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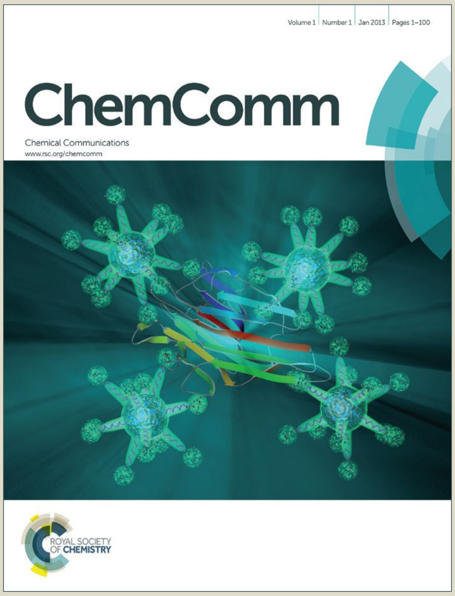

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ARTICLE

Topology-Guided Design of An Anionic bor-Network for Photocatalytic $[Ru(bpy)_3]^{2+}$ Encapsulation

Xuan Wang[a], Weigang Lu[a], Zhi-Yuan Gu[a], Zhangwen Wei[a], Hong-Cai Zhou[a]*

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An anionic metal-organic framework, PCN-99, has been synthesized through a topology-guided strategy; its underlying **bor** net is realized by the use of a tetrahedral $[In(COO)_4]^-$ node and a judiciously designed trigonal planar linker. In light of its anionic nature, the inherent cuboctahedral cage and 1D channel make PCN-99 an excellent matrix to encapsulate the photocatalytic $[Ru(bpy)_3]^{2+}$.

Introduction

The utilization of metal-organic frameworks (MOFs) for heterogeneous catalysis has been a hot topic in the past two decades.[1-5] MOFs are well-defined structures that can achieve exceptionally high porosity, which endows them with the capacity of hosting not only densely packed but also precisely positioned active sites for heterogeneous catalysis. To realize such an assembly of “molecular reactors”, a variety of suitable MOF scaffolds to accommodate catalytic centers of various sizes are needed.[6, 7] A significant amount of effort has been dedicated to rationally design MOFs with desired porosity and controlled cavity size and shape to tune the environment surrounding the active center of a catalyst.[4, 5, 8] Most recently, the rapid development of MOFs with permanent mesoporous cavities has prompted the study of encapsulation of bulky catalysts and ensuing catalytic properites.[8] The widely studied photoactive cation $[Ru(bpy)_3]^{2+}$ (bpy = bipyridine), in particular, is such a catalyst, which displays potential in both light harvesting and photocatalysis.[9] The difficulty in the recycling of photocatalyst, however, has delayed its practical applications.[10, 11] One approach to circumvent this issue is to design and synthesize heterogeneous photocatalysts, in which the catalytic centers are trapped in the solid form. $[Ru(bpy)_3]^{2+}$ encapsulation in MOFs have been studied through ligand design [6, 7, 12-16] and *in situ* entrapment[10, 17-20]. However, encapsulation of $[Ru(bpy)_3]^{2+}$ through post-synthetic ion exchange is relatively understudied, which is puzzling because the photocatalytic cation can be encapsulated easily and effectively.

Ionic MOFs are porous crystalline materials having either positively- or negatively-charged frameworks with trapped counterions inside the cavities. The charged frameworks provide strong electrostatic interactions to the guest molecules and, in most cases, function as templates for post-synthetic ion exchange;[21, 22] these unique properties make ionic MOFs promising for chemical sensing[23, 24] or ideal as highly efficient heterogeneous matrices.[25, 26] Nevertheless, the incorporation of large photoactive species has rarely been studied likely due to the lack of ionic MOFs with large pore apertures. [27, 28] Only a few ionic MOFs with cavities at mesoporous scale have been reported to date. [29, 30]

General approaches to obtain MOFs with desired topology and a larger cavity involve extension of the organic linkers. In this work a careful inspection of the net topology of the target framework may provide more insights into rational material design. With regard to ionic MOFs, indium-based MOFs are commonly constructed with either cationic building blocks $[In_3O(COO)_6]^+$ or anionic building blocks $[In(COO)_4]^-$.[21, 27, 31-40] For the sake of incorporation of cationic $[Ru(bpy)_3]^{2+}$, $[In(COO)_4]^-$ is our choice. Topologically, the $[In(COO)_4]^-$, a 4-connected tetrahedral node, could potentially form various high-symmetry nets when combined with other highly symmetric nodes.[41] The extension of btc (btc = 1,3,5-benzenetricarboylate) could theoretically produce an isorecticular ionic MOFs with large cavities.[30, 35] Therefore, tritopic carboxylates are chosen as the inorganic building units. Herein, we report the synthesis of an anionic MOF PCN-99 (PCN = porous coordination polymer) with a pore cavity at the mesoporous scale, spontaneous encapsulation of $[Ru(bpy)_3]^{2+}$ through ion exchange, and its photocatalysis in oxidative hydroxylation of arylboronic acids.

Results and discussion

Initially, the development of TATB (4,4',4"-s-triazine-2,4,6-triyl-tribenzoate), a trigonal planar linker, with 4-connected $[In(COO)_4]^-$ was attempted in the expectation of forming such an anionic MOF with large cavities, but to no avail. Similar endeavours have been reported with the achievement of a microporous anionic MOF.[42] This could be ascribed to the free rotation of carboxyphenyl rings in TATB, which prevents the three carboxylates from staying coplanar with each other (Figure 1a). Compared to the orientation preference of TATB, BTB (4,4’,4’’-benzene-1,3,5-triyl-tribenzoate) is even less likely

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[a] *Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012, USA.*

[b] Electronic Supplementary Information (ESI) available: [details of supplementary information about full experimental details, crystallographic data, TGA, and NMR spectra of products from aerobic oxidative hydroxylation reaction. CCDC 1431184]. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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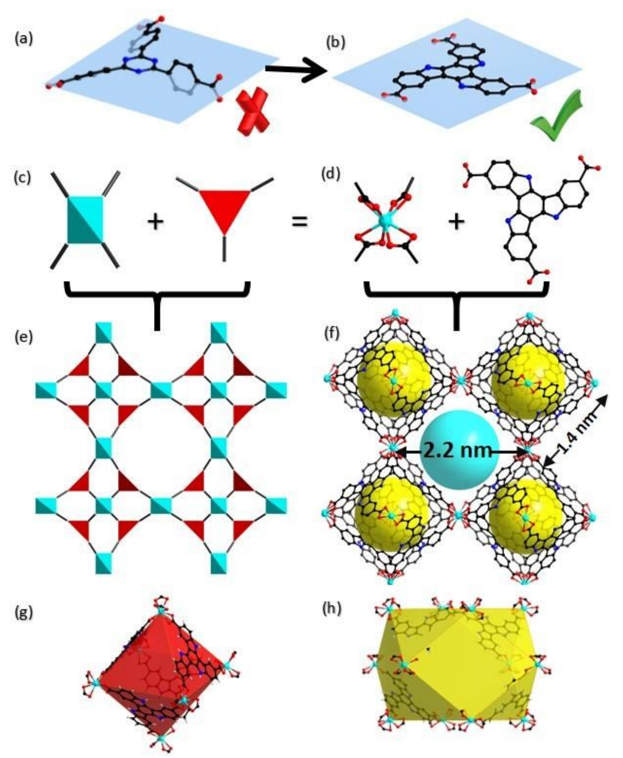

Figure 1. Design strategy of PCN-99; a) flexible conformation of TATB and b) coplanar conformation of DCTA; c), e) assembly of a T_d and coplanar trigonal nodes into a **bor** network; d), f) combination of 4-connected $[In(COO)_4]^-$ node（blue tetrahedral） and 3-conneted DCTA linker (red triangle) produces PCN-99; g) octahedron and h) cubooctahedron cages in PCN-99.

to have a coplanar conformation. Under the combination with $[In(COO)_4]^-$, three nets were interwoven to provide a **jcy** framework with micropores.[21] In order to minimize the structural variation caused by the flexibility of linkers, a strictly coplanar conformation must be adopted for the linker configuration. Therefore, guided by topological analysis using the known connectivity of metal nodes, a tritopic ligands 10, 15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole-3,8,13-tricarboxylate acid (H_3DCTA) was designed and synthesized (Figure 1b, Supporting information Section 2) Solvothermal reaction of $In(NO_3)_2\cdot H_2O$, H_3DCTA, and tetrafluoroboric acid in a mixture of *N,N-dimethylformamide* (DMF) and ethanol at 120 °C for 4 days yielded colourless cubic single crystals of PCN-99 (Supporting information Section 3).

In PCN-99, each indium center is coordinated by four carboxylate groups of DCTA linkers, making the framework negatively charged (Figure 1d). The counterions interact weakly with the framework and can be easily exchanged.[25, 27]A small octahedral cage is formed by six indium units and four DCTA linkers (Figure 1g). In addition, a large cuboctahedral cage comprised of twelve indium units and four linkers leads to a mesoporous cavity (Figure 1h, more detailed structural information in supporting information Section 4). Such a large pore is rarely reported for indium-based ionic MOFs. [29, 30] Moreover, this cage-based structure can help minimize the leaching of guest molecules, which was found in some MOFs used for enzyme immobilization.[43] At the topological level, PCN-99 adopts the bor topology, in which the connection of the coplanar tritopic linker DCTA and the $[In(COO)_4]^-$ node give rise to not only large cages but also 1D channels (Figure 1f). This eases the diffusion of the substrates during catalysis. Overall, this unique structural architecture imparts PCN-99 great potential in large catalyst encapsulation. Due the large pore aperture and ionic nature, the activation of PCN-99 for nitrogen adsorption measurement was not successful.

To evaluate the anionic nature of PCN-99, single crystals of PCN-99 were immersed in solutions of $[Ru(bpy)_3]Cl_2$ or congo red, respectively (Figure 2a, Supporting information Section 5). The colour of the congo red solution was retained after 24 hours, while the colour of the $[Ru(bpy)_3]^{2+}$ solution gradually turned from yellow to colourless, and the originally colourless PCN-99 at the bottom of vial turned orange. The decrease of $[Ru(bpy)_3]^{2+}$ concentration, a dramatic drop at 454 nm, is demonstrated by UV-Vis absorption

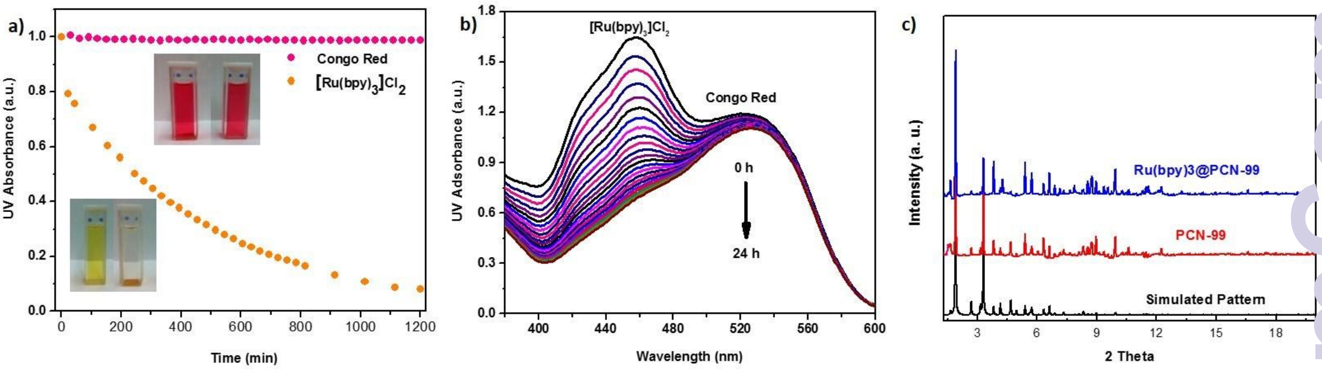

Figure 2. a) UV-Vis absorbance changes over time for PCN-99 in solutions of congo red and $[Ru(bpy)_3]Cl_2$, respectively; b) UV-Vis absorbance for PCN-99 in a mixture of $[Ru(bpy)_3]Cl_2$ and congo red in an equal molar; c) PXRD spectra of simulated pattern from crystal structure (black), as-synthesized PCN-99 (red), and $Ru(bpy)_3$@PCN-99 (blue)

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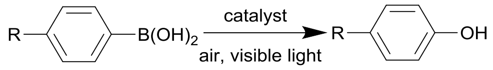
spectra, which is consistent with the trapping of cationic $[Ru(bpy)_3]^{2+}$ in the pores of PCN-99. Powder X-ray Diffraction (XRD) studies showed evidence that the crystallinity was well preserved during and after the guest inclusion (Figure 2c). The high absorption selectivity of $[Ru(bpy)_3]^{2+}$ owing to the strong electrostatic interactions over congo red was also witnessed in a equimolar-mixed environment. The diminishing absorption peak at 454 nm corresponds to the inclusion of $[Ru(bpy)_3]Cl_2$ while the consistent peak at 530 nm indicated the retention of congo red in the solution (Figure 2b, supporting information Section 5).

Arylphenols have been recognized as versatile intermediates in the chemical and pharmaceutical industry. Since $[Ru(bpy)_3]Cl_2$ has displayed excellent catalytic activities in aerobic oxidative hydroxylation of arylboronic acids, [6, 44] it is interesting to apply $Ru(bpy)_3$@PCN-99 in this type of chemistry as a heterogeneous catalyst within the scope of arylboronic acids (Supporting information Section 7). All conversions of the substrates exhibited relatively high efficiency (Table 1, supporting information Section 5b and Section7). Due to the fact that the framework structure impedes the access of substrates to a certain extent, so a reduced catalytic activity was observed for $Ru(bpy)_3$@PCN-99 compared to $[Ru(bpy)_3]Cl_2$ in homogenous solution (Table 1).. In the catalysis of $Ru(bpy)_3$@PCN-99, the influence of the Lewis acidity of metal cluster was excluded (Supporting information Section 8). As a result, the catalytic activity of $Ru(bpy)_3$@PCN-99 is due to the efficient encapsulation of $[Ru(bpy)_3]^{2+}$ active sites within the unique **bor** topology. Interestingly, comparable product conversions were also observed for the second use of catalyst with a small amount of $Ru(bpy)_3^{2+}$ leaching due to the partial decomposition of MOFs under basic condition (supporting information Section 9).

Table 1. Visible-light-induced aerobic oxidative hydroxylation of arylboronic acid. [a][b]



Entry	R-	Catalyst	Conversion
1	COOMe	$[Ru(bpy)_3]Cl_2$	71.9%
2	COOMe	$Ru(bpy)_3$@PCN-99	59.0%
3	Me	$[Ru(bpy)_3]Cl_2$	89.4%
4	Me	$Ru(bpy)_3$@PCN-99	65.4%
5	CHO	$[Ru(bpy)_3]Cl_2$	70.8%
6	CHO	$Ru(bpy)_3$@PCN-99	45.9%

[a] isolated yield.[b] Reaction Condition: **1a** (0.5mmol), catalyst (2 mol%), $^iPr_2NEt$ (2.0 equiv), DMF (5 mL), 36W fluorescence lamp irradiation, and open to air for 48 hour.

For practical applications, a reversible ion-exchange process is commonly required.[27, 45] Modulation of the relative concentration of different guest molecules shifts the dynamic equilibrium and consequently leads to release and recapture of the original guests. The release experiment was performed on the fully loaded $Ru(bpy)_3$@PCN-99. The release of $[Ru(bpy)_3]^{2+}$ was triggered by adding the same volume of saturated $NaNO_3$ solution (Figure 3) . The virtually complete release of $[Ru(bpy)_3]^{2+}$ could be achieved by increasing the volume of saturated $NaNO_3$ solution to 20 mL from the original 10 mL after 23 hours with the assist of gentle stirring (Figure 3). As the $[Ru(bpy)_3]^{2+}$ was replaced by the sodium ions, the yellow colour of the crystals gradually faded.

Conclusions

In this study, a trigonal coplanar linker was designed using topology guidance to produce an anionic **bor**-MOF PCN-99. In light of its anionic nature, the selective encapsulation of $[Ru(bpy)_3]^{2+}$ through ion exchange imparts $Ru(bpy)_3$@PCN-99 with heterogeneous photocatalytic activity toward the aerobic hydroxylation of arylboronic acid. Not only does this work exemplify a successful approach to customize MOF structures to accommodate a bulky photocatalyst, it also provides insights into the construction of ionic MOFs with large cavities. The post-synthetic ion-exchange can be a technically straightforward alternative to the modification of other ionic MOFs with catalytic units—as such, it could be tested with other types of ionic MOFs and catalytic ions. The specific matrix PCN-99 in this work is also interesting for its luminescence properties, which may be useful for chemical sensing.

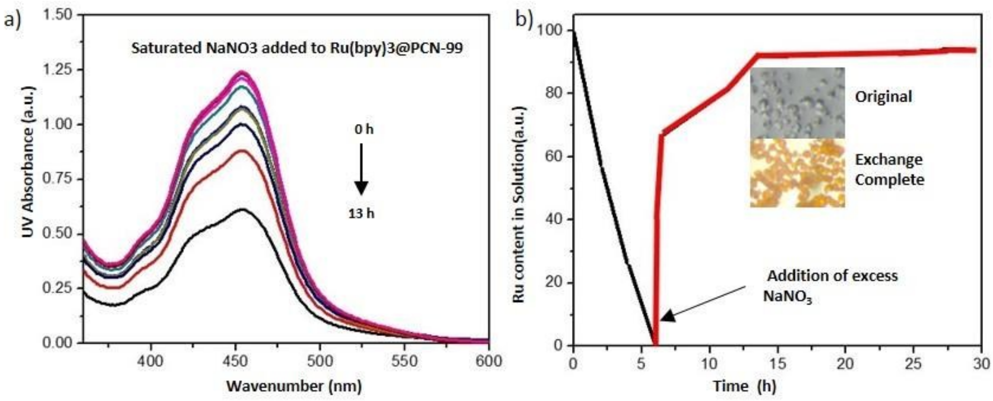


Figure 3: a) UV-Vis absorbance of $[Ru(bpy)3]^{2+}$ at different time after the addition of 20 mL of saturated $NaNO_3$ solution during the release experiment; b) trapping and releasing of $[Ru(bpy)3]^{2+}$ in PCN-99 in one-ion-change and release cycle.

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