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An in Situ Embedded Square-Planar $Cu^{II}/Ni^{II}N_4$ Metalloligand in Coordination Polymers for Visible-Light Photocatalysis

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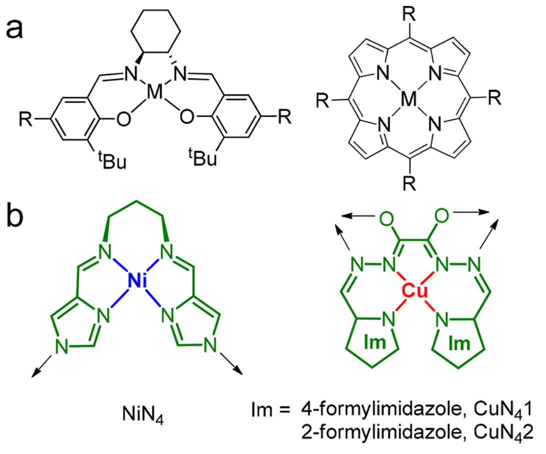
Supporting Information

ABSTRACT: Three coordination polymers (CPs) with square-planar $Cu^{II}/Ni^{II}N_4$ subunits were formed in one step by *subcomponent self-assembly*, giving rise to an unprecedented linking variety of in situ embedded metalloligands and Cu^I clusters. All CPs exhibit unusual visible-light adsorption. Enhanced photocatalytic activity and high selectivity were observed in the oxidation of benzene under visible-light irradiation.

Salen metal complexes, metalloporphyrins, and their derivatives with square-planar 4-coordinated structures have long been of interest to chemists because of their facile synthesis and unique accessible metal−substrate binding pockets with controllable steric and electronic properties.[1−4] Metallosalens/metalloporphyrins (see Chart 1a) can be built into crystalline coordination architectures[5−7] such as metallacycles,[3,8,9] rotaxanes,[10] cages,[11] metal−organic frameworks (MOFs), and one/two-dimensional (1D/2D) coordination polymers (CPs).[12−16] These supramolecular assemblies integrate the attractive properties of metallosalen/metalloporphyrin moieties and the well-defined compact or porous crystalline structures, giving rise to wide applications in fields such as catalysis,[14,15] separation,[11,13] photoluminescence,[9] and light-harvesting materials.[16,17] Given the remarkable function of salen/porphyrin metalloligands, it is highly worthwhile to construct MOFs/CPs with versatile metalloligands featuring square-planar 4-coordinated geometry and accessible metal sites as exhibited by salen/porphyrin metal complexes.

Chart 1. Structures of Metallosalens and Metalloporphyrins (a) and Square-Planar $Cu^{II}/Ni^{II}N_4$ Metalloligands in This Work (b)



So far, synthetic strategies compatible with metallosalen/metalloporphyrin struts include noncovalent encapsulation,[18] metalloligand self-assembly,[7,12−15] and postsynthetic modification/exchange,[14] which was developed in the research groups of Hupp,[6,19] Goldberg,[20] Zhou,[21] Cui,[11,13] Ma,[16] and others.[22−24] Our group has been exploring the Cu^I-based coordination chemistry,[25−29] introducing metal terpyridine complexes, metal pyrazolate cluster helicates,[30−32] and copper(I) metallosalen[33,34] through an in situ assembly and metalloligand strategy. In addition, the efficient photocatalytic activity of Cu^I-based compounds[35−37] and MOF/CP materials[33,34,38−40] was documented by us and other groups, including the degradation of organic pollutants,[33,34] hydrogen production,[38,39] and organic transformation[40] under visible-light irradiation. In an effort to explore the synthetic methodologies and properties of the extended crystalline structures combined with the outstanding merits of salen/porphyrin analogues and photoactive Cu^I clusters, we employ *subcomponent self-assembly* technology (in situ formation of coordination and covalent bonds simultaneously,[41,42] also reported in our work[43,44]) for the in situ assembly and embedding of metalloligands (Chart 1b) into the Cu^I network, yielding both accessible metal sites and photoactive Cu^I clusters. Unlike the predesigned metalloligand approach, versatile synthetic precursors can be applied in *subcomponent self-assembly*, giving diverse supramolecular assemblies. To the best of our knowledge, this work represents the first example of the in situ setup of square-planar $Cu^{II}/Ni^{II}N_4$ subunits in the CPs from single Cu^I ions or mixed metal ions in a one-step reaction.

Here we succeed in building $Cu^{II}/Ni^{II}N_4$ components (Chart 1b) into three CPs with 1D/2D coordination structures, $[(Ni^{II}N_4)_2(Cu^II)_5{\cdot}DMF]_n$ (**1**; DMF = dimethylformamide), $[(Cu^{II}N_41)(Cu^II)_2]_n$ (**2**), and $[(Cu^{II}N_42)_2(Cu^{II}I_2)]_n$ (**3**). They have been formulated and characterized on the basis of elemental analysis, IR spectroscopy, and thermogravimetric (TGA) and single-crystal X-ray diffraction analyses (see the Supporting Information, SI, for experimental details). Their optical response

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and visible-light-enhanced photocatalytic properties have been examined.

A single crystal of complex **1** (Table S1) was prepared by the four-component self-assembly of 4-formylimidazole, 1,3-diaminopropane, CuI, and $Ni(NO_3)_2 \cdot 6H_2O$ in a molar ratio of 4:2:5:2 in a DMF/ethanol mixture (3:1, v/v) at 120 °C for 3 days (see Figure 1a and the SI for details). X-ray diffraction analysis reveals that the Ni^{II} atom of the $Ni^{II}N_4$ subunit adopts a square-planar 4-coordinated configuration, which is coordinated to the discrete neutral Cu_5I_5 cluster by two deprotonated N atoms of imidazoles [$Cu^{I}-N_{imidazole}$, 1.96853(7)−2.00259(8) Å] in the asymmetric unit of **1** (Figure S1). In the unique structure of the Cu_5I_5 cluster (Figure 1c), four Cu^{I} atoms (Cu1, Cu2, Cu3, and Cu4) are arranged in the pseudocubane coordination geometry, with the supernumerary $Cu5^{I}$ atom sitting on one of the cubic faces. All Cu^{I} atoms in the Cu_5I_5 cluster of **1** adopt the tetrahedral 4-coordinated configuration and are connected by one μ_2-I, two μ_3-I, and two μ_4-I ions, wherein the $Cu3^{I}$ atoms are coordinated to four I^- anions and the other four Cu^{I} atoms act as nodes to bridge the ditopic $Ni^{II}N_4$ metalloligand with a bite angle of 121.71(4)° ($Cu^{I}\cdots Ni^{II}\cdots Cu^{I}$) for the construction of a double zigzag chain (Figure 1b). Along the *a* axis, 1D chains stack with each other to form tubular channels, where DMF molecules are trapped (Figure 1d).

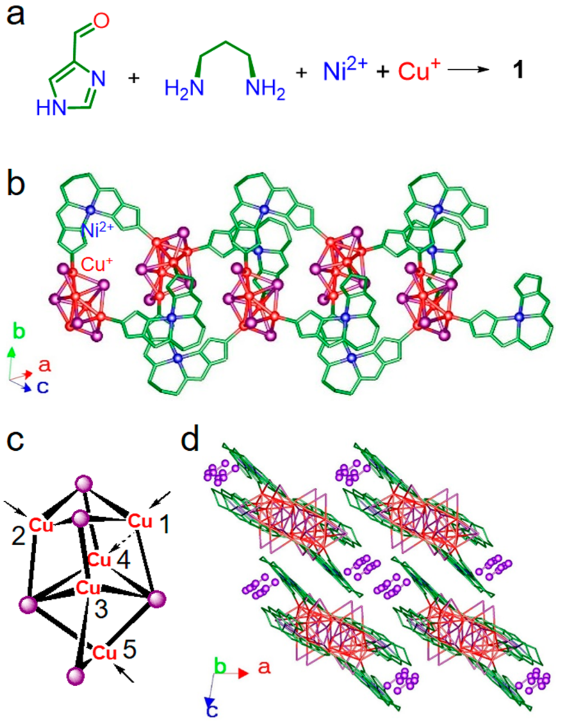

Figure 1. Illustration of the preparation and crystal structure of CP **1**: (a) synthesis of **1** via subcomponent self-assembly; (b) 1D double zigzag chain; (c) Cu_5I_5 cluster; (d) Three-dimensional packing of a 1D chain with trapped DMF molecules. Color code: I, purple; Cu, red; Ni, blue; C, N, and O, green. H atoms are omitted.

Efforts were also made to prepare the $Cu^{II}N_4$ motif. The in situ assembly of CuI, oxalyl dihydrazide, and 4-formylimidazole, in a molar ratio of 2:1:2, in an ethanol/water mixture (4:1, v/v) at 140 °C for 2 days (see the SI for details) yields dark-green complex **2**. The replacement of 4-formylimidazole with 2-formylimidazole under the same reaction conditions gave dark-green **3** (Figure 2a). Single-crystal X-ray diffraction analyses revealed (Table S1) that **2** is a mixed-valence 1D polymer and **3** presents a 2D Cu^{II}-based structure. Square-planar 4-coordinated $Cu^{II}N_4$ metalloligands (Chart 1b) in both polymers involve the in situ formation of imine bonds and the oxidation of Cu^{I} ions in the presence of O_2, with different coordination geometries. In complex **2**, $Cu^{II}N_4$1 behaves as a ditopic metalloligand (Figure S2) and was linked by Cu_2I_2 clusters along the *a* axis with a bite angle of 109.18(8)° ($Cu^{I}\cdots Cu^{II}\cdots Cu^{I}$), forming 1D zigzag chains (Figures 2b and S2). In complex **3**, $Cu^{II}N_4$2 acts as a tritopic metalloligand (Figure S3). Two adjacent $Cu^{II}N_4$2 units were chelated with the octahedral $Cu^{II}I_2$ cluster and bridged through I anions, giving an extended 2D layer network (Figures 2c and S3). Compared with the compact structure of **3**, $Cu^{II}N_4$ units in **2** feature highly accessible open sites in Cu^{II} centers. The successful one-step in situ construction of two functional moieties in CPs ($Ni^{II}N_4$ and Cu_5I_5 in **1**; $Cu^{II}N_4$ and Cu_2I_2 in **2**) promotes us to investigate their light absorption properties and photocatalytic activities.

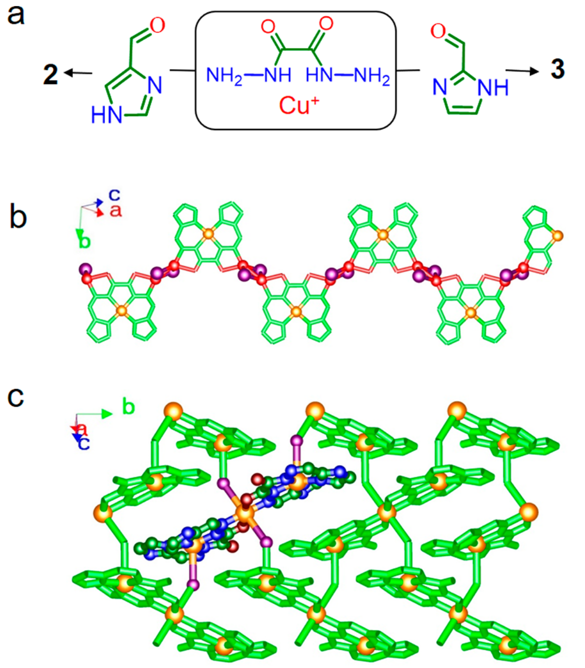

Figure 2. Illustration of the preparation and crystal structures of 1D/2D CPs **2** and **3**: (a) synthesis of **2** and **3** via subcomponent self-assembly; (b) 1D zigzag chain of **2**; (c) 2D layer structure of **3**. Color code: I, purple; Cu^{I}, red; Cu^{II}, gold; N, blue; C, green; O, red. H atoms are omitted.

All of these complexes were found to be highly stable in air and various solvents (water, DMF, ethanol, and acetonitrile; <0.5 mg/mL) for weeks, based on powder X-ray diffraction (PXRD) experiments (Figures S4−S6). Their thermal stabilities rise from 230 °C (**1**) to 342 °C (**3**) to 380 °C (**2**) according to TGA (Figure S7). The phase purity of the bulk samples was established by a comparison of their observed and simulated PXRD patterns. The optical response of **1**−**3** in the visible-light region was measured through UV−vis diffuse-reflectance spectra, and the maximum absorption wavelength ranges from 660 nm for **1** and 762 nm for **3** up to about 815 nm for **2** (Figure 3a), respectively. The values of the photon energy are listed in Table S2. The results indicate that the compounds can absorb photons with energy equal or higher than their highest occupied molecular orbital−lowest unoccupied molecular orbital gap.

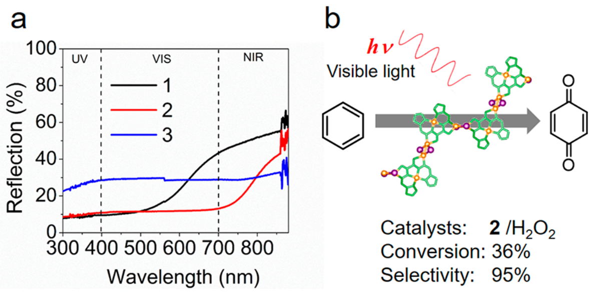

Figure 3. (a) UV−vis diffuse-reflectance spectra of CPs **1**−**3**. (b) Catalytic oxidation of benzene by **2** under visible-light irradiation.

Because direct and selective transformation of benzene is economically important and few photocatalysts have been reported for this reaction,[45,46] we here employed the oxidation of benzene to examine the photocatalytic activity of complexes **1** and **2** (Figure 3b). The reaction was conducted under visible-light irradiation using a 3 mmol % sample (per the $Cu^{II}N_4$ or $Ni^{II}N_4$ moiety) and 30% hydrogen peroxide as a catalyst and an oxidant, respectively (see the SI for details).[47,48] It was observed that only 1−15% conversion of benzene was obtained by **1**, **3**, and CuI in the presence or absence of light (Table S3 and Figures S8 and S9). In contrast to the poor activity of **1**, complex **2** exhibits enhanced photocatalytic activity with a moderate conversion of 37% and an excellent selectivity of 95% of 1,4-benzoquinone, which is higher than a conversion of 26% in the absence of light (Table S3). **2** was also recyclable and confirmed by the phase purity of the recovered sample's PXRD after three cycles (Figure S10). The activity comparison of **1** and **2** indicates that the combination of $Cu^{II}N_4$ moieties and Cu_2I_2 in the CP **2** is more favorable for this photoinduced reaction. Compared with the reported polymeric photocatalysts, the conversion (37%, **2**) and high selectivity rival that of $Au@TiO_2$[49] and Fe-g-C_3N_4[47] (with conversions of 62% and 11.9%, respectively, in the oxidation of benzene to phenol). To increase the photocatalytic efficiency for practical applications, the combination of metalloligands (ex., $Cu^{II}N_4$, $Fe^{III}N_4$,[50] etc.), photoactive Cu_2I_2 units[33,34,38,39] and high surface areas in porous networks might help tailor the catalytic system in our future work.

In summary, three 1D/2D polymeric materials with square-planar 4-coordinated $Cu^{II}/Ni^{II}N_4$ moieties were constructed by one-step subcomponent self-assembly. This synthetic methodology allows for the interweaving of multiple metal functional moieties in the coordination network from simple precursors through in situ assembly. It may be generalized for building target supramolecular architectures and functional materials with controllable properties because of the advantage of cost-effectiveness and energy efficiency. The photocatalytic activity test of CPs in the direct transformation of benzene pave the way for the future fabrication of porous Cu^{I} supramolecular hosts with diverse photoactive units, achieving higher catalytic efficiency in a cooperative way.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b03068.

Experimental details, crystal data, and physical measurements (PDF)

Accession Codes

CCDC 1589186−1589188 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The authors declare no competing financial interest.

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■ REFERENCES

(1) Cozzi, P. G. Metal-Salen Schiff base complexes in catalysis: practical aspects. *Chem. Soc. Rev.* **2004**, *33*, 410−421.

(2) Darensbourg, D. J. Making plastics from carbon dioxide: Salen metal complexes as catalysts for the production of polycarbonates from epoxides and CO_2. *Chem. Rev.* **2007**, *107*, 2388−2410.

(3) Beletskaya, I.; Tyurin, V. S.; Tsivadze, A. Y.; Guilard, R.; Stern, C. Supramolecular Chemistry of Metalloporphyrins. *Chem. Rev.* **2009**, *109*, 1659−1713.

(4) Drain, C. M.; Varotto, A.; Radivojevic, I. Self-Organized Porphyrinic Materials. *Chem. Rev.* **2009**, *109*, 1630−1658.

(5) Crane, A. K.; MacLachlan, M. J. Portraits of Porosity: Porous Structures Based on Metal Salen Complexes. *Eur. J. Inorg. Chem.* **2012**, *2012*, 17−30.

(6) Morris, G. A.; Nguyen, S. T.; Hupp, J. T. Enhanced activity of enantio selective (salen)Mn(III) epoxidation catalysts through supramolecular complexation. *J. Mol. Catal. A: Chem.* **2001**, *174*, 15−20.

(7) Lu, W. G.; Wei, Z. W.; Gu, Z. Y.; Liu, T. F.; Park, J.; Park, J.; Tian, J.; Zhang, M. W.; Zhang, Q.; Gentle, T., III; Bosch, M.; Zhou, H. C. Tuning the structure and function of metal-organic frameworks via linker design. *Chem. Soc. Rev.* **2014**, *43*, 5561−5593.

(8) Sun, S. S.; Stern, C. L.; Nguyen, S. T.; Hupp, J. T. Directed assembly of transition-metal-coordinated molecular loops and squares from salen-type components. Examples of metalation-controlled structural conversion. *J. Am. Chem. Soc.* **2004**, *126*, 6314−6326.

(9) Dong, J. Q.; Tan, C. X.; Zhang, K.; Liu, Y.; Low, P. J.; Jiang, J. W.; Cui, Y. Chiral NH-Controlled Supramolecular Metallacycles. *J. Am. Chem. Soc.* **2017**, *139*, 1554−1564.

(10) Narita, M.; Yoon, I.; Aoyagi, M.; Goto, M.; Shimizu, T.; Asakawa, M. Transition metal(II)-salen and -salophen macrocyclic complexes for rotaxane formation: syntheses and crystal structures. *Eur. J. Inorg. Chem.* **2007**, *2007*, 4229−4237.

(11) Xuan, W. M.; Zhang, M. N.; Liu, Y.; Chen, Z. J.; Cui, Y. A Chiral Quadruple-Stranded Helicate Cage for Enantioselective Recognition and Separation. *J. Am. Chem. Soc.* **2012**, *134*, 6904−6907.

(12) Cho, S. H.; Ma, B. Q.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. A metal-organic framework material that functions as an enantioselective catalyst for olefin epoxidation. *Chem. Commun.* **2006**, 2563−2565.

(13) Li, G.; Zhu, C. F.; Xi, X. B.; Cui, Y. Selective binding and removal of organic molecules in a flexible polymeric material with stretchable metallosalen chains. *Chem. Commun.* **2009**, 2118−2120.

(14) Shultz, A. M.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. Post-Synthesis Modification of a Metal-Organic Framework To Form Metallosalen-Containing MOF Materials. *J. Am. Chem. Soc.* **2011**, *133*, 13252−13255.

(15) Xi, W. Q.; Liu, Y.; Xia, Q. C.; Li, Z. J.; Cui, Y. Direct and Post-Synthesis Incorporation of Chiral Metallosalen Catalysts into Metal-Organic Frameworks for Asymmetric Organic Transformations. *Chem. - Eur. J.* **2015**, *21*, 12581−12585.

(16) Gao, W. Y.; Chrzanowski, M.; Ma, S. Q. Metal-metalloporphyrin frameworks: a resurging class of functional materials. *Chem. Soc. Rev.* **2014**, *43*, 5841−5866.

(17) Nakamura, Y.; Aratani, N.; Osuka, A. Cyclic porphyrin arrays as artificial photosynthetic antenna: Synthesis and excitation energy transfer. *Chem. Soc. Rev.* **2007**, *36*, 831−845.

(18) Bogaerts, T.; Van Yperen-De Deyne, A.; Liu, Y. Y.; Lynen, F.; Van Speybroeck, V.; Van Der Voort, P. Mn-salen@MIL101(Al): a heterogeneous, enantioselective catalyst synthesized using a 'bottle around the ship' approach. *Chem. Commun.* **2013**, *49*, 8021−8023.

(19) Shultz, A. M.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. A Catalytically Active, Permanently Microporous MOF with Metalloporphyrin Struts. *J. Am. Chem. Soc.* **2009**, *131*, 4204−4205.

(20) Krishna Kumar, R.; Balasubramanian, S.; Goldberg, I. Crystal engineering with tetraarylporphyrins, an exceptionally versatile building block for the design of multidimensional supramolecular structures. *Chem. Commun.* **1998**, 1435−1436.

(21) Feng, D. W.; Gu, Z. Y.; Li, J. R.; Jiang, H. L.; Wei, Z. W.; Zhou, H. C. Zirconium-Metalloporphyrin PCN-222: Mesoporous Metal-Organic Frameworks with Ultrahigh Stability as Biomimetic Catalysts. *Angew. Chem., Int. Ed.* **2012**, *51*, 10307−10310.

(22) Song, F. J.; Wang, C.; Falkowski, J. M.; Ma, L. Q.; Lin, W. B. Isoreticular Chiral Metal-Organic Frameworks for Asymmetric Alkene Epoxidation: Tuning Catalytic Activity by Controlling Framework Catenation and Varying Open Channel Sizes. *J. Am. Chem. Soc.* **2010**, *132*, 15390−15398.

(23) Ma, L. Q.; Falkowski, J. M.; Abney, C.; Lin, W. B. A series of isoreticular chiral metal-organic frameworks as a tunable platform for asymmetric catalysis. *Nat. Chem.* **2010**, *2*, 838−846.

(24) Kosal, M. E.; Chou, J. H.; Wilson, S. R.; Suslick, K. S. A functional zeolite analogue assembled from metalloporphyrins. *Nat. Mater.* **2002**, *1*, 118−121.

(25) Peng, R.; Li, M.; Li, D. Copper(I) halides: A versatile family in coordination chemistry and crystal engineering. *Coord. Chem. Rev.* **2010**, *254*, 1−18.

(26) Li, M.; Li, Z.; Li, D. Unprecedented cationic copper(I)-iodide aggregates trapped in "click" formation of anionic-tetrazolate-based coordination polymers. *Chem. Commun.* **2008**, 3390−3392.

(27) Ni, W. X.; Li, M.; Zhou, X. P.; Li, Z.; Huang, X. C.; Li, D. pH-Induced formation of metalloligand: increasing structure dimensionality by tuning number of ligand functional sites. *Chem. Commun.* **2007**, 3479−3481.

(28) Zhan, S. Z.; Li, M.; Hou, J. Z.; Ni, J.; Li, D.; Huang, X. C. Polymerizing Cluster Helicates into High-Connectivity Networks. *Chem. - Eur. J.* **2008**, *14*, 8916−8921.

(29) Zhan, S. Z.; Li, M.; Ng, S. W.; Li, D. Luminescent Metal-Organic Frameworks (MOFs) as a Chemopalette: Tuning the Thermochromic Behavior of Dual-Emissive Phosphorescence by Adjusting the Supramolecular Microenvironments. *Chem. - Eur. J.* **2013**, *19*, 10217−10225.

(30) Hou, J. Z.; Li, M.; Li, Z.; Zhan, S. Z.; Huang, X. C.; Li, D. Supramolecular helix-to-helix induction: A 3D anionic framework containing double-helical strands templated by cationic triple-stranded cluster helicates. *Angew. Chem., Int. Ed.* **2008**, *47*, 1711−1714.

(31) Wang, J. H.; Li, M.; Li, D. A dynamic, luminescent and entangled MOF as a qualitative sensor for volatile organic solvents and a quantitative monitor for acetonitrile vapour. *Chem. Sci.* **2013**, *4*, 1793−1801.

(32) Zhan, S. Z.; Li, M.; Zhou, X. P.; Ni, J.; Huang, X. C.; Li, D. From Simple to Complex: Topological Evolution and Luminescence Variation in a Copper(I) Pyridylpyrazolate System Tuned via Second Ligating Spacers. *Inorg. Chem.* **2011**, *50*, 8879−8892.

(33) Hou, Y. L.; Li, S. X.; Sun, R. W. Y.; Liu, X. Y.; Weng Ng, S.; Li, D. Facile preparation and dual catalytic activity of copper(I)-metallosalen coordination polymers. *Dalton Trans.* **2015**, *44*, 17360−17365.

(34) Hou, Y. L.; Sun, R. W. Y.; Zhou, X. P.; Wang, J. H.; Li, D. A copper(I)/copper(II)-salen coordination polymer as a bimetallic catalyst for three-component Strecker reactions and degradation of organic dyes. *Chem. Commun.* **2014**, *50*, 2295−2297.

(35) Hernandez-Perez, A. C.; Vlassova, A.; Collins, S. K. Toward a Visible Light Mediated Photocyclization: Cu-Based Sensitizers for the Synthesis of [5]Helicene. *Org. Lett.* **2012**, *14*, 2988−2991.

(36) Bissember, A. C.; Lundgren, R. J.; Creutz, S. E.; Peters, J. C.; Fu, G. C. Transition-Metal-Catalyzed Alkylations of Amines with Alkyl Halides: Photoinduced, Copper-Catalyzed Couplings of Carbazoles. *Angew. Chem., Int. Ed.* **2013**, *52*, 5129−5133.

(37) Creutz, S. E.; Lotito, K. J.; Fu, G. C.; Peters, J. C. Photoinduced Ullmann C-N Coupling: Demonstrating the Viability of a Radical Pathway. *Science* **2012**, *338*, 647−651.

(38) Wu, Z. L.; Wang, C. H.; Zhao, B.; Dong, J.; Lu, F.; Wang, W. H.; Wang, W. C.; Wu, G. J.; Cui, J. Z.; Cheng, P. A Semi-Conductive Copper-Organic Framework with Two Types of Photocatalytic Activity. *Angew. Chem., Int. Ed.* **2016**, *55*, 4938−4942.

(39) Shi, D. Y.; Zheng, R.; Sun, M. J.; Cao, X. R.; Sun, C. X.; Cui, C. J.; Liu, C. S.; Zhao, J. W.; Du, M. Semiconductive Copper(I)-Organic Frameworks for Efficient Light-Driven Hydrogen Generation Without Additional Photosensitizers and Cocatalysts. *Angew. Chem., Int. Ed.* **2017**, *56*, 14637−14641.

(40) Zhang, M. J.; Li, H. X.; Li, H. Y.; Lang, J. P. Copper(I) 5-phenylpyrimidine-2-thiolate complexes showing unique optical properties and high visible light-directed catalytic performance. *Dalton Trans.* **2016**, *45*, 17759−17769.

(41) Chichak, K. S.; Cantrill, S. J.; Pease, A. R.; Chiu, S. H.; Cave, G. W. V.; Atwood, J. L.; Stoddart, J. F. Molecular Borromean Rings. *Science* **2004**, *304*, 1308−1312.

(42) Nitschke, J. R. Construction, substitution, and sorting of metallo-organic structures via subcomponent self-assembly. *Acc. Chem. Res.* **2007**, *40*, 103−112.

(43) Zhou, X. P.; Liu, J.; Zhan, S. Z.; Yang, J. R.; Li, D.; Ng, K. M.; Sun, R. W. Y.; Che, C. M. A High-Symmetry Coordination Cage from 38- or 62-Component Self-Assembly. *J. Am. Chem. Soc.* **2012**, *134*, 8042−8045.

(44) Zhou, X. P.; Wu, Y.; Li, D. Polyhedral Metal-Imidazolate Cages: Control of Self-Assembly and Cage to Cage Transformation. *J. Am. Chem. Soc.* **2013**, *135*, 16062−16065.

(45) Shiraishi, Y.; Saito, N.; Hirai, T. Adsorption-driven photocatalytic activity of mesoporous titanium dioxide. *J. Am. Chem. Soc.* **2005**, *127*, 12820−12822.

(46) Fujihira, M.; Satoh, Y.; Osa, T. Heterogeneous Photocatalytic Oxidation of Aromatic-Compounds on Tio2. *Nature* **1981**, *293*, 206−208.

(47) Chen, X. F.; Zhang, J. S.; Fu, X. Z.; Antonietti, M.; Wang, X. C. Fe-g-C3N4-Catalyzed Oxidation of Benzene to Phenol Using Hydrogen Peroxide and Visible Light. *J. Am. Chem. Soc.* **2009**, *131*, 11658−11659.

(48) Conde, A.; Mar Diaz-Requejo, M.; Perez, P. J. Direct, copper-catalyzed oxidation of aromatic C-H bonds with hydrogen peroxide under acid-free conditions. *Chem. Commun.* **2011**, *47*, 8154−8156.

(49) Ide, Y.; Matsuoka, M.; Ogawa, M. Efficient Visible-Light-Induced Photocatalytic Activity on Gold-Nanoparticle-Supported Layered Titanate. *J. Am. Chem. Soc.* **2010**, *132*, 16762−16764.

(50) Li, J.; Yang, J.; Liu, Y. Y.; Ma, J. F. Two Heterometallic-Organic Frameworks Composed of Iron(III)-Salen-Based Ligands and d(10) Metals: Gas Sorption and Visible-Light Photocatalytic Degradation of 2-Chlorophenol. *Chem. - Eur. J.* **2015**, *21*, 4413−4421.