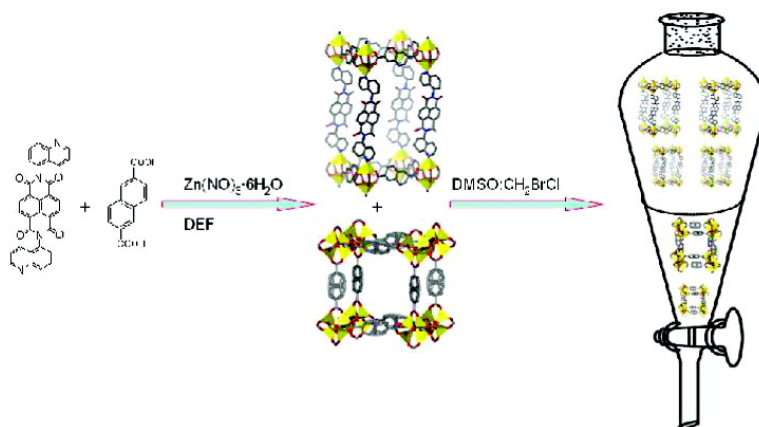## Communication

Separating Solids: Purification of Metal-Organic Framework Materials

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Separating Solids: Purification of Metal-Organic Framework Materials

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A tremendous development in the area of functional, nanostructured materials is the emergence of large numbers of structurally well defined, permanently microporous metal–organic framework materials (MOFs). Consisting of metal–ion or –cluster nodes and multitopic organic struts, such materials are often characterized by very large internal surface areas, low densities, and uniformly sized channels and pores.[1] Among the many applications that may capitalize on these extraordinary properties are gas storage,[2] chemical separations,[3] and selective catalysis,[4]

MOFs are generally synthesized via one-pot solvothermal methods. Since purification of the resulting network solids is not feasible via the methods usually employed by chemists (distillation, recrystallization, chromatography, sublimation, etc.), a premium is placed on discovering conditions that yield pure products. Typically, discovery entails systematically evaluating scores of reaction conditions that differ only slightly from initial or refined conditions (e.g., temperature, solvent composition, reactant concentrations, reaction time, and even reaction vessel size). Alternatively, if sufficiently large crystals of distinct morphology or color are obtained, they can be manually separated from undesired byproducts – albeit, often in painstaking fashion. Nevertheless, isolation of pure materials is essential; closely structurally related porous materials can often differ enormously in terms of properties and functional behavior.[5]

Here we report a method for rapidly purifying MOF materials and illustrate its applicability to three commonly encountered problems: (1) isolation of a desired crystalline MOF from a mixture containing a second compound comprising the same organic-strut and/or metal-ion building blocks, (2) separation of a desired mixed-strut material from a second crystalline MOF containing only a single type of strut, and (3) separation of a noninterpenetrating MOF from an otherwise identical material consisting of catenated networks. Briefly, the method takes advantage of MOF density differences such that one phase floats in a solvent of appropriate density while the other sinks. The method is both straightforward and broadly applicable. Furthermore, we find that it can be used to isolate even minor components (e.g., 15%) of mixed phases. Though this technique has occasionally been used to isolate *molecular* metal complexes, it is not well developed for metal–organic framework chemistry.[6]

CH_2BrCl was chosen as the parent solvent for each of the studies below because of its high density (1.99 g/cm^3) relative to most MOFs. Starting with a dense solvent allows the crude MOF mixture to float. Subsequently, a second miscible but lighter solvent is added until the appropriate density is reached and the MOF mixture separates into floating and sinking fractions. Powder X-ray dif-
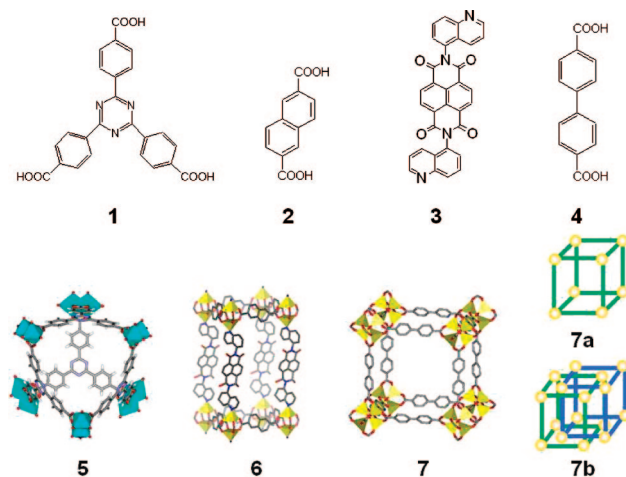

Figure 1. Representations of structures of struts and MOFs. **1**, 4,4′,4″-*s*-triazine-2,4,6-triyltribenzoate (TATB); **2**, 2,6-naphthalenedicarboxylate (NDC); **3**, *N,N*′-di-(5-aminoquinoline)-1,4,5,8-naphthalenetetracarboxydiimide (diQuNI); **4**: 4,4′-biphenyldicarboxylic acid (BPDC); **5**–**7**, see text. Zn(II) ions shown as tetrahedra. For clarity, interwoven networks are omitted.

fraction (PXRD) data can then be obtained for both fractions and afterward compared to candidate simulated PXRD patterns. This procedure should be completed within a few hours, that is, before significant solvent exchange with the porous MOFs takes place. Once a solvent of appropriate density is obtained, MOF separation occurs within a few tens of seconds.

Example 1. The 2-fold interpenetrated MOF, $Cu_3(TATB)_2(H_2O)_3$ (**5**; Figure 1), was obtained by reacting $Cu(NO_2)_2 \cdot 3H_2O$ with **1** in DMSO at 120 °C.[7] While capable of yielding pure **5** (diamond-shaped teal crystals), in our hands the method also sometimes produced a mixture of **5** and a second phase consisting of crystalline green needles that analyzed for twice the Cu content of **5**.[8] The mixture of compounds was purified by (a) sonicating, (b) filtering, (c) washing with DMSO, and (d) depositing in a separation funnel, followed by the addition of 1:5 (v:v) DMSO:CH_2BrCl.[9] Within seconds of the addition the teal crystals floated to the liquid surface and the green needles sank (Figure 2). The needles were removed and the procedure was repeated to ensure the purity of the desired top layer. The purified teal crystals were then collected. A single crystal X-ray structure as well as the PXRD pattern of the bulk sample (Figure 2) confirmed that the desired pure product (**5**) had been isolated.

Example 2. A new doubly interwoven, pillared-paddlewheel[10] MOF, $Zn_2(NDC)_2(diQuNI)$ (**6**, yellow crystals), was synthesized by reacting **2**, **3**, and $Zn(NO_3)_2 \cdot 6H_2O$ in diethylformamide (DEF). The crude product, however, was contaminated with a white crystalline material. **6** was purified similarly to **5**, but with a solution
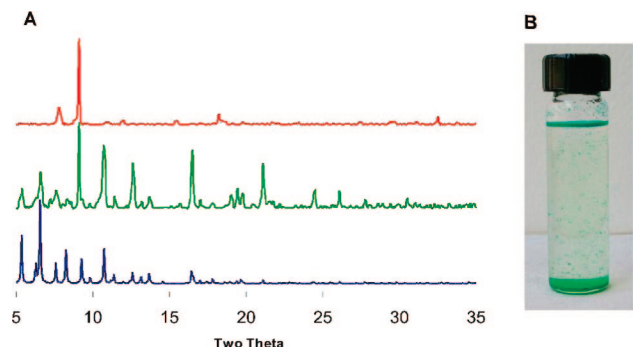
Figure 2. (A) Powder X-ray diffraction for example 1. Structure **5** simulation (bottom), **5** after separation (middle), and green needles impurities (top). (B) Photo of a vial after separation was achieved.
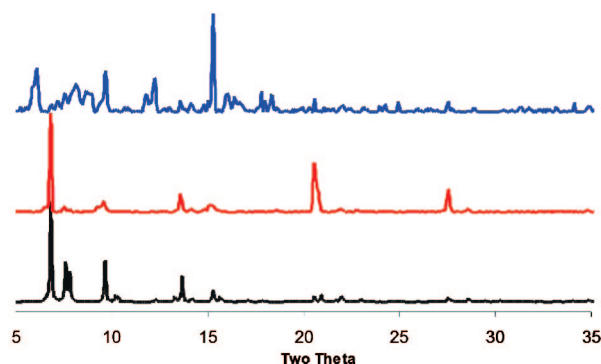

Figure 4. (A) Powder X-ray diffraction for example 3. **7a** simulation (bottom), **7a** after purification (middle), and **7b** (top). The asterisk (∗) indicates that the peak intensity is reduced by 80% in order to elucidate the rest of the spectrum. (B) Photo of vial after separation.

Supporting Information Available: Synthesis and characterization of **3** and **6**, including single crystal X-ray data for **6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org

Figure 3. Powder X-ray diffraction for example 2. Simulation of **6** (bottom), **6** after purification (middle), and white impurities (top).

of 2:5 (v:v) DMF:CH$_2$BrCl. The desired mixed-ligand compound floated while the contaminant sank. PXRD plots for both fractions are shown in Figure 3. The structure of **6** was established by single-crystal X-ray measurements (see Supporting Information). ^{1}H NMR of an acid-dissolved sample of the contaminant established that it contained NDC but not diQuNI; PXRD data are consistent with formation of an NDC-based cubic MOF or MOFs.[11]

Example 3. IRMOF-10 (**7a**, noncatenated structure)[11] was synthesized utilizing **4**, essentially as described by Yaghi et al.,[11] except that DMF replaced DEF as solvent. As is often the case in MOF syntheses, this seemingly minor change had significant consequences: **7a** was contaminated with substantial amounts of IRMOF-9 (**7b**), the 2-fold interwoven analogue of **7a**. The mixture was separated by using a 4:5:26 (v:v:v) solution of CH$_2$Cl$_2$:CHCl$_3$:CH$_2$BrCl. In this solution, IRMOF-10 floated while IRMOF-9 sank (Figure 4). A single-crystal X-ray structure for **7a** has not been reported. The PXRD of the sample, however, closely matches that described in ref . Finally, independently synthesized, pure samples of **7a** and **7b** were intentionally combined and then successfully density-separated.

In summary, rapid separation of mixtures of MOFs can be achieved via a solvent-based density-discrimination method. The method should prove widely applicable to the purification of MOFs. Although not considered here, the method should also be useful for separating MOFs from linear coordination polymers or insoluble metal salts. The only prerequisites are (a) density differences between product and impurities and (b) availability of an appropriate solvent. We believe this tool can substantially benefit those involved in MOF discovery and scale-up chemistry.
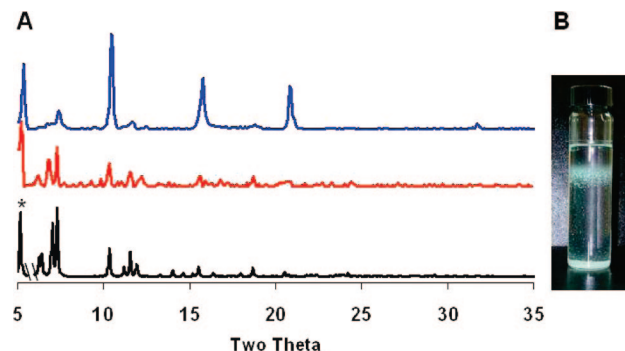
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(8) Yielded by 20 nominally identical reactions were the desired MOF in pure form (3 samples), brown amorphous material (5 samples), and a combination of the 2 crystalline materials in a range of ratios (12).
(9) The solvent composition required for the purification was initially ascertained by using pure CH$_2$BrCl and then adding DMSO until separation was triggered. The density of the solvent should lie between those of the materials to be separated. For verification, the densities of **5** and its impurity were determined via pycnometry and found to be 1.28 and 1.94 g/cm^3, respectively. The density of the solvent mixture was 1.82 g/cm^3.
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JA803097E