOF composite material that has extraordinary functions. Metal-Organic Frameworks for Electrocatalytic Reduction of Carbon Dioxide. N. Kornienko*, Y. Zhao*, C. S. Kley, C. Zhu, D. Kim, S. Lin, C. J. Chang, O. M. Yaghi, P. Yang, J. Am. Chem. Soc., 2015, 137, 14129-14135.Mesoscopic Constructs of Ordered And Oriented Metal-Organic Frameworks on Plasmonic Silver Nanocrystals. Y. Zhao, N. Kornienko, Z. Liu, C. Zhu, S. Asahina, T.-R. Kuo, W. Bao, C. Xie, A. Hexemer, O. Terasaki, P. Yang, O. M. Yaghi, J. Am. Chem. Soc., 2015, 137, 2199-2202.

Nanoscaled Porphyrinic MOFs for Photodynamic Therapy Application Jan Demel1, Daniel Buzek1, Kaplan Kirakci1, Jaroslav Zelenka2, Tomas Ruml2 and Kamil Lang3; 1Department of Materials Chemistry, Institute of Inorganic Chemistry, Rez, Czech Republic; 2University of Chemistry and Technology, Prague, Czech Republic.

Porphyrin containing MOFs attract attention due to their rigid geometry, variable structure, and their potential applications in catalysis, sensing, or luminescent materials. Recently, we showed that porphyrin-containing MOFs effectively produce singlet oxygen, O₁\(_{2}^(D)\), a reactive form of oxygen.¹ Singlet oxygen has cytotoxic effects and its ability to inactivate tumor cells is a basis for the applications in photodynamic therapy (PDT). In our work, we prepared nanoparticles of MOF-545/PCN-222, composed of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin units and Zr₂O₂(OH) secondary building units, and investigated their toxic/photoxic effects. Three different sizes of nanoMOF MOF-545/PCN-222, ranging from 30 to 300 nm, were prepared. The XRD patterns and textual parameters documented that pure MOF-545/PCN-222 phases were obtained in all cases. The shape and size distributions were determined by SEM and TEM measurements (Figure 1). UV-vis absorption and fluorescence measurements indicated that incorporated porphyrin units in the MOF framework keep suitable photophysical properties and productivity of O₁\(_{2}^(D)\). Dark toxicity as well as phototoxicity upon light irradiation was studied on the human cervix carcinoma HeLa cell line. The performed tests showed negligible dark toxicity of the MOF nanoparticles, whereas phototoxicity led to deactivation over 90 % of tumor cells. References[1] J. Demel, P. Kubat, F. Milange, J. Marrot, I. Cisarova, K. Lang, Inorg. Chem. 2013, 52, 2779–2786.


Crystalline solids dominate the field of metal–organic frameworks (MOFs), with access to the liquid and glass states of matter usually prohibited by relatively low temperatures of thermal decomposition. Recently, we demonstrated the melting of a three dimensional MOF belonging to the zeolitic imidazolate framework (ZIF) family, of chemical composition Zn(Im), (Im – C\(_{2}\)H\(_{4}\)N\(_{3}\)).¹ In this talk, I show how due consideration of framework chemistry may be used to expand the phenomenon of melting to other systems, linking crystal chemistry to framework melting temperature (T\(_{m}\)) and physical behaviour of the glass-forming liquids. Specifically, we show that the addition of ligand defects to ZIFs be used to lower T\(_{m}\) by over 150 °C.² ¹³C and ¹⁵N NMR measurements differentiate between electronic and steric effects of the inclusion of larger ligands, and highlight the additional strain imposed upon the crystalline systems by addition of larger dopant ligands as being responsible for the decrease in T\(_{m}\). The mechanism of melting is investigated by pair distribution function measurements and simultaneous molecular dynamics/DFT calculations, which provide pathways in generalizing the approach to other MOF systems. The macroscopic liquids produced are characterized using the same methods, and results summarized. Cooling of these ZIF liquids yields glasses, which are chemically and structurally distinct from the three other existing categories of melt-quenched glasses (inorganic nonmetallic, organic, and metallic), and retain the basic metal–ligand connectivity of their parent crystalline frameworks. Curiously, experimental positron annihilation spectroscopy measurements show that the glasses contain internal porosity and may be useful for molecular, and ionic transport applications.³ These results are also discussed, alongside the utility of a polymerization algorithm, which is able to predict the amorphous structures formed from given reactants. The work has important consequences for the growing list of potential applications for this burgeoning class of materials. First and foremost, melting opens up new routes to hybrid glasses, the chemical functionality of which may be altered by utilizing the chemical versatility of the crystalline MOF state. Through this work, we expect that the family of MOF-glasses (i.e., a new type of MQG) can be expanded for various applications.

SESSION C14: MOF Hybrids, Nanocomposites and Organic Networks—Amorphous MOFs

C: MOF Hybrids, Nanocomposites and Organic Networks
Chair: Xianhui Bu
Thursday Afternoon, September 15, 2016
International Ballroom IV/V

Structure Prediction of Amorphous MOFs and Porous Organic Polymer Membranes

Amorphous MOFs can be obtained through melt-quenching the hybrid frameworks to obtain a glass. The porosity and properties of such MOF glasses is poorly understood compared to that of crystalline materials. In part, this is due to the difficulty in obtaining a molecular level understanding of their structure, as it is not possible to collect a X-ray diffraction crystal structure. We have recently extended software originally developed by Colina et al. for the study of organic polymers (Theor. Chem. Acc., 2013, 132, 1) to the prediction of structures for the amorphous ZIF-4 material (a ZIF-4) (Chem. Commun. 2016, 52, 3750). Both the molecular modelling and positron annihilation lifetime spectroscopy found the porosity of a ZIF-4 to be intermediate between the open and dense crystalline forms ZIF-4 and ZIF-zni. Here we will discuss the extension of this approach to a series of amorphous MOFs, including MOF-5, UiO-66, ZIF-8 and HKUST-1. This will allow us to explore the potential porosity of these systems and to understand the key structural features that can influence their potential application as hybrid glasses for electronic, thermal or ionic conduction or separation membranes. Further, we explore the structural features such as the window sizes formed within the systems and also the degree to which dynamic motion of the structure can influence their performance. We believe the fundamental insight offered by studying this emerging class of materials is critical for uncovering their potential applications. In addition to discussing this series of amorphous MOF materials, we will also discuss application of this modelling approach to the design of high-permeance porous organic polymers for separation applications (Nature Materials, 2016, DOI: 10.1038/nmat4638).

Preserving Yttria-Stabilized Zirconia Nanomorphology at High Sintering Temperatures using an Amorphous Yttrium-Zirconium MOF

There is a major push to lower the operating temperature of solid oxide fuel cells (SOFCs) in order to substantially decrease performance degradation rates and cost. A key factor in improving low-temperature SOFC performance is to increase the density of electrochemically active sites in the porous ceramic electrode composites. Although increasing the porous ceramic scaffold surface area would directly increase the density of active sites in the electrodes, it is surprising that little progress has been made in this area. In fact, the most common SOFC scaffold, a porous yttria-stabilized zirconia (YSZ) film, typically has a surface area of 0.2-0.5 m²/g. Here we report a novel sintering method that creates and preserves YSZ scaffold surface areas up to 300 times higher than traditional methods via in-situ carbon templating of amorphous yttrium-zirconium metal organic frameworks (MOFs). Using UiO-66 and UiO-67 organic linkers, we realized amorphous MOFs that accommodated 13 mol% yttrium (Y³⁺) and 87 mol% zirconium (Zr⁴⁺). When we prepared crystalline UiO-66 and UiO-67, only 0.9 mol% Y and 0.4 mol% Y were present in the MOF, respectively. Therefore, only the amorphous form of the MOF was useful for our application. To create the carbon template in-situ, each MOF was sintered to 1200°C in argon. The carbon contents were 26 wt% for UiO-66 and 37 wt% for UiO-67, respectively. After removing the carbon by oxidation at 700°C in air, the surface areas were 27 m²/g and 60 m²/g for UiO-66 and UiO-67, respectively. The results demonstrate a promising and versatile application of amorphous MOFs.