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# In Situ Generation of Functionality in a Reactive Haloalkane-Based Ligand for the Design of New Porous Coordination Polymers

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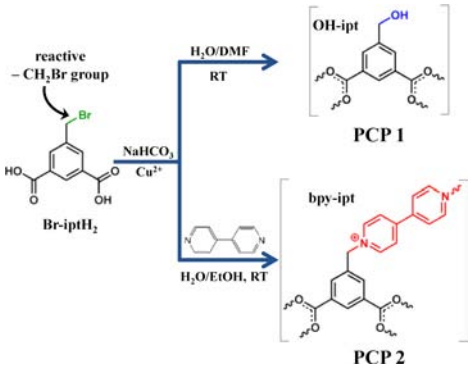
Supporting Information

**ABSTRACT:** Herein, we report new porous coordination polymers (PCPs) via a facile synthetic approach called "in situ generation of functionality in the ligand". Upon a synthetic process of PCPs, a neutral ($-CH_2OH$) or a cationic functionality ($-CH_2$-[4,4′-bipyridine]$^+$) was generated on a isophthalate ligand from a reactive haloalkane ($-CH_2Br$) moiety, affording two new PCPs. The PCPs have two-dimensional layered structures with large potential solvent-accessible voids for $CO_2$ adsorption.

The design and synthesis of new porous coordination polymers (PCPs) or metal−organic frameworks have long been fascinating to material scientists[1] for their widespread applications such as adsorption,[2] separation,[3] catalysis,[4] etc. In recent times, focus has been on the construction of PCPs with functional pores for targeting specific applications, such as selective adsorption,[2c] molecular recognition,[5] specific sensing,[6] etc. However, such ligand designs and their subsequent integration of functional groups into the targeted framework present synthetic challenges to material scientists. For applicable use of PCPs, the development of a facile synthetic process is necessary for the fabrication of new compounds with complex ligand systems. In this context, in situ ligand transformation is one of the promising methods to reduce synthetic steps and also to fabricate new functional pores that are otherwise inaccessible by the conventional stepwise synthesis.[7] Moreover, an in situ method is highly viable for the synthesis of multitopic organic ligands with a varying scale of denticity.[8] To date, many PCPs have been isolated via in situ ligand formation and exhibit interesting properties.[9] Benzyl halide (except fluoride), a reactive species, is known to undergo facile nucleophilic substitution reactions with versatile nucleophiles. When substitution reactions occur during PCP synthesis, there is large possibility of introducing various functional groups into the benzyl part. In particular, when a neutral nucleophile such as an amine group is substituted with a halide group, it is possible to introduce a positive charge into the ligand.[10] Therefore, we adopted the use of a precursor ligand with a benzyl bromide group and attempted to synthesize new PCPs via in situ modification.

Herein, we report two new PCPs, $\{[Cu(OH\text{-}ipt)(H_2O)]\cdot guest\}_n$ (**PCP1**) and $\{[Cu_2(bpy\text{-}ipt)_2(bpy)_{0.5}(H_2O)_3]\cdot(2NO_3)\cdot guest\}_n$ (**PCP2**), that have been assembled through in situ ligand transformation at room temperature (RT). To realize this, we employed a new dicarboxylate ligand, 5-(bromomethyl)-isophthalic acid (**Br-iptH$_2$**), functionalized with a reactive bromomethyl ($-CH_2Br$) backbone. The $-CH_2Br$ group transforms to a $-CH_2OH$ group during the synthesis of **PCP1**, while it reacts with 4,4′-bipyridine to generate an exotic single negatively charged isophalate ligand {5-(4,4′-bipyridinium methyl)isophthalate} in **PCP2** (Scheme 1). We have been able

**Scheme 1. Synthesis of PCPs via in Situ Transformation of the Br-iptH$_2$ Ligand to OH-ipt and bpy-ipt at RT**




to achieve transformation of a $-CH_2Br$ group to a $-CH_2OH$ group under mild reaction conditions at RT unlike at higher temperatures (>50 °C), which are usually employed (Figure S1 in the SI).[11]

**PCP1** was synthesized at RT by the slow diffusion of a *N*,*N*-dimethylformamide (DMF) solution of $Cu(NO_3)_2\cdot 3H_2O$ into an aqueous solution of **Br-iptH$_2$** in the presence of $NaHCO_3$, which kept the solution basic to accelerate the substitution reaction. Blue hexagonal crystals were collected after 10 days, washed with a DMF/$H_2O$ solution, and used for single-crystal X-ray diffraction (XRD) studies. In a similar fashion, **PCP2** was synthesized by the slow diffusion of an ethanol solution of $Cu(NO_3)_2\cdot 3H_2O$ into an aqueous solution of **Br-iptH$_2$** and **bpy** in the presence of $NaHCO_3$. Blue block-shaped crystals of **PCP2** formed after 7 days. Single-crystal XRD analysis suggests that **PCP1** and **PCP2** crystallize in space groups $R\bar{3}m$ and $P2_1/n$, respectively. Both compounds have two-dimensional (2D)

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structures (Figures 1 and 2) with potentially large accessible voids. Interestingly, **PCP1** has a (6,3)-kagomé topology with a

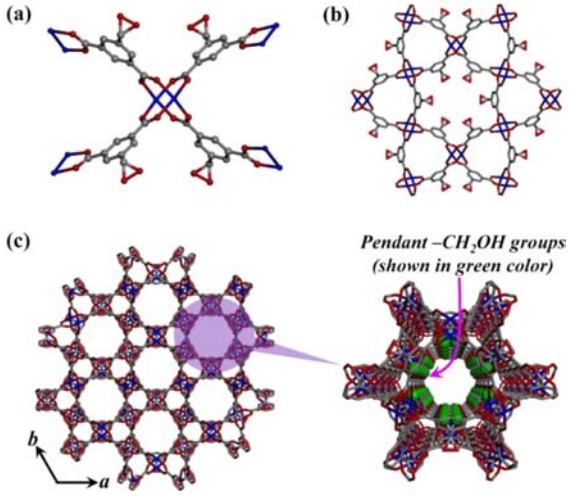


**Figure 1.** Crystal structure of **PCP1**: (a) $[Cu_2(CO_2)_4]$ building unit; (b) 2D kagomé layer composed of $[Cu_2(CO_2)_4]$ and **OH-ipt** (−OH is disordered); (c) framework structure of **PCP1** viewed along the crystallographic *c* direction showing hexagonal channels. An enlarged view (right-hand side) shows the location of pendant hydroxyl groups (large balls) in the nanochannel. Color specification: copper, blue; oxygen, red; carbon, gray (hydrogen atoms are not shown for clarity).

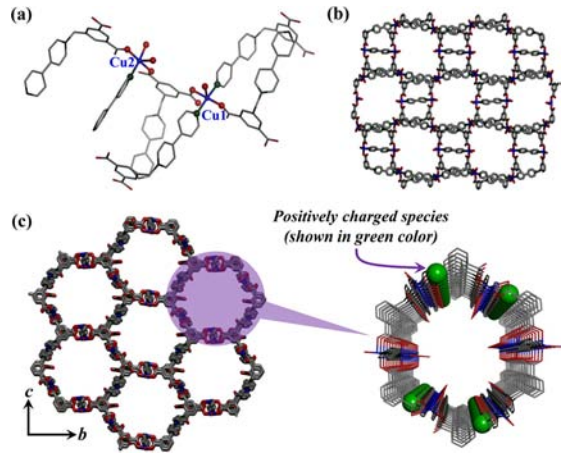


**Figure 2.** Crystal structure of **PCP2**: (a) coordination environment of two different copper(II) centers; (b) 2D layered structure of **PCP2**; (c) framework structure viewed along the crystallographic *a* direction showing large channels. Color specification: copper, blue; oxygen, red; carbon, gray; nitrogen, olive (hydrogen atoms are not shown for clarity).

$[Cu_2(CO_2)_4]$ secondary building unit (Figure 1a,b). Usually 2D compounds with kagomé topology pack in an AA fashion;[9g,12] however, **PCP1** packs in an unusual ABC fashion along the crystallographic *c* direction (Figure S2 in the SI). Upon analyzing the crystal structure in detail, we found profound influence of the $-CH_2OH$ group for the observed packing. The basic building unit of the framework is a $[Cu_2(CO_2)_4]$ core connected to four **OH-ipt** ligands and two water molecules. The coordinated water molecules of layer A interact with the $-CH_2OH$ group of **OH-ipt** of the neighboring layer B through hydrogen bonding (Figure S3 in the SI). This enforces layer B to displace by $^1/_3x + {}^1/_3y$ in the *ab* plane. At the same time, layer B locates itself at $^1/_3z$ toward the crystallographic *c* direction. As a consequence, to meet the crystallographic requirements, the third layer, C, is placed at $^2/_3x$, $^2/_3y$, $^2/_3z$ (coordinates are chosen with reference to *x*, *y*, *z* of layer A), thus leading to ABC-type packing in the crystal. This unusual ABC packing creates a highly porous structure with two distinguishable nanochannels along the crystallographic [211] and *c* directions (Figure S4 in the SI). The approximate dimensions of the nanochannels are 3 × 4 and 6 × 6 Å$^2$. It is important to mention that the pore surfaces of the nanochannels are decorated with $-CH_2OH$ groups from the **OH-ipt** ligand (Figure 1c). The surface also has copper(II) atoms coordinated by water molecules, the removal of which would potentially provide unsaturated copper(II) sites. The potential void space of the crystal, as calculated by *PLATON*[13] software, was found to be 5290 Å$^3$, which is approximately 60.6% of the unit cell volume.

**PCP2** also has a 2D layered structure (Figures 2 and S5 in the SI) that assembles with an unusual single negatively charged carboxylate ligand **bpy-ipt** formed in situ. The most plausible mechanism for formation of the **bpy-ipt** ligand is the nucleophilic attack of the pyridyl nitrogen atom of **bpy** on the $-CH_2Br$ group of **Br-iptH$_2$**. The multitopic **bpy-ipt** ligand features an unusual coordination mode through two carboxylate groups and a pyridyl group, which is never realized with a normal isophthlate ligand. The structure features two crystallographically independent copper centers with square-pyramidal geometry (Figure 2a). Cu1 is coordinated to four different **bpy-ipt** ligands in the equatorial plane with coordinations furnished by two carboxylate and two **bpy** moieties of the ligand. The fifth coordination at the axial position is provided by a water molecule. The coordination environment of Cu2 is different from that of Cu1, with two **bpy-ipt**, one **bpy**, and one water molecule occupying the equatorial plane. A water molecule at the axial position fulfills the square-pyramidal geometry requirement. Cu1 and Cu2 are connected via the isophthalate part of one **bpy-ipt** ligand to generate a 2D layered structure. Interestingly, in the 2D layer itself, the **bpy** ligand acts as a beam and connects two Cu2 centers, providing additional stability in the layer. Strong $\pi-\pi$ interaction of the benzene ring of the isophthalate moiety (Figure S6 in the SI) between the 2D layers leads to the formation of a three-dimensional (3D) supramolecular structure. The framework is cationic because of the monoanionic nature of the **bpy-ipt** ligand, and the residual charge is balanced by $NO_3^-$ counteranions in the structure (Figure S7 in the SI). The 3D supramolecular structure (Figure 2c) possesses large channels that are occupied with guest water molecules. The guest molecules were highly disordered in the channels and, hence, the *SQUEEZE*[14] tool was applied to refine the guest-free structure. The approximate dimensions of the nanochannels, calculated considering the van der Waals surface, are 11.5 × 11.5 Å$^2$ (Figure S8 in the SI). The potential solvent-accessible void in guest-free **PCP2** turns out to be ∼6000 Å$^3$, which is 62% of the unit cell volume.

Thermogravimetric analysis (TGA) suggests that **PCP1** and **PCP2** is stable up to 280 and 230 °C, respectively. The purity of the as-synthesized compounds was confirmed by powder XRD (PXRD) studies (Figures S10 and S11 in the SI). The desolvated PXRD of **PCP1** suggests a structural change upon guest removal. **PCP2** shows the unusual behavior of crystal-to-amorphous transformation[15] upon guest removal (Figure S11 in the SI). When heated at 120 °C for 12 h, **PCP2** transforms to an amorphous phase, as suggested by the PXRD pattern. The amorphous phase, when soaked in a 1:1 $H_2O$/EtOH solvent mixture for 24 h, returns to its original crystalline phase. Hence, it can be concluded that **PCP2** is reversible with respect to a crystal-to-amorphous phase change.


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The degassed PCPs, **PCP1′** and **PCP2′** were tested for their gas sorption behavior at low temperatures. As can be seen from Figure 3, the compounds show significant uptake of $CO_2$ gas at

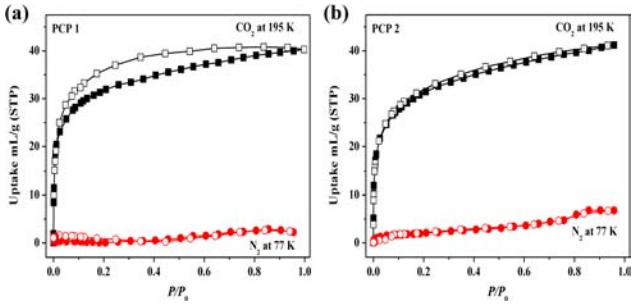


**Figure 3.** Gas-sorption isotherms of **PCP1** (a) and **PCP2** (b): $N_2$ at 77 K and $CO_2$ at 195 K. Closed symbols indicate adsorption and open symbols desorption. $P_0$ is the saturated vapor pressure of the adsorbates at the measurement temperatures.

195 K; however, they do not show any adsorption for $N_2$ gas at 77 K. Both PCPs show a type I $CO_2$ profile with steep uptake at the low-pressure region, suggesting the presence of an open channel in the degassed phase. The Brunauer−Emmett−Teller surface areas calculated from $CO_2$ sorption data for **PCP1** and **PCP2** turn out to be 147 and 144 $m^2\ g^{-1}$, respectively. In general, the sorption rate is influenced by factors such as the pore size, channel dimension, and surface functionality. In our case, because of the larger size of $N_2$ than of $CO_2$ (kinetic diameters: 3.64 and 3.3 Å for $N_2$ and $CO_2$, respectively), the diffusion rate of $N_2$ should be much slower in the 1D channel, resulting in no sorption of $N_2$ at low temperature (77 K).

In conclusion, we have carried out in situ generation of functionality with a reactive haloalkane-based ligand under mild reaction conditions to assemble two PCPs of copper(II). The PCPs have 2D layered structures, with **PCP1** featuring interesting 2D kagomé topology. **PCP2** shows an unusual reversible crystal-to-amorphous phase change with respect to guest removal. Our synthetic recipe has not only provided a facile synthetic pathway but also led to the assembly of porous **PCP2** with an unusual single negatively charged multitopic ligand **bpy-ipt**. The in situ generation of functionality should be a promising methodology for the integration of various chemical functionalities in PCPs.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

X-ray crystallographic file (CIF), experimental details, and NMR, TGA, and PXRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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