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

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Ternary supertetrahedral chalcogenolate clusters (SCCs) interlinked by multi-ordination with extra metal ions, or organic linkers. 3–7 Porous nized into extended frameworks individual clusters and related bulk materials. SCCs can be orga-
ized 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 S₆ groups. They were shown to act as both photocatalysts and hosts for hydrogen generation from water. 3 Each metal-ion-coordinated framework of [Sn₂(Zn₂Sn₆S₁₃)]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 (MOFs). 10,11 Feng et al. co-assembled imidazoles and In(–Cd)–S SCCs into microporous compounds with relatively high capacities to adsorb CO₂. 12 We present here a ternary chalcogenolate cluster of Cd₆Ag₄(SPh)₁₆(DMF)₄ (1) (DMF: N,N′-dimethylformamide) and its three-dimensional microporous assembly of [Cd₆Ag₄(SPh)₁₆(bpe)₄] (2) interlinked with rigid bpe (trans-1,2-bis(4-pyridyl)ethylene).

The discrete Cd₆Ag₄(SPh)₁₆(DMF)₄ cluster 1 was synthesized by the reaction of Cd(SPh)₂ and AgNO₃ in a solution of DMF. The organic 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 µ₃-SPh, and four µ₁-SPh ligands. The µ₃-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 µ₁-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. 18,19

Interpenetration generates small pores that are suitable for enhanced CO₂ adsorption from dilute gas mixtures. 20 The large voids
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 CO2 adsorption. The microporous framework 2 could adsorb CO2 at 11.95 cm³ g⁻¹; its specific surface area (S_BET) was moderate (186 m² g⁻¹ at 1 atm and 273 K). These values are comparable with the somewhat related compound SCIF-3. An ultramicroporous network of 6–8 Å pores was calculated for the three-dimensional frameworks of the semiconducting microporous framework 2 based on the clusters and the bpe linkers.

Heterometallic clusters are also promising precursors for the preparation of ternary nanocrystals such as CuInS2 and CuInSe2, which are efficient materials for solar cells. Interestingly, hybrid crystals of CdS–Ag formed upon the thermal decomposition of cluster 1 at 500 °C in a N2 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 CdAg2–xS compound. 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 charge transfer from SPh⁻ to Cd²⁺ 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(SPh)]ₙ. Its absorption onset at 352 nm (3.52 eV) was consistent with the work of Liu et al. 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. The value of the absorption onset for cluster 1 was similar to that of a related compound [Cd₁₀S₄(SPh)₁₂] with the same number of d⁰ centers.

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)
The wavelength of the intensity maximum ($\lambda_{\text{max}}$) 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.

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Notes and references