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A semiconducting microporous framework of Cd6Ag4(SPh)16 clusters interlinked using rigid and conjugated bipyridines†

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Ternary supertetrahedral chalcogenolate clusters were interlinked with bipyridines into a microporous semiconducting framework with properties qualitatively different from those of the original clusters. Both the framework and the clusters were effective photo-catalysts, and rapidly degraded the dye rhodamine B.

Supertetrahedral chalcogenide and chalcogenolate clusters (SCCs) have intriguing structures and size-dependent semiconducting and photocatalytic properties.[1,2] Their tetrahedral structure and multiple coordination sites allow them to assemble into extended and porous semiconductors with properties that are different from those of the individual clusters and related bulk materials. SCCs can be organized into extended frameworks via corner sharing, terminal co-ordination with extra metal ions, or organic linkers.[3–7] Porous zeolite-like chalcogenides have been synthesized from SCCs by corner-sharing S^{2-} groups. They were shown to act as both photo-catalysts and hosts for hydrogen generation from water.[8] An open metal-ion-coordinated framework of $\{Sn[Zn_4Sn_4S_{17}]\}^{6-}$ is a reported example of an ion-exchange material.[9] SCCs interlinked by multi-functional organic linkers are a class of metal–organic frameworks (MOF).[10,11] Feng *et al.* co-assembled imidazoles and In–(Cd)–S SCCs into microporous compounds with relatively high capacities to adsorb CO_2.[12] We present here a ternary chalcogenolate cluster of $Cd_6Ag_4(SPh)_{16}(DMF)_4$ (1) (DMF: *N,N′*-dimethylformamide) and its three-dimensional microporous assembly of $\{[Cd_6Ag_4(SPh)_{16}](bpe)_2\}$ (2) interlinked with rigid bpe (*trans*-1,2-bis(4-pyridyl)ethylene).

The discrete $Cd_6Ag_4(SPh)_{16}(DMF)_4$ cluster 1 was synthesized by reaction of Cd(SPh)₂ and AgNO₃ in a solution of DMF. The organic

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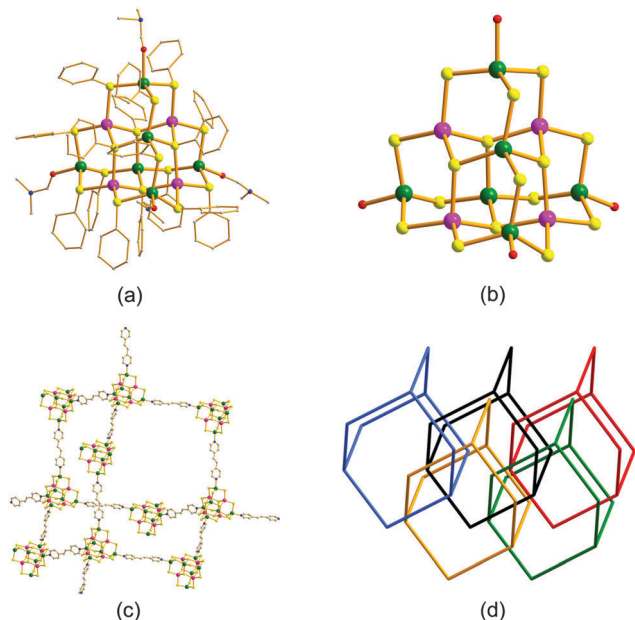
groups surrounding the clusters stabilized the structure and increased their solubility. Cluster 1 was soluble in DMF, slightly soluble in dimethyl sulfoxide (DMSO), and insoluble in other common solvents. Further reactions of cluster 1 most probably ligated its terminal Cd atoms with the nitrogen donors of the bpe linker in DMF to afford the microporous framework 2. Large crystals of both the cluster 1 and the microporous framework 2 crystallized upon the slow evaporation of DMF and were structurally determined by single-crystal X-ray diffraction. Cluster 1 showed a supertetrahedral (T3) structure with ten metal centers (six Cd, four Ag) coordinated with four terminal DMF, six μ_2-SPh, and four μ_3-SPh ligands. The μ_3-SPh ligand was not previously observed in SCCs. Balancing the charge of the neutral cluster suggests the presence of six Cd(II) and four Ag(I). The composition was confirmed by energy-dispersive X-ray spectroscopy, which gave a Cd : Ag : S atomic ratio of 6.4 : 4 : 16.2 (Fig. S1, ESI†). Cd(II) and Ag(I) are isoelectronic; therefore, their relative positions within the clusters cannot be determined by X-ray diffraction. Their positions were instead inferred by applying Pauling's electrostatic rule.[13] Each μ_3-SPh site within the cluster gave a bond valence of 1 when surrounded by two Ag(I) and one Cd(II). Therefore, the four Ag atoms were present in the core of the cluster in three possible arrangements (Fig. S2, ESI†). The Cd atoms were located in the two residual internal sites and the four terminal metal sites. This arrangement of metal atoms in the cluster was consistent with those of several other heterometallic SCCs that have metal atoms/ions of low valence deep within their structures.[14–16] The structure of the crystallized cluster 1 was solved with one possible arrangement for the inner Cd and Ag atoms (Fig. 1a and b). The microporous framework 2 crystallized in the tetragonal space group $I4(1)/a$. In the structure of the microporous framework 2, each cluster 1 was ligated four times via coordination of the terminal Cd atoms by the nitrogen donors of the rigid bpe ligands. The microporous framework 2 had a three-dimensional structure with a diamond topology that belonged to the *dia* net.[17] Fig. 1d shows five interpenetrated single frameworks within two layers in 2. Such interpenetrated arrangements are common in MOFs and covalent organic frameworks, particularly those with diamond topologies.[10,18,19]

Interpenetration generates small pores that are suitable for enhanced CO_2 adsorption from dilute gas mixtures.[20] The large voids

Fig. 1 (a) Molecular and (b) core structures of cluster 1 $Cd_6Ag_4(SPh)_{16}(DMF)_4$ showing one possible arrangement of silver atoms. Hydrogen atoms are omitted for clarity. Green, Cd; pink, Ag; yellow, −SPh; red, oxygen; blue, nitrogen; grey, carbon. (c) Non-interpenetrated visualization of the framework 2 $\{[Cd_6Ag_4(SPh)_{16}](bpe)_2\}$ based on clusters 1 interlinked by trans-1,2-bis-(4-pyridyl)ethylene (bpe). (d) Actual five-fold interpenetration that occurred in the three-dimensional frameworks of the semiconducting microporous framework 2 based on the clusters and the **bpe** linkers.

of 20 × 24 Å in a hypothetical non-interpenetrated version of the framework of 2 became occupied almost fully by the interpenetrations, leaving only very small pores. The porosity was determined by measuring CO_2 adsorption. The microporous framework 2 could adsorb CO_2 at 11.95 cm^3 g^{-1}; its specific surface area (S_{BET}) was moderate (186 m^2 g^{-1} at 1 atm and 273 K). These values are comparable with the somewhat related compound SCIF-3.[12] An ultramicroporous network of 6–8 Å pores was calculated for 2 using density functional theory and the CO_2 adsorption data (Fig. 2).

Heterometallic clusters are also promising precursors for the preparation of ternary nanocrystals such as $CuInS_2$ and $CuInSe_2$, which are efficient materials for solar cells.[21] Interestingly, hybrid crystals of CdS–Ag formed upon the thermal decomposition of cluster 1 at 500 °C in a N_2 atmosphere. (A diffraction pattern is shown in Fig. S3, ESI†) The cluster was thermally stable, showing a decomposition temperature of 320 °C; the microporous framework 2 was less stable due to the **bpe** (Fig. S6, ESI†). Selective control of the decomposition might allow cluster 1 to produce a ternary $Cd_xAg_{2-2x}S$ compound.[22] Further study of the decomposition of clusters such as 1 might yield new means to prepare hybrid or ternary semiconductors.

The microporous framework 2 showed much greater absorption in the visible range during solid-state UV/vis spectroscopy than did either starting material, $Cd(SPh)_2$ or cluster 1 (Fig. 3). The red shift is interpreted as a combined effect that arose from the proximity of the clusters and their interlinking by **bpe**. The microporous framework showed broad absorption at wavelengths of 200–600 nm, with a maximum at 305 nm and a shoulder peak at 420 nm. The high-energy absorption peak was assigned to the ternary clusters and the
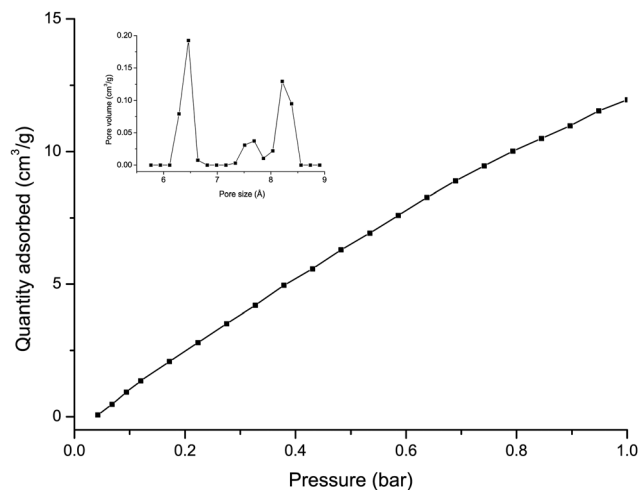

Fig. 2 CO_2 adsorption isotherm of the microporous semiconducting framework 2 $\{[Cd_6Ag_4(SPh)_{16}](bpe)_2\}_n$, recorded at 273 K. The inset shows the pore size distribution of 2 derived using density functional theory and the CO_2 adsorption isotherm.
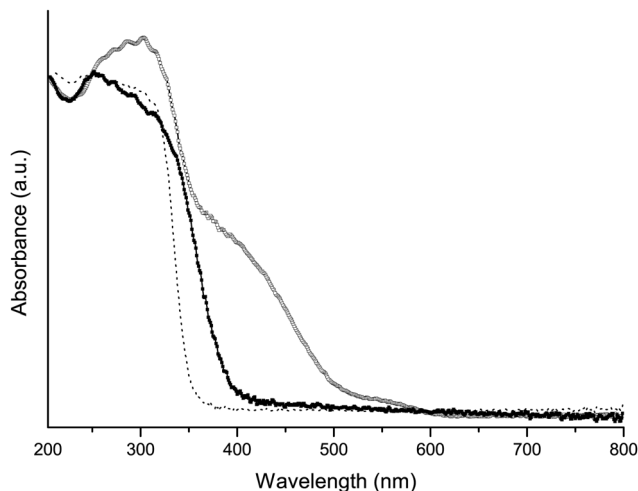

Fig. 3 Solid-state UV/vis absorption spectra of starting material $Cd(SPh)_2$ (dashed), cluster 1 $[Cd_6Ag_4(SPh)_{16}(DMF)_4]$ (■), and microporous framework 2 $\{[Cd_6Ag_4(SPh)_{16}](bpe)_2\}_n$ (□).

charge transfer from SPh^- to Cd^{2+} or Ag^+; the lower-energy shoulder peak was assigned to charge transfer between the conjugated **bpe** linkers and the clusters. The shoulder absorption peak was reduced in intensity when the framework was dispersed in DMF (not shown). The spectrum of the precursor $Cd(SPh)_2$ was typical for a semiconducting material with a polymeric structure of $[Cd_4(SPh)_8]_n$. Its absorption onset at 352 nm (3.52 eV) was consistent with the work of Liu et al.[23] The absorption spectrum of cluster 1 with its ten metal centers was red-shifted to higher wavelengths compared with the spectrum of the precursor (absorption onset 390 nm, 3.18 eV). The red shift was expected and rationalized by quantum confinement effects.[24] The value of the absorption onset for cluster 1 was similar to that of a related compound $[Cd_{10}S_4(SPh)_{12}]$ with the same number of d^{10} centers.[25]

Given the wide bandgap and the strong visible absorption shown by cluster 1 and microporous framework 2, both are expected to be active photocatalysts. Fig. 4 shows the removal of aqueous rhodamine B (RhB)
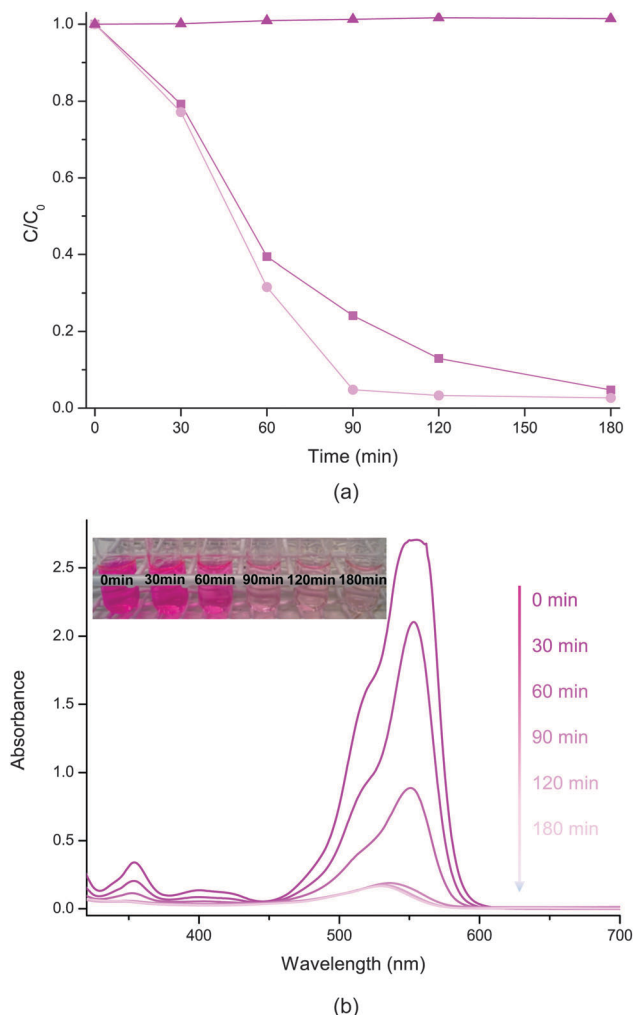
Fig. 4 (a) Decay of RhB concentration calculated from UV/vis absorbance at 555 nm, photocatalyzed by (■) cluster 1 – [Cd$_6$Ag$_4$(SPh)$_{16}$(DMF)$_4$], (●) microporous framework 2 – {[Cd$_6$Ag$_4$(SPh)$_{16}$(bpe)$_2$]$_n$, and also (▲) without catalyst; (b) UV/vis spectra and color images showing the decomposition of aqueous rhodamine B (4.2 × 10^{-5} M) photocatalyzed by the microporous framework 2.

after illumination. The clusters 1 reduced the dye concentration by 95% after illumination for 180 min. An aqueous dispersion of the microporous framework 2 was an effective photocatalyst; it reduced the concentration of RhB by 95% after illumination for 90 min. The improved photocatalytic activity of the microporous framework might be attributable to its hybrid structure and broad visible absorption, which facilitate the efficient use of incoming energy for the degradation. The photocatalytic performances of both 1 and 2 are comparable to some good photocatalysts for degradation of RhB, such as nanosized Bi$_2$WO$_6$.[26] Films of the microporous framework might be better photocatalysts than the dispersed sample due to their further enhanced visible absorption. A blank experiment without any catalyst showed no degradation. The characteristic adsorption band for RhB at 555 nm was chosen for observation of the photocatalytic degradation. The intensity of this band was reduced during successive illumination in the presence of catalysts, and the red solution quickly faded to pale pink (Fig. 4). The degradation of RhB can be explained by either the destruction of its conjugated structure or by deethylation.[27]

The wavelength of the intensity maximum (λ_{max}) was slightly blue-shifted (from 555 to 529 nm) upon successive illumination, indicating the destruction of the conjugated structure of RhB.

To conclude, a ternary chalcogenolate cluster with a supertetrahedral structure was synthesized and assembled into a solid, porous framework with diamond topology and five-fold interpenetration. The rigid linker **bpe** aided the formation of a three-dimensional, porous structure, and likely contributed to the emergence of new properties in the framework, leading to a significant red shift of the absorption of the porous framework. Both the cluster 1 and the microporous framework 2 displayed wide band gaps, and were effective photocatalysts under illumination by visible light. We expect that similar clusters and linkers can be crystallized from solutions of DMF into potentially useful structures such as semiconducting films.

Notes and references

1 H. Li, A. Laine, M. O'Keeffe and O. M. Yaghi, *Science*, 1999, **283**, 1145–1147.
2 P. Feng, X. Bu and N. Zheng, *Acc. Chem. Res.*, 2005, **38**, 293–303.
3 H. Li, J. Kim, T. L. Groy, M. O'Keefe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 4867–4868.
4 M. Yaghi, Z. Sun, D. A. Richardson and T. L. Groy, *J. Am. Chem. Soc.*, 1994, **116**, 807–808.
5 P. Vaqueiro and M. L. Romero, *J. Am. Chem. Soc.*, 2008, **130**, 9630–9631.
6 N. Zheng, X. Bu, J. Lauda and P. Feng, *Chem. Mater.*, 2006, **18**, 4307–4311.
7 J. Xie, X. Bu, N. Zheng and P. Feng, *Chem. Commun.*, 2005, 4916–4918.
8 N. Zheng, X. Bu, H. Vu and P. Feng, *Angew. Chem., Int. Ed.*, 2005, **44**, 5299–5303.
9 M. J. Manos, R. G. Iyer, E. Quarez, J. H. Liao and M. G. Kanatzidis, *Angew. Chem., Int. Ed.*, 2005, **44**, 3552–3555.
10 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keefe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319–330.
11 S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334–2375.
12 T. Wu, R. Khazhakyan, L. Wang, X. Bu, S.-T. Zheng, V. Chau and P. Feng, *Angew. Chem., Int. Ed.*, 2011, **50**, 2536–2539.
13 L. Pauling, *J. Am. Chem. Soc.*, 1929, **51**, 1010–1026.
14 S. Dehnen and M. K. Brandmayer, *J. Am. Chem. Soc.*, 2003, **125**, 6618–6619.
15 W. Su, X. Huang, J. Li and H. Fu, *J. Am. Chem. Soc.*, 2002, **124**, 12944–12945.
16 D. F. Back, G. N. M. De Oliveira, R. A. Burrow, E. E. Castellano, U. Abram and E. S. Lang, *Inorg. Chem.*, 2007, **46**, 2356–2358.
17 M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782–1789.
18 B. Kesanli, Y. Cui, M. R. Smith, E. W. Bittner, B. C. Bockrath and W. Lin, *Angew. Chem., Int. Ed.*, 2005, **44**, 72–75.
19 F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klöck, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 4570–4571.
20 J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477–1504.
21 S. L. Castro, S. G. Bailey, R. P. Raffaelle, K. K. Banger and A. F. Hepp, *Chem. Mater.*, 2003, **15**, 3142–3147.
22 J. Chaturvedi, S. Singh, S. Bhattacharya and H. Nöth, *Inorg. Chem.*, 2011, **50**, 10056–10069.
23 Y. Liu, F. Boey, L. L. Lao, H. Zhang, X. Liu and Q. Zhang, *Chem.–Asian J.*, 2011, **6**, 1004–1006.
24 V. N. Soloviev, A. Eichhöfer, D. Fenske and U. Banin, *J. Am. Chem. Soc.*, 2001, **123**, 2354–2364.
25 M. Bendova, M. Puchberger and U. Schubert, *Eur. J. Inorg. Chem.*, 2010, 3299–3306.
26 H. Fu, C. Pan, W. Yao and Y. Zhu, *J. Phys. Chem. B*, 2005, **109**, 22432–22439.
27 P. Lei, C. Chen, J. Yang, W. Ma, J. Zhao and L. Zang, *Environ. Sci. Technol.*, 2005, **39**, 8466–8474.