

## Mn<sup>II</sup>-based MIL-53 Analogues: Synthesis Using Neutral Bridging $\mu_2$ -Ligands and Application in Liquid-Phase Adsorption and Separation of C6–C8 Aromatics

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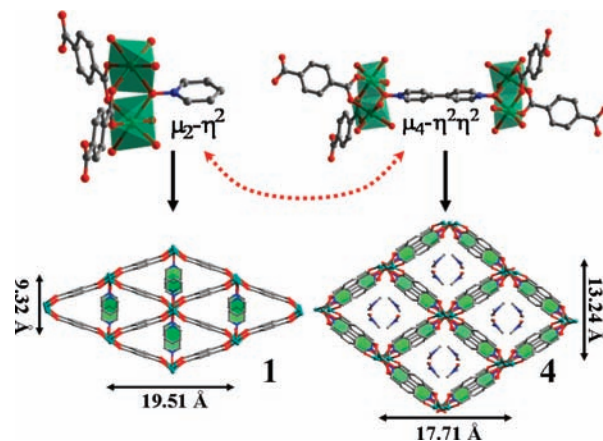
The C6–C8 aromatics, known as monoaromatic hydrocarbons and mostly abbreviated as BTEX standing for benzene, toluene, ethylbenzene, and the three xylene isomers, are major industrial raw materials in plastic, synthetic rubber, and synthetic fiber manufacture.<sup>1</sup> On the other hand, BTEXs are ubiquitous in numerous sites including areas used for fuel operations, refineries, gasoline stations, gasification sites, and groundwater reservoirs and display carcinogenic and neurotoxic potentials.<sup>2</sup> Microporous materials, such as zeolites and MOFs,<sup>3</sup> are promising materials for the recovery of these pollutants and the separation of BTEXs targeted to individual chemicals with high purity.

As an important subsidiary group of metal–organic frameworks (MOFs) and promising candidates for gas adsorption, the MIL-53 (M<sup>III</sup>) systems developed by Férey and co-workers have received intensive attention owing to their remarkable framework flexibility.<sup>4</sup> The framework flexibility is termed as “breathing effect”, and some frameworks show abnormal expansions (contractions) toward exhaling (inhaling) guest species.<sup>5</sup> Similar to MOFs, both the metallic sites and 1,4-benzenedicarboxylate (BDC) linkers in MIL-53 systems have been the targets for modifications in order to impart desired properties.<sup>6</sup> However, much less attention has been paid to modifying  $\mu_2$ -OH that bridged the metal cations along the chains.<sup>7</sup> Besides  $\mu_2$ -OH, doubly bridging oxygen atoms ( $\mu_2$ -oxo) and neutral ligands appeared in the structural analogues of MIL-53 such as MIL-47(V<sup>IV</sup>),<sup>4b</sup> MOF-71,<sup>8</sup> and MIL-53(Fe<sup>II</sup>).<sup>9</sup> The different charges of the metal cations necessitate the variation of  $\mu_2$  groups so that their neutral frameworks could be maintained. In this work, we report the synthesis of four Mn<sup>II</sup>-based MIL-53 analogues [MIL-53(Mn<sup>II</sup>)] using pyridine *N*-oxide and its derivatives (PNOs) as neutral  $\mu_2$  ligands. The adsorption and separation of C6–C8 aromatics using one evacuated porous MIL-53(Mn<sup>II</sup>) as an absorbent were investigated via crystal to crystal transformations.

Compounds **1–4**, formulated as Mn(BDC)L<sup>*n*</sup> for **1–3** (L<sup>1</sup> = pyridine *N*-oxide (PNO), L<sup>2</sup> = 4-methyl-pyridine *N*-oxide, L<sup>3</sup> = 3,5-dimethyl-pyridine *N*-oxide) and Mn<sub>2</sub>(BDC)<sub>2</sub>L<sup>4</sup>•(DMF)<sub>2</sub> for **4** (L<sup>4</sup> = 4,4'-bipyridine-*N,N'*-dioxide (BPNO), DMF = dimethyl formamide) (Figure S1, Supporting Information), were prepared under solvothermal conditions using Mn(NO<sub>3</sub>)<sub>2</sub> aqueous solution, H<sub>2</sub>BDC, and corresponding L<sup>*n*</sup> as precursors in DMF at 120 °C. Details of synthesis are provided in Supporting Information (SI). Despite the hygroscopic nature of PNOs, compounds **1–4** are stable in atmospheric conditions for at least six months. All four compounds are insoluble in common organic solvents, but they do decompose in water. The occluded DMF molecules in **4** can be exchanged by ethanol molecules yielding **4**<sub>eth</sub> or completely removed giving **4**<sub>vac</sub>.

Single-crystal X-ray diffraction analysis revealed that compounds **1–4** are built up from infinite chains of corner-sharing MnO<sub>6</sub> octahedra interconnected by organic moieties, which is similar to those of MIL-53 systems, and the net of them is *sra*.<sup>8</sup> In Table S1 (SI), a summary of crystallographic data of these four compounds along with **4**<sub>vac</sub> as

well as guest-exchanged products of **4** is provided. The structure of **1** is illustrated in Figure 1 since **2** and **3** are isostructural to **1**. The one-dimensional (1D) channels in compounds **1–3** are blocked by pendant PNOs as shown in Figure 1 and Figure S2 (SI). The structural evolutions from **1** to **3** along with the increase of the substituent methyl group in PNOs could be ascribed to  $\pi$ – $\pi$  interactions, one of the noncovalent interactions playing pivotal roles in many fields such as chemistry, biology, and material science,<sup>10</sup> between two adjacent digonal pendant groups and explained using a simple electrostatic model.<sup>11</sup> Further explanation toward this is provided in SI.



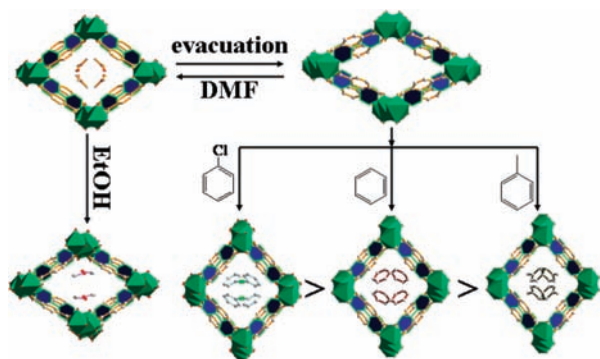
**Figure 1.** Mn<sup>II</sup>-based MIL-53 frameworks with pendant PNO (**1**) and BPNO incorporated into the skeleton (**4**). The occluded molecules in **4** are DMF. Color code: green, Mn; red, O; blue, N; 50% gray, C.

In compound **4**, the manganese oxide chains are further interconnected by BPNO units besides BDC (Figure 1). Its structure can be also viewed as evolved from **1** by connecting two closest  $\mu_2$ -PNO molecules of adjacent manganese oxide chains in **1** to form a BPNO molecule. This extra connection exerts forces to the manganese oxide chains and results in the corrugation of the linear –Mn–Mn–Mn– chains in **1–3** accompanied with an even more severe COO distortion (Figure S3, SI). The advantage of this connection is that the blocking of the channels by pendant  $\mu_2$  ligands in **1–3** could be avoided. The delimited channel sizes change from 9.32 to 13.24 Å and 19.51 to 17.71 Å, respectively, as shown in Figure 1. The open 1D channels in **4** are occupied by DMF molecules. Despite being incorporated into the framework skeleton, the adjacent bi- $\mu_2$  BPNO ligands still interact with each other via  $\pi$ – $\pi$  interactions, which spread throughout the whole crystal, with a closest 4.606 Å centroid-centroid distance and a severe offset (Figure S2, SI). It is worthy of noting that BPNO has a  $\mu_4$ - $\eta^2$ - $\eta^2$  connection mode toward Mn<sup>2+</sup> in **4**. Such mode is unusual for BPNO in constructing coordinative framework polymers.<sup>12</sup>

Thermal gravimetric analysis and X-ray thermodiffraction of sample **4** indicate that these compounds show high thermal stability

(Figure S4 and S5, SI). Standard N<sub>2</sub> sorption measurements revealed that no appreciable pore could be detected for 1–3 as expected from the single X-ray diffraction analysis. The low hydrogen adsorption isotherm of 4 shows a reversible hydrogen sorption, and the adsorbed amount of hydrogen corresponds to ~1.0 wt % at 1 bar and 77 K (Figure S6, SI), suggesting a favorable interaction of H<sub>2</sub> with the host framework.<sup>6a</sup>

Although the occluded DMF molecules could be exchanged by a small molecule, e.g. ethanol, or removed by evacuation processes (see SI and Figure 2), they could not be exchanged by big molecules such as benzene or toluene directly. Therefore 4<sub>vac</sub> was chosen for studying its adsorption and separation of C6–C8 aromatics. Upon immersing 4<sub>vac</sub> into liquids including benzene, toluene, xylenes, ethylbenzene, and chlorobenzene, only C6–C7 molecules could be intercalated, and crystals of 4<sub>ben</sub>, 4<sub>tol</sub>, and 4<sub>chl</sub> were obtained (Table S1, SI). Single-crystal structural analysis shows that the intercalated molecules have definite positions in the channels and fill the channels pairwise. Along each channel, there are two symmetrically equivalent positions available for the pairs. Furthermore, when 4<sub>vac</sub> was immersed into a mixture of benzene and toluene with 1:1 volume ratio, only benzene could be selectively adsorbed. These results clearly demonstrate that 4<sub>vac</sub> could be a potential adsorbent for the separation of C6, C7, and C8 aromatics in liquid phase.<sup>3b,13</sup> A higher chlorobenzene selectivity of 4<sub>vac</sub> over benzene (Figure 2) was also observed in a process similar to that using benzene and toluene.



**Figure 2.** Guest exchange of 4 with EtOH and selective absorptions of C6–C8 aromatics by single crystals of 4<sub>vac</sub>.

For selective adsorption and separation of C6–C8 aromatic using 4<sub>vac</sub> as adsorbents, the  $\pi$ – $\pi$  interactions including the guest–guest and guest–linker interactions are considered to play key roles for the crystal to crystal transformations. The three occluded aromatics in 4<sub>ben</sub>, 4<sub>tol</sub>, and 4<sub>chl</sub> tend to form antiparallel dimers to facilitate the dipole–dipole interactions.<sup>14</sup> Besides intermolecular parallel displaced (PD)  $\pi$ – $\pi$  interactions, they can also interact with BDC rings with nearly isoenergetic T-shaped configurations.<sup>14,15</sup> There is only one T-shaped  $\pi$ – $\pi$  interaction between each toluene molecule and the phenyl ring of BDC linker, while there are two T-shaped  $\pi$ – $\pi$  interactions for benzene and chlorobenzene (Figure S7). In addition, one C–H...Cl hydrogen bonding between each chlorobenzene and the BPNO can be formed (Figure S7, SI). These two interactions might be responsible for the selectivity trend (chlorobenzene > benzene > toluene) of 4<sub>vac</sub>. As we already noticed, all three aromatics present as dimers in order to have high packing densities within the 1D channels.<sup>3b</sup> The dimeric C8 aromatics are unlikely favored within the channels as the number of guest–host T-shaped  $\pi$ – $\pi$  interactions might be reduced when more electron-donating substituent groups were attached to the benzene rings, a case having already occurred in 4<sub>tol</sub>. Another dominant factor for filling guest molecules in the 1D channel

of 4<sub>vac</sub> is likely to be the packing efficiency. Increasing the number of electron-donating substituent groups also leads to an increase of intermolecular repulsions of their dimers that might make the dimensional sizes of these dimers too large to be accommodated by the 1D channels in 4<sub>vac</sub>.

In summary, we succeeded in preparing MIL-53(Mn<sup>II</sup>) single crystals using PNOs as  $\mu_2$ -ligands. A porous crystal 4 could be formed using BPNO as a bi- $\mu_2$ -ligand. Its evacuated form 4<sub>vac</sub> showed selective adsorptions toward C6–C8 aromatics due to the different degrees of guest–linker interactions.

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**Supporting Information Available:** Experimental details and data, CIF files, thermal ellipsoid of crystal structures of 1–4, TGA and powder X-ray diffractions for 1–4, X-ray thermodiffraction and the H<sub>2</sub> sorption isotherms for 4, and the views of the noncovalent interactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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