

Nano Research

February • 2021

Volume 14 · Number 2



Q K 2 1 2 3 3 5

Special issue: Future Directions of Reticular Chemistry

Guest Editors: Yue-Biao Zhang, Qiaowei Li, Hexiang Deng, Omar M. Yaghi

Let the light be a guide: Chromophore communication in metalorganic frameworks

Hierarchical assemblies of molecular frameworks—MOF-on-MOF epitaxial heterostructures

Two-dimensional d- π conjugated metal-organic framework based on hexahydroxytrinaphthylene



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Contents

Editorial

Reticular chemistry at the atomic, molecular, and framework scales

Yue-Biao Zhang^{1,*}, Qiaowei Li^{2,*}, and Hexiang Deng^{3,*}

¹ ShanghaiTech University, China

² Fudan University, China

³ Wuhan University, China

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Review Articles

Let the light be a guide: Chromophore communication in metal-organic frameworks

Corey R. Martin, Preecha Kittikhunnatham, Gabrielle A. Leith, Anna A. Berseneva, Kyoung Chul Park, Andrew B. Greytak, and Natalia B. Shustova*

University of South Carolina, USA



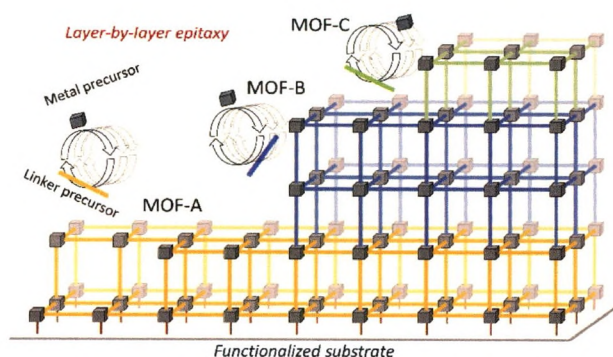
Metal-organic framework motifs promote efficient chromophore communications and unveil the potential for a promising library of futuristic materials for advancing nanoscale photonics and portable electronics.

338–354

Hierarchical assemblies of molecular frameworks—MOF-on-MOF epitaxial heterostructures

Ritesh Haldar and Christof Wöll*

Karlsruhe Institute of Technology (KIT), Germany



Synthetic strategies and applications of hierarchical metal-organic framework (MOF)-on-MOF epitaxial heterostructures are reviewed.

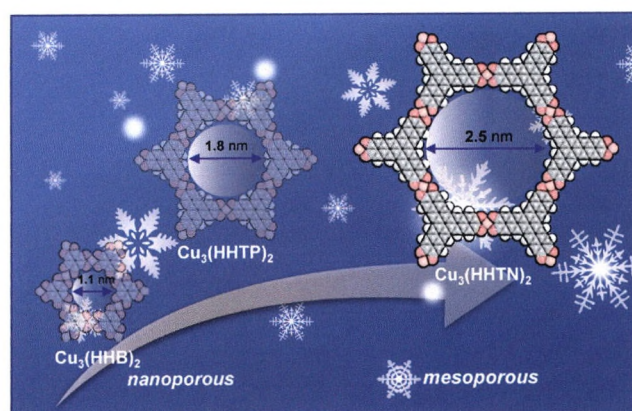
355–368

Research Articles

Two-dimensional d- π conjugated metal organic framework based on hexahydroxytrinaphthylene

Zheng Meng and Katherine A. Mirica*

Dartmouth College, USA

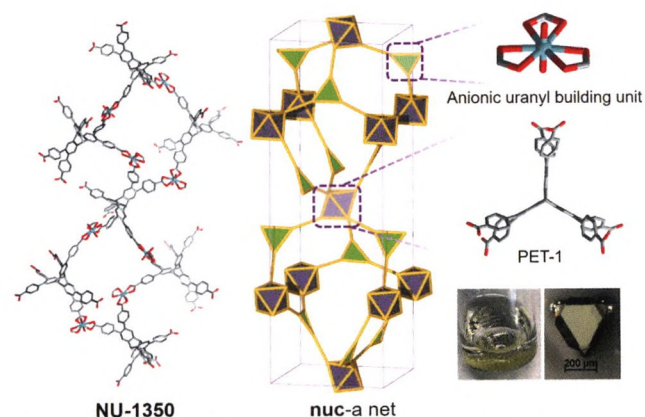


A novel d- π conjugated two-dimensional metal-organic framework $\text{Cu}_3(\text{HHTN})_2$ using a new ligand 2,3,8,9,14,15-hexahydroxytrinaphthylene was synthesized. The resulting material has a pore aperture of 2.5 nm, tunable electrical conductivity, and temperature-dependent band gap ranging from 0.75 to 1.65 eV.

369–375

Reticular exploration of uranium-based metal-organic frameworks with hexacarboxylate building units

Zhijie Chen^{1,*}, Penghao Li¹, Xuan Zhang¹, Mohammad Rasel Mian¹, Xingjie Wang¹, Peng Li¹, Zhichang Liu¹, Michael O’Keeffe², J. Fraser Stoddart^{1,3,4}, and Omar K. Farha^{1,*}

¹ Northwestern University, USA² Arizona State University, USA³ Tianjin University, China⁴ University of New South Wales, Australia

Three uranium-based metal-organic framework (MOF) structures were synthesized from trigonal planar uranyl nodes and triptycene-based hexacarboxylate ligands with variable arm lengths.

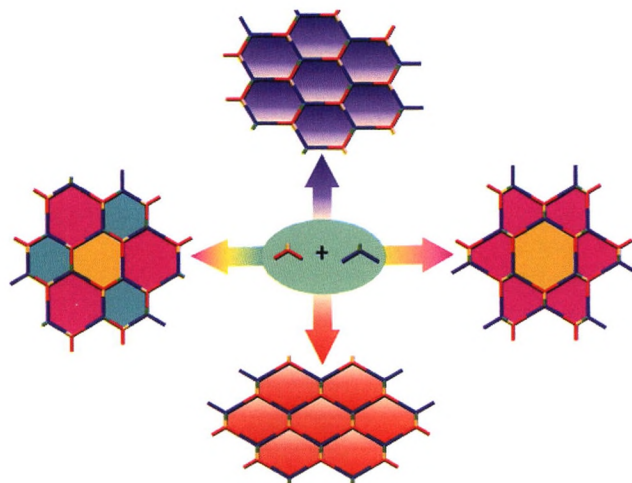
376–380

Effects of connecting sequences of building blocks on reticular synthesis of covalent organic frameworks

De-Li Ma^{1,2}, Cheng Qian^{1,2,*}, Qiao-Yan Qi², Zhong-Ri Zhong¹, Guo-Fang Jiang^{1,*}, and Xin Zhao^{2,*}

¹ Hunan University, China

² Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China



A model system has been established to demonstrate how connecting sequences of building blocks exert an influence on the reticular synthesis of covalent organic frameworks.

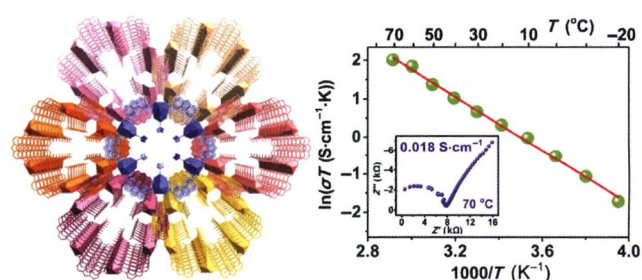
381–386

High proton conductivity in metalloring-cluster based metal-organic nanotubes

Quanjie Lin¹, Yingxiang Ye¹, Lizhen Liu¹, Zizhu Yao¹, Ziyin Li¹, Lihua Wang¹, Chulong Liu^{1,*}, Zhangjing Zhang^{1,2,*}, and Shengchang Xiang^{1,2,*}

¹ Fujian Normal University, China

² Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, China



The inner surface of metalloring-cluster based metal-organic nanotubes (MONTs) is decorated with uncoordinated carboxylic acid groups, which can obviously enhance the proton conductivities of MONTs.

387–391

Discovery of Zr-based metal-organic polygon: Unveiling new design opportunities in reticular chemistry

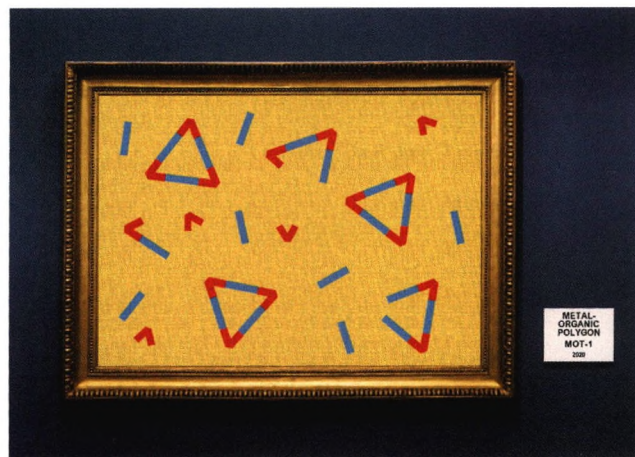
Jiyeon Kim¹, Dongsik Nam¹, Hiroshi Kitagawa², Dae-Woon Lim^{2,†,*}, and Wonyoung Choe^{1,*}

¹ Ulsan National Institute of Science and Technology, Republic of Korea

² Kyoto University, Japan

[†] Present address: Yonsei University, Republic of Korea

392–397



This manuscript reports a triangular metal-organic polygon as a new member of Zr-based metal-organic materials. The interplay of the geometrically frustrated ligand and secondary building unit opens up new design opportunities.

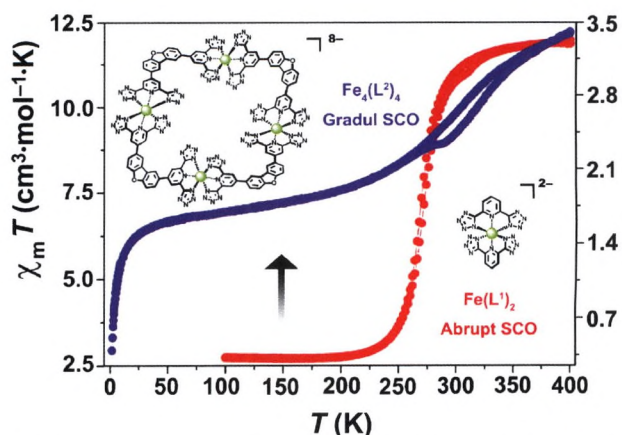
From a mononuclear FeL_2 complex to a Fe_4L_4 molecular square: Designed assembly and spin-crossover property

Zhuo Wang^{1,2}, Li-Peng Zhou^{1,2}, Li-Xuan Cai^{1,2}, Chong-Bin Tian^{1,2,*}, and Qing-Fu Sun^{1,2,*}

¹ Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, China

² University of Chinese Academy of Sciences, China

398–403



The spin-crossover (SCO) performance can be improved through linking the mononuclear $\text{Fe}(\text{L}^1)_2$ SCO centers into polynuclear systems $\text{Fe}_4(\text{L}^2)_4$.

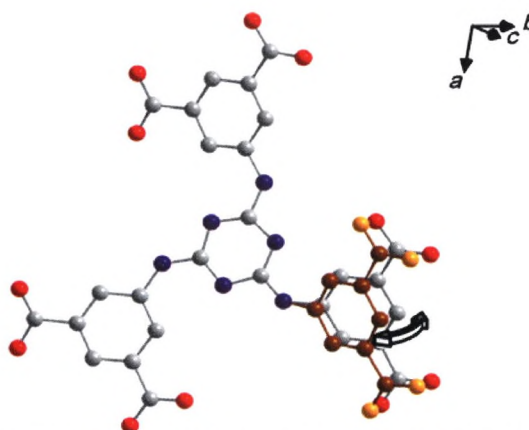
Large anisotropic negative thermal expansion in Cu-TDPAT metalorganic framework: A combined *in situ* X-ray diffraction and DRIFTS study

Mehrdad Asgari¹, Ilia Kochetygov¹, Hassan Abedini^{1,2}, and Wendy L. Queen^{1,*}

¹ École Polytechnique Fédérale de Lausanne (EPFL) - Valais Wallis, Switzerland

² Petroleum University of Technology (PUT), Iran

404–410

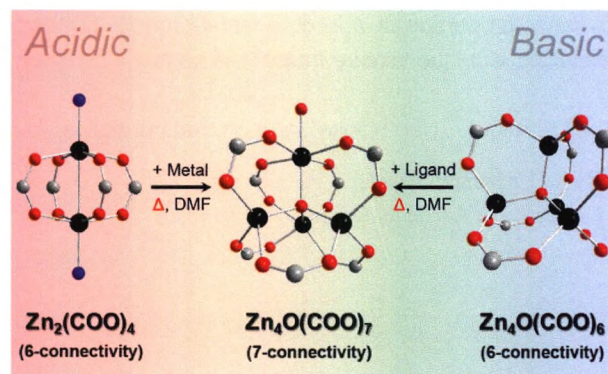


Cu-TDPAT (H_6TDPAT = 2,4,6-tris(3,5-dicarboxyphenylamino)-1,3,5-triazine), a stable and versatile metal-organic framework with promising adsorption performance, shows unusual negative thermal expansion properties. We shed light on the mechanism of the observed negative thermal expansion (NTE) by a combination of comprehensive *in situ* characterization techniques.

Solid-state phase transformations toward a metal–organic framework of 7-connected Zn_4O secondary building units

Jaehui Kim, Junsu Ha, Jae Hwa Lee*, and Hoi Ri Moon*

Ulsan National Institute of Science and Technology (UNIST),
Republic of Korea



Multiple transformative routes toward a metal–organic framework (MOF) of 7-connected $\text{Zn}_4\text{O}(\text{COO})_7$ secondary building units (SBUs) can be realized by controlling the SBU geometry via the addition of either basic or acidic moieties.

411–416

Applying reticular synthesis to the design of Cu-based MOFs with mechanically interlocked linkers

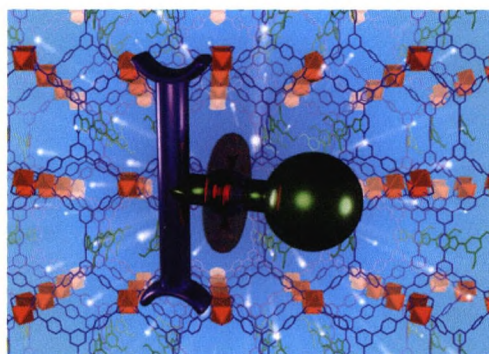
Alexander J. Stirk¹, Benjamin H. Wilson¹, Christopher A. O’Keeffe¹,
Hazem Amarne², Kelong Zhu³, Robert W. Schurko⁴, and
Stephen J. Loeb^{1,*}

¹ University of Windsor, Canada

² The University of Jordan, Jordan

³ Sun Yat-Sen University, China

⁴ Florida State University, USA



The concept of reticular synthesis was used to design rigid T-shaped linkers and their [2]rotaxane analogs based on a triphenylene tetracarboxylate strut akin to that used for the iconic metal–organic framework (MOF) material **NOTT-101**. Single-crystal X-ray diffraction was used to characterize four new Cu(II)-based MOFs prepared using these new linkers; **UWCM-12** (fof), β -**UWCM-13** (loz) and **UWCM-14** (lil) contain “naked” linkers and **UWDM-14** (lil), analogous to **UWCM-14** (lil), contains a [2]rotaxane linker. The loz topology found for β -**UWCM-13** (loz) is the first example of this net. Variable-temperature, ^2H solid-state NMR spectroscopy was used to probe the motion of the 24-membered macrocycle threaded onto the rigid backbone in **UWDM-14**.

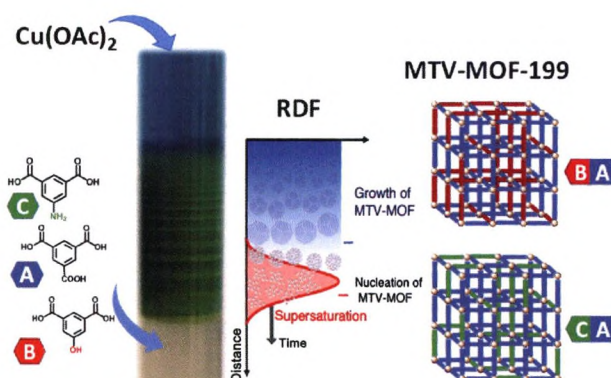
417–422

Controlled growth and composition of multivariate metal–organic frameworks-199 via a reaction-diffusion process

Razan Issa¹, Fayrouz Abou Ibrahim¹, Mazen Al-Ghoul^{1,2,*},
and Mohamad Hmadeh^{1,*}

¹ American University of Beirut, Lebanon

² McGill University, Canada



Multivariate MOF-199 structures are successfully synthesized via the reaction diffusion framework (RDF). The resulting functionalized and defected metal–organic frameworks (MOFs) are employed as efficient adsorbents for dye removal from water.

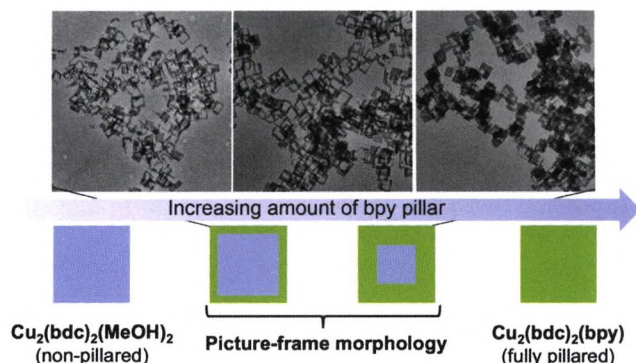
423–431

Dynamic properties of a flexible metal-organic framework exhibiting a unique “picture frame”-like crystal morphology

Kenji Sumida^{1,2}, Nao Horike¹, and Shuhei Furukawa^{1,*}

¹ Kyoto University, Japan

² University of Adelaide, Australia



A flexible metal-organic framework (MOF) of $\text{Cu}_2(\text{bdc})_2(\text{bpy})$ is shaped into “picture-frame”-like crystal morphology, which is correlated to the dynamic properties to vary between rigid, elastic, and shape memory modes.

432–437

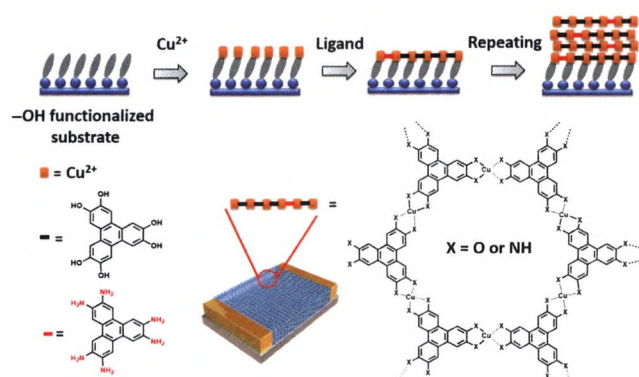
Layer-by-layer assembled dual-ligand conductive MOF nano-film with modulated chemiresistive sensitivity and selectivity

Ai-Qian Wu¹, Wen-Qing Wang¹, Hong-Bin Zhan¹, Lin-An Cao², Xiao-Liang Ye², Jia-Jia Zheng³, Pendyala Naresh Kumar², Kashi Chiranjeevulu², Wei-Hua Deng², Guan-E Wang², Ming-Shui Yao^{2,3,*}, and Gang Xu^{2,*}

¹ Fuzhou University, China

² Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, China

³ Kyoto University, Japan



We demonstrate a dual-ligand design strategy to modulate the performance of electronically conductive metal-organic framework (EC-MOF) thin film with a spray layer-by-layer assembly method. The high quality nano-film of 2,3,6,7,10,11-hexaiminotriphenylene (HITP) doped Cu-HITP enables the precise modulation of the chemiresistive sensitivity and selectivity.

438–443

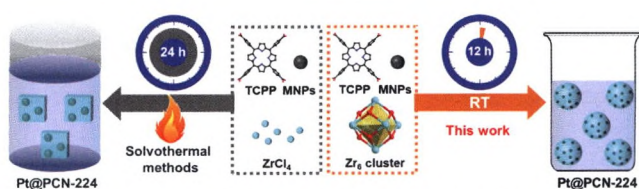
Rapid room-temperature synthesis of a porphyrinic MOF for encapsulating metal nanoparticles

Huihui He¹, Luyan Li³, Yang Liu¹, Meruyert Kassymova³, Dandan Li^{2,*}, Liangliang Zhang^{1,*}, and Hai-Long Jiang³

¹ Northwestern Polytechnical University (NPU), China

² Anhui University, China

³ University of Science and Technology of China, China



We successfully prepared a porphyrinic metal-organic framework (MOF), PCN-224-RT, as a support for encapsulating metal nanoparticles via a directly stirring method at room temperature. The rapid and simple method in this work is favorable in reference to traditional solvothermal methods.

444–449

Nickel phosphonate MOF as efficient water splitting photocatalyst

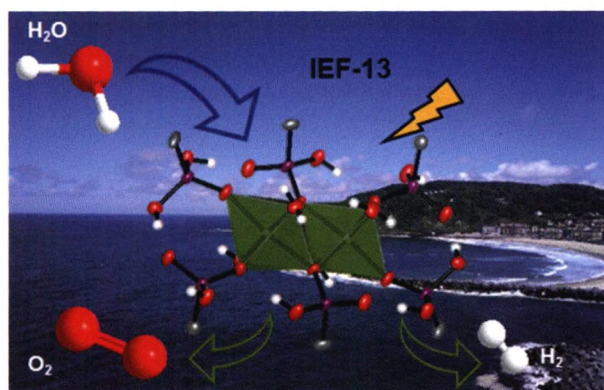
Pablo Salcedo-Abraira^{1,2}, Sérgio M. F. Vilela¹, Artem A. Babaryk¹, María Cabrero-Antonino³, Pedro Gregorio¹, Fabrice Salles⁴, Sergio Navalón³, Hermenegildo García^{3,*}, and Patricia Horcajada^{1,*}

¹ Advanced Porous Materials Unit (APMU), Spain

² Universidad Complutense de Madrid, Spain

³ Universitat Politècnica de València, Spain

⁴ Université Montpellier, France



A novel robust microporous two-dimensional (2D) Ni-phosphonate metal-organic framework (MOF) has been prepared, exhibiting without co-catalyst stable photocatalytic activity in hydrogen evolution and overall water splitting.

450–457

Heterogeneous catalysts with programmable topologies generated by reticulation of organocatalysts into metal-organic frameworks: The case of squaramide

Anna Broto-Ribas¹, Claudia Vignatti¹, Alicia Jimenez-Almaraz², Javier Luis-Barrera², Zahra Dolatkhan², Felipe Gándara³, Inhar Imaz^{1,*}, Rubén Mas-Ballesté^{2,4,*}, José Alemán^{2,4,*}, and Daniel MasPOCH^{1,5,*}

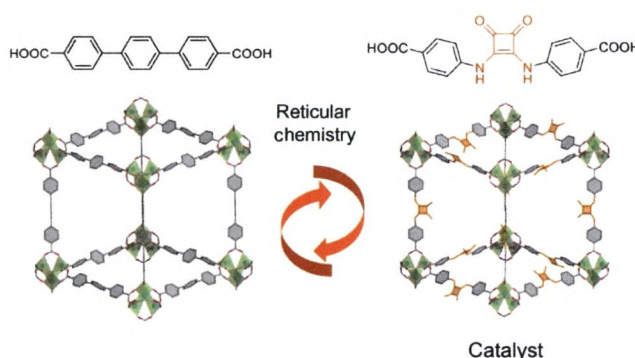
¹ CSIC and The Barcelona Institute of Science and Technology, Spain

² Universidad Autonoma de Madrid, Spain

³ Consejo Superior de Investigaciones Científicas (CSIC), Spain

⁴ Campus Universidad Autonoma de Madrid, Spain

⁵ Institutio Catalana de Recerca i Estudis Avancats (ICREA), Spain



A series of metal-organic framework (MOF)-based catalysts with programmable topologies are generated by incorporating squaramide organocatalysts, using reticular chemistry and exploiting MOF-structural data from Cambridge Structural Database.

458–465

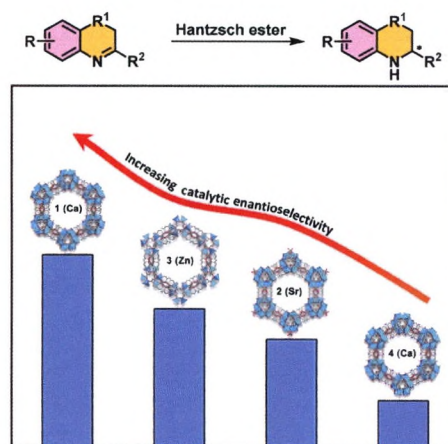
Chiral metal-organic frameworks with tunable catalytic selectivity in asymmetric transfer hydrogenation reactions

Xu Chen¹, Zhiwei Qiao², Bang Hou¹, Hong Jiang¹, Wei Gong¹, Jinqiao Dong¹, Hai-Yang Li³, Yong Cui¹, and Yan Liu^{1,*}

¹ Shanghai Jiao Tong University, China

² Guangzhou University, China

³ Zhengzhou University, China



We have demonstrated that the enantioselectivity of metal-organic framework (MOF) catalysts in asymmetric transfer hydrogenation of heteroaromatic imines could be rationally tuned by changing the electronegativities of metal ions and modifying the steric hindrance of ligand structures of MOFs.

466–472

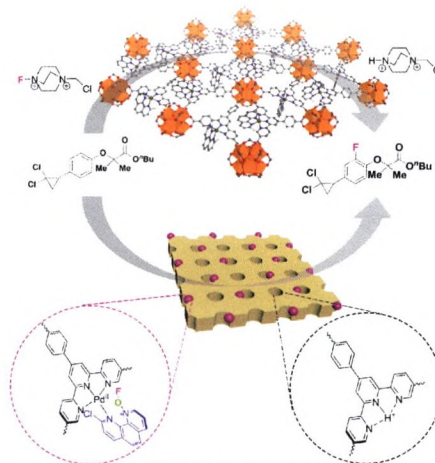
Metal-organic layers as reusable solid fluorination reagents and heterogeneous catalysts for aromatic fluorination

Wenjie Shi^{1,2}, Lingzhen Zeng¹, Lingyun Cao¹, Ying Huang¹, Cheng Wang^{1,*}, and Wenbin Lin²

¹ Xiamen University, China

² University of Chicago, USA

473–478



A Pd-functionalized two-dimensional metal-organic layer (MOL) was developed as a heterogeneous catalyst and a reusable solid reagent to fluorinate a broad scope of aromatic compounds. The MOL stabilized a highly reactive N-fluoroxy-phenanthroline coordinated on Pd as the active center in the solid reagent, highlighting new opportunities in fluorination chemistry with MOLs.

Direct aerobic oxidation of monoalcohol and diols to acetals using tandem Ru@MOF catalysts

Songwei Zhang^{1,3}, Jerry Pui Ho Li^{1,5}, Jingpeng Zhao², Dan Wu², Biao Yuan¹, Willinton Yesid Hernández², Wen-Juan Zhou², Tao He^{1,4}, Yi Yu¹, Yong Yang^{1,*}, Vitaly Ordonsky^{2,*}, and Tao Li^{1,*}

¹ ShanghaiTech University, China

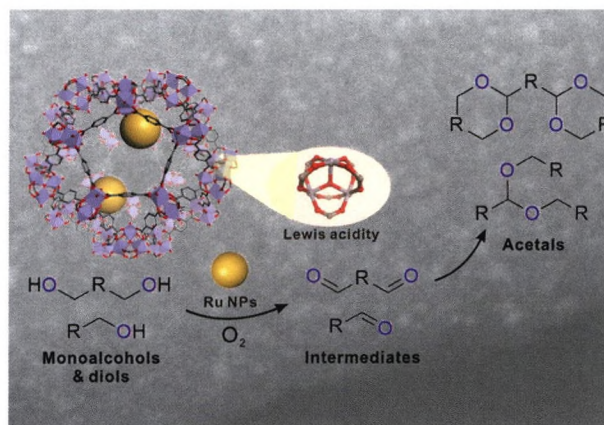
² Eco-Efficient Products and Processes Laboratory (E2P2L), China

³ University of Chinese Academy of Sciences, China

⁴ Shanghai Advanced Research Institute, Chinese Academy of Sciences, China

⁵ Queen's University Belfast, UK

479–485



The existing methods usually rely on a two-step process in which alcohols are first oxidized to aldehydes over metal catalysts (Ru, Pt, Pd) and then acetalized using acids. Hereby we report a Ru@MOF tandem catalyst containing ultra-fine Ru nanoparticles (< 2 nm) for direct alcohol to acetal conversion of monoalcohols and diols with no formation of carboxylic acids.

Single-atom Pd catalyst anchored on Zr-based metal-organic polyhedra for Suzuki-Miyaura cross coupling reactions in aqueous media

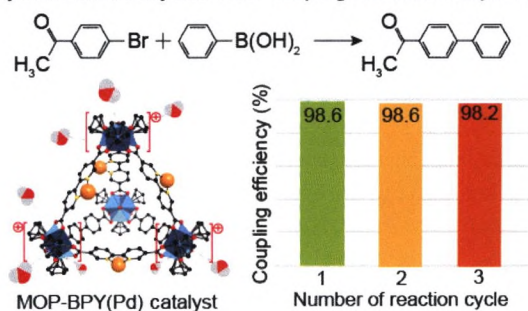
Seongsoo Kim¹, Seohyeon Jee², Kyung Min Choi^{2,*}, and Dong-Sik Shin^{2,*}

¹ Kangwon National University, Republic of Korea

² Sookmyung Women's University, Republic of Korea

486–492

Catalysis for Suzuki-Miyaura cross coupling reactions in aqueous media



The discrete cages of metal-organic polyhedra anchoring single Pd atom successfully catalyse a Suzuki-Miyaura cross coupling reaction with various substrates in aqueous media.

Highly efficient multi-metal catalysts for carbon dioxide reduction prepared from atomically sequenced metal organic frameworks

Celia Castillo-Blas^{1,†}, Consuelo Álvarez-Galván^{2,*}, Inés Puente-Orench^{3,4}, Alba García-Sánchez⁵, Freddy E. Oropeza⁵, Enrique Gutiérrez-Puebla¹, Ángeles Monge^{1,*}, Víctor A. de la Peña-O'Shea^{5,*}, and Felipe Gándara^{1,*}

¹ Materials Science Institute of Madrid (CSIC), Spain

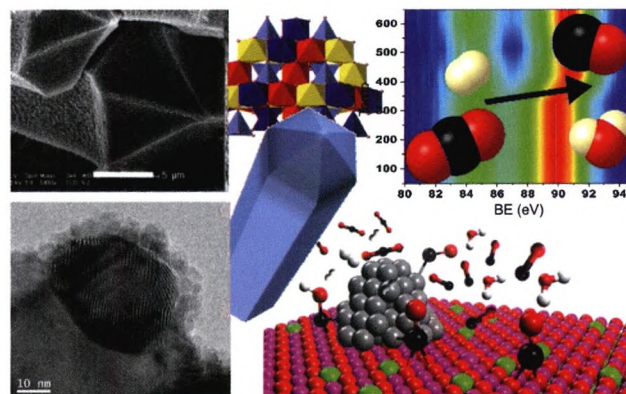
² Instituto de Catálisis y Petroleoquímica (CSIC), Spain

³ Instituto de Ciencia de Materiales de Aragón, Spain

⁴ Institut Laue Langevin, France

⁵ Photoactivated Processes Unit IMDEA Energy Institute, Spain

[†] Present address: University Autonomous of Madrid, Spain



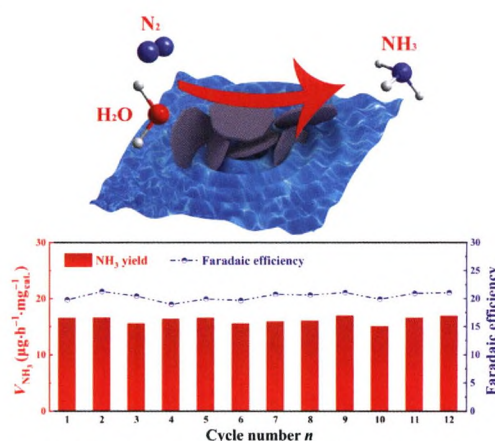
Precision at the atomic level exerted in metal-organic frameworks (MOFs) allows control on the formation of complex nanomaterials with enhanced reactivity: Supported metal nanoparticles are formed from MOF derived multi-metal oxides, and are efficient catalyst for the reduction of carbon dioxide in the reverse water-gas shift reaction.

493–500

Oxygen vacancy engineering of calcium cobaltate: A nitrogen fixation electrocatalyst at ambient condition in neutral electrolyte

Xinyu Chen, Ke Li, Xiaoxuan Yang, Jiaqi Lv, Sai Sun, Siqi Li, Dongming Cheng, Bo Li, Yang-Guang Li, and Hong-Ying Zang*

Northeast Normal University, China



Herein, a calcium metalate catalyst CaCoO_x nanoplates with oxygen vacancies was synthesized and used as an electrocatalyst for nitrogen reduction reaction (NRR) for the first time, whose morphology can be controlled by the calcination temperature and the heating rate. Under the optimal conditions, the CaCoO_x catalyst achieved the yield of nitrogen conversion to ammonia of 16.25 μg·h⁻¹·mg_{cat}⁻¹ and showed good stability even after 12 times recyclability.

501–506

A microporous aluminum-based metal-organic framework for high methane, hydrogen, and carbon dioxide storage

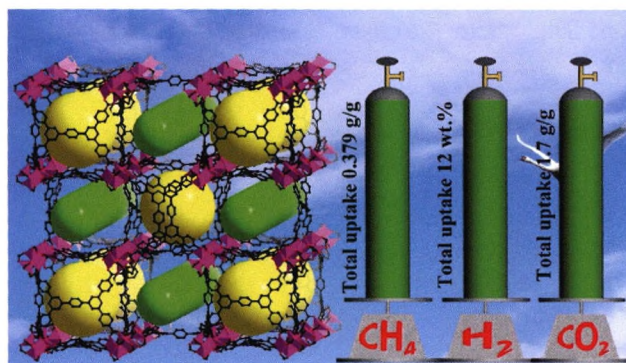
Bin Wang^{1,2}, Xin Zhang², Hongliang Huang⁴, Zhangjing Zhang¹, Taner Yildirim³, Wei Zhou³, Shengchang Xiang^{1,*}, and Banglin Chen^{2,*}

¹ Fujian Normal University, China

² University of Texas at San Antonio, USA

³ National Institute of Standards and Technology, USA

⁴ Tianjin Polytechnic University, China



In this work, we explored the methane, hydrogen, and carbon dioxide storage capacities of a stable microporous aluminum-based metal-organic framework with large surface area and pore volume.

507–511

A robust soc-MOF platform exhibiting high gravimetric uptake and volumetric deliverable capacity for on-board methane storage

Gaurav Verma¹, Sanjay Kumar^{1,†,*}, Harsh Vardhan¹, Junyu Ren¹, Zheng Niu¹, Tony Pham^{1,‡}, Lukasz Wojtas¹, Sydney Butikofer^{1,⊥}, Jose C Echeverria Garcia¹, Yu-Sheng Chen², Brian Space¹, and Shengqian Ma^{1,*}

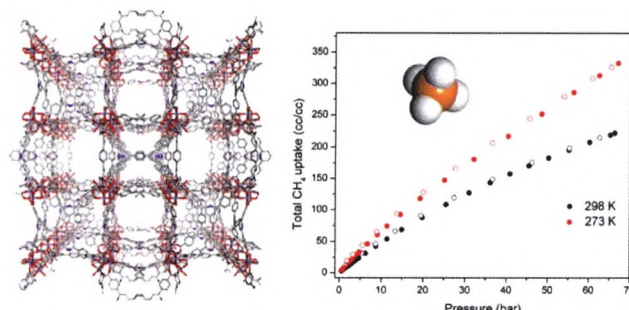
¹ University of South Florida, USA

² The University of Chicago, USA

[†] Present address: Multani Mal Modi College, India

[‡] Present address: The University of Tampa, USA

[⊥] Present address: University of Illinois at Urbana-Champaign, USA



An iron-based square-octahedron (soc) topology metal-organic framework (soc-MOF) shows high gravimetric uptake and volumetric deliverable capacity for methane storage at 65 bar and room temperature.

512–517

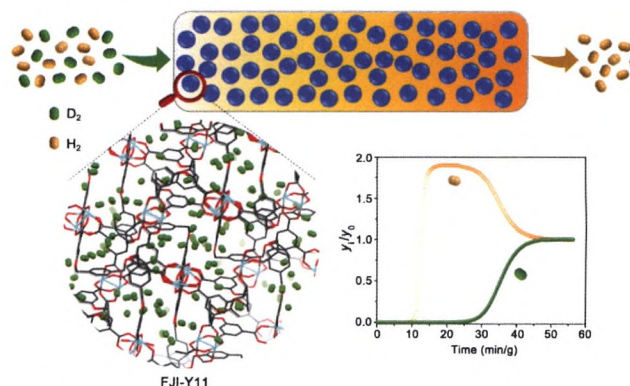
Highly effective H₂/D₂ separation in a stable Cu-based metalorganic framework

Yanan Si^{1,3}, Xiang He^{2,*}, Jie Jiang², Zhiming Duan², Wenjing Wang¹, and Daqiang Yuan^{1,*}

¹ Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, China

² Shanghai University, China

³ University of the Chinese Academy of Sciences, China



Efficient hydrogen isotope separation is achieved by using the dynamic low-temperature breakthrough device, in which a mixed gas of H₂/D₂/Ne (10/10/80, vol.%) flowed over the packed column of activated FJI-Y11 with a total flow of 10 mL/min at 77 K and 1 bar.

518–525

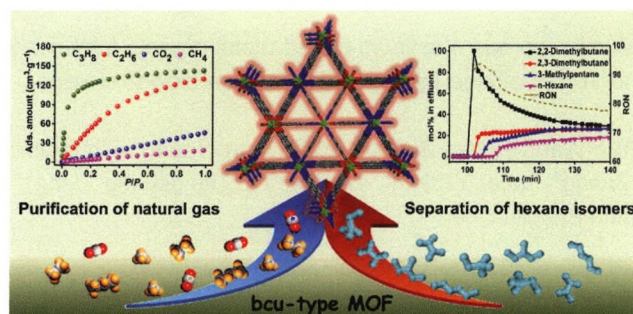
Separation of hexane isomers by introducing “triangular-like and quadrilateral-like channels” in a bcu-type metal-organic framework

Dongmei Wang^{1,2}, Xinglong Dong³, Yu Han^{3,*}, and Yunling Liu^{1,*}

¹ Jilin University, China

² Zhejiang Normal University, China

³ King Abdullah University of Science and Technology, Kingdom of Saudi Arabia



A novel bcu-type metal-organic framework (MOF) Zn₉(tba)₉(dabco)₃ (H₂tba = 4-(1H-tetrazol-5-yl)-benzoic acid; dabco = 1,4-diazabicyclo[2.2.2]octane) with triangular-like and quadrilateral-like channels was designed and assembled based on reticular chemistry strategy. Resulting from the synergetic contributory of sieving effect and diffusion, Zn₉(tba)₉(dabco)₃ exhibits highly effective separation ability for hexane isomers.

526–531

Efficient hexane isomers separation in isorecticular bipyrazolate metal-organic frameworks: The role of pore functionalization

Rebecca Vismara^{1,†}, Corrado Di Nicola², Rodrigo Gil-San Millán³, Kostiantyn V. Domasevich⁴, Claudio Pettinari^{2,5}, Jorge A. R. Navarro^{3,*}, and Simona Galli^{1,6,*}

¹ Università dell'Insubria, Italy

² University of Camerino, Italy

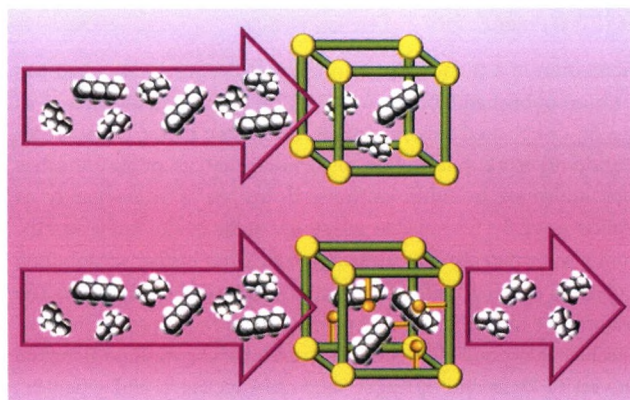
³ Universidad de Granada, Spain

⁴ Taras Shevchenko National University of Kyiv, Ukraine

⁵ Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), Italy

⁶ Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Italy

[†] Present address: University of Liverpool, UK



Pore functionalization in a series of robust isorecticular zinc-bipyrazolate frameworks possessing square one-dimensional channels gives rise to selective hexane isomers adsorption interactions leading to efficient gas separation, as proven by experimental and computational studies.

532–540

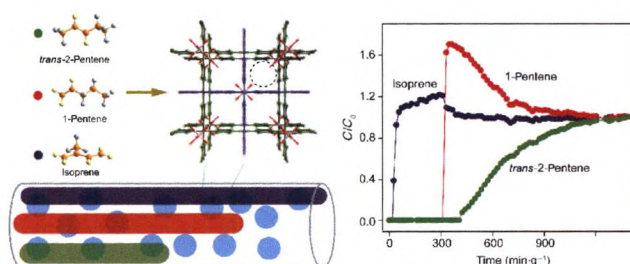
Remarkable separation of C5 olefins in anion-pillared hybrid porous materials

Ying Yu¹, Lifeng Yang^{1,2}, Bin Tan³, Jianbo Hu^{1,2}, Qingju Wang¹, Xili Cui^{1,2,*}, and Huabin Xing^{1,2}

¹ Zhejiang University, China

² Institute of Zhejiang University - Quzhou, China

³ CHN Energy, China



Anion-pillared hybrid porous materials with well-distributed anion-based electrostatic environment and responsive flexible skeleton exhibit remarkable separation and regeneration performance for C5 olefin mixtures of *trans*-2-pentene, 1-pentene and isoprene.

541–545

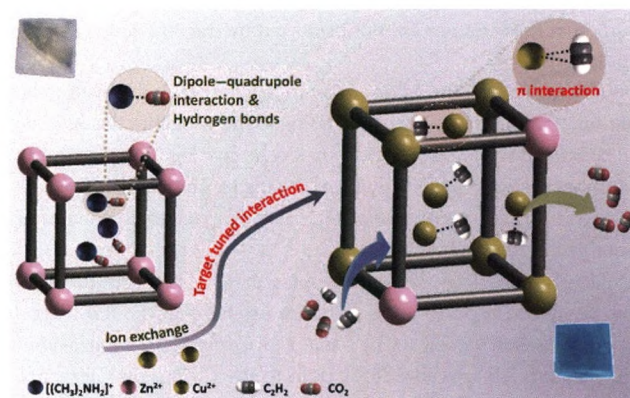
A chemically stable nanoporous coordination polymer with fixed and free Cu²⁺ ions for boosted C₂H₂/CO₂ separation

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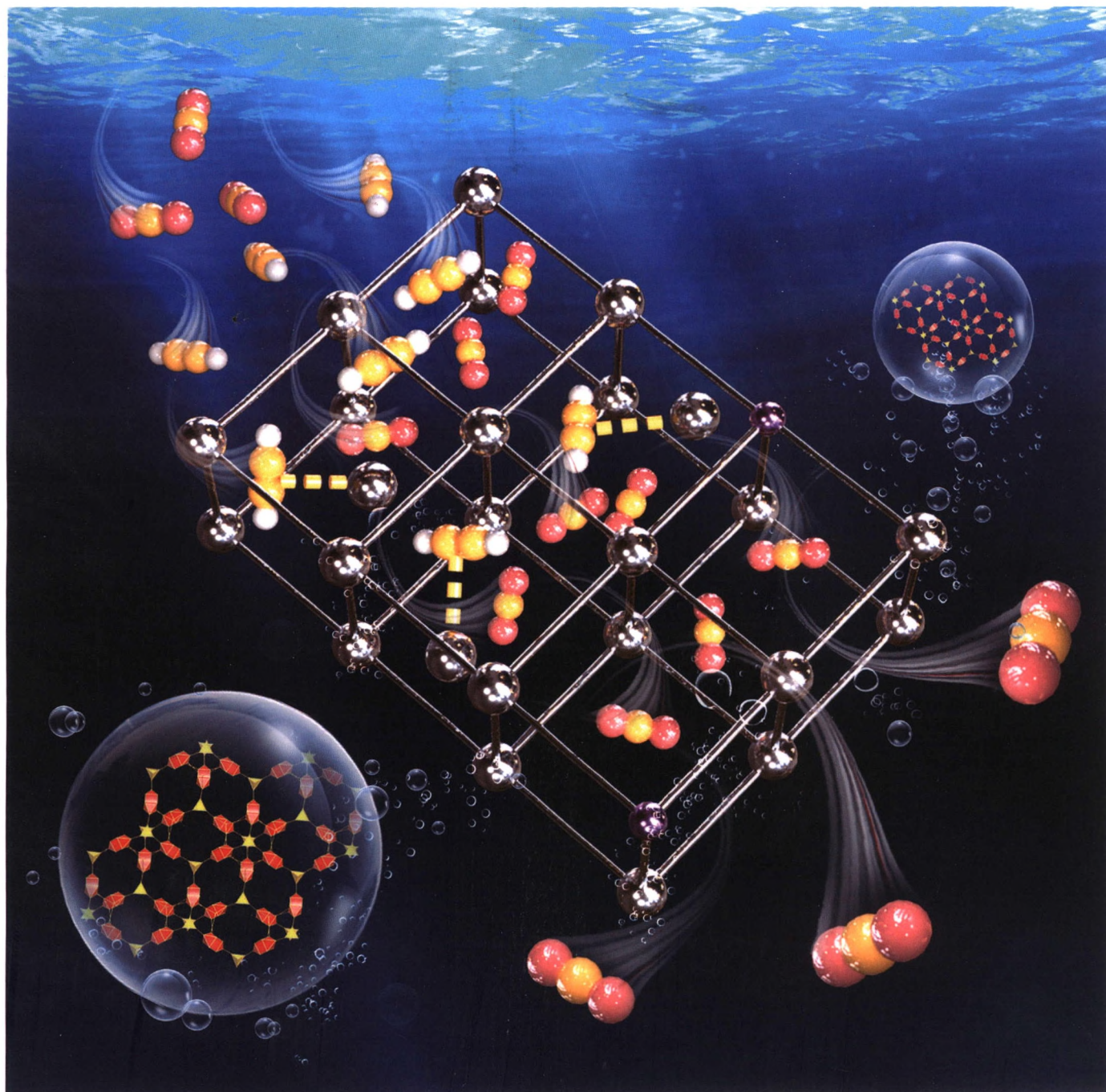
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³ Yancheng Teachers University, China



A new chemically stable nanoporous coordination polymer adsorbent with fixed and free Cu ions was prepared through post-synthetic approach, which shows excellent C₂H₂/CO₂ separation, along with enhanced C₂H₂ capacity.

546–553



纳米研究(英文版)(月刊, 2008年创刊) 第14卷 第2期 2021年2月出版

Editors-in-Chief Yadong Li, Shoushan Fan

Sponsored by Tsinghua University & Chinese Chemical Society

Edited by Nano Research Editorial Office

Published by Tsinghua University Press

Address Xueyan Building,
Tsinghua University,
Beijing 100084, China

Website www.theNanoResearch.com & www.springer.com/journal/12274

Online Manuscript Submission, Review and Tracking System www.editorialmanager.com/nare

主管单位 中华人民共和国教育部

主办单位 清华大学

中国化学会

主 编 李亚栋 范守善

编 辑 《纳米研究》编辑部

出版发行 清华大学出版社有限公司

印刷单位 北京地大彩印有限公司

ISSN 1998-0124



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