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# Postmodification of a supramolecular organic framework: visible-light-induced recyclable heterogeneous photocatalysis for the reduction of azides to amines

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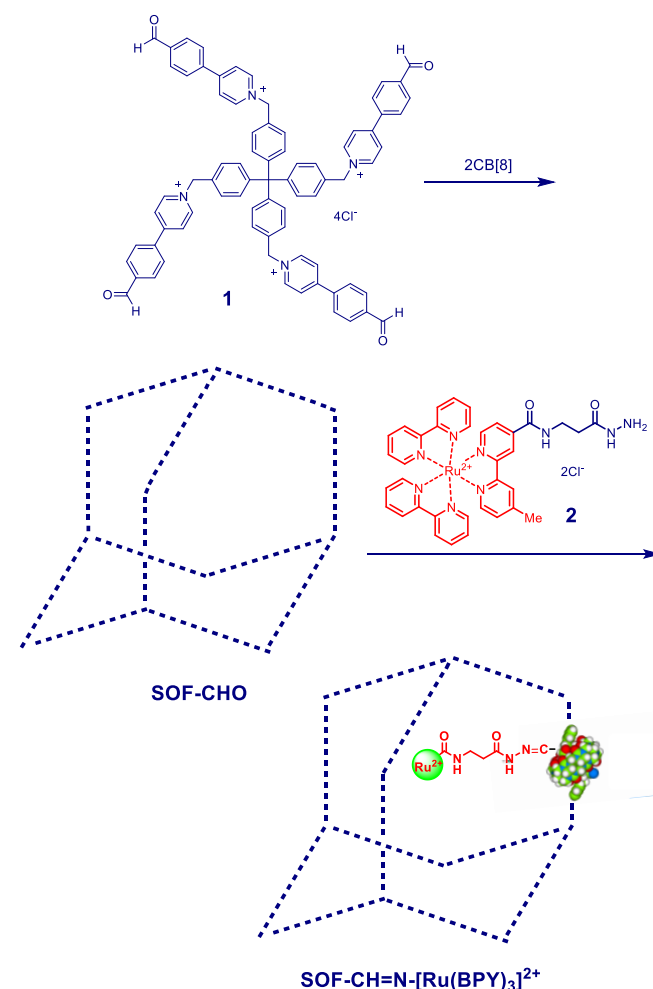
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**We present the postmodification of a diamondoid 3D supramolecular organic framework (SOF) to append [Ru(BPY)<sub>3</sub>]<sup>2+</sup> groups through the formation of hydrazone bond. The resulting SOF works as an efficient recyclable heterogeneous catalyst for visible-light-induced reduction of aromatic azides to amines.**

Postsynthetic modification (PSM) represents a useful approach for the functionalization of porous materials to lead to new properties and/or applications.<sup>1,2</sup> In this context, great effort has been devoted to the modification of metal-organic frameworks (MOFs).<sup>3</sup> Examples involving the modification of covalent organic frameworks have also been reported (COFs).<sup>4</sup> In most cases, the modification has been achieved by covalently connecting a rationally designed functional group to a well-established framework.<sup>2,3</sup> Desirably, the resulting frameworks retain their crystallinity and porosity while the specific activity of the attached functional groups is maintained or even amplified by the frameworks. We and other groups have recently developed the homogeneous self-assembly strategy for the generation of supramolecular organic frameworks (SOFs) from organic building blocks in water.<sup>5-8</sup> Several SOFs have exhibited interesting functions, including homo- and heterogeneous adsorption of ionic and neutral guests,<sup>6d-g,7a</sup> catalysis,<sup>6e</sup> drug delivery,<sup>6f,g</sup> and stepwise fluorescence enhancement.<sup>7b</sup> As the formation of SOFs occurs in water, it is highly desirable to employ aqueous-compatible ligating chemistry for facile introduction of additional functional groups to the interior of the frameworks, which would further extend their potentials in designing new porous materials. Here we report that the PSM strategy can be used to covalently introduce the [Ru(BPY)<sub>3</sub>]<sup>2+</sup> unit to the interior of an

3D diamondoid SOF through the formation of hydrazone bond, which allows for efficient visible-light-induced recyclable heterogeneous conversion of azides to amines.



**Fig. 1** The formation of 3D diamondoid SOF-CHO from **1** and CB[8] and its postsynthetic modification with [Ru(BPY)<sub>3</sub>]<sup>2+</sup>-attached acylhydrazine **2** to afford SOF-CH=N-[Ru(BPY)<sub>3</sub>]<sup>2+</sup>.

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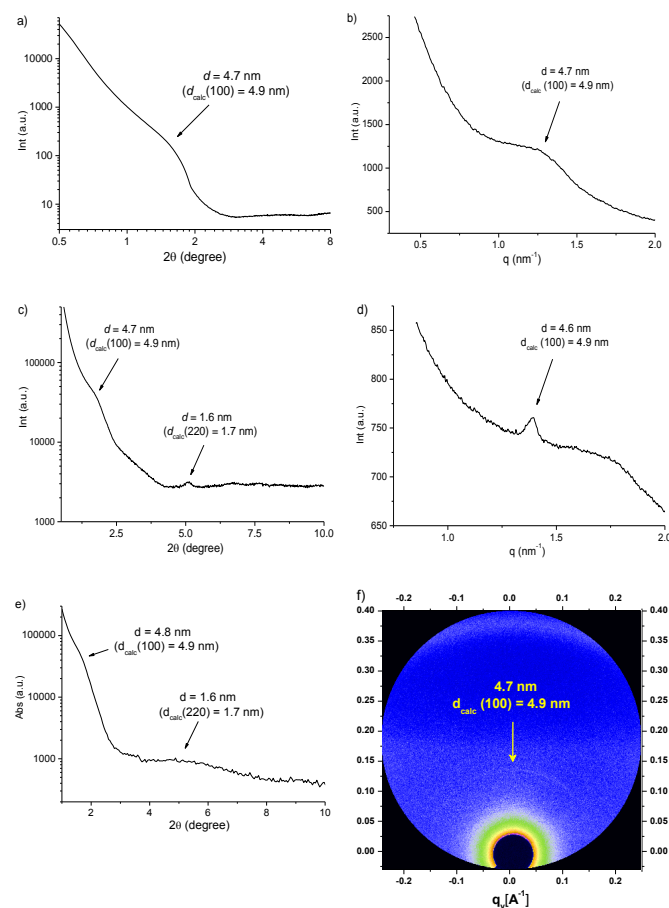
Electronic Supplementary Information (ESI) available: Synthesis and characterization of new compounds, photochemical reaction details and <sup>1</sup>H and <sup>13</sup>C NMR and other additional spectra. See DOI: 10.1039/x0xx00000x

Previous studies revealed that tetrahedral molecules that contain four peripheral 4-phenylpyridinium units bearing the OMe, SMe, NMe<sub>2</sub>, CN or CH<sub>2</sub>OH group at the 4-position of the benzene rings could co-assemble with cucurbit[8]uril (CB[8]) in water to afford 3D SOFs.<sup>6d,f</sup> For PSM of this series of SOFs, tetramer **1** (Fig. 1), which bears four aldehyde groups, was prepared to co-assemble with CB[8] to afford the new diamondoid system **SOF-CHO** (Fig. 1). The aldehyde group was expected to form hydrazone bonds by reacting with [Ru(BPY)<sub>3</sub>]<sup>2+</sup>-bearing acylhydrazide **2** in water. The aqueous-based reaction has been demonstrated in the preparation of a variety of COFs and dynamic combinatorial libraries.<sup>9,10</sup>

CB[8] has a very limited solubility (< 20  $\mu$ M) in water.<sup>11</sup> Upon mixing with **1**, its solubility was remarkably increased (> 2.0 mM). The <sup>1</sup>H NMR spectrum of the 1:2 solution of **1** and CB[8] (2 mM) in D<sub>2</sub>O displayed a set of low-resolution signals (Fig. S1, ESI), which was similar to that of the mixture of other tetrahedral molecules and CB[8].<sup>6d,f</sup> The 1:2 stoichiometry was confirmed by Job's plot obtained from fluorescence quenching experiments (Fig. S2, ESI), as well as fluorescence titration experiments using the control compound *N*-benzyl-4-(4-formylphenyl)pyridin-1-ium bromide (**3**, ESI), which showed an inflection point at [CB[8]]/[**3**] = 2 (Fig. S3, ESI).<sup>6a,d</sup> Using <sup>1</sup>H NMR competition method,<sup>12</sup> we determined the apparent association constant (*K*<sub>a</sub>) for the 2:1 complex between the 4-phenylpyridinium (PhPy) units of **1** and CB[8] in 50 mM CD<sub>3</sub>CO<sub>2</sub>Na buffer (pD = 4.74) to be  $1.3 \times 10^{14} \text{ M}^{-2}$ , which was comparable to that of other reported SOFs of the identical framework.<sup>6d,f</sup> Dynamic light scattering (DLS) experiments for the 1:2 solution of **1** (1.0 mM) and CB[8] in water gave rise to the hydrodynamic diameter (*D*<sub>H</sub>) value of 108 nm (Fig. S4, ESI), supporting the formation of large supramolecular entity [**1**•(CB[8])<sub>2</sub>]<sub>n</sub>. Notably, the *D*<sub>H</sub> value did not decrease at lowered concentrations after the samples were diluted and incubated for 8 hours (Fig. S5, ESI). This result implied that the supramolecular entities were very stable and their disassembling was kinetically slow. Two-dimensional (2D) <sup>1</sup>H NMR diffusion-ordered spectroscopic (DOSY) experiment for the 1:2 solution of **1** (1.0 mM) and CB[8] in D<sub>2</sub>O indicated that both components diffuse at the same diffusion coefficient (*D*) of  $3.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  (Fig. S6, ESI), further supporting the formation of the large supramolecular entity [**1**•(CB[8])<sub>2</sub>]<sub>n</sub>. The value was also considerably smaller than that of pure **1** at the same concentration ( $2.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) (Fig. S7, ESI). All the above observations indicated that, similar to other tetrahedral molecules of the identical backbone, **1** also complexed with CB[8] to afford a new 3D SOF derivative (**SOF-CHO**, Fig. 1).

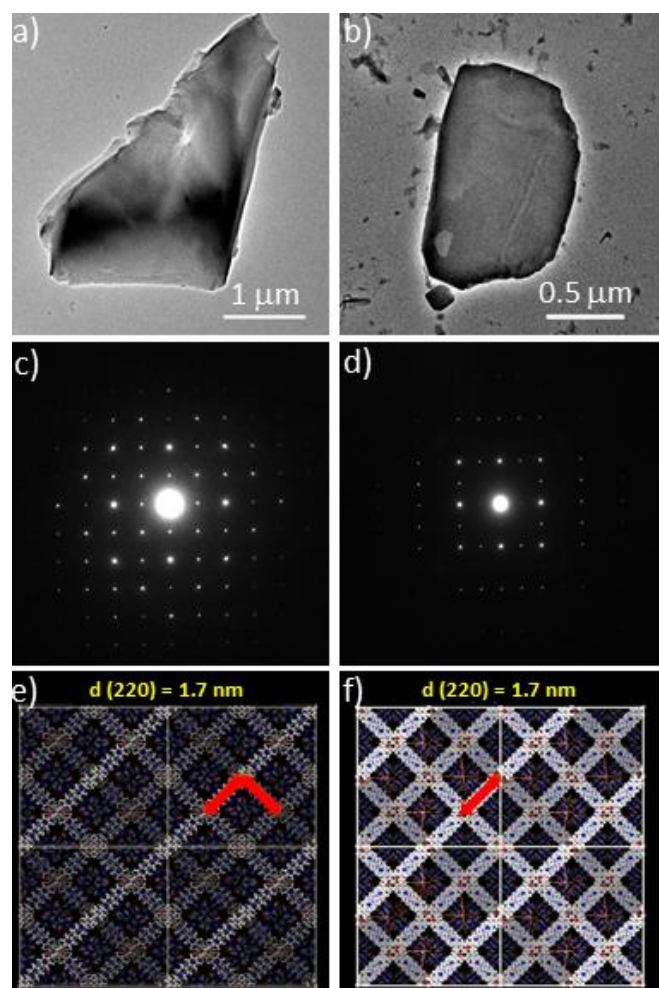
Synchrotron X-ray diffraction (XRD) and small-angle X-ray-scattering (SAXS) experiments for the aqueous solution of (1.2CB[8])<sub>n</sub> both revealed a broad, but discernible peak corresponding to the *d*-spacing around 4.7 nm (Fig. 2a,b). The peak matched well with the calculated {100} spacing (4.9 nm) of the modelled network, which was obtained according to reported method.<sup>6d,13</sup> The results supported that the nanoscale supramolecular entity [**1**•(CB[8])<sub>2</sub>]<sub>n</sub> existed as an ordered framework **SOF-CHO** (Fig. 1). Similar to that of other reported diamondoid SOFs,<sup>6d,f</sup> the peak of **SOF-CHO** in both profiles is broad, presumably reflecting the dynamic nature of this self-assembled framework. Slow evaporation of the solution at room temperature first afforded hydrogels, which further solidified into microcrystals, as was evidenced by the transmission electron microscopic (TEM)

image (Fig. 3a). The synchrotron XRD and SAXS profiles of the microcrystals exhibited a broad peak around 4.7 and 4.6 nm (Fig. 2c,d), respectively, which also corresponded to the {100} spacing. Moreover, the XRD profile of the same sample also showed another relatively sharp peak centred at 1.6 nm (Fig. 2c). This peak was ascribed to that of the {220} spacing (1.7 nm) of the framework. Two-dimensional synchrotron X-ray scattering for the solid sample also revealed one scattering peak with *d*-spacing of 4.7 nm (Fig. 2f), which again matched well with the calculated value of the {100} spacing. Thermogravimetric analysis showed that **SOF-CHO** microcrystals were stable at  $\leq 300^\circ \text{C}$  (Fig. S8, ESI).



**Fig. 2** Solution-phase a) synchrotron XRD ([**1**] = 1.0 mM) and b) SAXS of **SOF-CHO** ([**1**] = 1.0 mM) in water, c) XRD and d) SAXS of solid-state **SOF-CHO**, e) XRD of **SOF-CH=N-[Ru(BPY)<sub>3</sub>]**, and f) 2D synchrotron X-ray scattering of solid-state **SOF-CHO**. The value for the broad peak in a-e was attributed by choosing the position that was highest above the straight line defined by the two saddle points of the peak.

Transmission electron microscopy (TEM) of the solid sample of **SOF-CHO** showed the microcrystal morphology (Fig. 3a). Selected area electron diffraction (SAED) experiment exhibited a pattern pointing to the {220} lattice spacing (1.7 nm) (Fig. 3c), which matched exactly with the simulated data (1.7 nm) (Fig. 3e) and thus further supported the microcrystallinity of the sample. Elemental mapping analysis for the microcrystals confirmed the compositions of the C, N, O and Br elements (Fig. S9, ESI).



**Fig. 3** a,b) TEM images of solid-state **SOF-CHO** and **SOF-CH=N-[Ru(BPY)<sub>3</sub>]<sub>3</sub>**, c,d) SAED patterns of solid-state **SOF-CHO** and **SOF-CH=N-[Ru(BPY)<sub>3</sub>]<sub>3</sub>**, and e,f) model illustration of the above two SAED patterns with the reciprocal lattice observed for the {220} facet.

**SOF-CHO** ([1] = 1.0 mM) was then treated with compound **2** of different molar amounts ([2]:[1] = 0.3, 0.4, 0.6, 0.8, and 1.0) in water at room temperature. The reactions reached equilibrium after 24 hours, as evidenced by <sup>1</sup>H NMR spectrum in D<sub>2</sub>O. The O=CH signal of **1** weakened notably (Fig. S10, ESI), which indicated that the aldehyde groups partially converted into the hydrazone groups. However, quantitative evaluation of the conversion by <sup>1</sup>H NMR spectroscopy was impossible due to the low resolution of the spectra. Dialysis experiments were thus carried out for the reaction mixtures (2.0 mL) of **SOF-CHO** ([1] = 1.0 mM) and **2**, whose concentration was 0.3, 0.4, 0.6, 0.8, and 1.0 mM, respectively, which corresponded to 7.5, 10, 15, 20, and 25 mole% of the concentration of the aldehyde units of **1**. In a typical procedure, an 2 mL mixture solution was laid for 24 hours and then added to a dialysis bag (1 kDa molecular weight cut-off, 8 mm flat-width) which was immersed in water (25 mL). The whole solution was subjected to shaking for 48 hours and the outside water was renewed one time per 6 hours. It was found that after 48 hours, the dialysis of **2** did not occur anymore because the outside water kept colourless six hours later after the last renewal, which implied that there was

no free **2** in the dialysis bag. By recording the adsorption of the [Ru(BPY)<sub>3</sub>]<sub>3</sub><sup>2+</sup> complex in the outside waters using UV-vis spectroscopy, we could determine that 4.6, 4.7, 5.2, 5.1, and 5.3 mole% of the aldehyde units of **1** reacted with **2** to afford [Ru(BPY)<sub>3</sub>]<sub>3</sub><sup>2+</sup>-appended **SOF-CH=N-[Ru(BPY)<sub>3</sub>]<sub>3</sub>** through the formation of the hydrazone bond. The synchrotron XRD profile of the solid-state sample obtained by evaporation of the last solution sample exhibited two broad, but discernible peaks around 4.8 and 1.7 nm (Fig. 2e), respectively, which could be assigned to the {100} and {220} spacings. These results showed that, after the introduction of the [Ru(BPY)<sub>3</sub>]<sub>3</sub><sup>2+</sup> unit, the periodicity of the framework was still maintained to a considerable extent. TEM image of **SOF-CH=N-[Ru(BPY)<sub>3</sub>]<sub>3</sub>** also showed its microcrystallinity (Fig. 3b). Its SAED pattern, being 1.7 nm for the {220} lattice spacing (1.7 nm) (Fig. 3d), again matched the simulated datum (Fig. 3f), indicating that the framework maintained its periodicity after the attachment of the [Ru(BPY)<sub>3</sub>]<sub>3</sub><sup>2+</sup> unit.

**Table 1.** Visible light-induced reduction of aromatic azides to amines using **SOF-CH=N-[Ru(BPY)<sub>3</sub>]<sub>3</sub>** as the photocatalyst

<b>SOF-CH=N-[Ru(BPY)<sub>3</sub>]<sub>3</sub></b>				<b>2</b>	
X	Turn	Time (h)	Yield (%)	Time (h)	Yield (%)
4-CN	1	18	99	30	99
	2	21	98		
	3	49	98		
	4	120	93		
3-CN	1	8	99	9	99
	2	15	99		
	3	64	96		
	4	100	79		
4-CO <sub>2</sub> H	1	9	99	12	99
	2	15	93		
	3	42	88		
	4	120	65		
4-CO <sub>2</sub> Me	1	6	99	8	99
	2	7.5	92		
	3	23	88		
4-Cl		38	99	18	99
4-F		48	99	28	99
4-CF <sub>3</sub>		20	99	8	99
4-CONHC <sub>5</sub> H <sub>11</sub>		18	99	18	99
4-Me		38	43	28	69
4-OMe		38	20	38	43
2-naphthylazide		38	99	38	99

We then investigated the activity of **SOF-CH=N-[Ru(BPY)<sub>3</sub>]<sub>3</sub>** in heterogeneous visible-light-induced photocatalysis, using the conversion of aromatic azides to the related amines as a model reaction.<sup>14,15</sup> In a typical reaction, **SOF-CH=N-[Ru(BPY)<sub>3</sub>]<sub>3</sub>** (5 mg, 4.6mol%) was suspended in 5 mL of dichloromethane and n-hexane (1:1) in which **4x**, Hantzsch ester (0.15 mmol, 1.5 equiv), i-Pr<sub>2</sub>NEt (1.0 mmol, 10 equiv) and HCO<sub>2</sub>H (1.0 mmol, 10 equiv) were present, and the reaction flask was irradiated with a 26 W compact fluorescent light (CFL) bulb by keeping a distance of 20 cm. The yield of the resulting amines was monitored by HPLC analysis. The

results are provided in **Table 1**. For comparison, homogeneous reduction of all the azides by control **2** of the same molar amount of Ru(II) were also conducted under the identical conditions. It can be found that, for azidobenzenes that bear an electron-withdrawing group, the two catalysts exhibited comparable, efficient activity and the reactions all took place in nearly quantitative yields, even though the reaction time might be different. For azidobenzenes that bear an electron-rich group (Me or OMe), both catalysts are less active, which is not unexpected considering that the electron-rich group would decrease the electron-accepting capacity of the azido group. Notably, for these two azides, **2** led to pronouncedly higher yield of the amines. The reduction of 2-azidonaphthalene could also be realized quantitatively, boding well that the catalyst works for other aromatic azides.

The recyclability of the SOF catalyst was further studied for 4-CN, 3-CN, 4-CO<sub>2</sub>H, and 4-CO<sub>2</sub>Me-bearing azidobenzenes. The catalyst could be recovered by simply centrifuging and then removing the solution, and used for three to four times. For 4-cyano-1-azidobenzene, the yield of the amine was still high (93%) after recycling for four times. For other three substrates, the yield of the amines was reduced considerably after recycling for three or four times. Partial loss of the catalyst during the recovering operation, irradiation-caused partial decomposition of the complex, and/or partial hydrolysis of the hydrazone bond might account for this reduction of the yield.

In summary, we have demonstrated that supramolecular organic framework can be functionalized through postmodification of the tetrahedral building block by forming hydrazone bonds. The attachment of the functional group [Ru(BPY)<sub>3</sub>]<sup>2+</sup> did not destruct the regularity of the framework, while the appended [Ru(BPY)<sub>3</sub>]<sup>2+</sup> group exhibited efficient recyclable photocatalytic activity for the reduction of aromatic amides to the related amines. Although the catalytic activity decreased, to a varying extent, after recycling for three to four times, the result demonstrates the usefulness of the postmodification strategy for quickly introducing additional functional groups to the self-assembled frameworks. One following effort is to replace the peripheral aldehyde group with the amino group to build the framework. In this way, simple acylation of the group will lead to the attachment of stable covalent bonding-linked functional groups, which may exhibit increased catalysis recyclability or other properties.

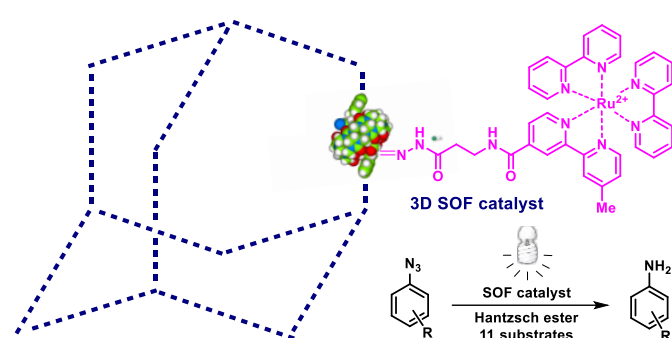
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## Postmodification of a supramolecular organic framework: visible-light-induced recyclable heterogeneous photocatalysis for the reduction of azides to amines

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Postmodification has been utilized to introduce [Ru(BPY)<sub>3</sub>]<sup>2+</sup> to 3D SOF to prepare a catalyst for visible light-induced recyclable heterogeneous photoreduction of aromatic azides into amines.