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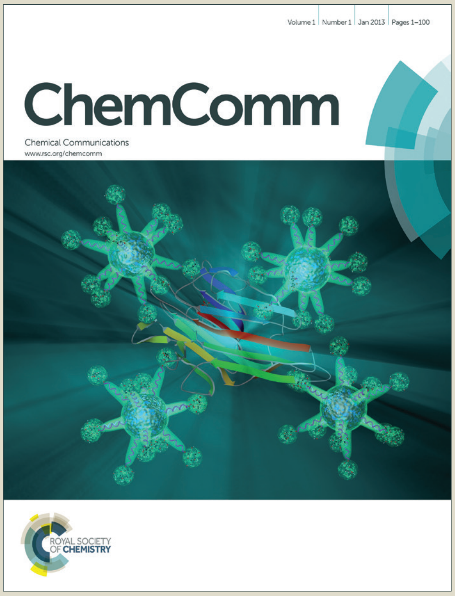

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Robust, Catalytic Metal-Organic Framework with Open 2,2'-Bipyridine Sites

Honghan Fei,[a] and Seth M. Cohen[a]

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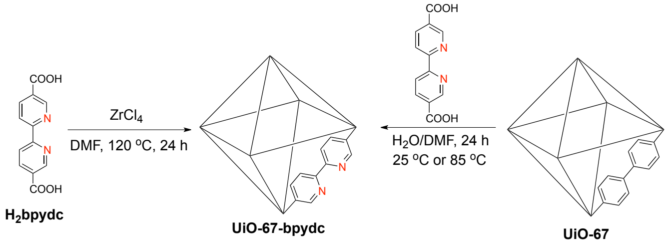
We report two synthetic approaches to a highly crystalline Zr(IV)-based metal-organic framework (MOF) containing open 2,2'-bipyridine (bpy) chelating sites. The resulting UiO-67-bpydc readily complexes $PdCl_2$ to produce a MOF that exhibits efficient and recyclable catalytic activity for the Suzuki-Miyaura cross-coupling reaction.

Metal-organic frameworks (MOFs), an emerging class of crystalline microporous materials, have attracted extensive attentions for their potential applications in gas absorption/storage,[1,2] catalysis,[3] molecular separation,[4] chemical sensing[5] and drug delivery.[6] Introducing open metal-binding sites into MOFs is of substantial interest, as such sites may add properties that facilitate applications such as enhanced gas sorption or catalysis.[7,8] The direct solvothermal synthesis of frameworks bearing such sites has been achieved, but can be hard to predict and even harder to design.[9,10] Postsynthetic methods are another approach that can use covalent modification to produce such sites.[11] Here, a rare example that uses either direct solvothermal (presynthetic) preparation or postsynthetic exchange (PSE) is shown to produce a widely used metal-binding motif into a robust MOF.

2,2'-Bipyridine (bpy) is one of the most widely used bidentate chelators in transition metal coordination chemistry. In standard solution chemistry, homoleptic metal tris(bpy) complexes exhibited important photophysical and photochemical properties.[12] A few reports have described the incorporation of free bpy into MOFs.[13-15]

Previous reports have described the direct incorporation of 2,2'-bipyridine-5,5'-dicarboxylic acid (H_2bpydc) into MIL-53 (MIL = Materials Institute Lavoisier), taking advantage of the hard-soft Lewis acid-base mismatch of the bpy ligand with the Al(III) cations used to form this framework.[13] The resulting framework (MOF-253) was well characterized, but suffered from poor crystallinity and gave surprisingly low porosity upon metalation with Ru(II) (~80 m^2/g Brunauer-Emmett-Teller (BET) surface area with only 13% of bpydc sites metalated).[16] An interpenetrated Zn(II)-based MOF with open bpy sites was constructed with *N,N*'-bis(4-pyridyl)-2,2'-bipy-5,5'-dicarboxamide and metalation with copper led to an interesting crosslinking reaction with two bpy units connected by tetrahedral Cu(I) centers.[15] In other work, Lin and co-workers could dope the synthesis of UiO-67 (UiO = University of Oslo) with metalated bpydc, achieving ~3-4 mol% loading of catalytically active, bpy-derived species (Re and Ru).[14]

Herein, we described two fundamentally different strategies, direct MOF formation and PSE, to incorporate the H_2bpydc ligand into the highly robust UiO-67 platform.[17] Importantly, both synthetic approaches allow for functionalization of this MOF in a controllable manner, allowing for H_2bpydc incorporation to be varied from 0 to 100%. The resulting UiO-67-bpydc MOFs are highly crystalline and demonstrate high porosity after activation. Quantitative metalation with palladium is achieved to give 'Pd(bpy)Cl_2' species on the struts of the MOFs. The metalated MOFs are highly crystalline and porous, exhibiting efficient, heterogeneous, and recyclable catalysis of Suzuki-Miyaura cross-coupling reactions.



Scheme 1. Synthesis of UiO-67-bpydc using direct synthesis and postsynthetic exchange.

Presynthetic functionalization of UiO-67 with H_2bpydc was achieved by direct solvothermal synthesis using different molar ratios of H_2bpydc and 4,4'-biphenyldicarboxylic acid (H_2bpdc) with $ZrCl_4$ and acetic acid (as a modulator, Figure S1) at 120 °C in *N,N'*-dimethylformamide (DMF) for 24 h, after modification to the previous report (Scheme 1).[18] The resulting white crystalline solids were washed with copious amount of DMF and methanol, and the yield after activation under vacuum ranged from 88-94% based on $ZrCl_4$. Examination by ^{1}H NMR spectroscopy upon digestion of this UiO-67-bpydc$_x$/bpdc$_{1-x}$ ($0 \leq x \leq 1$, x indicating the amount of bpydc incorporation) series with dilute HF in d^6-DMSO showed that the ratio of linkers in these MOFs varied according to the ratio of the linkers used in the starting solution (Figure 1). Powder X-ray diffraction (PXRD) of these MOFs confirmed their isoreticular nature and high crystallinity (Figure 1). Importantly, scanning electron microscopy (SEM) revealed that these UiO-67-bpydc$_x$/bpdc$_{1-x}$ materials form a single, phase-pure product with homogeneous particle morphology with crystal sizes ~1 μm (Figure S2). In addition, BET surface areas (N_2 gas at 77K) of UiO-67-bpydc$_{0.5}$/bpdc$_{0.5}$ (containing 50% bpydc, 2346±134 m^2/g) and UiO-67-bpydc (containing 100% bpydc, 2051±102 m^2/g) are very close to unfunctionalized UiO-67 (2299±54 m^2/g), showing the expected high surface areas of these materials. The characterization data along with the high yield of these direct, solvothermal syntheses clearly indicated that the hard-soft mismatch of the bpy ligand and Zr(IV) allows for the formation of UiO-67-bpydc$_x$/bpdc$_{1-x}$ in a facile and controllable fashion.[13]

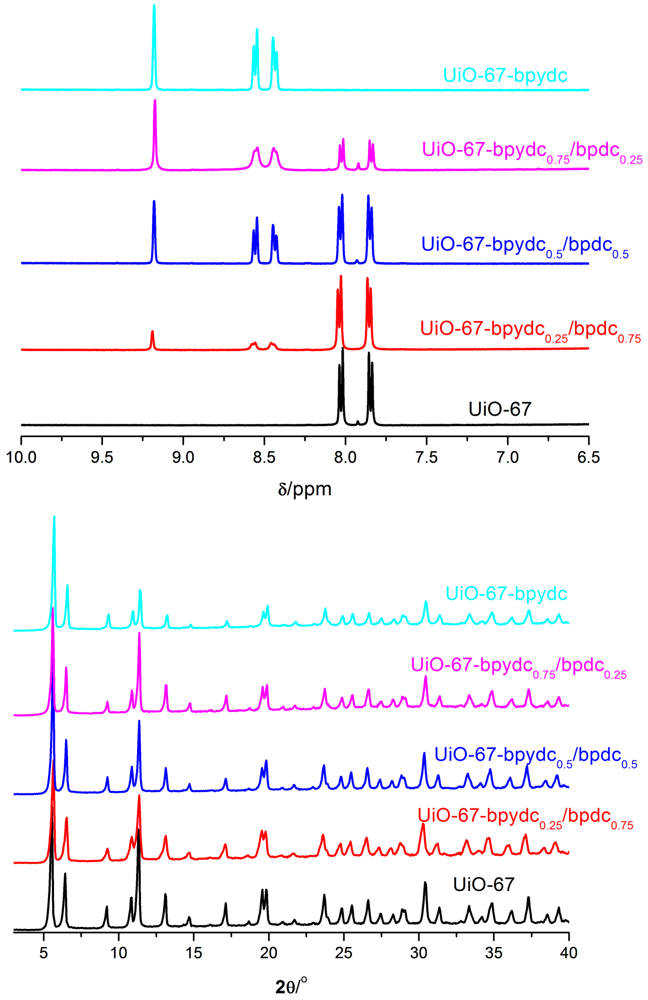


Figure 1. ^{1}H NMR (HF/d^6-DMSO digested, top) and PXRD (bottom) of UiO-67-bpydc containing different amounts of the bpydc ligand. These MOFs were synthesized under direct solvothermal conditions.

With these findings in hand, it was not surprising to observe that H_2bpydc could also successfully incorporated into UiO-67 via PSE, much like other metal chelating groups reported previously.[19,20] Incubating UiO-67 in a H_2O/DMF (v/v=4:1) solution containing 5 equiv of H_2bpydc at 25 °C or 85 °C afforded 36% or 73% incorporation of bpydc, respectively (Figure S3). BET surface areas of UiO-67-bpydc$_{0.36}$/bpdc$_{0.64}$ (via PSE) and UiO-67-bpydc$_{0.73}$/bpdc$_{0.27}$ (via PSE) were 2243±159 m^2/g and 2101±205 m^2/g, close to UiO-67 and indicating good porosity and the PXRD patterns of these materials were indicative of high crystallinity (Figure S4).

Accessibility of the bpy chelating sites in synthesized UiO-67-bpydc$_x$/bpdc$_{1-x}$ (prepared by direct solvothermal methods) to transition metals was evidenced by postsynthetic metalation with Pd. Incubation of UiO-67-bpydc$_{0.5}$/bpdc$_{0.5}$ in acetonitrile solution containing $PdCl_2(CH_3CN)_2$ at 65 °C afforded nearly quantitative metalation of all the bpy sites as confirmed by energy-dispersed x-ray spectroscopy (EDS) (Figure S5). EDS suggested 1:0.52:1.01 atomic ratio of Zr:Pd:Cl, supporting the formulation of the material as $Zr_6O_4(OH)_4(PdbpydcCl_2)_3(bpdc)_3$ (Table S1). Moreover, SEM and PXRD supported the underlying framework is maintained upon metalation, and EDS elemental mapping of post-metalation UiO particles exhibited a consistent and even distribution of Zr, Pd, and Cl (Figure S6, S7). UiO-67-Pdbpydc$_{0.5}$/bpdc$_{0.5}$ showed a reasonably BET surface area (1651±135 m^2/g), which is consistent with Pd complexion in the lattice. This BET surface area is significantly higher than other reported MOFs with over 10% metalated bpy sites.[13,14,16] UiO-67-bpydc was also metalated under the same conditions and EDS suggested a 94% metalation yield, with SEM confirming retention of the UiO-67 topology. However; the PXRD pattern showed a loss of high angle reflections (Figure S6) and the material was found to be non-porous to N2. Therefore, it appears that metalation of the fully functionalized UiO-67-bpydc causes some loss of integrity in the MOF.

Having successfully achieved a highly robust, porous and crystalline MOF with reactive Pd sites, the ability of this material to act as a solid-state catalyst was explored. UiO-67-Pdbpydc$_{0.5}$/bpdc$_{0.5}$ was used to carry out the Suzuki-Miyaura cross-coupling reaction between aryl halides and arylboronic acids. As a benchmark reaction, phenylboronic acid and 4-bromotoluene were chosen as the substrates to form 4-phenyltoluene. As shown in Table 1, incubating a mixture of reactants, K_2CO_3, and UiO-67-Pdbpydc$_{0.5}$/bpdc$_{0.5}$ as catalyst at 95 °C led to the 89% yield of cross-coupled product (Figure S8). Meanwhile, pristine UiO-67 and UiO-67-bpydc$_{0.5}$/bpdc$_{0.5}$ (without metalation) gave no conversion. A homogeneous control was carried out using $PdCl_2$ and $Pd(OAc)_2$, which gave a lower yield (51~54%) under the same reaction conditions. Commercially available Pd loaded on carbon (10% Pd/C) was employed as well, but also gave a lower (63%) yield. More importantly, leaching of Pd of UiO-67-Pdbpydc$_{0.5}$/bpdc$_{0.5}$ into the reactant solution was examined by inductively coupled plasma-optical emission spectroscopy (ICP-OES), showing that less than 0.1 ppm Pd and less than 0.1 ppm Zr present in the reaction solution, overcoming the known leaching problem of Pd/C.[21] The heterogeneity and stability of this MOF catalyst was also examined by hot filtration of the catalyst after 2 h, resulting in no further increase in product formation after 14 h. UiO-67-Pdbpydc$_{0.5}$/bpdc$_{0.5}$ can also be recovered from the reaction mixture by centrifugation and washed with copious amount water and MeOH for separation from K_2CO_3. The recovered catalysts was used in successive runs of Suzuki coupling and no decrease in yield (>85%) was observed even after three successive runs. PXRD and SEM characterization of UiO-67-Pdbpydc$_{0.5}$/bpdc$_{0.5}$ after catalysis showed the MOF still possessed high crystallinity, highlighting the robust nature of the Pd-grafted UiO catalyst (Figure S9, S10).

In conclusion, a rare example of open bpy sites directly introduced, by both presynthetic and postsynthetic approaches, has been presented using the UiO-67 MOF as a host. The resulting MOFs show high crystallinity in this versatile platform. Metalation produced an immobilized Pd(bpy)Cl_2 species on the MOF strut that exhibited heterogeneous and recyclable catalysis for the Suzuki-Miyaura cross-coupling reaction. Compared with commercially available Pd/C catalysts, this porous solid showed significantly enhanced catalytic efficiency with low catalyst loading and low Pd leaching.

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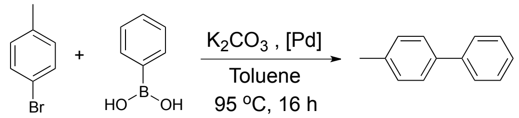
Table 1. Suzuki-Miyaura Coupling Reaction of 4-bromotoluene and phenylboronic acid.[i]



Entry	Catalyst	Pd (mol%)	MOF (mol%)	Yield (%)[ii]
1	blank	0	5	0
2	UiO-67	0	5	0
3	UiO-67-bpydc$_{0.5}$/bpdc$_{0.5}$	0	5	0
4	PdCl_2	2.5	0	54(3)
5	Pd(OAc)$_2$	2.5	0	51(6)
6	Pd/C (10 wt% Pd)	2.5	0	63(7)
7	UiO-67-Pdbpydc$_{0.5}$/bpdc$_{0.5}$	2.5	5	89(1)

[i] Reaction conditions: 4-bromotoluene (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol) in 5 mL toluene was heated at 95 °C for 16 h. [ii] Yield based on GC-MS analysis, an average value of three runs (error in parentheses).

Notes and references

[a] Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, USA 92093. Email: scohen@ucsd.edu

† Electronic Supplementary Information (ESI) available: [Experimental details of synthesis and catalysis, additional characterizations]. See DOI: 10.1039/c000000x/

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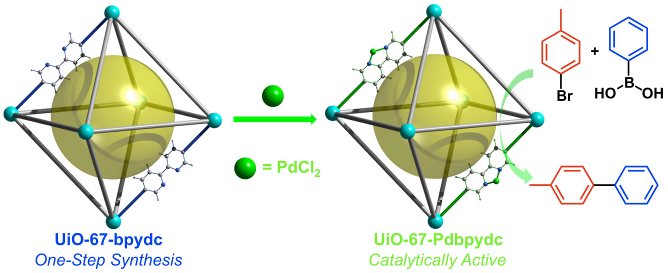

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