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Solvatochromic Behavior of a Nanotubular Metal−Organic Framework for Sensing Small Molecules

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Supporting Information

ABSTRACT: A nanotubular metal−organic framework (MOF), $\{[(WS_4Cu_4)I_2(dptz)_3]\cdot DMF\}_n$ (dptz = 3,6-di-(pyridin-4-yl)-1,2,4,5-tetrazine, DMF = *N,N*-dimethylformamide) for sensing small solvent molecules is presented. When accommodating different solvent molecules as guests, the resulting inclusion compounds exhibit different colors depending on the solvent guests, and more interestingly, the band gaps of these solvent-included complexes are in linear correlation with the polarity of the guest solvents. The solvent molecules can be sensed by the changes of UV−vis spectra of the corresponding inclusion compounds, showing a new way of signal transduction as a new kind of sensor. The sensing by such a MOF occurs within the channel-containing material rather than on the external surface.

Porous metal−organic frameworks (MOFs) composed of metal ions or metal clusters as nodes and multitopic organic ligands as linkers have received considerable attention due to scientific interest in the creation of nanometer-sized spaces and for their potential applications in sensor, separation, gas storage, and catalysis technologies.[1] Besides porosity, pore size and shape, pore-surface functionalization is a key factor for tailoring properties of some materials such as sensors and catalysts.[1a−c] Two strategies can be considered in the functionalization of pore surfaces, one is using functional ligands to introduce guest-accessible functional organic sites on the pore surface (such as using chiral ligands to introduce chiral sites), and another is immobilization of open metal sites (such as for Lewis acid catalysis or specific gas adsorption).[2] As for developing sensing materials, the decisive task is to realize signal transduction; that is, when contacting to an analyte, the material should exhibit specific and detectable changes in refractive index, redox potential, impedance, piezoresistance, or other properties. In the MOF-based cases where sensing has been described, the signal transductions employed luminescence quenching or enhancement after incorporating certain analytes in the pores,[3] but researches of other manners of signal transductions are comparatively few.[4]

In pursuing new sensing materials, we have been attracted by the effect of solvatochromism, which represents a phenomenon where the position or shape of UV−vis−near-IR absorption bands of some organic compounds can be influenced by surrounding environment such as liquid, solid surfaces, etc. The shifts of optical absorption bands of the solvatochromic compounds in different solutions are dependent quantitatively on the polarity of solvents (refer to the overall solvation capability or solvation power).[5] On the basis of the unique solvent dependence, we anticipate that if the solvatochromic effect can be introduced into a solid porous material, a solvent molecule, when entering the cavities, can induce a certain shift of the optical absorption band of the host material, and this material can thus be used as a new type of sensor to probe this solvent molecule by measuring its change in optical absorption spectra.

The solvatochromic porous MOFs are quite few because of the challenge of generating both stable pores and solvatochromism in one material. In the reported cases, the solvatochromism originates from the d−d transitions of metal centers, and strong solvatochromism is always accompanied by large changes in the coordination sphere of metals and the overall structures of MOFs upon changing solvent guests.[6,7] In this work, we designed the use of a solvatochromic organic ligand to construct a porous MOF. This ligand should also be multidentate for generating a high dimensional structure; 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine (dptz) is a good candidate (see Supporting Information). Cu^I was chosen as the metal center, since its filled-shell d^{10} electronic configuration offers opportunities to observe other low-lying electronic transitions.[8] Excitingly, a nanotubular MOF $\{[(WS_4Cu_4)I_2(dptz)_3]\cdot DMF\}_n$ (**1**⊃DMF, DMF = *N,N*-dimethylformamide) is obtained by treatment of dptz with $(NH_4)_2WS_4$ and CuI, which exhibits reversible solvatochromic response upon incorporating different solvent guests by changing into specific colors (shifts of optical adsorption band) with high sensitivity, and the dptz ligand plays an important role in the solvatochromic response of **1**.

X-ray crystallographic analysis of **1**⊃DMF revealed that one WS_4^{2-} dianion chelates four Cu^+ atoms by the S atoms forming a saddle-shaped $WS_4Cu_4^{2+}$ heterothiometallic cluster unit (Figure S1). Each Cu^+ atom is tetrahedrally coordinated and has two coordination sites pointing outward the cluster unit. The overall eight peripheral sites of one $WS_4Cu_4^{2+}$ unit are occupied by two I^- and six dptz molecules (Figure 1a). Ligands between adjacent two $WS_4Cu_4^{2+}$ units are paired up with strong $\pi-\pi$ interactions between tetrazine rings [3.578(2) Å]. The $WS_4Cu_4^{2+}$ units are, acting as tetrahedral nodes, linked by two paired ligands and two single ligands with four adjacent units into a diamondoid network (Figure S2). Six diamondoid networks associate together

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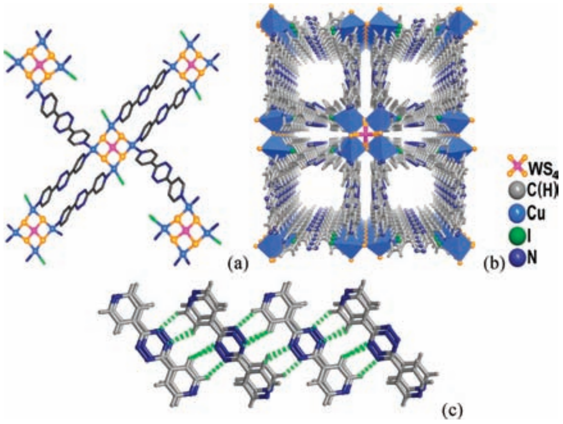

Figure 1. (a) The coordination environment of the $WS_4Cu_4^{2+}$ unit. (b) The perspective view of the nanotubular structure of **1**. (c) Hydrogen bonds between paired ligands of interpenetrated networks (green dashed lines).

with the $WS_4Cu_4^{2+}$ units of each net arranged parallel, forming square-shaped nanotubes along the *c* direction (Figure 1b). Strong C−H···N hydrogen bonds are formed between the paired dptz ligands of the interpenetrated networks with an average C···N distance of 3.291(2) Å (Table S1), which stabilize the overall nanotubular architecture (Figure 1c). The inner cross-section of the nanotube is 5.4 × 5.3 Å taking van der Waals radii into consideration. Highly disordered DMF molecules reside in the tubes.

TG analysis and powder X-ray thermo-diffraction showed that the DMF guests can be removed from **1**⊃DMF at 100 °C, and the resulting solvent-free framework is stable up to 170 °C (see SI). Exchanging DMF guests with more volatile solvent CH_3OH afforded compound **1**⊃CH_3OH, where the CH_3OH guests can be easily removed below 60 °C. **1**⊃CH_3OH can retain its single crystallinity by being heated at 60 °C under vacuum for 10 h, enabling a crystal structure determination for the desolvated compound **1′**. X-ray analysis revealed an intact nanotubular skeleton, but the pore size expands slightly to 5.7 Å × 5.3 Å and the cell volume increases by 1.5%. The C−H···N hydrogen bonds between networks are weakened in **1′** with average C···N distance of 3.371(2) Å.

When the dark red sample **1**⊃DMF was immersed in CH_3CN or $CHCl_3$, the resulting compound **1**⊃CH_3CN changes to bright red color, but **1**⊃$CHCl_3$ changes to totally black. Using other solvents, acetone, H_2O, CH_3OH, and C_2H_5OH, the resulting inclusion compounds change to different colors depending on the solvent guests included. While in solvent THF or DMSO, the porous compound **1** is slowly dissolved. The UV−vis spectra and photographs of these inclusion compounds are shown in Figure 2, the UV−vis absorption bands are well consistent with their colors.

Literature values of Reichardt's solvent polarity[5] parameters E_T^N and band gaps of the solvent-included compounds are incorporated in Table S2. The band gaps show excellent linear correlation with the E_T^N values of solvents (Figure 2, right). The best fits of band gaps against the E_T^N values are obtained by separately plotting nonhydroxylic solvents (slope, 2.989; correlation coefficient, 0.996) and hydroxylic solvents (slope, 0.607; correlation coefficient, 0.977). Such good solvent dependence indicates that **1** can be powerful for sensing these solvents. With the increasing of solvent guests' polarity [$CHCl_3$ < ··· < CH_3CN or C_2H_5OH < CH_3OH < H_2O], the absorption bands are blue-shifted showing a negative solvatochromic effect, and the different dependence of **1** on the hydroxylic and nonhydroxylic solvents should be ascribed to the different hydrogen-bond donor abilities of these two kinds of solvents.[9]

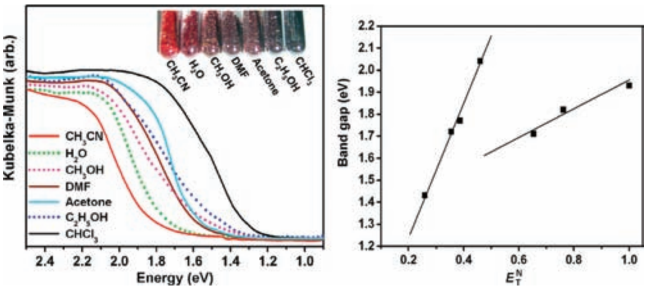

Figure 2. Left: The UV−vis spectra and photograph of the inclusion compounds **1**⊃solvent. Right: Band gaps of the inclusion compounds against the solvent E_T^N values.

To estimate the effect of dptz ligand on the solvatochromic response of **1**, comparing tests were performed with an analogous MOF $\{[WS_4Cu_4(bpy)_4][WS_4Cu_4(bpy)_2I_4]\}_n$, (**2**, bpy = 4,4′-bipyridine), which is similar to **1** in both structure and composition.[10] After the guest exchanging processes with the same solvents used for **1**, the colors and UV−vis spectra of the obtained inclusion compounds **2**⊃solvent revealed that no solvatochromic effect occurred for **2** (see SI). Although the solvatochromism of **1** and dptz ligand originate from different transitions (MLCT transition for **1** and $\pi \rightarrow \pi^*$ transition for dptz), the result indicates that the dptz ligand plays an important role in the solvatochromic response of **1**, which should be ascribed to its strong π-acceptor property and labile electronic structure to solvent polarity.[11]

From compound **1**⊃CH_3CN to **1**⊃$CHCl_3$, the absorption bands are red-shifted up to 245 nm showing very high sensitivity to solvent guests. To determine whether sensing by **1** occurs predominantly within the channel-containing material or instead on the external surface, competitive size selectivity studies were performed. We chose 1,4-dioxane, which has larger size but smaller polarity (E_T^N = 0.146) than DMF (E_T^N = 0.386). Placing crystals **1**⊃DMF in 1,4-dioxane for 5 days, the UV−vis absorption spectrum of the result compound is nearly the same to that of **1**⊃DMF, and the 1,4-dioxane molecules cannot get into the pores to exchange the DMF guest (see SI). These results show that the shift of UV−vis absorption band is mostly based on the solvents within the cavities and the effect of the external surface is negligible. The sieving function of the micropores of **1**, which allows small molecules to go through, while blocking larger ones, will be powerful in distinguishing the molecules having similar polarity but different sizes than the pores.

The sensing of small solvent molecules by the desolvated sample **1′** is much more efficient than by any forms of **1**⊃solvent. **1′** can change to specific colors (UV−vis spectra) within 1 min after being emmersed in different liquid solvents at 15 °C. **1′** also responds to solvent vapors but at a much slower speed. The durability of **1** was tested by measuring the optical absorption spectra of five cycles of **1′** ↔ **1**⊃CH_3OH (immersing and desolvating) and **1**⊃$CHCl_3$ ↔ **1**⊃CH_3OH (solvent exchanging): no significant change in the spectra was observed. Besides sensitivity, selectivity, and reusability, the porous MOF-based material **1** is also stable and does not contaminate the analyte.

In conclusion, we have demonstrated a porous MOF exhibiting solvatochromic response upon incorporating different solvent guests, and the excellent dependence of the optical absorption bands of this compound on the polarity of solvent guests is powerful for sensing these solvent molecules. The coupling of solvatochromism and porosity in a solid material has interesting prospects for the development of new sensing materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental detail, X-ray crystallographic files for **1** and **1′**, further descriptions of the structure for **1** and **2**, photograph of the crystals, PXRD, TGA, and UV—vis spectra of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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