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A Tale of Two Trimers from Two Different Worlds: A COF-Inspired Synthetic Strategy for Pore-Space Partitioning of MOFs

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Abstract: *The introduction of a symmetry- and size-matching pore-partitioning agent in the form of either a molecular ligand, such as 2,4,6-tri(4-pyridinyl)-1,3,5-triazine (**tpt**), or a metal-complex cluster, into the hexagonal channels of MIL-88/MOF-235-type (the **acs** net) to create **pacs**-type (partitioned **acs**) crystalline porous materials is an effective strategy to develop high-performance gas adsorbents. We have developed an integrated COF–MOF coassembly strategy as a new method for pore-space partitioning through the coassembly of $[(M_3(OH)_{1-x}(O)_x(COO)_6]$ MOF-type and $[B_3O_3(py)_3]$ COF-type trimers. With this strategy, the coordination-driven assembly of the **acs** framework occurred concurrently and synergistically with the COF-1-type condensation of pyridine-4-boronic acid into a C_3-symmetric trimeric boroxine molecule. The resulting boroxine-based **pacs** materials exhibited dramatically enhanced gas-sorption properties as compared to nonpartitioned **acs**-type materials and are among the most efficient NH_3-sorption materials.*

Metal–organic frameworks (MOFs) are crystalline porous materials with intriguing structural characteristics[1] and have attracted intense attention in the last two decades for various applications, such as gas sorption,[2] separation,[3] and catalysis.[4] Pore-space partitioning has been shown to be a versatile design strategy for constructing crystalline porous materials (CPMs) with much enhanced chemical stability and gas-sorption properties.[5] A prominent platform involves the introduction of C_3-symmetric pore-partitioning agents into hexagonal channels of MIL-88/MOF-235-type structures,[6] also known as the **acs** net, to form 9-connected **pacs** frameworks.[7] The flexibility of the **acs** parent framework enables a large number of pore-partitioning agents to be used within the channel. To expand the **pacs** system, novel strategies for designing symmetry-matching C_3 partitioning agents are needed, some of which have been demonstrated, including: 1) the insertion of individual **tpt**-type ligands to prepare **tpt-pacs** (tpt = 2,4,6-tri(4-pyridinyl)-1,3,5-triazine) materials, 2) the coassembly of **acs** frameworks with in situ formed metal–ligand clusters based on isonicotinate and 1,2,4-triazolate with monomeric, dimeric, and trimeric metal cores,[7] and 3) a postsynthetic modification and cyclotrimerization approach to introduce tpt, 2,4,6-tri(4-pyridinyl)-1,3,5-benzene (tpbz), and 2,4,6-tri(4-pyridinyl)-1,3,5-cyclohexane (tpc).[8]

Covalent organic frameworks (COFs) are a new class of crystalline porous materials built up by covalent bonds between light elements (B, C, N, O, Si).[9] Organic building units are linked covalently into extended 2D or 3D nets. Various chemical strategies have been reported for the construction of COFs, including: 1) boron–oxygen-based linkages, such as the B_3O_3 boroxine 6-ring or BO_2C_2 boronate ester 5-ring,[10] 2) C=N imine-based linkages,[11] 3) $(CN)_3$ triazine-based linkages,[12] and 4) other methods, such as imidization.[13] These chemical reaction strategies have led to the rapid growth of COF materials. However, the integration of such COF chemistry with coordination-driven MOF chemistry,[14] especially as it relates to the pore-space-partition method, has not been explored.

In this study, we integrated COF-1 chemistry (Figure 1a),[10] also known as the self-condensation of boronic acids, with MOF chemistry to develop a novel pore-partition method, which led to the synthesis of a new family of pore-partitioned materials. Our method makes use of pyridine-4-boronic acid, which is introduced as a monomer into a MIL-88-type reaction system. During the reaction, a new pore-partitioning ligand, the trimer of pyridine-4-boronic acid, is formed as 2,4,6-tri(4-pyridinyl)-1,3,5-boroxine (**tpb**; Figure 1b). The simultaneous operation of two totally different reactions requires all components to function cooperatively. Metal ions coordinate with pyridine-4-boronic acid (or its trimer) at the N side during formation of a metal trimer $(M_3(OH)_{1-x}(O)_x(COO)_6)$ (Figure 1c), and the condensation of three boronic acids occurs at the B side to form a C_3-symmetric pore-partitioning ligand. Crystal structures of In–Co-based materials were determined by single-crystal X-ray diffraction (Table 1).

The trimer of pyridine-4-boronic acid, **tpb**, has never been made before, maybe because it contains both Lewis acid and base sites (B and N), thus pointing to the possibility of further intermolecular assembly. The successful trimer formation highlights a synergistic effect of the simultaneous MOF and COF assembly and a significant difference between standard COF chemistry and the COF-type chemistry reported herein.

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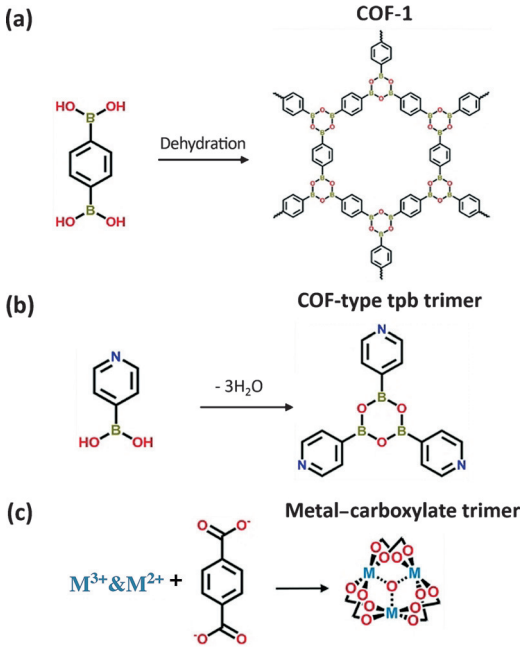

Figure 1. a) Condensation reaction of benzene-1,4-diboronic acid to prepare COF-1. b) Pyridine-4-boronic acids self-assemble into **tpb** through covalent bonds. c) Metal–carboxylate trimer formation through coordination bonds.

In COF-1, the two sides of the boronic acids are identical, whereas in our approach, the two sides are different. Under normal chemical conditions, the B site in the targeted trimer has the tendency to bond to the N site of the pyridyl group, thus leading to competing reactions. In this study, the coordination framework preferentially occupied the N side of pyridine-4-boronic acid or tpb trimer, thus precluding any undesirable B–N coordination interaction (see Figure S11 in the Supporting Information).

The **tpb-pacs** family has the general framework formula $[(M1)_{1+x}(M2)_{2-x}(OH)_{1-x}(O)_x(L1)_3](L2)$, in which $[(M1)_{1+x}(M2)_{2-x}(OH)_{1-x}(O)_x(L1)_3]$ represents the parent **acs** framework (M1 = In^{3+}, Fe^{3+}; M2 = Co^{2+}, Mg^{2+}, Ni^{2+}; L1 = BDC, NH_2BDC, NO_2BDC, and 26NDC in CPM-100a, CPM-100b, CPM-100c, and CPM-100d, respectively). CPM-100a has been made with different metal combinations, denoted as CPM-100a-InCo, CPM-100a-FeMg, CPM-100a-FeNi. L2 is the condensation product **tpb**. A **tpt-pacs** CPM $[In_{1.2}Co_{1.8}(OH)_{0.8}O_{0.2}(BDC)_3]$tpt, denoted as tpt-InCo-BDC (or CPM-83-InCo), was also prepared.[7,15]

The characteristic feature of the **pacs** platform is its great potential for adapting to a variety of pore-partitioning agents and design strategies. The formation of **tpt-pacs** is an OMS-eliminating process (OMS = open metal site) owing to the formation of a 3,9-connected net with three open metal sites occupied by pyridyl groups from tpt. Triazolate-cluster-partitioned **trz-pacs** represents an OMS-shifting design. While **trz-pacs** is also a 3,9-connected framework in which azolate ligands occupy all open metal sites on the parent framework, the open metal sites formed on metal–ligand complexes in the channel centers can reach up to 18 per unit cell. A totally different feature is shown in this study through pore-space partitioning. Through the MOF–COF synergistic reaction, open metal sites on the framework are occupied by pyridyl groups, and boron Lewis acid sites are exposed through boronic acid condensation (Figure 2). The new partitioning agent **tpb** contains three B sites, providing six Lewis acid sites (LAS) per unit cell (ca. 1.55 LAS/nm^3). Boron Lewis acid sites are favorable adsorbents for Lewis base gases, such as ammonia, owing to the B–N coordinative process.

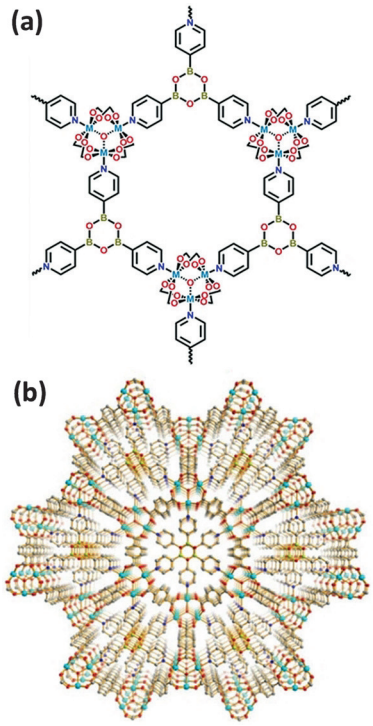

Figure 2. Alternating **tpb** trimers and metal-cluster trimers a) in the *ab* layer of CPM-100 and b) viewed down the *c* axis.

The thermal and hydrothermal stability of all seven compounds

Table 1: Crystal data of the CPM-100 series of **pacs**-type porous materials.

Material[a]	Framework formula[b]	*a*, *b* [Å]	*c* [Å]	*R* (*F*)
CPM-100a-InCo	$In_{1.8}Co_{1.2}(OH)_{0.2}O_{0.8}(BDC)_3$tpb	17.015 (5)	15.303 (9)	0.0560
CPM-100a-FeMg[c]	$Fe_{1.7}Mg_{1.3}(OH)_{0.3}O_{0.7}(BDC)_3$tpb	16.908 (2)	14.847 (2)	–
CPM-100a-FeNi[c]	$Fe_{1.6}Ni_{1.4}(OH)_{0.4}O_{0.6}(BDC)_3$tpb	16.883 (2)	14.848 (2)	–
CPM-100b	$In_{1.7}Co_{1.3}(OH)_{0.3}O_{0.7}(NH_2BDC)_3$tpb	17.055 (2)	15.333 (5)	0.0617
CPM-100c	$In_{1.1}Co_{1.9}(OH)_{0.9}O_{0.1}(NO_2BDC)_3$tpb	17.077 (3)	15.153 (3)	0.0695
CPM-100d	$In_{1.5}Co_{1.5}(OH)_{0.5}O_{0.5}(26NDC)_3$tpb	17.043 (3)	21.000 (4)	0.0807
tpt-InCo-BDC	$In_{1.2}Co_{1.8}(OH)_{0.8}O_{0.2}(BDC)_3$tpt	16.945 (5)	15.329 (5)	0.0332

[a] Space group of all compounds: $P6_3/mmc$. [b] BDC = benzene-1,4-dicarboxylate, NH_2BDC = 2-aminobenzene-1,4-dicarboxylate, NO_2BDC = 2-nitrobenzene-1,4-dicarboxylate, 26NDC = naphthalene-2,6-dicarboxylate, tpb = 2,4,6-tri(4-pyridinyl)-1,3,5-boroxine. [c] The unit cell was determined by powder diffraction by using the indexing program DICVOL06.

was studied (see Figures S2 and S12). Overall, these materials showed much enhanced stability as compared to nonpartitioned MIL-88-type materials. Furthermore, greater hydrothermal stability can be achieved for boroxine rings owing to their confinement within the channels.

Seven newly synthesized CPMs were chosen as adsorbents for gas-adsorption studies. Sorption isotherms for C_2H_2, C_2H_4, C_2H_6, CH_4, CO_2, and NH_3 uptake were measured. The following systematic trends among these new materials were explored: 1) changing the L1 ligand with a fixed M1/M2 combination (In/Co), 2) varying the M1/M2 combination (In/Co, Fe/Mg, Fe/Ni) with a fixed L1 ligand (BDC), and 3) changing the pore-partitioning agent (**tpt** or **tpb**) with fixed L1 (BDC) and M1/M2 (In/Co).

It is notable that the uptake of five gases in **tpb-pacs** materials was dramatically enhanced as compared to **acs** materials (see Figure S6 and Table S3 in the Supporting Information). At 1 bar and 273 K, the CO_2 uptake ranged from 3.96 to 6.32 mmol g^{-1} in **tpb-pacs** (Figure 3a). These values are higher than the CO_2 uptake of the best-performing gas sorbent in **acs**-type Mg_2V-MIL-88 (4.25 mmol g^{-1}),[5] which is already a highly optimized **acs**-type material. In most cases, **acs**-type materials are rather poor gas-sorption materials, even though their swelling effects are of great interest.

The C_2H_2 uptake of the new materials reported herein could be tuned from 5.61 to 10.45 mmol g^{-1} at 1 bar and 273 K (Figure 3b). Under the same conditions, the C_2H_2 uptake of CPM-100a-FeMg (5.25 mmol g^{-1} at 273 K) is nearly twice that of Mg_2V-MIL-88 (3.28 mmol g^{-1} at 298 K).[5] This effective gas-sorption enhancement is attributed to the pore-partitioning agent **tpb**, which increases the robustness of the framework as well as the number of binding sites.[16] The C_2H_4 and C_2H_6 (1 bar, 273 K) uptake could be enhanced from 3.8 to 6.89 mmol g^{-1} and from 3.39 to 7.5 mmol g^{-1}, respectively (see Figure S4). The uptake of CH_4 was tuned from 0.55 to 1.71 mmol g^{-1} at 1 bar and 273 K (see Figure S5).

For NH_3, at 1 bar and 298 K, the NH_3 uptake could be tuned from 7.85 to 12.56 mmol g^{-1} in the order 26NDC, BDC, NO_2BDC, NH_2BDC, and from 11.66 to 13.01 mmol g^{-1} in the order In/Co, Fe/Mg, Fe/Ni (Figure 4a). There was no evident adsorption loss after four cycles (see Table S1). The NH_3

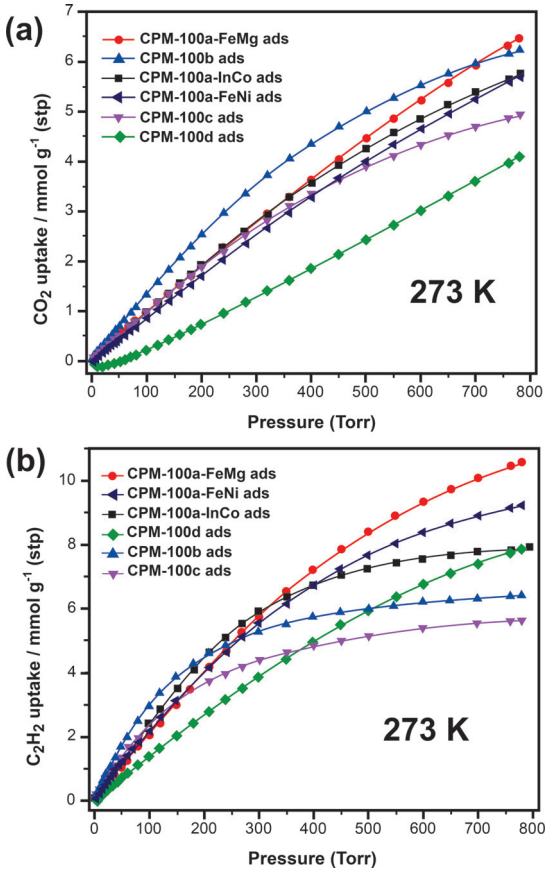

Figure 3. Gas-sorption isotherms of a) CO_2 and b) C_2H_2 at 273 K.

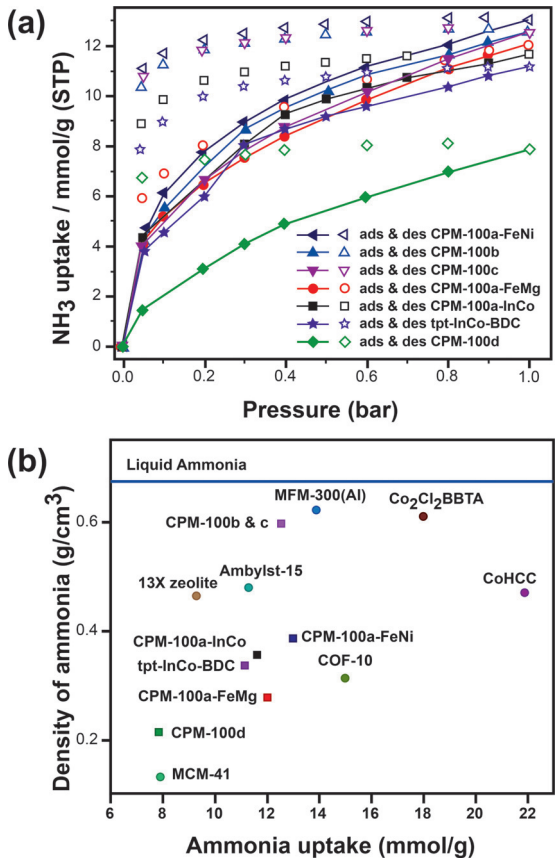

Figure 4. a) NH_3-sorption isotherm at 298 K. b) Comparison of the density of NH_3 between CPM-100, other materials, and liquid ammonia.

packing density in CPM-100b and CPM-100c (0.598 and 0.597 g cm^{-3}) is comparable to that of the top two materials MFM-300(Al) and Co_2Cl_2BBTA (0.622 and 0.610 g cm^{-3}; Figure 4b; see also Table S2).[17] According to DFT calculations, the adsorption site B possesses a large binding energy of −43 kJ mol^{-1}. The distance between N in ammonia and B in **tpb** is approximately 2.45 Å, thus indicating a strong interaction between B and N (see Figure S10), which results in an adsorption enhancement with respect to **tpt-pacs** materials.

In summary, an integrated MOF–COF synthesis method has been developed as a new pore-space-partition strategy, which led to a novel family of **pacs** materials, named **tpb-pacs**. It differs from previous syntheses of **tpt-pacs** and **trz-pacs** by combining simultaneous coordination assembly and covalent assembly, thus leading to **pacs** materials with exposed boron Lewis acid sites. A gas-sorption study showed that **tpb-pacs** exhibited high-performance gas-sorption properties for common gasses and showed impressive NH_3 uptake. Importantly, this method represents the first step in concurrently introducing C_3-symmetric fragments in COFs into structures (other possibilities include boronate ester, imine, and hydrazine linkages). Further materials and applications based on this strategy need to be explored.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: boronic acids · covalent organic frameworks · materials science · metal–organic frameworks · pore-space partitioning

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