Halide enhancement of the luminescence of $Cd_{10}S_4$ thiolate clusters

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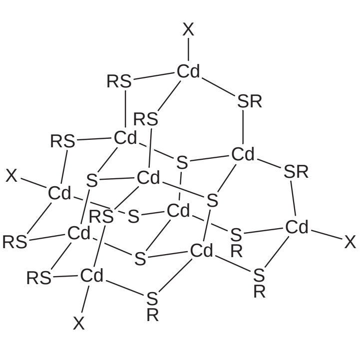
New halide-substituted cluster anions $[Cd_{10}S_4X_4(SR)_{12}]^{4-}$ (R = Ph, X = I, 2a; R = *p*-MeC_6H_4, X = I, 3a or Br, 3b) of the $[Cd_{10}S_4(SR)_{16}]^{4-}$ family have been prepared and characterized; investigations of their luminescence show that the introduction of the halide groups produces red shifts and significant enhancements in their emission intensities.

Semiconductor quantum dots are colloidal semiconductor particles, *ca.* 10–200 Å in diameter, that exhibit interesting optoelectronic properties due to quantum confinement of photogenerated electron–hole pairs.[1] Synthetic challenges in the field include narrowing the size distribution of the particles, and effective capping of surface atoms. A ‘bottom-up’ approach to the synthesis of well defined quantum dots begins with molecular clusters based on a semiconductor core.[1a] For CdS, one of the most studied quantum dot materials, molecular clusters having 10, 17 and 32 cadmium atoms in the core have been synthesized.[2] Here, we report the synthesis, crystallographic and spectroscopic characterization of new halide substituted molecular clusters derived from the $Cd_{10}S_4(SR)_{12}$ core. The halide ligands profoundly affect the spectral distribution and intensity of the observed photoluminescence relative to that of the parent cluster anion $[Cd_{10}S_4(SPh)_{16}]^{4-}$ **1**.

The new cluster anions $[Cd_{10}S_4X_4(SR)_{12}]^{4-}$ (R = Ph, X = I, **2a**; R = *p*-MeC_6H_4, X = I, **3a** or Br, **3b**) were synthesized by a modification of the procedure used for the synthesis of the parent $[Cd_{10}S_4(SPh)_{16}]^{4-}$.[2b]† The structures of **3a** and **3b** were determined crystallographically as their NEt_4 salts,‡ and an ORTEP diagram of **3b** is shown in Fig. 1. The cluster has S_4 symmetry and the $[Cd_{10}S_4(SR)_{12}]$ core of **3a** and **3b** is similar to those of the parent **1**.[2b]

The principal difference between **3a**,**b** and **1** is the presence of a terminally coordinated halide ligand on each of the four external cadmium atoms of the cluster.

The compounds are colorless to pale yellow, and the principal features in the UV–VIS spectra are intraligand bands at 250–300 nm.[3] The tetramethylammonium salt of the parent cluster **1** has been reported to show weak broad luminescence at *ca.* 530–550 nm in acetonitrile.[4] Under our conditions the parent cluster **1** emits broadly at *ca.* 430 nm. Interestingly, the halide clusters **2a, 3a** and **3b** show considerably more intense emission, readily visible to the naked eye under ultraviolet illumination, with apparent maxima at *ca.* 490 and 540 nm (Fig. 2). For **3b**, emission spectra were also acquired on a single crystal taken from the diffractometer and was found to be identical to that taken in DMSO solution. For all compounds, the excitation spectra had maxima in the range 350–390 nm, lying in the absorption tail of the much more prominent intraligand bands.



R = Ph; X = SPh, **1** or I, **2a**
R = C_6H_4Me-*p*; X = I, **3a** or Br, **3b**

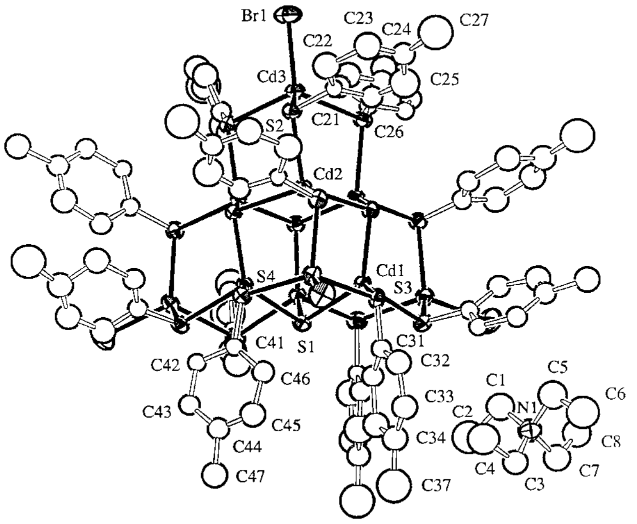


Fig. 1 An ORTEP diagram of the molecular structure of $[NEt_4]_4[Cd_{10}S_4(SC_6H_4Me\text{-}p)_{12}Br_4]$, **3b**.

The existence of multiple excited states, the domination of observed broad emission by a low-lying state with low oscillator strength, and the large Stokes shift have been documented in the case of a Cd_{32} cluster, and it was speculated that its *ca.* 500 nm emitting state was an intrinsic charge transfer state within the cluster.[2e] Calculations of the ground and excited states of the related Cd_4 cluster $[Cd_4(SPh)_{10}]^{2-}$ suggest that the lowest energy transition in this molecule is more localized, a

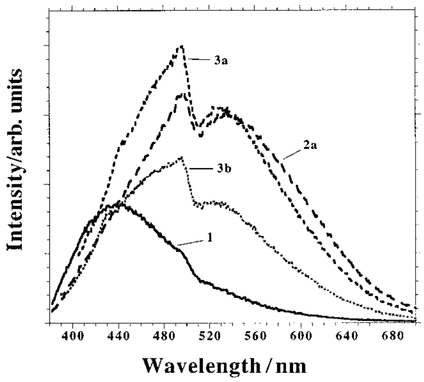


Fig. 2 Uncorrected emission spectra of 1.7 × 10^{-3} M **1**, 1.7 × 10^{-3} M **2a**, 1.6 × 10^{-3} M **3a** and 1.8 × 10^{-3} M **3b** in DMSO solution at room temperature. To ensure sample purity, single crystals of each compound, characterized by X-ray diffraction, were dissolved in DMSO and data was acquired within hours of dissolution. The excitation wavelengths employed were the maxima for each compound: 350 nm for **1**, 360 nm for **2a,** 380 nm for **3a** and 390 nm for **3b**. All other parameters were identical.

mixture of thiolate to Cd 5s ligand-to-metal charge transfer (LMCT) and intraligand charge transfer bands.[5] The sizes of Cd_{10} clusters reported here are in between these; time-resolved spectroscopy experiments are in progress to elucidate the details of the electronic structure of the halide–Cd_{10} clusters.§

Copper(I) halide clusters of the type $Cu_4X_4L_4$ also show complex emission spectra, and *ab initio* calculations have demonstrated that the two observed emissive states are likely halide-to-ligand charge transfer and 'cluster-centered' states; the cluster-centered states are a complex mixture of halide-to-metal charge transfer and metal-centered states.[6] For some of the compounds in this series, the emission spectra are insensitive to the nature of the halide, which was rationalized on the basis of competing trends in halogen electronegativities and ionization energies.[6] In these Cu_4 clusters, the electronic states of the halide are crucial to the photoluminescence of the cluster. Our results clearly demonstrate that halide ligands produce a strong enhancement in the intensity of photoluminescence from the excited states of our Cd_{10} clusters.

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Notes and references

† *Synthesis* of $[NEt_4]_4[Cd_{10}S_4I_4(SC_6H_4Me\text{-}p)_{12}]\bullet 2H_2O$ **3a**: $Cd(NO_3)_2\bullet 4H_2O$ (0.767 g) in MeOH (15 mL) was added to a solution of *p*-thiocresol (0.943 g) and triethylamine (1.146 mL) in methanol (15 mL) at 25° C. Then NEt_4I (0.474 g) in MeOH (15 mL) was added. After all the precipitate had dissolved, the solvent was removed *in vacuo*. The residue was dissolved in acetonitrile (35 mL) and powdered sulfur (0.048 g) was added to the clear solution at 25 °C. This reaction was complete in < 2 min. Isolated yield (24% based on Cd). ^{113}Cd NMR (CD_3CN) δ 559.54 (6 Cd), 434.28 (4 Cd). Anal. Calc: C, 36.71; H, 4.46; N, 1.48. Found: C, 37.12; H, 3.90; N 1.70%. Compound **2a** was prepared similarly using benzenethiol in place of *p*-thiocresol. Compound **3b** was prepared similarly to **3a** by substituting NEt_4Br for NEt_4I. For **3b**: ^{113}Cd NMR (CD_3CN) δ 560.86 (6 Cd), 411.57 (4 Cd).

‡ The compounds $[NEt_4]_4[Cd_{10}S_4I_4(SC_6H_4Me\text{-}p)_{12}]\bullet 2H_2O$ **3a** and $[NEt_4]_4[Cd_{10}S_4Br_4(SC_6H_4CH_3)_{12}]$ **3b** both crystallize in the tetragonal crystal system: space group $P\bar{4}2_1c$. For **3a**: M = 3795.31, $a = b$ = 20.1542(8) Å, c = 18.7192(5) Å, Z = 2, 1545 reflections, R = 0.048, λ = 0.71069 Å, D_c = 1.61 g cm^{-3}, μ(Mo-Kα) = 23.71 cm^{-1}, T = 293 K. For **3b**: M = 3571.27, $a = b$ = 20.3321(6) Å, c = 18.9573(7) Å, Z = 2, 1524 reflections, R = 0.051, λ = 0.71069 Å, D_c = 1.56 g cm^{-3}, μ (Mo-Kα) = 26.84 cm^{-1}, T = 293 K. Anion **1** was also characterized crystallographically in the form of its NEt_3H salt: space group $P\bar{4}2_1c$. For $[NEt_3H][Cd_{10}S_4(SC_6H_5)_{16}]$, **1**: M = 3489.89, $a = b$ = 20.3001(3) Å, c = 18.0263(5) Å, Z = 2, 2084 reflections, R = 0.040, λ = 0.71069 Å, D_c = 1.56 g cm^{-3}, μ(Mo-Kα) = 17.27 cm^{-1}, T = 293 K. CCDC 182/1147.

§ The smallest CdS molecular cluster that has been reported to be emissive is $[Cd_4(SC_6H_4NO_2)_{10}]^{2-}$, which emits at 500 nm, albeit with a lifetime of *ca.* 200 ps or shorter; the transition has been assigned as a cluster-to-nitrobenzene charge transfer. D. I. Yoon, D. C. Selmarten, H. Lu, H.-J. Liu, C. Mottley, M. A. Ratner and J. T. Hupp, *Chem. Phys. Lett.*, 1996, **251**, 84. For the NMe_4 salt of **1** the emissive state has been assigned as metal-to-ligand charge transfer; see ref. 4*a*. Ref. 4*a* also reports very weak emission from $[Cd_4(SC_6H_5)_{10}]^{2-}$, with a wavelength maximum at *ca.* 500 nm and a lifetime of *ca.* 400 ps.

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