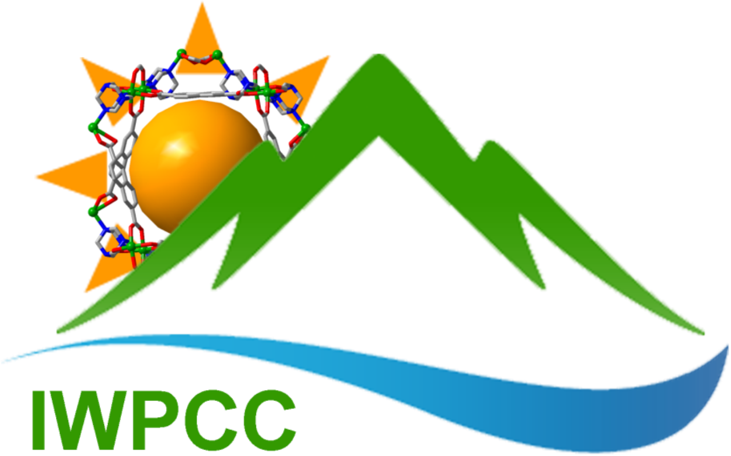
Book of Abstracts

International Workshop on Porous Coordination Compounds



September 19–23, 2016, Altay, Russia

Nikolaev Institute of Inorganic Chemistry,
Siberian Branch of the Russian
Academy of Sciences

www.niic.nsc.ru

International Workshop on Porous Coordination Compounds

September 19-23, 2016, Altay, Russia

The scientific program of IWPCC covers key areas of modern fundamental and applied research in the field of porous compounds. Plenary lectures from leading scientists, oral and poster presentations from young scientists will be presented at the Workshop.

Organizing committee

- Vladimir P. Fedin, Co-Chairman, Corr-member of RAS, Prof., Director of NIIC SB RAS, Novosibirsk, Russia
- Martin Schröder, Co-Chairman, Prof., Vice-President of the University of Manchester, United Kingdom
- Danil N. Dybtsev, Conference secretary, NIIC SB RAS, Novosibirsk, Russia
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- Anastasia M. Cheplakova (cheplakova@niic.nsc.ru)
- Tatyana K. Koltunova (koltunova@niic.nsc.ru)

The workshop is supported by the Grant of the Government of the Russian Federation (No. 14.Z50.31.0006, leading scientist – Martin Schröder).

International Workshop on Porous Coordination Compounds

September 19-23, 2016, Altay, Russia

PROGRAM

September, 19th		
8:00–8:30	Breakfast	
8:30–16:30	Bus trip to Altay	~8 h
16:30–17:30	Accommodation in “Aya” hotel	45 min
18:00–19:00	Dinner	

September, 20th		
9:00–9:10	Opening Ceremony Vladimir P. Fedin, Martin Schröder	10 min
Chairman: Hiroshi Kitagawa		
9:10–9:55	Kimoon Kim. New Approaches to Modular Porous Materials	45 min
9:55–10:40	Christian Serre. New Horizons of Robust Metal Organic Frameworks	45 min
Coffee break, 20 min		
Chairman: Kimoon Kim		
11:00–11:45	Hiroshi Kitagawa. Dimensional Crossover in Coordination Chemistry	45 min
11:45–12:10	Daewoon Lim. Porous Metal-Organic Framework and Their Composites for Energy Application	25 min
12:10–12:25	Alexandr Sapianik. Rational Synthesis of Metal-Organic Frameworks from a Pre-Organized Heterometalic Carboxylate Building Blocks	15 min
Lunch, 1 h 35 min		

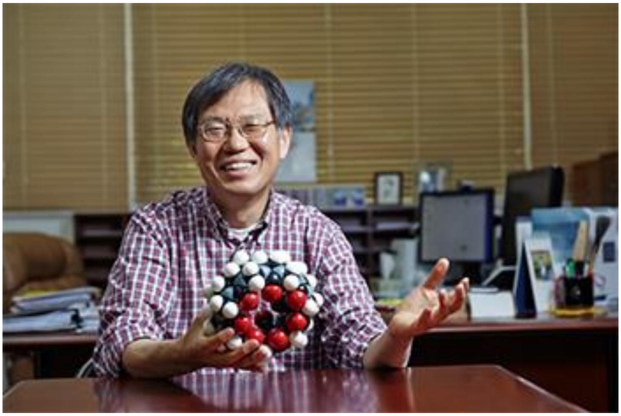
Chairman: Christian Serre		
14:00–14:45	Hiroshi Nishihara. Coordination Nanosheet (CONASH) – Synthesis, Structure and Functions	45 min
14:45–15:30	Masaki Kawano. Redox-Active Coordination Networks	45 min
Coffee break, 20 min		
Chairman: Hiroshi Nishihara		
15:50–16:15	Konstantin A. Kovalenko. Metal Clusters Inclusion into MIL-101 and Functional Properties of Inclusion Compounds	25 min
16:15–16:40	Daniil I. Kolokolov. Dynamics in Confinement: Observation, Characterization and Possible Use	25 min
16:40–16:55	Naoki Ogiwara. Control of Molecular Rotor Rotational Frequencies in Porous Coordination Polymers Using a Solid-Solution Approach	15 min
16:55–17:10	Ken-ichi Otake. High Proton Conduction of Four-Legged Metal–Organic Nanotube Complex with Hydrophobic Nanochannel	15 min
17:10–18:00	Posters and Discussion	50 min
18:00–21:00	Conference Dinner	

September, 21st		
Chairman: Sujit K. Gosh		
9:00–9:45	Martin Schröder. Supramolecular Chemistry of Porous Metal-Organic Materials: Dynamics, Storage and Separations	45 min
9:45–10:30	Dirk Volkmer. Functional MFU-4-Type Metal-Organic Frameworks Comprising Open Metal Sites	45 min
10:30–10:45	Anastasia M. Cheplakova. Imparting High Proton Conductivity to Metal-Organic Framework Materials	15 min
Coffee break, 20 min		
Chairman: Yong Cui		
11:05–11:50	Hyungphil Chun. Toward New MOFs of Sufficient Interest: Case Study on 2,5-DOBDC Phases of Titanium(IV) and Zirconium(IV)	45 min
11:50–12:15	Ekaterina N. Zorina-Tikhonova. Formation of Heterometallic Coordination Polymers Based on {Cu(Me$_2$mal)$_2$} Fragment	25 min
12:15–12:10	Evgenia S. Bazhina. Design of Polynuclear Architectures Based on Mononuclear Fragment of Oxovanadium(IV) and Substituted Malonate Anions	25 min
Lunch, 1 h 20 min		
Chairman: Dirk Volkmer		
14:00–14:45	Sujit K. Ghosh. Porous Coordination Compounds as Chemical Sensors, Fuel Cell Membrane and Pollutant Adsorbents	45 min
14:45–15:30	Yong Cui. Heterogenization of Chiral Metallosalen Catalysts Over Frameworks	45 min

15:30–15:45	Tatyana K. Koltunova. Lithium- and Magnesium-Carboxylate Coordination Polymers	15 min
Coffee break, 20 min		
Chairman: Hyungphil Chun		
16:05–16:30	Sergei S. Sapchenko. Urotropine-Containing Metal-Organic Frameworks: from Design to Functional Properties	25 min
16:30–16:55	Marina S. Zavakhina. Halochromic Coordination Polymers Based on Chromeazurol B Dye	25 min
16:55–17:20	Alena M. Sheveleva. EPR Spin Probe Methodology for Investigation of Structure Transitions and Gas Adsorption in MOF	25 min
17:20–17:35	Marina O. Barsukova. An Unexpected Hysteretic Sorption Behavior in Microporous Metal-Organic Frameworks	15 min
17:35–17:45	Closing Remarks Vladimir P. Fedin, Martin Schröder	10 min
18:00–21:00	Dinner	

September, 22nd		
9:30–16:30	Sightseeing, some hiking	
18:00–19:00	Dinner	

September, 23th		
8:30–16:30	Bus trip to Novosibirsk	~8 h
16:30–17:30	Accommodation in local hotel	45 min



KIMOON KIM

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Kimoon Kim received his B.S. degree from Seoul National University (1976), MS degree from Korea Advanced Institute of Science and Technology (1978), and Ph.D. degree from Stanford University (1986). After two year postdoctoral work at Northwestern University he started his own academic career at Department of Chemistry, Pohang University of Science and Technology (POSTECH) in 1988 where he is now Distinguished University Professor (POSTECH Fellow). Since 2012, he has also been director of the Center for Self-assembly and Complexity (CSC), Institute for Basic Science (IBS). His current research focuses on developing novel functional materials and devices based on supramolecular chemistry. In particular, his group has been working on a wide variety of functional materials based on cucurbiturils, a family of pumpkin-shaped macrocyclic molecules, and organic or metal-organic porous materials useful for catalysis, separation and gas storage. His work has been recognized by a number of awards including Izatt-Christensen Award (2012). He has been a member of the Korean Academy of Science and Technology since 2000.

CHRISTIAN SERRE

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Christian Serre, 46 years old, is an engineer from the Ecole Supérieure de Physique et de Chimie Industrielles de Paris. He obtained a PhD in Inorganic Chemistry in 1999 at University of Versailles St Quentin, France. After a post-doctoral fellowship in the USA in 2000 within the CNRS-Rhodia Inc. joint laboratory, he moved to a permanent CNRS research position in 2001 in the 'Porous Solids' research group in Versailles. Since 2009, he is currently CNRS research director at the head of the Porous Solid Group in Versailles. He recently started in 2016 a new porous materials institute in Paris at the Ecole Normale Superieure and ESPCI engineer school. He received the CNRS bronze medal in 2006, a European Research Council starting grant in 2008 devoted to the bioapplications of Metal Organic Frameworks, the Solid State Chemistry award of the French chemical society in 2010 and very recently the Fonde de l'Etat award from the French academy of sciences. His research topics deal with the synthesis, structure determination and applications, particularly in biomedicine, of Metal Organic Frameworks. He is currently coauthor of more than 256 articles and 16 patents with >25000 citations (h factor of 73).

HIROSHI KITAGAWA

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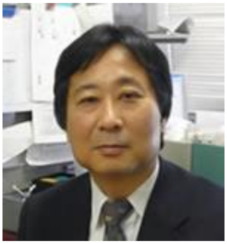
Hiroshi Kitagawa finished his Ph.D course in 1991 and received his Ph.D. from Kyoto University in 1992. He moved to Institute for Molecular Science (IMS) as an assistant professor in 1991, Japan Advanced Institute of Science & Technology (JAIST) as an assistant professor in 1994, University of Tsukuba as an associate professor in 2000, and Kyushu University as a professor in 2003. In 2009, he returned back to the original laboratory at Kyoto University. He held a visiting appointment at Davy-Faraday Research Laboratory, Royal Institution of Great Britain (1993-1994). He was a chair of the 5th Chemical Sciences and Society Summit (CS3), 2013. He is now Deputy Executive-Vice President for Research at Kyoto University. He is engaged at Japan Science & Technology Agency (JST) as a Research Director of ACCEL and a Research Supervisor of Science and Creation of Innovative Catalysts, PRESTO. His research fields are solid-state chemistry, coordination chemistry, nano-science, low-dimensional electron system, and molecule-based conductors. He was awarded *The Chemical Society of Japan Award for Creative Work* (2010), *Inoue Prize for Science* (2011), *Marco Polo della Scienza Italiana* (2013), and *The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology* (2016).



HIROSHI NISHIHARA

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Hiroshi Nishihara received D. Sc. in 1982 from the University of Tokyo. He was appointed research associate of Department of Chemistry, Faculty of Science and Technology at Keio University in 1982, and he was promoted lecturer in 1990, and associate professor in 1992. Since 1996, he has been a professor of Department of Chemistry, School of Science at The University of Tokyo. He also worked as a visiting research associate in the Prof. Royce W. Murray's group of Department of Chemistry at The University of North Carolina at Chapel Hill (1987-1989), and as a researcher of PRESTO, JRDC (1992-1996). He has received Professorship of University of Bordeaux I (France) in 2005, that of University of Strasbourg (France) in 2009, and Distinguished Lectureship of Hong Kong Baptist University in 2012.

He received *Young Scholar's Lectureship, The Chemical Society of Japan* in 1994, *The Chemical Society of Japan Award for Creative Work* in 2003, *Docteur Honoris Causa from University of Bordeaux* in 2011, *Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology* in 2014, *Japan Society of Coordination Chemistry Award* in 2015, and *Chemical Society Japan Award* in 2016. He was the leader of a Grant-in-Aid for Scientific Research on Innovative Areas "*The Coordination Programming – Science of Super-molecular Structure and Creation of Chemical Elements*" (area abbr.: Coordination program) from 2009 to 2014, and that of JST CREST project "*Creation of Organic-Inorganic Hybrid 2D Materials, Coordination Nanosheets, with Innovative Electronic, Photonic, and Chemical Functions*" from 2015 to 2021.

MASAKI KAWANO

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Masaki Kawano is professor at Chemistry Department, Tokyo Institute of Technology. He received his PhD degree from Waseda University in 1993. After working at Waseda University (1992–1994, as research associate), University of Wisconsin-Madison in the US (1994–1997, as postdoctoral fellow), Tokyo Institute of Technology (1997–2003, as postdoctoral fellow), the University of Tokyo (2003-2004, as lecturer; 2004-2009, as associate professor), and POSTECH (2009-2015, as professor), he moved to his current position in 2015. His major research interests include *in situ* crystallography, *ab initio* powder structure analysis, kinetic assembly and coordination polymers. His awards and honors are *The Lectureship Award of Young Generation Special Forum (Chemical Society of Japan)* (2002), *The UK-JAPAN researchers exchange program (JST)* (2005), *Chemistry Innovation UT GCOE Lectureship (2008), The CSJ Award for Creative Work (Chemical Society of Japan)* (2009), *Rising Star Research Support Program in POSTECH (2011), Yamada Foundation Award 2015* and *Nagase Foundation Award 2016.*

MARTIN SCHRÖDER

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Martin Schröder obtained his BSc from the University of Sheffield and PhD from Imperial College, London, and was a postdoctoral fellow at the ETH, Zurich and University of Cambridge. He has held academic appointments at the University of Edinburgh and University of Nottingham. In 2015 he was appointed Vice-President and Dean of the Faculty of Science and Engineering and Professor of Chemistry at the University of Manchester. He has won a number of RSC prizes including the Corday Morgan Medal and Prize, the Tilden Lectuership and awards for Chemistry of the Transition Metals, and for Chemistry of the Platinum Group Metals. He has been awarded a Royal Society Wolfson Merit Award, a Leverhulme Research Fellowship and an Honorary Doctorate from Tallinn Technical University, and has held ERC Advanced and Proof of Concept Grants. He is a member of Academia Europaea. His research lies in the area of coordination and supramolecular chemistry with specific focus on porous metal organic framework materials for energy applications and clean technologies.

DIRK VOLKMER

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Dirk Volkmer obtained his Dr. of Science in Inorganic Chemistry from the University of Münster (Westphalia), Germany. He spent the academic years 1995–1996 as Feodor Lynen post-doctoral fellow at the Université Louis Pasteur (Strasbourg (France), with Prof. Jean-Marie Lehn). During the period of 1996 – 2004 he stayed as a so-called “Habilitand” (= German academic equivalent to an Assistant Professor) at the University of Bielefeld (Germany, with Achim Müller), including a short stay from 1998–1999 at the Weizmann Institute of Science (Rehovot (Israel), with Prof. Lia Addadi), where he went as a Minerva fellow.

From 2004–2010 he became Associate Professor at the University of Ulm (Germany), after which he accepted his present position as Full Professor and Chair of Solid State and Materials Chemistry at the Institute of Physics, University of Augsburg (Bavaria, Germany).

His main research interests lie in coordination chemistry and in the design of biologically inspired materials, both being merged into functional porous framework materials. Applications range from sorption and gas separation, activation of small molecules, heterogeneous catalysis to sensors and nanodevices. In 2008 he received the Merckle (Ratiopharm) Award for the development of biomimetic materials.

HYUNGPHIL CHUN

Hyungphil Chun is professor of Department of Applied Chemistry in Hanyang University, Republic of Korea. He received his PhD from University of Houston, Texas, USA in 2000. He moved to Max-Planck-Institut für Strahlenchemie, Mülheim an der Ruhr, Germany as a research fellow, Center for Smart Supramolecules, POSTECH, Korea as a senior research scientist in 2002 and Department of Applied Chemistry, Hanyang University, Korea as an assistant in 2005. His interests cover synthesis of new metal-organic frameworks and molecular solids for applications in gas storage and separation.

SUJIT K. GHOSH

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Sujit Kumar Ghosh is associate professor in IISER Pune, Pashan, India. He received his PhD in Chemistry from the Indian Institute of Technology (IIT) Kanpur, India in 2006. He then spent three years at Kyoto University (Japan) as a JSPS and CREST postdoctoral fellow before joining IISER Pune in 2009. His group is working on the development of MOF based chemical sensors, anion adsorbents, hydrocarbon separation and ion conductors.

YONG CUI

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Yong Cui received a PhD in chemistry in 1999 from Fujian Institute of Research on the Structure of Matter, CAS. He carried out his postdoctoral research at the University of Science and Technology of China (1999–2000), at the University of North Carolina (2001–2002) and at the University of Chicago (2003–2005). He joined the Shanghai Jiao Tong University in 2005, where he is now a professor of chemistry. His research interest lies in the fields of supramolecular chemistry and chiral material.

NEW APPROACHES TO MODULAR POROUS MATERIALS

Kimoon Kim

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In recent years, considerable efforts have been devoted to the creation of mesopores over 5 nm in MOFs. So far, such mesoporous MOFs are produced by direct synthetic methods including ligand extension, template-assisted synthesis, imperfect crystallization (defect formation), and etc. Since these methods require rather elaborated synthetic procedures, it is highly desirable to develop a simple and reliable method to produce mesoporous MOFs. Furthermore, porous materials having both micro- and mesopores are expected to be useful for many practical applications, but the synthesis of MOFs with such hierarchical pore structures in a controlled manner is still challenging.

We recently reported a new approach to the synthesis of hierarchical micro- and mesoporous metal-organic frameworks (MOFs) from microporous MOFs by a simple hydrolytic post-synthetic procedure [1]. As a proof of concept, we synthesized a new microporous MOF, POST-66(Y), and studied its transformation into a hierarchical micro- and mesoporous MOF by water treatment. This method produced mesopores in the range of 3 to 20 nm in the MOF while maintaining the original microporous structure, at least in part. The degree of micro- and mesoporosity can be controlled by adjusting the time and temperature of hydrolysis. The resulting hierarchical porous MOF, POST-66(Y)-wt, can be utilized to encapsulate nanometer-sized guests such as proteins and the enhanced stability and recyclability of an encapsulated enzyme has been demonstrated.

While MOFs and covalent-organic frameworks (COFs) have been extensively studied over the last two decades, relatively little attention has been paid to organic molecular porous materials, even though they have potential benefits over extended frameworks such as processability and easy functionalization. Recently, we reported the porphyrin boxes (**PB-1** and **PB-2**), rationally designed porous organic cages with a large cavity using well-defined and rigid 3-connected triangular and 4-connected square shaped building units [2]. **PB-1** has a cavity as large as 1.95 nm in diameter and shows high chemical stability in a broad pH range (4.8 to 13) in aqueous media. The crystalline nature as well as cavity structure of the shape persistent organic cage crystals were intact even after complete removal of guest molecules, leading to one of the highest surface area (1370 m^2/g) among the known porous organic molecular solids. The size of cavities and windows of the porous organic cages can be modulated using different sized building units while maintaining the topology of the cages, as illustrated with **PB-2**. Interestingly, **PB-2** crystals showed unusual N_2 sorption isotherms as well as high selectivity for CO_2 over N_2 and CH_4. We are currently studying other interesting properties of the new organic cages such as selective ion transport, and exploring their applications including construction of hierachical nanostructures.

This work was supported by Institute for Basic Science (IBS).

1. Y. Kim et al. *Angew. Chem. Int.*, **2015**, *54*, 13273.
2. S. Hong et al. *Angew. Chem. Int.*, **2015**, *54*, 13241.

NEW HORIZONS OF ROBUST METAL ORGANIC FRAMEWORKS

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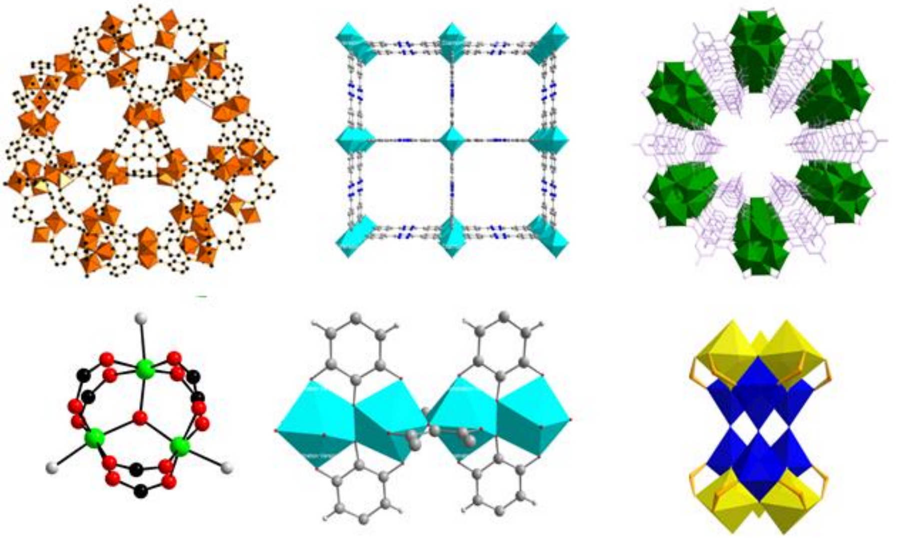
Metal-organic frameworks based on high valence metal ions (e.g. Fe^{3+}, Al^{3+}, Cr^{3+}, Ti^{4+} or Zr^{4+}) have been intensively studied within the past few years mainly due to their good thermal and enhanced chemical stabilities [1]. These cations are known for their strong binding affinities towards oxygen containing functional groups (-COOH, -OH, O2-), which results often in much better stability of their related MOFs compared to the other metal ions. However, porous structures based on these elements are still scarce mostly due to their very high chemical reactivity in solution preventing from any sufficient crystal growth [3].



These materials are nevertheless of a great interest for separation, catalysis or biomedicine due to their large range of properties depending mainly on their structural (pore size, pore architecture, flexibility or rigidity) or chemical (Lewis, BrØnsted, redox, photoactive metal sites, organic functional groups) features. Herein we will show (i) how topical metal(III) polycarboxylate MOFs can be functionalized or activated carefully to enhance their properties or (ii) how one can target new structures to obtain even more robust metal (III/IV) architectures bearing sometimes unique properties. We will propose relationships between their structural, chemical or optical features and their most interesting properties (separation, catalysis, conductivity…) [4].

1. T. Devic, C. Serre, *Chem. Soc. Rev.*, **2014**, 43, 6097-6115.
2. P. Horcajada *et al. Chem. Rev.*, **2012**, *112(2)* 1232.
3. a) M. Dan-Hardi, et al, *J. Am. Chem. Soc.* **2009**, 131, 10857 – 10859. b) S. Yuan et al. *Chem. Sci.*, **2015**, 6, 3926-3930. c) B. Bueken, et al., *Angew. Chem. int. Ed.* **2015**, 127, 14118 –14123. d) C. Serre et al., *Chem. Mater.*, **2006**, 18, 1451-1457.
4. a) A. Cadiau et al., *Adv. Mater.* **2016**, *27(32)*, 4775-4780; b) M. Daturi et al., *under revision*; c) J.W. Yoon et al., *under revision*; d) S. Wang et al., *submitted.*

DIMENSIONAL CROSSOVER IN COORDINATION CHEMISTRY

Hiroshi Kitagawa

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Here, we demonstrate a bottom-up approach for the fabrication of well-defined dimensional-crossover nano-architectures with high tunability using metals and organic molecules as building blocks or linkers [1-8]. We succeeded in rationally constructing assemblies; (1) ladders and tubes which are located in dimensional-crossover region between 1D and 2D, (2) surface metal–organic frameworks (SurMOFs) which are located in dimensional-crossover region between 2D and 3D, and (3) nanoparticles coated with MOFs or polymers which are located in dimensional-crossover region between 0D and 3D.

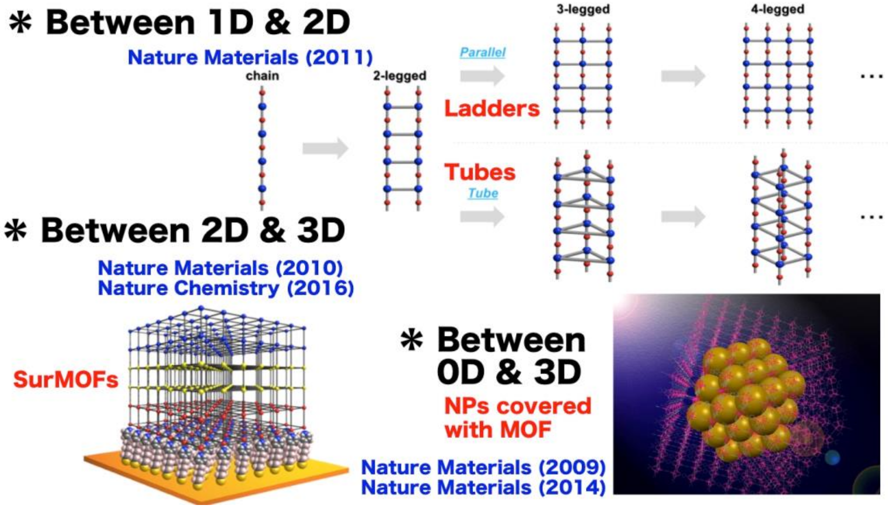
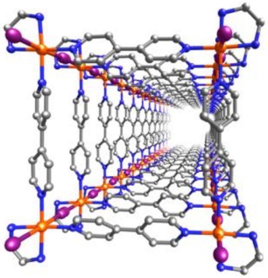


Figure 1. Materials research in dimensional crossover regions.

Recently, we have developed several square prism-shaped metal-organic nanotubes with aside of 0.5 - 2 nm. A uniform 1D channel with aside of 2 nm is fabricated inside the tube, and H_2O and alcohol can be selectively adsorbed. Its optical gap is about 0.76 eV of semiconductive region, and X-ray and theoretical studies revealed its unique electronic structure of charge-density-wave (CDW) quartets. In addition, its electronic states can be successively controlled by exchanges of structural components and guest molecules. The results presented here demonstrate a rational route to the creation of nanotubes with high tunability of structures and electronic states, and might also offer valuable insights into multifunctional nanomaterials. In addition, our recent study on proton transport properties is presented and proton diffusion in a confined water-nanotube of hydrophobic nanochannel is discussed by a pulse field gradient NMR study.



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2. G. Li, H. Kobayashi, J. M. Taylor, R. Ikeda, Y. Kubota, K. Kato, M. Takata, T. Yamamoto, S. Toh, S. Matsumura, H. Kitagawa. *Nature Materials*, **2014**, *13*, 802.
3. K. Otsubo, Y. Wakabayashi, J. Ohara, S. Yamamoto, H. Matsuzaki, H. Okamoto, K. Nitta, T. Uruga, H. Kitagawa. *Nature Materials*, **2011**, *10*, 291.
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5. R. Makiura, T. Yonemura, T. Yamada, M. Yamauchi, R. Ikeda, H. Kitagawa, K. Kato, M. Takata. *Nature Materials*, **2009**, *8*, 467.
6. T. Yamada, K. Otsubo, R. Makiura, H. Kitagawa. *Chem. Soc. Rev.*, **2013**, *42*, 6655.
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8. K. Otsubo and H. Kitagawa. *CrystEngComm*, **2014**, *16*, 6277.

COORDINATION NANOSHEET (CONASH) – SYNTHESIS, STRUCTURE AND FUNCTIONS

Hiroshi Nishihara

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Single-layer 2D materials have attracted much attention because of their unique physical and chemical properties. We have synthesized coordination nanosheets (CONASHs) comprising metal ions and organic π-ligands by the interfacial coordination reactions (Fig. 1) [1,2].

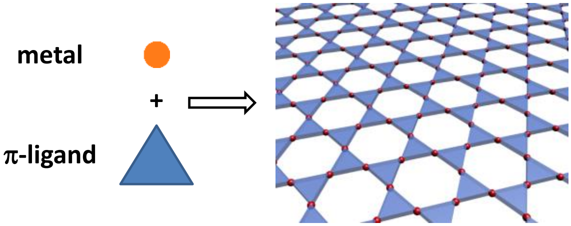

Fig. 1. Coordination nanosheet.

For example, a liquid−liquid interfacial reaction of nickel(II) acetate in an aqueous phase with benzenehexathiol in an organic phase produced semiconducting sheets containing bis(dithiolato)nickel moieties with one micrometer thickness. A single-layer nanosheet with 0.6 nm thickness was successfully synthesized using a gas−liquid interfacial reaction [3]. Modulation of the oxidation state and the electronic conductivity of the coordination nanosheet was achieved using redox reactions [4]. Bis(dithiolato)palladium nanosheet was prepared by a modified interfacial method inhibiting the formation of Pd nanoparticles [5].

A series of multilayered coordination nanosheets comprising 1,3,5-tris(4-(2,2′:6′,2″-terpyridyl)phenyl)benzene and iron(II) or cobalt(II) ions was synthesized by liquid/liquid interfacial coordination reactions. The resultant nanosheet had a flat, smooth morphology and was several hundreds of nanometers thick [6]. Upon its deposition on an indium tin oxide (ITO) electrode, the nanosheets underwent a reversible and robust redox reaction (Fe^{3+}/Fe^{2+} or Co^{2+}/Co^{+}) accompanied by a distinctive color change. Electrochromism was achieved in a solidified device composed of the nanosheet, a pair of ITO electrodes, and a polymer-supported electrolyte. The combination of Fe^{2+} and Co^{2+} nanosheets in one device deposited on each ITO electrode demonstrated dual-electrochromic behavior.

We also synthesized coordination nanosheets featuring a photoactive bis(dipyrrinato)zinc(II) complex motif by an interfacial reaction between a three-way dipyrrin ligand and zinc(II) ions [7]. The bis(dipyrrinato)zinc(II) nanosheet deposited on a SnO_2 electrode functions as a photoanode in a photoelectric conversion system.

1. R. Sakamoto, K. Takada, X. Sun, T. Pal, T. Tsukamoto, E. J. H. Phua, A. Rapakousiou, K. Hoshiko, H. Nishihara, *Coord. Chem. Rev.* **2016**, *320-321*, 118.
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REDOX-ACTIVE COORDINATION NETWORKS

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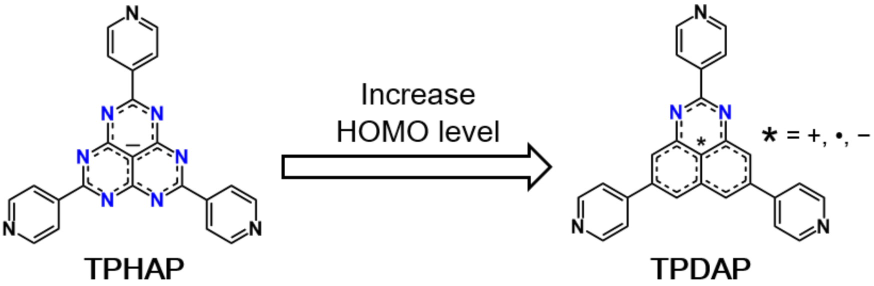
Our research interests include creating functional interactive pores. Especially, by controlling the weak intermolecular interactions, we kinetically generate interactive porous coordination networks which will not be obtained by conventional thermodynamic control like solvothermal synthesis. In sharp contrast to the thermodynamic synthesis of coordination networks, kinetically trapped metastable networks were not paid much attention, because it is very difficult to analyze crystal structures. Recently we have demonstrated that it is possible to perform ab initio powder structure determination of porous coordination networks using low resolution data [1]. In addition, we designed an interactive ligand, tripyridyl hexaazaphenalene (TPHAP), which was aimed to show the importance of multi-interactivity of the ligand for kinetic network formation [2]. Indeed, we elucidated that totally different coordination networks can be selectively prepared using the same starting materials by thermodynamic and kinetic control [3,4]. Moreover, we can prepare another type of coordination networks from the kinetic product which can be prepared



instantly and in a large scale. Recently we designed and prepared interactive as well as redox active ligands [5].

A redox-active porous coordination network can provide a potential-tunable space to achieve numerous benefits, including catalytic activity, selective molecular trapping, and tunable electronic/magnetic materials. The redox center of a conventional redox-active network typically consists of metal ions rather than organic ligands. A few redox-active ligands have been synthesized, using mostly TCNQ, TTF, pyrene, or naphthalene diimide skeletons. Because TPHAP is not redox-active, we designed another tripyridyl ligand, 2,5,8-tri(4-pyridyl)1,3-diazaphenalene (TPDAP) to introduce redox activity while keeping the same molecular shape as TPHAP [5]. In this talk, we will introduce selective preparation of redox active porous networks and their redox properties [6].

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SUPRAMOLECULAR CHEMISTRY OF POROUS METAL-ORGANIC MATERIALS: DYNAMICS, STORAGE AND SEPARATIONS

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The storage, sequestration and selective binding of fuel gases in a safe and compact form represents a significant current challenge. There is wide-ranging interest in the development of stable materials that can store and release hydrogen, carbon dioxide, sulphur dioxide, methane and hydrocarbons with fast kinetics and high reversibility over multiple cycles. Porous co-ordination framework compounds have enormous potential in this regard. We report the synthesis, structural characterisation and gas adsorption studies of a range of metal-organic materials derived from stable carboxylate-linked complexes that exhibit high porosity and surface area coupled with high storage capacities and selectivities [1]. Of particular interest are *in situ* structural and dynamic studies of gas-loaded materials that define the binding of substrates within pores at a molecular level [2].

The synthesis, structure and properties of a unique non-amine-containing porous solid MFM-300(M) (M = Al, Bi, In V, Sc, Cr, Fe) and doped analogues in which hydroxyl groups within the pores bind selectively to CO_2, SO_2, acetylene and ethylene are also described. MFM-300 exhibits highly selective uptake of CO_2 versus N_2, CH_4, H_2, CO, O_2, Ar, and *in situ* powder X-ray diffraction (PXRD), neutron diffraction and inelastic neutron scattering (INS) studies, combined with density functional theory (DFT) modelling, reveal that these hydroxyl groups bind CO_2 and SO_2 *via* the formation of $O{=}X{=}O(\delta\text{-})\cdots H(\delta\text{+})—O$ hydrogen bonds [3]. These are reinforced further by weak supramolecular interactions with C-H hydrogen atoms on the phenyl rings. This offers exciting potential for the application of new capture systems based on the soft binding of CO_2 and SO_2 via the use of an “easy-on“ and “easy-off“ model.

This work has been extended to the study of the storage and binding of acetylene and ethylene which bind to the metal-organic host *via* hydrogen bonding between hydroxyl group and the π-electron density of the unsaturated guest [4]. Excellent gas capacities and selectivities between alkane vs alkene vs alkyne are observed, representing a methodology for purification of ethylene.

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FUNCTIONAL MFU-4-TYPE METAL-ORGANIC FRAMEWORKS COMPRISING OPEN METAL SITES

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Since 2009, metal-organic frameworks (MFU-4 family [1], CFA-1 [2]) have been developed in our group, that comprise unique “Kuratowski-type”[3] coordination units. The structural and functional relationship between these frameworks and the versatile class of scorpionate complexes will be presented with special attention drawn to function (i.e. quantum sieving, [4] band-gap engineering [5], activation of small molecules [6]). A rational approach towards catalytically active MOFs is proposed, which rests on the tridentate facial coordination of redox-active metal centers in frameworks giving rise to open and flexible coordination sites, suitable for the development of functionally diverse heterogeneous catalysts and sensor materials.

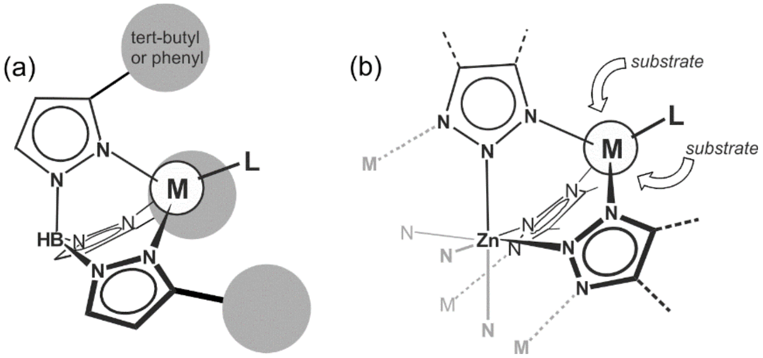

Fig. 1. (a) Scorpionate complex; (b) Secondary building (“Kuratowski-type”) unit from MFU-4 & CFA-1 comprising open metal sites (M = transition metal, L = ligand)

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TOWARD NEW MOFS OF SUFFICIENT INTEREST: CASE STUDY ON 2,5-DOBDC PHASES OF TITANIUM(IV) AND ZIRCONIUM(IV)

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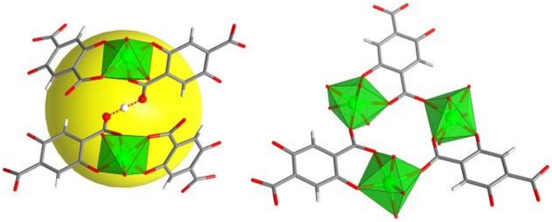
Study on porous coordination networks known as MOFs has seen an exponential growth in last decade, and the main focus in the field of the molecule-based crystalline porous materials has apparently shifted from de novo synthesis toward advanced applications. Further developments from this point on, however, would require an expanded portfolio of hydrothermally stable MOFs that can be readily synthesized from simple building blocks. In this regard, the logic behind the synthesis of new MOFs in our lab in the past will briefly be revisited before current efforts with Ti and Zr are introduced. The behavior of these high-valent metal ions under solvothermal synthetic conditions is only poorly understood, and thus the metal ions resist systematic synthesis with simple ligands. Recently, our lab has discovered that a relatively simple, but painstaking control during conventional solvothermal reactions with 2,5-dihydroxyterephthalic acid produces phase-pure MOFs for Ti(IV) and Zr(IV). Their structures determined by single-crystal X-ray crystallography, shown in part, and preliminary data on stabilities as porous MOFs will be presented.



POROUS COORDINATION COMPOUNDS AS CHEMICAL SENSORS, FUEL CELL MEMBRANE AND POLLUTANT ADSORBENTS

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Metal–organic frameworks (MOFs) or Porous Coordination Polymers (PCPs) are well known for their high surface area and a designable structure with specific host–guest chemistry. MOFs score over conventional porous materials owing to their distinct advantages of tuneable electronic properties, designable pore channels and controllable functionalization. These features go well with the requisites in materials sought for application in several domains including chemical sensing, capture of environmentally toxic molecules and as solid-state ion conductors. The engineering of MOFs for targeted application is an active aspect of current research; some of the examples in this regard will be discussed in detail.

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HETEROGENIZATION OF CHIRAL METALLOSALEN CATALYSTS OVER FRAMEWORKS

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The incorporation of catalytically active chiral molecules like metallosalen and BINOLate complexes into MOFs has been recognized as an efficient strategy for heterogeneous asymmetric catalyst design and synthesis with considerable impact. Besides crystalline structures and high catalyst loadings, spatial control of reactive sites engendered by frameworks could often dramatically enhance reactivity by precluding self-quenching or facilitating coorperativity in confined space, thus offering advantages over other immobilized catalyst systems. However, the heterogenized catalysts are typically less effective than their homogeneous analogs, and success examples of chiral MOF catalysts especially those for asymmetric catalysis and framework confinement effect on incorporated molecular catalysts are still scarce [5]. Given their intrinsic features and excellent asymmetric catalytic behavior, metallosalen and biphenol are expected to be ideal functional struts in chiral functional MOFs. We report here the assembly of chiral MOFs from metallosalen or biphenol complexes and show that they are efficient heterogeneous catalysts for asymmetric organic transformations [1-4].

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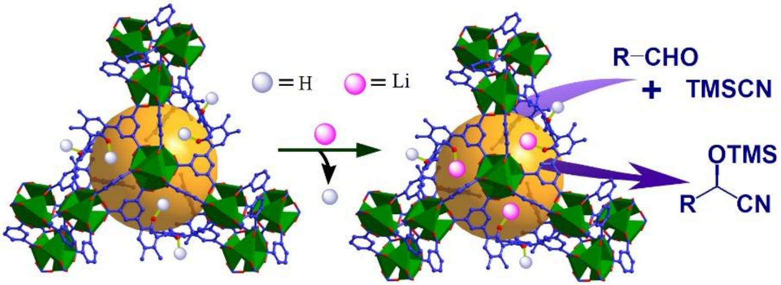

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POROUS METAL-ORGANIC FRAMEWORK AND THEIR COMPOSITES FOR ENERGY APPLICATION

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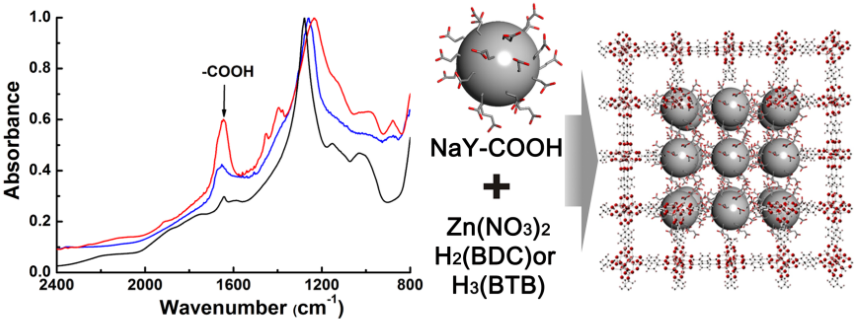
Porous metal organic frameworks (MOFs) have been attractive as an emerging crystalline micro-porous material because of their various potential applications such as gas storage, separation, sensor, heterogeneous catalysis, proton conduction, and fabrication of nanoparticles [1] which are attributed to their exceptional porosity, large surface area and tunability. Although they have a potential for applications of interest it is required to enhance their physicochemical properties for the practical application. Synthesis of composite materials composed of MOFs and one or more materials such as metal nanoparticles (NPs), quantum dots, polymer, graphene oxide, carbon nanotubes, and biomolecules including other MOFs is considered as one of approaches [2]. This strategy not only complement the weakness of individual materials but also represent a new property with the synergistic effect.

Herein we present a synthesis of new MOF composites (nano particles with MOF and zeolite with MOFs), charaterization and their potential application [3,4]. These materials provide a first stepping stone toward the synthesis of various composites that have potential application to the hydrogen storage and size selective ionic hydrogenation catalyst.



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RATIONAL SYNTHESIS OF METAL-ORGANIC FRAMEWORKS FROM A PRE-ORGANIZED HETEROMETALLIC CARBOXYLATE BUILDING BLOCKS

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Chemistry of metal-organic frameworks (MOFs) is a recently emerged but already developed field of modern science. Rational design of metal-organic frameworks (MOFs) based on polynuclear metal nodes from the corresponding molecular complexes is a rare sight, compared to the overwhelming number of examples of the *in situ* self-assembly mechanisms.

Tetranuclear pivalates $[Li_2M_2(piv)_6(py)_2]$ ($M = Co^{2+}$, Ni^{2+}, Zn^{2+}, …) are an interesting example of bimetallic complexes which could be obtained by a simple procedure and feature a number of functional properties, such as magnetism or luminescence. Because of a robust structure and fixed geometry of the carboxylate ligand these complexes are excellent candidates for heterometallic building blocks of the multifunctional porous MOFs. Using them as synthons we have obtained a wide range of new metal-organic frameworks based on initial carboxylic fragments $\{Zn_2Li_2(COO)_6\}$, $\{Li_2Co_2(COO)_6\}$ (Fig. 1) as well as binuclear $\{ZnLi(COO)\}$, $\{CoLi(COO)\}$.

Most promising isoreticular compounds $[Li_2Zn_2(R\text{-}bdc)_3(bpy)]$ (where R – H, Br, NO_2, NH_2 substituents in the aromatic ring of terephthalate linker) were characterized by measuring sorption properties, luminescence and framework dynamic. Interestingly, a fascinating interplay of the luminescence properties, depending on the excitation wavelength as well as the nature of the aromatic guest molecules was discovered (Fig. 1). Despite the isostructural nature of all four MOFs, three compounds (but not with NO_2 substituent) feature extensive hysteresis between the adsorption and desorption curves at low pressures during the nitrogen isotherm measurements likely due to pressure-induced framework dynamics. The functional substituents (R) in microporous MOFs decorate the inner surface and also control the volume of micropores, the surface area as well as affect both the gas uptakes and the adsorption selectivity. The highest CO_2 and CH_4 absorption at ambient conditions (106 and 23 $cm^3{\cdot}g^{-1}$ at 273 K, 1 bar) are well above typical values for microporous MOFs.

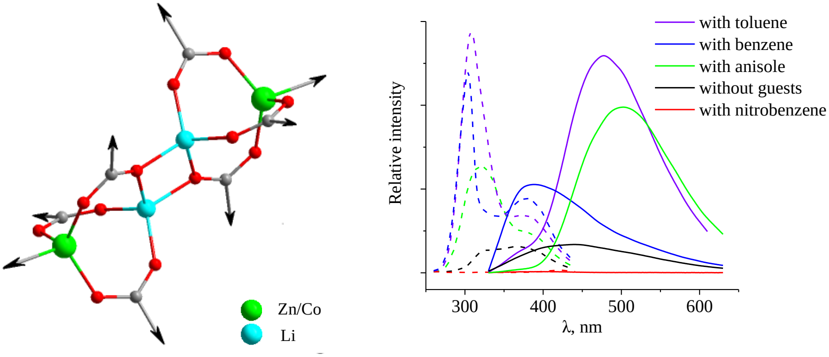

Fig. 1. 8-connected secondary building unit from heterometallic pivalate complex (left). Spectra of emission and excitation (right) of compound $[Li_2Zn_2(bdc)_3(bpy)]$ (λ_{Ex} = 320 nm).

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METAL CLUSTERS INCLUSION INTO MIL-101 AND FUNCTIONAL PROPERTIES OF INCLUSION COMPOUNDS

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Recently, Férey, Serre et al. have reported the synthesis of mesoporous coordination polymer MIL-101. It possesses a rigid zeotype crystal structure with extremely large surface area (~3800 m^2/g) and large nanocages (~3.4 nm) [1]. Importantly, this material is resistant to air, water, common solvents and thermal treatment (up to 320 °C). All these features allow one to consider MIL-101 as a promising support for immobilization of different nanosized guests, e.g. clusters, polyoxometallates, nanoparticles.

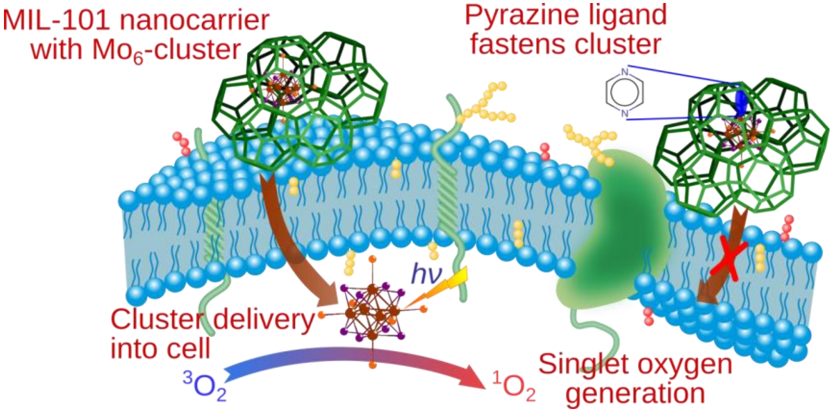
The inclusion of $[Re_4S_4F_{12}]^{2-}$ clusters results in producing additional polar centers inside MIL mesopores, thus increasing more than twice the number of hydrogen binding sites [2, 3].

Inclusion compounds containing luminescent $[Mo_6Cl_{14}]^{2-}$ and $[Re_6S_8(CN)_6]^{4-}$ clusters reveal unusual excitation properties during cooling down to 20 K: the irradiation maximum is shifted to the long wavelength region and the intensity increases ~4 times [4].

One of the advantages of MOFs is the possibility of their postsynthetic modification. For example, the substitution of aqua-ligands by functional ligand is feasible. We used ditopic 4,4'-bipyridyl and pyrazine for the coordination to chromium atom [5, 6]. The second nitrogen atom of the ligands is able to coordinate and anchor cluster complexes inside the porous matrix.

We used luminescent $K_4[\{Re_6(\mu_3\text{-}S)_8\}(HCOO)_6]$ and $(Bu_4N)_2[\{Mo_6I_8\}(NO_3)_6]$ cluster complexes with labile ligands in order to introduce into pristine and modified MIL-101. The luminescence and sorption properties of compounds obtained as well as their stability were studied. Because cluster complexes possess red long-lived photoluminescence, the reactive oxygen species generation was investigated.

The MTT study revealed a low cytotoxicity of pristine chromium metal-organic framework and molybdenum cluster inclusion compounds both with and without pyrazine strut. Confocal microscopy confirmed that MIL-101 performed as a nanocarrier for octahedral metal cluster complexes, that could penetrate through the cellular membrane from MIL-101 nanoparticles adhered to the external surface of the cell, though in the case of strongly bonded cluster complexes to MIL-101-pyz matrix *via* pyrazine ligand the penetration did not occur. Furthermore, photoinduced reactive oxygen species generation in living cells by the released from MIL-101 cluster complexes was established.



This work was supported by the Grant of the Government of the Russian Federation (No. 14.Z50.31.0006, leading scientist – Martin Schröder).

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DYNAMICS IN CONFINEMENT: OBSERVATION, CHARACTERIZATION AND POSSIBLE USE

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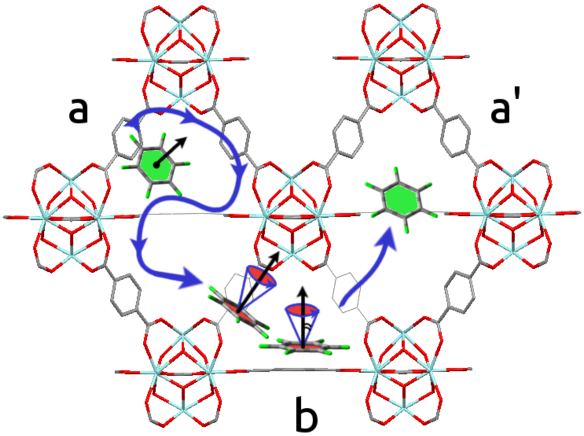
The phenomenon of dynamics in confined state is tightly bound to the dynamical processes that occur in porous materials and condensed (solid) state. In conditions when the available space for a given molecule shrinks to it is own size or just several times more its behavior undergoes a drastic change affecting such basic properties like molecular ordering in the system, the possible reaction pathways, but primarily the transport phenomena. This is especially important for new functional materials based on microporous coordination materials, such as metal-organic frameworks. For many applications like the proton conductors, molecular sieves and heterogeneous catalysts, the dynamics of confined species regulates the core functionality of the system.

This report is regards several practical examples in different fields of applications of microporous materials where the confinement plays a particularly important role. The main focus will be put on the combined use of different experimental techniques to probe the mobility of the confined molecular species and the importance of use of the structural data as a reference to build a realistic motional mechanism.

In particular, on the example of the benzene species adsorbed inside the UiO-66 MOF pores, it will be shown how the quasi-elastic neutron scattering coupled with solid state ^{2}H NMR can be used as a universal tool box to probe molecular dynamics in very broad range of time and length scales. So, it will be demonstrated how by considering the temperature evolution of ^{2}H NMR spectra line shapes and T_1, T_2 relaxations of the deuterated benzene we are able to understand both the mechanism of the reorientation and give the characteristic rates and barriers of the motions.



Inside UiO-66 pore benzene molecules propagate by jump exchange between cages (**a-b-a’**). The rotational dynamics in the tetrahedral cage (**b**) is much more hindered compared to the larger octahedral one (**a, a’**).

Finally some possible ways to use and control of the confinement effect will be discussed.

This work was supported by Russian Foundation for Basic Research (grant no. 14-03-91333) and by the Deutsche Forschungsgemeinschaft (grant HA 1893/16).

CONTROL OF MOLECULAR ROTOR ROTATIONAL FREQUENCIES IN POROUS COORDINATION POLYMERS USING A SOLID-SOLUTION APPROACH

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Rational design to control the dynamics of molecular rotors in crystalline solids is of interest because it offers advanced materials with precisely tuned functionality such as dielectric [1], magnetic [2], and optical properties [3]. To date, a few studies have demonstrated change of the rotor rotational frequency in crystals by modifying the substituent groups around the rotors [4]; however, this strategy has not provided continuous change of the frequency due to the limited range of available substituent derivatives.

Porous coordination polymers (PCPs) constructed of metal ions and organic ligands have great potential as crystalline solids that can allow the control of molecular rotor dynamics due to their porosity, which provides sufficient space for the rotation of organic ligands [5]. The shape and volume of the pores affects the rotational frequency of the ligands.

We employed the control of the rotational frequency of rotors in flexible PCPs using a solid-solution approach (Figure 1) [6]. Solid-solutions of the flexible PCPs [{Zn(5-nitroisophthalate)$_x$(5-methoxyisophthalate)$_{1-x}$(deuterated 4,4′- bipyridyl)}(DMF·MeOH)]$_n$ with an interdigitated structure allow continuous modulation of cell volume of the pores by changing the solid-solution ratio x.

We monitored the rotational frequency of rotors (pyridyl rings of the 4,4′-bipyridyl group) in the PCPs via ^{2}H solid-state NMR (Figure 2). Systematic modification of the solid-solution ratio x of the PCPs effectively modulates the void spaces in the PCPs from small space to large space and results in continuous changes of the rotational frequency from 10^3 Hz to 10^6 Hz without the need to vary the temperature. This is attributable to continuous changes in the local environment around the molecular rotors provided by variation of the isostructures.

Furthermore, this strategy should be applicable for the control of the functional dynamics of molecular rotors in other flexible porous materials The fine-tuning of ligand dynamics in the crystalline framework is related to the functions of dielectricity and ion conductivity, and the control of dynamics of these functional groups aligned in crystals is the next challenge.

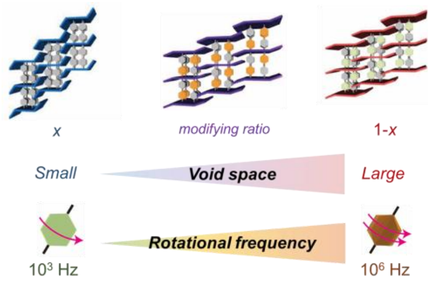

Fig. 1. Control of the rotational frequency of molecular rotors in flexible porous MOFs using a solid-solution approach.

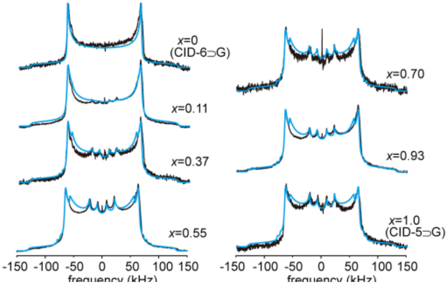

Fig. 2. ^{2}H solid-state NMR spectra for [{Zn(5-nitroisophthalate)$_x$(5-methoxyisophthalate)$_{1-x}$(deuterated 4,4′- bipyridyl)}(DMF·MeOH)]$_n$.

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HIGH PROTON CONDUCTION OF FOUR-LEGGED METAL–ORGANIC NANOTUBE COMPLEX WITH HYDROPHOBIC NANOCHANNEL

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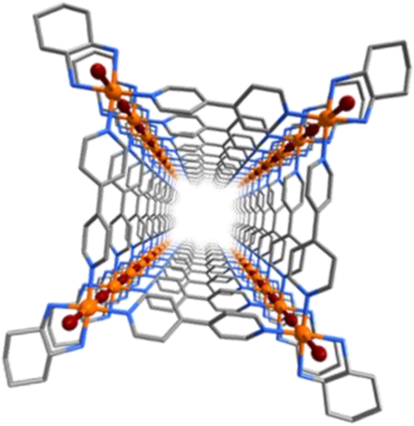

Figure 1. The crystal structure of 1 (100 K). Orange and brown spheres indicate platinum and bromide, respectively. Counteranions (SO_4^{2-}) and crystallization waters are omitted

Recently, research on proton conducting materials has attracted much attention due to its importance for both practical application and fundamental research. In particular, to study discrete one-dimensional (1D) channel systems is important for understanding biological systems, such as proton pump proteins [1,2]. In this study, we have focused on nanotube compounds based on halogen-bridged metal complexes (MX-chain) [3, 4, 5]. We have synthesized 4-legged MX-tube typed platinum complex $[Pt(dach)(bpy)Br]_4(SO_4)_4$ (**1**) (dach = 1,2-diaminocyclohexane bpy = 4,4’-bipyridine) and determined its crystal structure using single-crystal X-ray crystallography (SCXRD) (Figure 1). **1** has 1D hydrophobic nanochannel with a pore aperture size of ca. 1 nm and shows large water sorption uptakes. In addition, within the hydrophobic nanochannel, the included water molecules form a 1D hydrogen-bonded ice nanotube composed of water tetramers and octamers below 200 K as confirmed by variable temperature SCXRD studies. The proton conductivity measure-ments were performed using a single-crystal of 1 with two gold electrodes attached to the two sides of the single crystal along the channel direction (Figure 2). Upon increasing the relative humidity (RH) from 40 to 95%, the proton conductivity was significantly increased over three or ders of magnitude. At 55 °C and 95% RH, **1** showed the high conductivity of 1.7×10^{-2} S cm^{-1}. From the result of temperature dependence, activation energy was estimated to be about 0.3 eV, which indicates that the mechanism of the conduction can be explained by the Grotthuss model. For further investigation on the proton conducting mechanism, solid-state ^{1}H NMR measurements and theoretical calculations were also conducted. Details are reported.

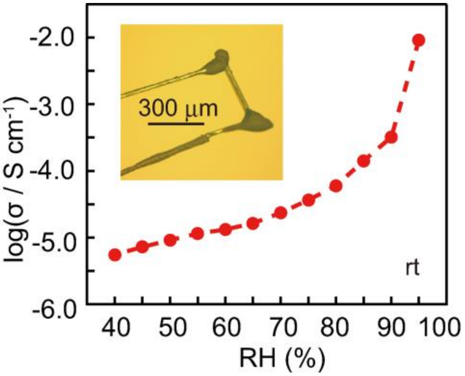

Figure 2. Humidity dependence of proton conductivity of 1. Inset shows the experimental setup.

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IMPARTING HIGH PROTON CONDUCTIVITY TO METAL-ORGANIC FRAMEWORK MATERIALS

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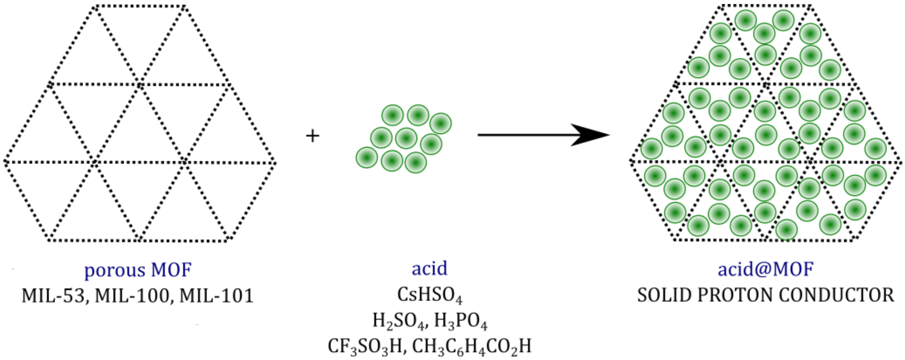
Metal-organic frameworks (MOFs) have been intensively investigated due to their unique functional properties, *e.g.* gas sorption, catalysis, luminescence and proton conductivity.

One of the approaches to impart a certain property to metal-organic framework material is inclusion of functional guest molecules. This approach proved to be promising and allows getting material with high proton conductivity (up to $1{\cdot}10^{-1}$ $Sm{\cdot}cm^{-1}$) as well. However, inclusion of highly acidic species (strong acids and acidic salts) requires the MOFs having enhanced hydrolytic stability. Cr-based MOFs of MIL family are among them.



For example, the (1−x)$CsHSO_4$–xCr-MIL-101 (x=0–0.07) hybrid compounds had decreased temperature of superionic phase transition and increased (up to 2 orders of magnitude) proton conductivity compared to $CsHSO_4$ with the proton conductivity of 10^{-7}–10^{-2} S/cm at the temperature range 50–200 °C [1].

The material "strong acid"@Cr-MIL-101 turned out to be stable during multiple measurements and demonstrate high proton conductivity [2,3]. So, the proton conductivities of H_3PO_4@MIL-101 and H_2SO_4@MIL-101 at 150 °C and dry atmosphere were found to be $\sigma=3\cdot10^{-3}$ $Sm\cdot cm^{-1}$ and $\sigma=1\cdot10^{-2}$ $Sm\cdot cm^{-1}$, respectively. The spectroscopic investigation of CF_3SO_3H@MIL-101 showed that proton transfer occurred via relay (Grotthuss) mechanism within the droplets of acid solution accompanied by their continuous reorganization.

The next step was to study the influence of the amount of loaded acid and the structure of the MOF. Thus, decreasing of the amount of loaded H_3PO_4 led to the significant drop of the conductivity to $\sigma=2\cdot10^{-6}$ $Sm\cdot cm^{-1}$. Similar hybrid materials based on MIL-53 and MIL-100 were synthesized. The measurements confirmed that MOF structure affected both values of proton conductivity and its temperature behavior.

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FORMATION OF HETEROMETALLIC COORDINATION POLYMERS BASED ON $\{Cu(Me_2mal)_2\}$ FRAGMENT

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The ability of malonic acid (H_2mal) anions to form stable six-membered chelate rings with metal atoms substantially predetermines the structure and properties of the complexes with malonate-dianions. These features of *d*-metal malonates, Cu^{II} in particular, make it possible to use them as metal-containing moieties in order to construct heteronuclear ionic, molecular, or polymeric systems.

The great majority of published works is devoted to the studies of the complexes with anions of unsubstituted malonic acid. Much less is known about the synthesis of *d*-metal derivatives with anions of substituted analogues of malonic acid that easily may turn out to be convenient blocks in construction of heterometallic systems. By varying the substituents in the malonate dianion, the nature of the heterometal, and the synthetic conditions, it is possible to obtain compounds with a certain composition and structure. Coordination polymers of this type can be interesting as sorbents for gases and organic substrates, biological-active compounds or precursors for complex oxides [1,2].

Mononuclear dianion $\{Cu(Me_2mal)_2\}^{2-}$ have been used as building block for synthesis of six new coordination polymers: $\{Li_2(H_2O)_2(H_2O)[Cu(Me_2mal)_2]\}_n$ (**1**), $\{Na_2(EtOH)_2[Cu(Me_2mal)_2]\}_n$ (**2**), $\{K_8(H_2O)_6[Cu(H_2O)(Me_2mal)_2]_2[Cu_2(Me_2mal)_4]\}_n$ (**3**),

$\{K_2M(H_2O)_5(H_2O)_3[Cu(Me_2mal)_2][Cu(H_2O)(Me_2mal)_2]\}_n$ (M = Mg^{II} (**4**) or Ni^{II} (**5**); isostructural compounds), and $\{K_4Co_3(H_2O)_8(H_2O)_4(OH)_2[Cu(H_2O)(Me_2mal)_4]_2\}_n$ (**6**). It was shown, that the structure of the compounds depends on nature and ionic radius of heterometal. In particular, the complex dimensionality growths from 1D to 2D and 3D with increasing the radius of *s*-metal in compounds **1**, **2**, and **3**, respectively. Partial replacement of K^+ in **3** by Mg^{2+}, Ni^{2+} and Co^{2+} leads to formation of heterometallic coordination polymers **4** and **5** with 2D structure, and 3D complex **6**.

Also we have shown that binding a dianionic $\{Cu(Me_2mal)_2\}^{2-}$ moiety with barium ions gives 3D polymeric structures $[BaCu(Me_2mal)_2(H_2O)_x]_n$ (x = 1(**7**) or 5 (**8**)). It was found that thermal decomposition of **7** led to sequential formation of **8**, new coordination polymer $[BaCu(Me_2mal)_2]_n$ (**9**) and barium cuprate $BaCuO_2$ depending on heating conditions. It was shown that compounds **7**–**9** were 3D-coordination polymers and differed, besides their composition, by the environment of barium(II) ion and the quantity of bridging groups, that linked copper(II) and barium(II) ions [1].

ENZ thanks Russian Foundation of Basic Research (16-33-60179), NVG, AAS, MAK and ILE thank Russian Science Foundation (14-23-00176).

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DESIGN OF POLYNUCLEAR ARCHITECTURES BASED ON MONONUCLEAR FRAGMENT OF OXOVANADIUM(IV) AND SUBSTITUTED MALONATE ANIONS

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On example of oxovanadium(IV) compounds it was shown that the use of substituted malonate anions in the synthesis of heterometallic compounds with the atoms of *s*- and *d*-elements enables the formation of polynuclear architectures as well as molecular complexes. The dimension of polymeric structures of the obtained compounds depends on the size of the hydrocarbyl substituent in malonate anion, nature of the metal atom and the reaction conditions.

The reactions of $VOSO_4 \cdot 3H_2O$ with the substituted malonates (cyclopropane-1,1-dicarboxylate, dimethylmalonate, cyclobutane-1,1-dicarboxylate, butylmalonate) of alkali earth metals ML (M = Ba^{2+}, Sr^{2+}, Ca^{2+}; L = $cpdc^{2-}$, Me_2mal^{2-}, $cbdc^{2-}$, $Bumal^{2-}$) in the molar ratio of 1:2 in water lead to formation of compounds of general formula $[M_x(VO)_x(L)_{2x}(H_2O)_y]_n$ (where x = 1-3, y = 1-13). In crystals of these compounds there are polynuclear architectures which dimensionality changes from 1D to 3D. These architectures are built from mononuclear dianions $[VOL_2(H_2O)]^{2-}$ or $[VOL_2]^{2-}$, where vanadium(IV) atom coordinates two anions of dicarboxylic acid (L) in chelate mode. An exception is the example of complex $\{[Sr(H_2O)_8][VO(Me_2mal)_2]\}_n$, in which structure all of dimethylmalonate dianions show only bridging coordination and form layered polymeric structure. In the series of the obtained compounds, when varying acid anion and *s*-element, the increasing of substituent size and decreasing of cationic radius of alkali earth metal lead to the increase of dimensionality and packing density of the carboxylate compounds.

Passing to the alkali metal salts M_2L (M = K^+, Na^+, Li^+; L = Me_2mal^{2-}, $cbdc^{2-}$, $Bumal^{2-}$) we obtained from water solutions 2D and 3D structures of general formula $[M_{2x}(VO)_x(L)_{2x}(H_2O)_y]_n$ (where x = 1-3, y = 0-15). Re-crystallization of Li–V^{IV} compounds from ethanol resulted in transformation of 3D structure $[Li_2(VO)(Me_2mal)_2]_n$ into the 2D coordination polymer $[Li_2(VO)(Me_2mal)_2(H_2O)(EtOH)]_n$ and abnormal decrease of the layered polymer $[Li_2(VO)(Bumal)_2(H_2O)_{5.5}]_n$ dimensionality with the formation of molecular complex $[Li_4(VO)_2(Bumal)_4(H_2O)_8]\cdot H_2O$. The interaction of 3D polymer $[K_4(VO)_2(cbdc)_4(H_2O)_4]_n$ with $Mg(NO_3)_2\cdot 6H_2O$ in water gives the product of partial substitution of potassium cations $[KMg_{0.5}(VO)(cbdc)_2(H_2O)_8]_n$ with 1D polymeric crystal structure.

In the systems V^{IV}-3d-metal 1D polymeric chains $[M^{II}(VO)L_2(H_2O)_5]_n\cdot nH_2O$ (L = Me_2mal^{2-}, $Bumal^{2-}$; M^{II} = Mn, Co, Cd) $[M^{II}(VO)(cbdc)_2(EtOH)_2(H_2O)_3]_n$ (M^{II} = Mn, Co, Ni) form. During the synthesis of the carboxylate complexes V^{IV}-Zn^{II} it was found that in the system with $cbdc^{2-}$ the decrease of dimensionality occurs and dinuclear molecular complex $[Zn(VO)(cbdc)_2(H_2O)_5]\cdot H_2O$ forms. At the same time in the systems with Me_2mal^{2-} and $Bumal^{2-}$ heterometallic products are not isolated.

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LITHIUM AND MAGNESIUM-CARBOXYLATE COORDINATION POLYMERS

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The area of metal-organic frameworks (MOFs) has become one of the fastest growing fields in chemistry because of unique functional properties of these compounds, and particularly superior adsorption characteristics. Porous MOFs based on light metals carboxylates, e. g. Li^+ and Mg^{2+} are promising materials for the storage of fuel gases such as methane and hydrogen in a safe and compact form suitable for mobile applications. However the number of Li- and Mg-based porous structures is low compared to the number of MOFs based on transition metals. Thus the synthesis of new structures is important not only from the point of view of applications but also of fundamental science.

In this work we describe the synthesis and structural characterizations of a number of metal-organic materials based on the lithium- and magnesium cations with terephthalic (H_2bdc), trimesic (H_3btc) and azobenzene-4,4'-dicarbolyxic (H_2abdc) acids. All materials were obtained by the solvothermal method. The single crystals of lithium products were obtained by heating of either $LiOH{\cdot}H_2O$ or $LiBH_4$ and different aromatic polycarboxylic acids in N,N-dimetylformamide, ethanol or their mixtures with water. The magnesium products were obtained by the heating of $Mg(NO_3)_2{\cdot}6H_2O$ or $Mg(ClO_4)_2{\cdot}6H_2O$ and the azobenzene-4,4'-dicarbolyxic acid in N,N-dimetylformamide or N-methylpyrrolidone. The crystal structures of the reported compounds were solved by the single-crystal X-ray diffraction method and confirmed by the thermogravimetric, elemental and X-ray powder diffraction analysis.

The **$[Li_3(btc)(H_2O)]$**, synthesized from $LiBH_4$ and H_3btc in EtOH/H_2O mixture, demonstrates a ligand-centered luminescence which intensity significantly increases after the dehydration at 200 °C (Fig. 1).

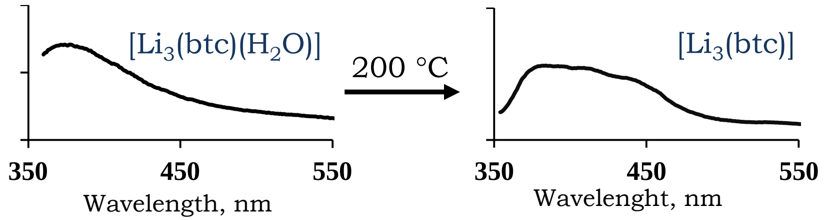

Fig 1. The luminescence spectra of **$[Li_3(btc)(H_2O)]$** before and after activation.

The crystallization of a particular polymorph from “Mg^{2+} + $abdc^{2-}$“ systems turned out to depend on a solvent and the anion of the salt. In particular, **$[Mg_3(DMF)_3(abdc)_3]\cdot DMF\cdot 2H_2O$** was synthesized from $Mg(NO_3)_2\cdot 6H_2O$ and H_2abdc in DMF. This compound possess channels of about 5Å and solvent-accessible free volume calculated by PLATON of more than 50% and is potentially porous (Fig. 2).

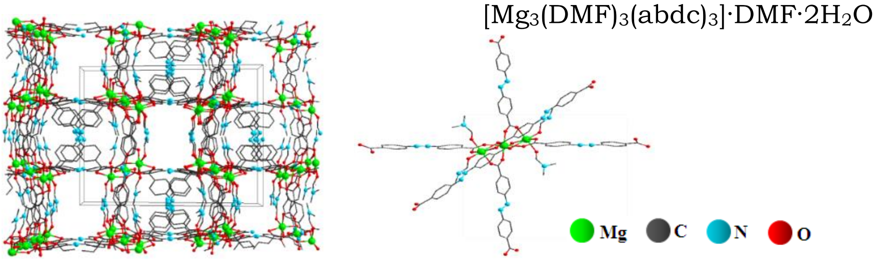

Fig 2. The structure of building Mg_3-block and the spatial image of channels of $[Mg_3(DMF)_3(abdc)_3]\cdot DMF\cdot 2H_2O$.

This work was supported by the Grant of the Government of the Russian Federation (No. 14.Z50.31.0006, leading scientist – Martin Schröder).

UROTROPINE-CONTAINING METAL-ORGANIC FRAMEWORKS: FROM DESIGN TO FUNCTIONAL PROPERTIES

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Chemistry of metal-organic frameworks (MOFs) is a rapidly developing area of modern coordination and materials chemistry. Many of the reported MOFs are permanently porous and show excellent sorption, catalytic and luminescent properties.

Urotropine (hexamethylenetetramine) has been widely used as a linker in the construction of MOFs [1], but only a few of them feature open porous structures. We argue that if used together with a space-creating rigid ligand, the urotropine would be a viable target to generate directly, without the need for synthetic post-modification, free N-donors with open channels of porous solids. Herein we report few porous urotropine-contaning materials.

$[Zn_4(dmf)(ur)_2(ndc)_4]$ (**1**, ur = urotropine, H_2ndc = 2,6-naphtalenedicarboxylic acid) contains a system of 1D channels of two types. The bigger hexagonal channels with characteristic dimensions 9.5×11 Å decorated with basic non-coordinated nitrogen atoms of the urotropine fragment. The lesser ellipsoidal channels (4×5 Å) contain Lewis acidic zinc centers coordinated to dmf molecules. Use of S_4N_4 eliminates the coordinated DMF from these channels and leads to biporous framework $[Zn_4(ur)_2(ndc)_4]$, which demonstrates a high selectivity in separation of the bicomponent S_4N_4-benzene mixture [2]. The solid-state luminescent properties of compound **1** depend on the guest molecules. The benzene molecules enhance the framework luminescence, while ferrocene effectively quenches it [3].

$[Zn_{11}(H_2O)_2(ur)_4(bpdc)_{11}]$ (**2**, H_2bpdc = 4,4′-biphenyldicarboxylic acid) contains a system of intersected channels with non-coordinated nitrogen centers. Their characteristic aperture is *ca.* 7×9 Å.

The sorption properties of compounds **1** and **2** towards N_2, H_2, CO, CO_2 and acetylene were investigated. Their pronounced affinity to CO_2 and C_2H_2 was demonstrated. The critical role of non-coordinated nitrogen atoms of urotropine for facilitating the interaction between CO_2/acetylene and the framework was further confirmed by the DFT calculations [4].

The metal–organic framework $(H_3O)_2[Zn_4(ur)(Hfdc)_2(fdc)_4]$ (**3**, H_2fdc = furan-2,5-dicarboxylic acid) incorporates cryptand-like cavities. The unique structural features of the compound allowed us to separate and optically detect the heavy alkali metal cations of Rb^+ and Cs^+ from their light analogues. The reported data are the first example of effective employing of MOF materials for environmentally challenging problems of alkali metals detection.

This work was supported by the Grant of the Government of the Russian Federation (No. 14.Z50.31.0006, leading scientist – Martin Schröder).

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HALOCHROMIC COORDINATION POLYMERS BASED ON CHROMEAZUROL B DYE

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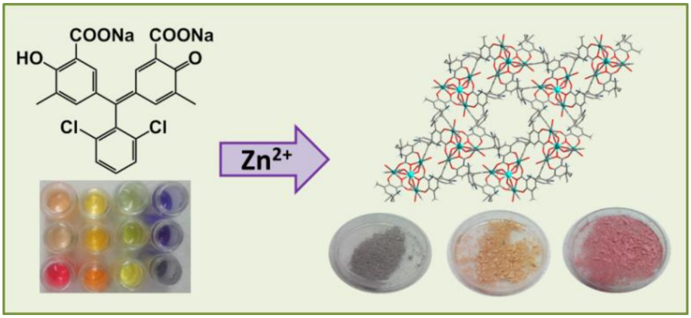
Chromeazurol B (Na_2HL) is a well-known dye based on a hydroxytriarylmethane core. One of the interesting phenomena, observed for such organic molecules with both a developed system of conjugated bonds and H-donor/acceptor groups, is their ability to change the light absorption in the visible region in different acidity of the environment. Depending on a protonation level, Chromeazurol B exists in one of four different forms, each having a distinct color thus demonstrating visual pH-sensitivity (halochromism). This molecule, if incorporated into a coordination polymer as a linker, could function as halochromic detector within the resultant MOF material. Two carboxylate functional groups make Chromeazurol B suitable for the synthesis of coordination polymers in the reactions with metal cations.

Two new coordination polymers $[NaZn_4(H_2O)_3(L)_3]\cdot3THF\cdot3H_2O$ (**1**) and $[Zn_3(H_2O)_3(\mu_2\text{-}OH_2)(\mu_3\text{-}OH)(HL)_2(H_2L)]\cdot2THF\cdot3H_2O$ (**2**) incorporating the Chromeazurol B linkers were prepared by the solvothermal reactions of zinc acetate with organic dye. The structure of **1** comprises pentanuclear heterometallic $\{Zn_4Na\}$ nodes, linked by six L^{3-} anions into layered structure with honeycomb topology. **2** crystallizes as a double-chain ribbon (ladder) structure with two types of metal SBU: mononuclear Zn cation and tetranuclear Zn_4 cluster. Hydroxocarboxylate linker bears its ability to change color in acidic media to the resulting polymers. The coordination of Zn(II) to donor groups of the

Chromeazurol B ligand does not change its ability to accept the protons from the acidic environment. Both coordination polymers **1** and **2** show pH-sensitivity in water solution which can be observed visually. The color of crystals of both compounds reversibly changes from violet to orange by varying the pH of the media from neutral to acidic, respectively. The crystalline stability of **1** in broad range of acidity/basicity of the atmosphere was examined by powder X-ray diffraction analysis.

The halochromic properties of $[NaZn_4(H_2O)_3(L)_3]\cdot3THF\cdot3H_2O$ towards HCl vapors of different acidity were systematically investigated. Chrome pure blue and coordination polymer **1** show different level of protonation in the air and in hydrochloric acid vapors of different concentration. This is accompanied by significant changes in color and can be observed with naked eye. The as-synthesized powdered sample of **1** reversibly changes its color from violet to orange and pink while exposing to air or vapors of 2M and 7M HCl, respectively. The protonation of Chromeazurol B anions at each color stage was examined by diffuse reflectance spectroscopy. The remarkable stability of the crystalline coordination polymers in acidic atmosphere, reversible and reproducible character of the color changes provides unique opportunities for these compounds in the design of multifunctional sensor materials.



This work was supported by the Grant of the Government of the Russian Federation (No. 14.Z50.31.0006, leading scientist – Martin Schröder).

EPR SPIN PROBE METHODOLOGY FOR INVESTIGATION OF STRUCTURE TRANSITIONS AND GAS ADSORPTION IN MOF

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Metal-organic frameworks (MOFs), a novel class of micro and meso-porous materials, have attracted much attention due to their high practical importance in industry and medicine. MOFs can have rigid and flexible structures, consisting of metal clusters linked together with organic ligands, and exhibit unique and interesting properties. For example, MOFs are promising candidates for hydrogen storage materials and, due to their large surface area, can constitute novel catalytic materials. Such applications require detailed knowledge about pore properties and the behavior of guest molecules confined in such systems. In this research we focused on electron paramagnetic resonance (EPR) methods for investigation of MOF materials.

We have shown that post-synthetic adsorption of stable nitroxide radicals, followed by EPR detection, is a powerful approach for studying the breathing behavior and guest-host interactions in structurally-flexible MOFs.[1] The huge advantage of the new approach is the ability to use the negligible amounts of guest molecules to probe the MOF's interior, without altering the framework structure. For example, by embedding three derivatives of TEMPO (4-oxo-TEMPO, 4-hydroxo-TEMPO, 4-acetamido-TEMPO) in the MIL-53(Al) framework, we could monitor structural “breathing” of this MOF with temperature in order to gain deeper understanding of underlying guest-host interactions.[2] Different substituents in piperidine ring led to different mobility and reactivity of corresponding nitroxides. The obtained EPR data and Molecular Dynamics (MD) calculations showed that the efficiency of nitroxide radical reaction with μ2-hydroxo group of MIL-53(Al) strongly correlates with the character of its molecular motion, and the reversibility of this reaction upon structural “breathing” is a general phenomenon. Also we have tried experimental approach for detection of gas behavior inside the MOF by EPR of spin probe. As a probe TEMPO molecule was used. CW and Pulse EPR techniques were applied for TEMPO@ZIF-8 system loaded with different gases. Molecular dynamic calculations were made for qualitative explanation of experimental results.

We are grateful to the Russian Foundation for Basic Research (№ 14-03-00224) and the RF President's Grant (MD-276.2014.3) for financial support.

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AN UNEXPECTED HYSTERETIC SORPTION BEHAVIOR IN MICROPOROUS METAL-ORGANIC FRAMEWORKS

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Metal-organic frameworks (or MOFs) are a class of crystalline coordination compounds with 1, 2, or 3D structures consisting of metal ions or clusters connected by rigid organic bridging ligands. A great interest in the chemistry of these compounds comes from numerous possible applications in gas storage and separation, heterogeneous catalysis and the development of the photoactive materials.

Herein we report three microporous metal-organic coordination polymers: two isostructural MOFs $[Mn_3(pdc)_2(Hpdc)_2]\cdot G$ (**1**) and $[Mg_3(pdc)_2(Hpdc)_2]\cdot G$ (**2**), and $[Sc(pzc)_2(H_3O^+)]\cdot G$ (**3**) (H_2pdc – 2,4-pyridinedicarboxylic acid, H_2pzc – 2,5-pyrazinedicarboxylic acid). Structures of compounds **1** and **3** were determined by the single-crystal X-ray diffraction technique. Structural identity of compounds **1** and **2** was revealed by PXRD studies.

Compounds **1** and **2** contain trinuclear secondary building blocks, connected to each other by bridging pdc^-/pdc^{2-} fragments forming a microporous structure. According to the PLATON calculations, the accessible volume is 49%, and characteristic pore size is 6×3 Å. Interestingly, that both compounds practically don’t adsorb N_2, but adsorb CO_2. Moreover, only for compound **1** we observed a significant hysteresis between sorption and desorption isotherms (Fig. 1*a*), what is probably connected with sieving effect caused small pore size. It is worth to compare the obtained results with another pair of microporous isostructural MOFs [Mn(HCOO)$_2$] and [Mg(HCOO)$_2$] [1,2]. Like compounds **1** and **2** they are built from manganese and magnesium correspondingly and have similar structures, however both of them demonstrate the same sorption behaviour.

Compound **3** contains of Sc(III) cations playing role of tetrahedral nodes coordinated by four bidentate pzc^{2-} anions. Obtained material has 2D intersecting channels with characteristic pore size 3×3 Å and accessible volume of 40 % (according to the PLATON calculations). Like previous two compounds this compound doesn't adsorb N_2 and H_2, but, what is more interesting, it adsorbs CO_2 and N_2O. Sorption isotherms of these gases have stepwise character with notable hysteresis between sorption and desorption isotherms (Fig. 1*b*) which are probably connected with structure rearrangement.

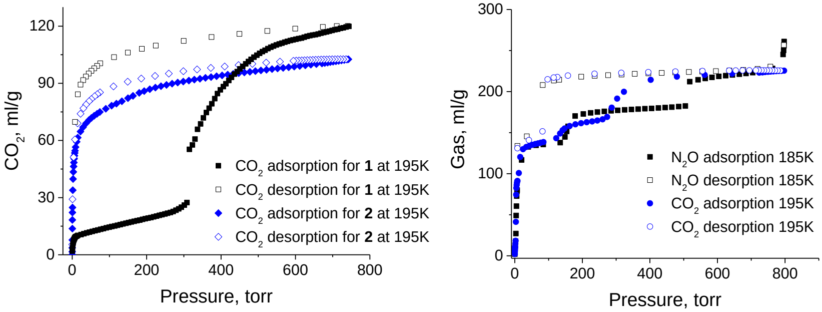

Figure 1. a) CO_2 sorption isotherms of compounds **1** and **2** at 195 K. b) CO_2 and N_2O sorption isotherms of compound **3** at 195 and 185 K respectively.

This work was supported by the Grant of the Government of the Russian Federation (No. 14.Z50.31.0006, leading scientist – Martin Schröder).

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PREPARATION OF Pd NANOPARTICLES EMBEDDED IN CAVITIES OF ISORETICULAR MOFS

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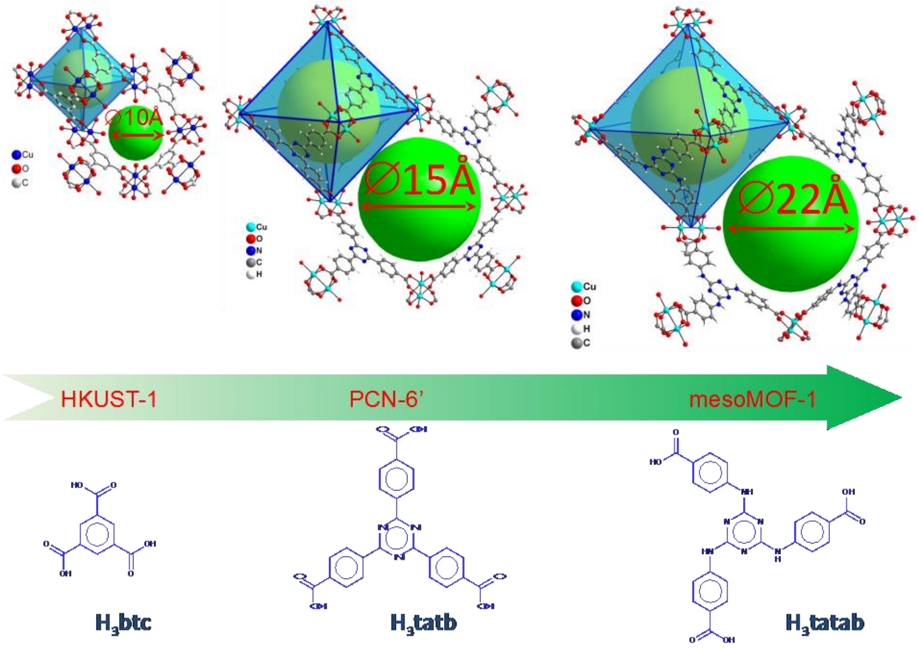
Porous metal-organic frameworks (MOFs) attract large attention of the researchers due to their wide perspectives for using in separation technologies, gas sorption and storage, for creating prolonged action or prolonged release medicines, as catalysts or supports for the catalytically active particles. Using the bridging organic ligands of different lengths, but being similar in nature, location and type of functional groups isoreticular MOFs could be prepared with the similar ways of metal centers interconnection, but with different geometric parameters *e.g.* pore widths and volumes. Incorporating of metal nanoparticles (NP) into MOF's cages is interesting for catalysts production with enhanced activity and selectivity in hydrogenation, coupling and condensation reactions and other processes. On the other hand the catalytic properties of metal NP depend strongly on particle size and shape.

This work is devoted to study the inclusion of palladium nanoparticles into the cavities of isoreticular MOFs of HKUST-1 family. Using porous copper(II) carboxylates with increasing pore apperture we wish to obtain Pd nanoparticle calibrated by size because the growth of the nanoparticle (and therefore its shape and size) is limited by the cage. The oxalate complex $(NH_4)_2[Pd(C_2O_4)_2]$ was chosen as the precursor compound. The key property of the complex is low temperature decomposition (below 150 °C) resulting in Pd NP as an only solid residue.

There were difficulties in synthesis of pure crystalline phases of enlarged MOFs. The main problem is quite low yield which is about several mg.

Several attempts to scale up the synthesis were absolutely unsuccessful. The further research was continued with HKUST-1 only.

Inclusion compounds of Pd-complex and HKUST-1 were synthesised by double solvent method, which allows obtaining NP exclusively in the cavities of MOFs without the formation of large aggregates on their surface. The resulting sample Pd@HKUST-1 was fully characterized including elemental analysis, X-ray diffraction, thermal analysis, and gas sorption.



SORPTION EFFECTS ON PERMANENTLY POROUS POLYTHIOPHENE DICARBOXYLATE MOFs

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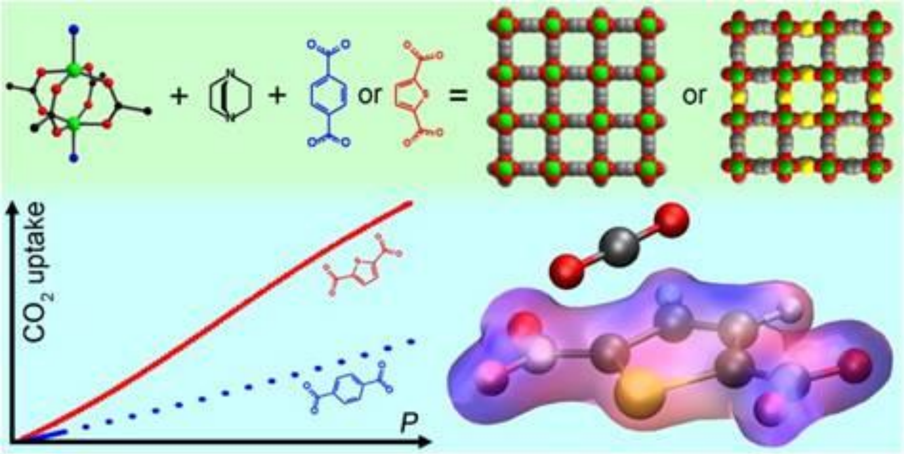
Three isoreticular porous MOFs based on Zn_2–paddle wheels, connected through thiophenedicarboxylate moieties and N-donor linkers (L) $[Zn_2(tdc)_2L]$ are synthesized and characterized. Apart from some structural differences these frameworks are very similar to the prototypic Zn(II) terephthalate $[Zn_2(bdc)_2dabco]$ compound and so does the general porous properties (pore size, volume, specific surface area). However, the substitution of terephthalate by thiophene linker doubles the carbon dioxide adsorption as well as CO_2/N_2 adsorption selectivity. The CO_2 uptake of $[Zn_2(tdc)_2dabco]$ achieves the best values reported in the literature although the compound possesses no basic Lewis functions nor open metal sites, which is manifested by a low isosteric heat of adsorption. The quantum chemical calculations confirm the definitive role of heterocyclic and, particularly, sulfur atoms in CO_2 binding *via* induced dipole interactions. These results emphasize the feasibility of van-der-Waals interactions to effective CO_2 binding while maintaining low heat of adsorption and a general hydrophobicity of the porous material. More importantly, the incorporation of heterocycles into porous structures may be a practical way to improve the adsorption properties of the already known materials.

In this connection, the interest in MOFs based on polythiophene systems grows quite naturally. The logical extension of the strategy presented is the study of such sorption effects on metal-organic frameworks based on polycyclic thiophene carboxylates. Particular attention has been paid to developing the synthesis of new porous metal-organic frameworks thieno[3,2-b]thiophene-2,5-dicarboxylates (3,2b-TTDC-MOFs) and thieno[2,3-b]thiophene-2,5-dicarboxylates (2,3b-TTDC-MOFs). On the other hand, H_2(3,2-b)TTDC and H_2(2,3-b)TTDC is of considerable interest because of their full geometric analogy to terephthalic acid. An original strategy to develop more effective sorbent is to increase the number of sorption sites per unit of new type ligand. The use of metal ions with a higher charge to develop MOFs results in good thermal and chemical stability of the material. Using Zr^{4+} and linker containing double amount of sorption sites should give highly stable framework possessing enhanced gas sorption and selectivity. - Despite this, to date the chemistry metal-organic framework based on H_2(3,2-b)TTDC and H_2(2,3-b)TTDC is very poor.



This work was supported by the Grant of the Government of the Russian Federation (No. 14.Z50.31.0006, leading scientist – Martin Schröder).

MODIFICATION OF Cr-MIL-101: SYNTHESIS AND CATALYTIC PROPERTIES

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Metal-organic coordination polymers are considered as promising materials for storage and gas separation, catalysis and other applications. One of the advantages of MOF if to compared with other porous materials is the possibility of their modification by the general specifically solvable problems.

Mesoporous chromium(III) terephthalate MIL-101 $[Cr_3O(H_2O)_2X(bdc)_3]\cdot nH_2O$ (X = F, NO_3; bdc — terephthalate ions $(-n\text{-}C_6H_4(COO)_2{}^{2-})$, n≈10–15) is a coordination polymer with high hydrolytic and thermal stability. A feature of MIL-101 is the ability to undergo dehydratation to form a coordination unsaturated sites (CUS), which can coordinate other ligands. There was thus obtained a series of modified frameworks (Figure 1) – MIL-101-pyz, MIL-101-bpy, MIL-101-dabco, MIL-101-pip, and MIL-101-ED.

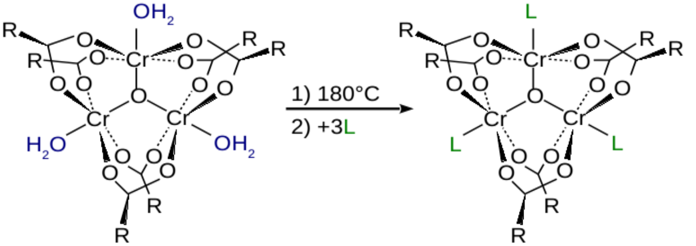

Figure 1. Modification of MIL-101.

Ditopic organic N-donor ligands as 1,4-diazabicyclo [2,2,2] octane, 4,4'-bipyridyl, pyrazine, piperazine, and ethylenediamine were used to modification of MIL-101 so that the first nitrogen atom is coordinated to a chromium atom, and the second – is able to act as a primary catalytic center.

The study of the catalytic properties of modified MOFs were performed on the model of Henry reaction (condensation of benzaldehyde with nitromethane, Figure 2).

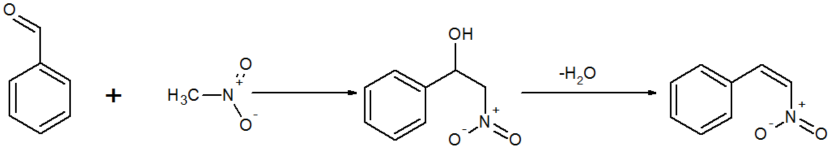

Figure 2. Scheme of Henry reaction

The reaction proceeds with high yield and selectivity by using MIL-based catalysts. In the case of MIL-101-dabco the main product is 2-nitro-1-phenylethanol, in the case of MIL-101-pip and MIL-101-ED the main product is 1-nitro-2-phenylethylene, whereas MIL-101-pyz and MIL-101-bpy have shown negligible catalytic activity. The different catalytic activity of MIL-101-L catalysts is explained by various basicity of modifying ligands. The catalyst's stability after run was confirmed by element analysis, X-Ray powder diffractometry and by reusing in the next run. Therefore MIL-101-L compounds behave as true heterogeneous catalysts and can be used repeatedly without suffering a loss of the catalytic properties.

This work was supported by the Grant of the Government of the Russian Federation (No. 14.Z50.31.0006, leading scientist – Martin Schröder).

A METAL–ORGANIC FRAMEWORK AS A FACILE PLATFORM FOR SELECTIVE UPTAKE AND DETECTION OF ALKALI METAL CATIONS

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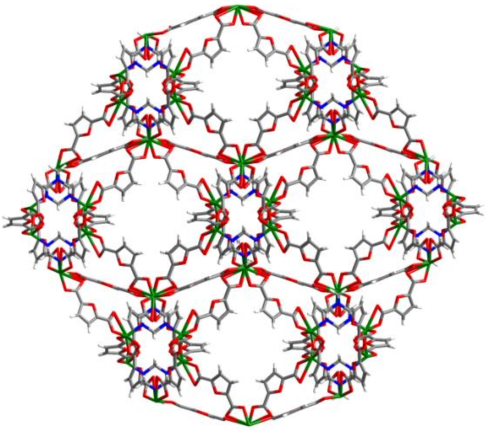
Alkali metals belong to one of the most technically and physiologically relevant elements. Since some biological processes are controlled by the concentration of the alkali metal cations (e.g. Na^+/K^+-ATPase solute pump regulation), it is no surprise, that group I cations belong to one of the most popular objects for the development of new optical sensors [1].

Here we report a metal-organic coordination polymer $(H_3O)_2[Zn_4(ur)(Hfdc)_2(fdc)_4]$ (**ZFU**) which demonstrates alteration of its solid-state luminescent properties depending on the nature of alkali metal cations present in specific cryptand-like cages in polymeric crystal structure.

Anionic metal-organic framework **ZFU** constructed from zinc(II), 2,5-furandicarboxylate and urotropine comprises two types of micropores (Fig. 1). First type hydrophobic pores are filled by disordered solvent molecules and don’t show any alkali-metal selectivity. Second type hydrophilic pores (Fig. 2) have an oxygen environment of ~0,6 nm radii and contain hydroxonium cations which can be selectively substituted with alkali-metal cations.

Ionic substitution products were obtained by soaking **ZFU** in MNO_3 (M = IA group cations) solutions in N-methylpyrrolidone. The substitution to alkali metals caused changes in solid-state luminescence intensity and its quantum yield.



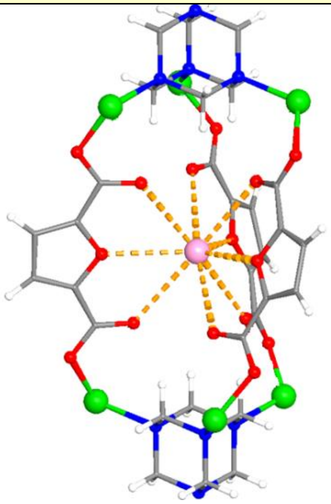


Fig. 1. ZFU crystal structure Fig. 2. cryptand-like cage in ZFU

ZFU shows particularly high selectivity towards Rb^+ and Cs^+ cations over light alkali metal species (Li^+, Na^+, K^+). Moreover, the most significant luminescent response was observed upon the inclusion of these heavy alkaline metal cations. The experimental data suggest compound **ZFU** can be a perspective material for the development of selective luminescent sensors for heavy alkali metal cations.

This work was supported by the Grant of the Government of the Russian Federation (No. 14.Z50.31.0006, leading scientist – Martin Schröder).

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THIEN-THIOPHENE DICARBOXYLATE BUILDING BLOCKS AS GEOMETRICAL ANALOGUES OF TEREPHTHALATE. NEW POROUS MATERIALS, SYNTHESIS, PROPERTIES AND PROSPECTS

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Martin Schröder[1,3], Danil N. Dybstev[1,2], Vladimir P. Fedin[1,2]

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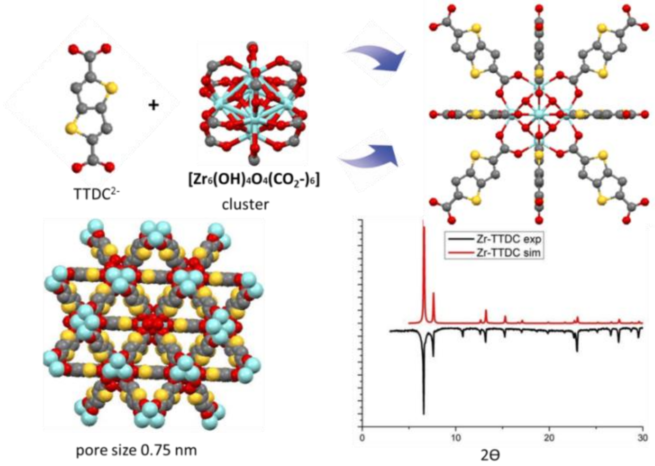

MOFs based heterocyclic carboxylates containing in its composition fused thiophene groups are small, and the systematic study of the properties of such a framework is missing. Despite this, in recent years there has been an increase in the intensity of work in this direction. Recent studies have shown that the material $[Zn_2(tdc)_2dabco]$ thiophene group probably is the cause of increased adsorption capacity of the frame with respect to carbon dioxide. In this connection, the interest in MOFs based on polythiophene systems grows quite naturally. However, these precursors are very scarce. In this connection, polythiophene condensed carboxylic acids are deficient. Because of this, it increased urgency of developing a simple easily reproducible method of synthesis of the ligands of this family from available precursors. In this work, we report the development of an effective one-step method high yield for producing H_2(3,2b)TTDC and H_2(2,3b)TTDC by oxidation of the starting dialdehyde (H_2TTDA) with freshly prepared Tholens reagent.

Today it is also known that the thiophene group consisting Zr-MOF significantly increase sorption capacity porous framework with respect to various gases including carbon dioxide. Increasing the sorption capacity is associated with a local dipole moments present in the thiophene group as well as the features of the electronic structure of conjugated heterocyclic ligands. On the other hand H_2(3,2b)TTDC it is of considerable interest because of its full geometric analogy terephthalic acid. The study of various systems with the participation of H_2(3,2b)TTDC in the future promises rich results in the form of many new porous frameworks, which replaces the ligand (3,2b)TTDC structural terephthalate. Despite this, to date the chemistry metal-organic framework based (3,2b)TTDC is very poor. In this work, we report the development of a new porous material based on zirconium and TTDC ($[Zr_6(OH)_4(O)_4(TTDC)_6]\cdot G$), which is a structural analog of UiO-66.

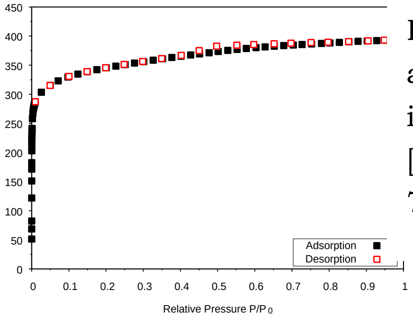

Figure 1. Nitrogen adsorption-desortion isotherm on $[Zr_6O_4(OH)_4((3,2b)TTDC)_6]$ at 77 K.

This work was supported by the Grant of the Government of the Russian Federation (No. 14.Z50.31.0006, leading scientist – Martin Schröder).

Bi(III) IMMOBILIZATION INSIDE POROUS METAL-ORGANIC FRAMEWORK: TOWARD ENHANCED PHOTOCATALYTIC PERFORMANCE

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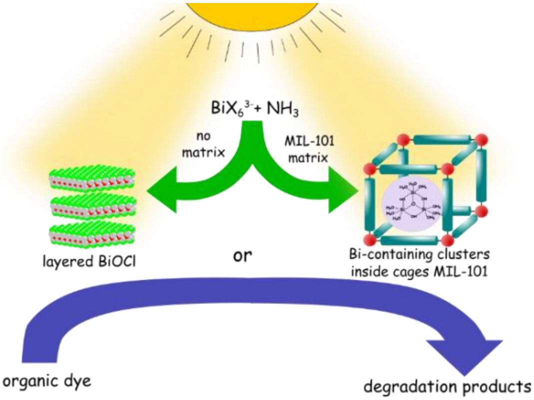
Development of highly efficient photocatalysts is one of challenges of modern inorganic and material chemistry. Applications cover such areas as wastewater treatment, air purification, photocatalytic water splitting for ecological benign production of hydrogen, selective and efficient chemical synthesis. Among the huge class of materials with photocatalytic performance, there is a large family of bismuth oxohalides BiOX (X = Cl, Br and I) attracting much attention due to their structural diversity and high catalytic activity under UV and visible light irradiation. The key factors affecting the catalyst activity are morphology, surface area and size of particles. There are many approaches to control morphology and particle size during synthesis but a difficult problem is to keep that size and morphology intact during catalyst applying. From this point of view, impregnation of photocatalyst into a stable porous matrix offers a suitable solution. Crystalline porous metal-organic frameworks are good candidates to be a catalyst's supports due to huge diversity of topologies, regularity of their structure, high porosity, enough stability and accessibility via simple hydrothermal synthesis.

In this work, we present the original hybrid catalysts based on mesoporous chromium(III) terephthalate $[Cr_3OF(H_2O)_2(bdc)_3]\cdot nH_2O$ (MIL-101; bdc — terephthalate anion $C_6H_4(COO)_2^{2-}$, $n \approx 15-20$) with embedded bismuth(III) particles which reveals superb photocatalytic activity in degradation of organic dyes as model pollutants. Bi(III)-containing species inside MIL-101 cages were obtained by two step approach including impregnation of metal-organic framework by Bi(III) salt in acidic media with following fixing of Bi(III)-containing particles by ammonia solution. Two different Bi-containing sources ($BiCl_3$ and BiOBr) were used to obtain Bi(III)-X@MIL-101 (X = Cl, Br) with different sensitivity to UV and visible light. It is well known that the substitution of Br for Cl leads to shift of optimal light wavelength of photocatalytic activity to higher values. Only a small amount of bismuth was determined by elemental analysis: from 0.09 to 0.13 Bi atoms per MIL-101 formula unit or about 1–1.5 Bi atoms per mesocage of MIL-101. EXAFS data indicates the formation of small oxo-hydroxo Bi-clusters inside MIL-101.

The photocatalytic activity of Bi(III)-X@MIL-101 was tested on a degradation of organic dyes. Solutions of methyl red or methylene blue were fully discolored after 30–50 min of irradiation by Hg lamp. The kinetics of the processes is described by the first-order law with rate constants 0.037 min^{-1} and 0.11 min^{-1} for X = Cl and Br, respectively. The specific activity of Bi(III)-Cl@MIL-101 exceeds those of pure BiOCl in 5−6 times. The catalysts stability was confirmed by elemental analysis and powder XRD after catalytic tests as well as solutions was examined for no leaching of both Bi or Cr. The stable performance of catalysts was demonstrated in 4–7 catalytic cycles. It was demonstrated that Bi(III)-Br@MIL-101 possesses photocatalytic activity under visible light irradiation while Bi(III)-Cl@MIL-101 is active only under UV light.

This work was supported by the Grant of the Government of the Russian Federation (No. 14.Z50.31.0006, leading scientist – Martin Schröder).



SYNTHESIS AND CRYSTAL STRUCTURES OF THE INCLUSION COMPOUNDS OF A POROUS METAL-ORGANIC POLYMERS WITH CYMANTRENE AND 2-CYCLOPENTENE-1-ONE

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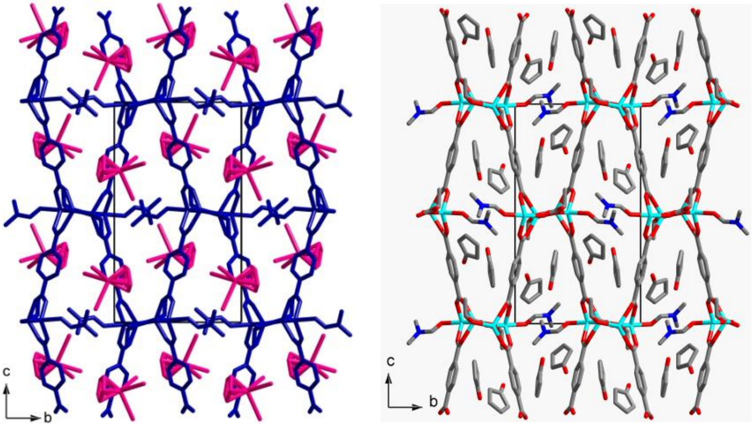
Porous metal-organic coordination polymers (MOCPs) have a number of unique properties, including a high specific surface area. Such compounds have attracted much attention due to numerous possibilities of the structural and functional design of these compounds and prospects for creating new generation functional materials based on them. Nowadays, these are first of all materials suitable for reversible sorption followed by the storage of gases of various nature, materials for selection and purification of various organic compounds, as well as for catalysis. Another new and important aspect being elaborated nowadays is the use of a system of voids and channels in porous MOCPs as nanoreactors to carry out chemical (photochemical) reactions in them. It is also interesting to study the dynamic behavior of guest molecules depending on the size and shape of the channel and on the guest nature. In the present work, we report the synthesis and crystal structure of the inclusion compounds based on previously obtained homochiral porous MOCP ($[Zn_2(dmf)(bdc)(lac)]$) with 2-cyclopentene-1-one (C5H6O)[1] and cymantrene[2]: $[Zn_2(dmf)(bdc)(lac)]\cdot[Mn(C_5H_5)(CO)_3]$ **(1)**, $[Zn_2(dmf)(bdc)(lac)]\cdot C_5H_6O$ **(2)** (DMF = N,N′-dimethylformamide, H_2bdc = terephthalic acid,H_2lac = S-lactic acid, C_5H_5= cyclopentadienyl).



This work was supported by the Grant of the Government of the Russian Federation (No. 14.Z50.31.0006, leading scientist – Martin Schröder).

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ULTRA-SLOW DYNAMICS OF FRAMEWORK LINKER IN MIL-53 (AL) AS A SENSOR FOR DIFFERENT ISOMERS OF XYLENE

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MIL-53 (Al) is an important example of the metal−organic frameworks (MOFs) with a flexible framework capable to efficiently separate *ortho* and *para* isomers of xylene at moderate temperatures. The batch adsorption and breakthrough experiments have demonstrated that the *o-/p*-xylenes separation factor was ~ 3.5 at saturation conditions and T = 298 K [1,2]. The MIL-53 MOF contains mobile terephthalate phenylene fragments that can be used as dynamical probe to investigate the guest-host interactions and the origin of the separation selectivity. ^{2}H NMR spin alignment echo technique was applied for the first time to identify and characterize an ultra-slow motion (0.1-1 kHz) in MOFs.

Xylene isomers influence the mobility of the linkers in a different way causing drastic discrepancy in its rates of motion. It has been established that phenylenes rotation perform one order of magnitude slower in the presence of *o*-xylene (k_{ortho} = 70 s^{-1}) compared to the same rotation in the presence of the other isomer, *p*-xylene (k_{para} = 800 s^{-1}) at T ~ 373 K. This is explained by the stronger interaction of *ortho* isomer with the linker than *para* isomer. However, this difference in rotation rates is irregular and depends on the temperature (Figure 1).

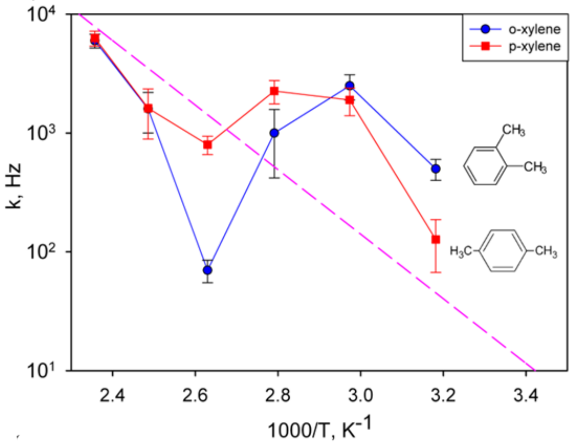

Figure 1. Temperature dependence of the rate constants k of phenylene fragment rotation for the MIL-53(Al) loaded with o-xylene (blue ●) and p-xylene (red ■). The dashed line shows the expected rotational rates extrapolated from high temperature 2H NMR solid echo experiments reported in [3].

This finding offers understanding molecular mechanism of *p*- and *o*- xylene separation by this MOF: stronger interaction of *o*-xylene with organic linker compared to *p*-xylene provides separation of these isomers on MIL-53.

This work was supported by Russian Foundation for Basic Research (grant no. 14-03-91333) and by the Deutsche Forschungsgemeinschaft (grant HA 1893/16).

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INVESTIGATION OF GUEST-HOST INTERACTION UNDER GAS SORPTION IN THE $Zn_{2-x}Cu_x(bdc)_2(dabco)$ WITH EPR SPECTROSCOPY

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Metal–organic frameworks (MOFs) represent a new class of porous crystals, which has attracted chemist and material scientists worldwide due to their extraordinary physicochemical and mechanical properties and potential applications in energy and biomedicine fields. One of the applications of MOFs are adsorptive separation and gas storage which are very important in industry. Generally, for this purposes solid materials such as zeolites, activated carbons, or silica gels are used as adsorbents. With an ever increasing need a more efficient, energy-saving, and environmentally benign process must be found.

$Zn_2(bdc)_2(dabco)$ have a potential application for hydrogen, carbon dioxide and hydrocarbon storage. For investigation this MOF using EPR spectroscopy our colleagues synthesized magnetically diluted $Zn_{2-x}Cu_x(bdc)_2(dabco)$, where Zn/Cu ratio equal 1000.

In this work we study interaction $Zn_{2-x}Cu_x(bdc)_2(dabco)$ with H_2, CO_2 and cyclohexane using pulse EPR spectroscopy. We also present data on relaxation parameters of Cu sites interacting with molecules of this compound.

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