Porous material for absorption and luminescent detection of aromatic molecules in water†

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Received (in Cambridge, UK) 1st December 2005, Accepted 10th February 2006
First published as an Advance Article on the web 27th February 2006
DOI: 10.1039/b517002h

A two-dimensional porous framework, which was formed from neutral discrete hexanuclear copper clusters *via* self-assembly, exhibited highly selective absorption of aromatic molecules in water with special fluorescent response.

Porous compounds have been the focus of recent research interest because of their potential applications in several technological areas such as molecular adsorption and separation processes, heterogeneous catalysis and artificial storage.[1] One of the current challenges in the synthesis of such porous materials is to functionalize them, so that they are suitable for specific host–guest interactions and practical applications.[2,3] The use of molecular metal clusters as building blocks in the assembly of nanometer-sized materials is an attractive synthetic approach, since the structural integrity of the building units can be maintained throughout the reaction, and the desired physical properties can be imparted to solid-state materials.[4] Furthermore, as compared with mononuclear complexes, cluster-based building blocks are larger in size, which is particularly attractive for making porous structures potentially useful for guest recognition and separation. Despite such high expectations, there is very little literature precedent of metal-cluster arrays that are assembled *via* intercluster interactions.[5] In an effort to extend this synthetic approach to the creation of novel cluster-based porous materials and ultimately to explore the properties of such supramolecules, here we report a new luminescent active conceptual nanotubular solid constructed from modules of a hexanuclear copper cluster *via* van der Waals interactions along with its selective absorption of and luminescent response towards aromatic molecules.

Reaction of ligand HL, 5,6-diphenyl-1,2,4-triazine-3-thiol[6] with $Cu(CH_3CN)_4(ClO_4)$ (molar ratio = 1 : 1) in a DMSO solution afforded the corresponding hexanuclear Cu_6S_6 cluster **1** $Cu_6L_6\cdot(H_2O)(DMSO)$ in a high yield.‡ X-ray structure analysis§ indicated that the neutral cluster lay in a special position with crystallographic S_6 symmetry and consisted of six copper(I) centers bridged by six deprotonated ligands (Fig. 1). The center of the cluster can be described as two centro-related chair Cu–S–Cu–S–Cu–S hexagonal rings stacked one above the other. Each copper(I) center was coordinated to two thiolate sulfur atoms and one nitrogen of a triazine ring from three different ligands with Cu–S bond lengths being 2.197(1) and 2.292(1) Å and the Cu–N bond length being 1.991(3) Å. Each ligand coordinated to three copper atoms using a bridging thiolate sulfur atom and a monodentate nitrogen atom and linked the two Cu_3S_3 hexagonal rings together. The shortest Cu–Cu separation of 2.75 Å is shorter than the sum of the van der Waals radii of two copper atoms (2.8 Å), therefore, the cluster **1** had the potential to exhibit critical photophysical properties that were closely related to the increase of copper–copper interaction in the excited state.[7] The six triazine rings belonged to three stacking pairs. The shortest inter-planar atom···atom separation was 3.23 Å with the dihedral angle being 21° for each stacking pair (rings A and B), respectively. The twelve benzene rings spread outside the cluster to give an overall Ferris wheel appearance for constructing porous materials using inter-aromatic interactions.[8]

Each cluster connected three neighbors of the phenyl rings through cooperative intermolecular van der Waals interactions featuring a two-dimensional (6,3) sheet (Fig. 1b) with twelve phenyl rings from three different clusters interacting in a pairwise manner to form the 3-connected nodes. The shortest intercluster

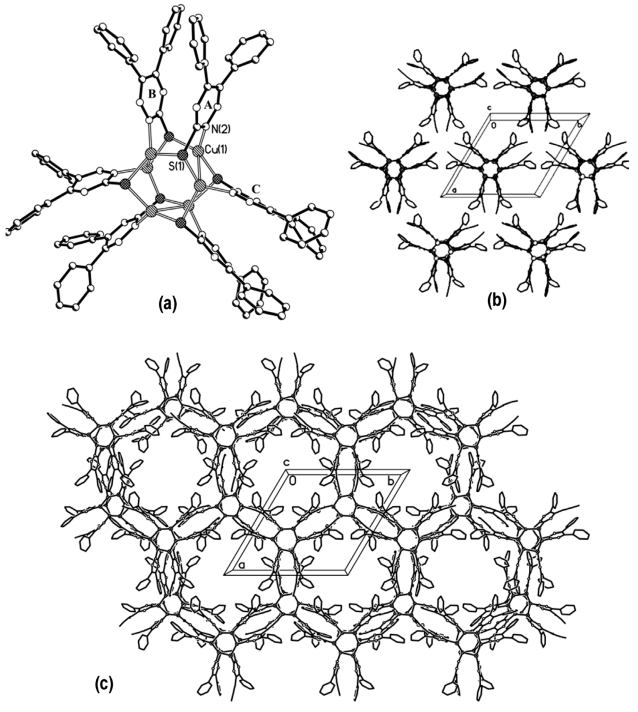

Fig. 1 Molecular structure of hexanuclear copper cluster **1** (a) and the packing pattern of the clusters viewed along the channel axis c showing the intercluster interactions (b) and nanochannels with porous structure (c).

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† Electronic supplementary information (ESI) available: Thermogravimetric analysis of **1**; powder X-ray diffraction pattern of solid **2**; luminescence spectra of solid **2** after absorption of various aromatic molecules; time-dependence of luminescence of solid **2** after absorption of toluene. See DOI: 10.1039/b517002h

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atom–atom separation was 3.45 Å. Adjacent sheets were centrosymmetrical related and stacked in the ···ABAB··· fashion featuring 1D channels with nanometer size (Fig. 1c). The tunnel has a hexagonal shape with the edge about 1.2 nm and a pore with the net inside diameter about 1.2 nm also. The size and shape of the pore were similar to those of the single-walled carbon nanotube. The low calculated density of (ρ_c = 1.17 g·cm^{-3}) compared to that of analogues (ρ_c = 1.5–1.85 g·cm^{-3})[7,9] suggested a porous structure, however, crystallography itself did not prove that the solid behaved as a nanotunnel. The most important factor in seeking and developing new molecular-based porous and tunnel materials is whether the frameworks of such materials are stable even after removal of guest molecules.[1,2]

Thermogravimetric analysis (TGA) of compound **1** revealed a slow weight loss of 4.8% below 150 °C corresponding to the liberation of a DMSO molecule and a water molecule per cluster (calcd. as 4.6%). Over the temperature range of 150–310 °C, almost no weight loss was observed. Beyond this temperature, a weight loss step between 315 °C and 600 °C was observed and attributed to the decomposition of the framework (see ESI). The powder X-ray diffraction pattern of the desolvated solid **2**, which was obtained by drying the crystals under vacuum for 6 h at 120 °C and identified by the elemental analyses and TGA, revealed that the positions of the most intense lines remained unchanged relative to the simulated pattern based upon the single-crystal data of the compound **1**, indicating the tunnel framework was retained in the absence of guest molecules (see supporting material). It is worth noting that although the van der Waals interactions have energies only in the range of 2–20 kJ·mol^{-1}, such interactions have the potential to assemble smaller and simpler fragments into desired cavities under favorable conditions, which is important in host–guest chemistry and has applications in chemistry, biology and materials science.[3]

The desolvated solid **2** has poor solubility in most organic solvents. Putting **2** (50 mg) into 50 mL H_2O, toluene, benzene, n-hexane, cyclohexane, methanol, ethanol and acetone, respectively, and stirring for 6 hours afforded new crystalline solids. Thermogravimetric analysis and elemental analyses suggested that the desolvated solid **2** could absorb benzene and toluene molecules efficiently with the saturated host : guest mole ratio about 1 : 3,[10] but was not able to absorb water, n-hexane or cyclohexane, methanol and ethanol solvents *etc.* It was suggested that the specific π–π stacking and C–H···π interactions focused by the guest aromatic molecules on the channel core provided greater stability and milder absorption conditions than those necessary in the large-cavity systems, as in the case of metal-organic frameworks, thus selectivity for aromatic molecules was achieved. On the basis of X-ray powder diffraction studies, the robust nanotabular porous material did maintain its structural integrity upon removal and selective sorption of guest molecules within the channels, and sorption/desorption cycles could be repeated many times in the porous materials as in conventional zeolites.

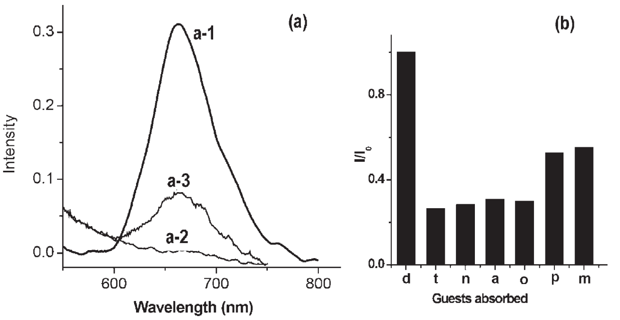

Fig. 2 Luminescence spectra of the desolvated solid **2** (a-1), after immersing it in a toluene solution for 6 h (a-2); and after immersing it in an aqueous solution of toluene (0.5 wt%) for 6 h (a-3); and the relative fluorescence intensity of porous solids that absorbed diverse guests (d: desolvated solid **2**; t: toluene; n: nitrobenzene; a: aniline; o: *o*-dimethylbenzene; p: *p*-dimethylbenzene and m: *m*-dimethylbenzene, respectively) (b).

Generally, Cu_6S_6 clusters exhibit interesting luminescent properties[7] such as high luminescence efficiency and stable luminescence even at higher temperatures. Solid-state absorption of desolvated solid **2** exhibited a broad peak at about 400–500 nm, which was the part of an LMCT (S→Cu) transition overlapped with the intra-ligand absorption.[9] While compound **1** did not exhibit any obvious luminescence in the solid-state, as shown in Fig. 2a, the luminescent spectrum of desolvated solid **2** exhibited a cluster-center (CC) band at 660 nm (excited at 460 nm). The large Stokes shift implied that the configuration coordination mode at the excited state minimum had a large distortion from the ground-state configuration and reflected the strong electron-lattice coupling. Since the critical photophysical properties of the clusters were highly dependent on the Cu–Cu distance within the cluster, emission intensities could be modified by changing the intra-cluster Cu–Cu separation through inclusion of interacting guests. In fact, luminescent measurements (Fig. 2a) of aromatic molecular absorbed powders did not exhibit any obvious luminescence intensities, indicating that aromatic molecules such as benzene and toluene in the porous structure could quench the luminescence of the cluster efficiently. Clearly, the cluster-based porous material should be amenable to absorption and luminescent detection.[11]

To investigate the possible application in sensing aromatic molecules in water, sorption/desorption cycles were repeated using the simulacrum of wastewater (0.5% toluene aqueous solution)[12] to replace pure toluene. Fig. 2a shows the luminescence spectrum of a solid obtained by stirring the desolvated solid in 0.5% toluene aqueous solution for 6 h. The luminescent quenching process clearly demonstrated the absorption of aromatic molecules. TGA measurements exhibited a slow weight loss of about 8.0% below 150 °C which confirmed the presence of toluene molecules. The host : guest mole ratio was 1 : 3 for the saturated sorption solid, which was observed by stirring the desolvated solid in 0.5% toluene aqueous solution for 24 h and identified by the complete quenching of the luminescence. These results indicated that the nanotubular porous material has the potential to separate toluene molecules in water.

Fig. 2b shows the fluorescence intensities of solids that were obtained by stirring the desolvated solid **2** in 0.5% aqueous solution containing various aromatic compounds such as nitrobenzene, aniline, *o*-, *p*- and *m*-dimethylbenzene for 6 h. The presence of the monosubstituted benzene derivatives toluene, nitrobenzene, aniline reduced the luminescent intensity to a quarter of its original level. It seemed that the luminescent quenching was not influenced by the existence of electronic donor or acceptor groups. Meanwhile, the presence of *o*-, *p*- and *m*-dimethylbenzene caused quite different luminescent intensities which suggested that the guest molecule size was not the main factor influencing the quenching process. Probably, the monosubstituted and *o*-dimethylbenzene rings possessed advantageous π–π stacking and C–H···π driving force with the porous backbone on account of their suitable conformations, thus Cu–Cu separation was enlarged and as a result, cluster-center (CC) luminescence of Cu_6L_6 was quenched effectively, while the methyl groups positioned in *p*- and *m*-dimethylbenzene weakened the potential aromatic–aromatic interactions.

Furthermore, the concentration effects and the quantitative response to a fluorescence change upon absorption of guest aromatic molecules were studied. For a 0.5% toluene aqueous solution, while the luminescence was tracked after stirring solid **2** for 6 h, time-dependence investigations demonstrated that the fluorescent intensity could be half quenched after 1.5 h stirring, whereas at a higher concentration level (1%), the fluorescent intensity was half quenched within 1 hour (see supporting material). In comparison, the luminescent signal responded to pure organic solution immediately. Since porous solid **2** is hydrophobic and has a lower density than water, it is quite difficult to immerse and syncretize the solid **2** within the aqueous solution. To maintain the response a number of hours has to be costed for syncretizing the porous solid within the measured solution and at the same time a high concentration level ($\geqslant$ 0.5%) of the aromatic compounds is needed.

In summary, a new strategy to design functional porous material was provided, from which a two-dimensional porous framework which exhibited highly selective absorption of aromatic molecules in water with special fluorescent response was achieved. Investigations to improve the sensitivity, such as the minimization of the concentration limit of aromatic wastes and the time for absorption by employing appropriate technology including depositing the solid in a suitable film are in progress.

This work was supported by the National Natural Science Foundation of China and the Education Ministry of China.

Notes and references

‡ **1**: The ligand HL (0.05 mmol, 0.013 g) and Cu(I)($CH_3CN)_4ClO_4$ (0.05 mmol, 0.016 g) were mixed in DMSO (2 mL). Crystals formed by slow diffusion of diethyl ether into the above solution were filtrated, washed with ether and dried in air. Yield: 86%. Elemental analysis (%) for **1**: calcd for $(C_{15}H_{10}N_3SCu)_6\cdot(C_2H_6SO)\cdot(H_2O)$, C 53.6, H 3.3, N 12.2; found: C 53.8, H 3.5, N 12.0. Uv/vis (diffuse reflectance spectrum λ_{max}): 460 nm. The desolvated powder **2** was obtained by heating the crystalline solid at 120 °C under vacuum for 6 h. Calcd for $C_{15}H_{10}N_3SCu$, C 55.0, H 3.1, N 12.8; found: C 55.3, H 3.3, N 13.0.

§ *Crystal data*: $C_{92}H_{68}Cu_6N_{18}O_2S_7$, Mr = 2063.3, crystallized in the trigonal space group $P\text{-}31c$ with a = 19.861(3) Å, c = 17.094(4) Å, V = 5839.8(17) Å^3, Z = 2, T = 293(K), ρ_{cald} = 1.173 Mg·m^{-3}, μ = 1.244 mm^{-1}, F(000) = 2096. Intensity data were collected on a Bruker CCD system. The structure was solved by direct methods. There were 28149 measured reflections of which 3440 reflections (R_{int} = 0.087) were independent and all are included in the refinement. R_1 = 0.061, wR_2 = 0.163 for 2400 observed reflections with $I \geqslant 2\sigma(I)$, and R_1 = 0.094, wR_2 = 0.179, GOOF = 1.010 for all data. 71 restraints were used in the refinement to constrain the positions and isotropical parameters of the atoms in the disordered phenyl rings and lattice DMSO and water molecules. CCDC 292207. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517002h

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