

## Spectroscopic and photophysical studies of apparent cluster-to-organic-acceptor charge transfer in a molecular cadmium sulfide assembly

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### Abstract

A nitrobenzene (NB) decorated cadmium sulfide cluster,  $[\text{Cd}_4(\text{S-NB})_{10}][\text{N}(\text{CH}_3)_4]_2$ , has been prepared and examined spectroscopically. The assembly exhibits an intense cluster-to-attached-acceptor charge-transfer band at 376 nm. Observation of back electron transfer (nitrobenzene to cluster) via time resolved luminescence yields a rate constant of  $\geq 5 \times 10^9 \text{ s}^{-1}$ . Raman studies show that seven vibrational modes are coupled to the electron transfer reaction and that those exhibiting the greatest initial-state/final-state displacements are the Cd–S and N–O stretches. Despite the activity of  $\nu_{\text{Cd-S}}$ , however, the electron donor is more appropriately characterized as an individual sulfur atom, rather than a delocalized assembly.

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### 1. Introduction

Light-induced charge transfer (CT) from nanocrystalline semiconductor particle dispersions or films to molecular acceptors forms an integral part of potential or emerging energy conversion strategies [1–3] and water decontamination strategies [4–6]. Generally these strategies involve semiconductor band-gap excitation, followed by charge separation via surface localization and ultimately, interfacial hole (valence band) or electron (conduction band) transfer [1–6]. Here we describe in preliminary terms an alternative *direct* study of CT between a cad-

mium sulfide based cluster and a covalently attached molecular acceptor (nitrobenzene). (We note the existence of prior studies involving metal chalcogenide cluster to methyl viologen CT (weak outer-sphere CT between ion-paired species [7,8]) and metallo-cyanide to titanium dioxide CT (colloidal particles exhibiting bulk electronic properties) [9–11].) The system examined here,  $\text{Cd}_4(\text{S-NB})_{10}^{2-}$  (**1**) (S–NB is the 4-nitrothiophenolate anion), is a simple derivative of  $\text{Cd}_4(\text{SC}_6\text{H}_5)_{10}^{2-}$  (**2**). Synthesis of the latter has been described by Dance et al. [12]. Cluster **2** (and by inference, **1**) is among the smallest of several well-defined cadmium/sulfur (thiolate) clusters [12–16] and is the smallest to feature the adamantanoid structure of bulk cadmium sulfide. Much of the current interest in small clusters centers on optical manifestations of ‘quantum confinement’ phe-

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nomena<sup>2</sup> [18–21], where the magnitudes of the phenomena are necessarily cluster size dependent. Quantum confinement should also play a role in CT processes. In any case, covalent attachment of the acceptor to the cadmium sulfide cluster leads to intense donor–acceptor CT absorption. The high absorption intensity, in turn, provides a basis for weak, but detectable, CT emission, and for the exploitation of other informative spectral methods.

## 2. Experimental

Compound **1** was synthesized as the tetramethylammonium salt by using Dance's method for **2** [6], except that (a) 4-nitrothiophenol (recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–hexanes) was used in place of thiophenol, and (b) the reaction mixture (methanol solution) was heated to boiling to enhance solubility. The crude product was purified by recrystallization from CH<sub>3</sub>CN; yield: 63%. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN)  $\delta$ : 7.64 (d,  $J = 9.0$  Hz, 20H), 7.44 (d,  $J = 9.0$  Hz, 20H), 3.05 (s, 24H). FAB mass spectrum (*m*-NBA, *m/e*): 2065 [(M–[(CH<sub>3</sub>)<sub>4</sub>N]<sup>2+</sup>)]<sup>2–</sup> (8), 1835 (15), 1415 (100). Elemental analysis calculated for C<sub>68</sub>H<sub>64</sub>N<sub>12</sub>O<sub>20</sub>S<sub>10</sub>Cd<sub>4</sub>: C, 38.20; H, 3.09; N, 7.89. Found: C, 38.17; H, 3.01; N, 7.86.

Resonance Raman measurements were made on a combination double monochromator/spectrograph (Spex Triplemate 1877) featuring a 1-in. UV-enhanced CCD camera (Spex Spectrum One) as detector. The excitation source was a Coherent Innova 400 Ar<sup>+</sup> laser whose output was typically attenuated to ca. 100 mW. Optically dilute samples were examined in methanol as solvent by using a windowless flow cell. Care was taken in the Raman experiments to ensure that neither thermal nor photochemical sample degradation occurred. While **1** was found to be unstable with respect to deep UV irradiation, it proved remarkably photochemically robust during both near-UV and visible region irradiation.

Electronic absorption spectra were obtained with a CARY 14 spectrometer, which had been rebuilt and computerized by OLIS. Stark spectra were obtained with the CARY 14 spectrometer by using a power supply and detection scheme patterned after that described by Boxer [22]. Stark samples were examined in a 1:5 (v/v) CH<sub>3</sub>CN–methyltetrahydrofuran glass (77 K) contained in a cell constructed with Kapton spacers and fluorine-doped SnO<sub>2</sub> coated glass. Corrected emission spectra were collected in methanol with a PTI-QM2 spectrofluorimeter. Time-resolved emission measurements were made by single photon counting methods, based on excitation at 380 nm with the frequency-doubled output of a mode-locked Ti:sapphire laser.

Electrochemical measurements (cyclic voltammetry) were made in methanol in a standard three-electrode cell by using a PAR 273 potentiostat. Potentials are reported vs. SCE.

## 3. Results and discussion

Fig. 1 compares electronic absorption spectra for **1** and **2** in methanol as solvent. The pertinent features are (a) a far-UV absorption (common to both) that we assign to overlapping sulfur-to-cadmium CT

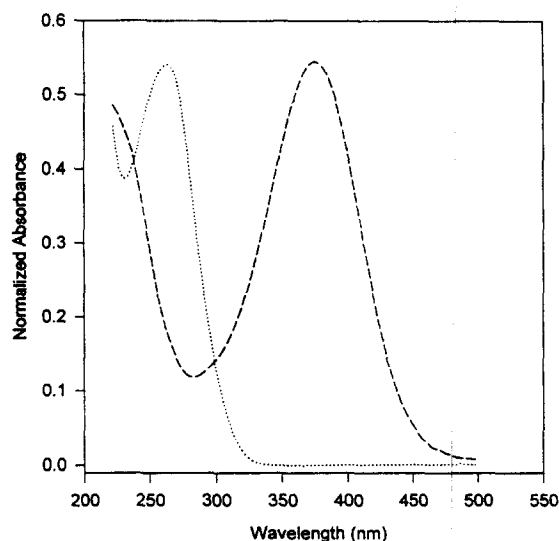
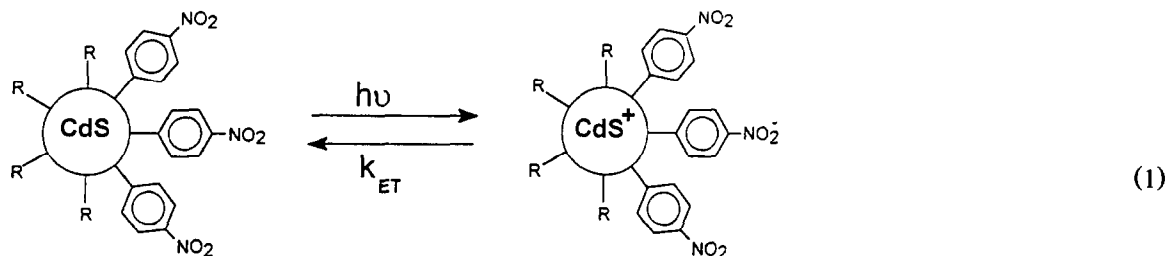


Fig. 1. Electronic absorption spectra for Cd<sub>4</sub>(SC<sub>6</sub>H<sub>5</sub>)<sub>10</sub><sup>4–</sup> (---) and Cd<sub>4</sub>(S–NB)<sub>10</sub><sup>4–</sup> (—) in methanol as solvent.

<sup>2</sup> A quantum confinement description implies the existence of electronic band structure. The smallest thiolate-capped cluster clearly displaying such structure is apparently Cd<sub>20</sub>S<sub>13</sub>(SC<sub>6</sub>H<sub>5</sub>)<sub>22</sub><sup>8–</sup> [17]. Species **1**, therefore, is probably best viewed as a limiting molecular analog of the larger quantum-confined entities.

and (nitro)thiophenol  $\pi$ - $\pi^*$  transitions, and (b) a near-UV absorption ( $\lambda_{\text{max}} = 376$  nm), observed only for **1** and assigned as a cluster-to-nitrobenzene CT transition (shown schematically in Eq. 1). The extremely large extinction for the feature at 376 nm

( $\epsilon = 136\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) no doubt reflects both the multiplicity of nearly degenerate electron acceptors and the strong  $\pi$  interaction through the benzene thiolate.



The longer-wavelength CT assignment has been confirmed via electric field effect (electronic Stark effect) measurements [22–25] on isotropic samples. While the Stark spectrum in Fig. 2 exhibits the expected squared dependence of intensity upon field strength, it appears – at a first glance – to be dominated by a first-derivative, rather than second-derivative component of the absorbance spectrum. (A substantial second-derivative component is expected when significant CT effects, and therefore, ground-state/excited-state dipole moment differences, exist.) A more thorough evaluation shows that the spectrum is actually comprised chiefly of interfering second-derivative components from two overlapping electronic transitions. Two CT transitions are, in fact, expected based on distinct ‘bridging’ (Cd–SR–Cd) and ‘capping’ (Cd–SR) thiolate geometries [12]. Quantitative analysis of the Stark experiment is in progress.

Additional experiments involving normal and resonance Raman scattering (514.5 and 351 nm excitation, respectively; see Fig. 3) provide specific information about vibrations coupled to the CT reaction. From the excitation wavelength dependence of the intensity of the scattering spectrum, several modes are clearly resonance (CT transition) enhanced. Analysis of scattering intensities (351 nm excitation; instrument response corrected) using time-dependent wavepacket propagation methods [26–32] yields the estimates for normal coordinate displacements ( $\Delta$ ) shown in Table 1. These displacements are identi-

cally those required in a Franck–Condon sense for cluster-to-nitrobenzene CT. Notably, the largest displacements are associated with Cd–S and N–O stretches. Also shown in Table 1 are estimated contributions by each fundamental mode to the total vibrational reorganization energy ( $\chi_{\text{vib}}$ ) for reaction 1. (The analysis protocol was similar to that described by Zink and Shin [31] and by Lu et al. [33], except that explicit account was taken of solvent effects (in both a Franck–Condon sense and an inhomogeneous line broadening sense) via the method recently described by Myers [34]). Briefly, optimized normal coordinate displacements were obtained from a simultaneous best fit of calculated scattering and luminescence spectra to experimental spectra (where a full time-dependent analysis of initial state and final state wavepacket overlaps was employed). (Fig. 4 illustrates the quality of the fit for the Raman data.) To reproduce the structureless emission spectrum (Fig. 5; below) an empirical damping factor of  $10 \text{ cm}^{-1}$ , a solvent reorganization energy ( $\lambda_s$ ) of  $2000 \text{ cm}^{-1}$  and an  $E_{00}$  value of  $23\,920 \text{ cm}^{-1}$  were required. In any case, a fit based on emission (presumably a single electronic transition) rather than absorbance (multiple electronic transitions) was expected to circumvent, to some extent, complications (e.g., excess spectral broadening) associated with the existence of multiple, overlapping CT transitions.

As indicated above, **1** emits from the putative cluster-to-acceptor CT excited state, with an apparent

Table 1

Preliminary structural and Franck–Condon charge transfer data for  $\text{Cd}_4(\text{S-NB})_{10}^{2-}$ 

Raman shift ( $\text{cm}^{-1}$ )	Relative scattering intensity	$ \Delta $	$\chi'_{\text{vib}}$ <sup>a</sup>	Preliminary assignment [36,37]
325	0.38	1.7	460	$\nu_{\text{Cd-S}}$
726	0.08	0.76	210	?
851	1.00	1.1	470	$\delta_{\text{N-O}}$ (symmetric deformation)
1089	$\sim 0.4$ <sup>b</sup>	$0.3$ <sup>b</sup>	$40$ <sup>b</sup>	$\nu_{\text{C-S}}$ coupled to $\nu_{\text{C-N}}$
1113	0.07	0.57	180	$\nu_{\text{C-N}}$
1333	6.2	1.6	1700	$\nu_{\text{N-O}}$
1571	1.10	0.47	170	$\nu_{8a'}$
2177	0.91	–	–	combination band (851 + 1333)
2419	0.67	–	–	combination band (1089 + 1333)
2655	1.74	–	–	$2\nu_{\text{N-O}}$

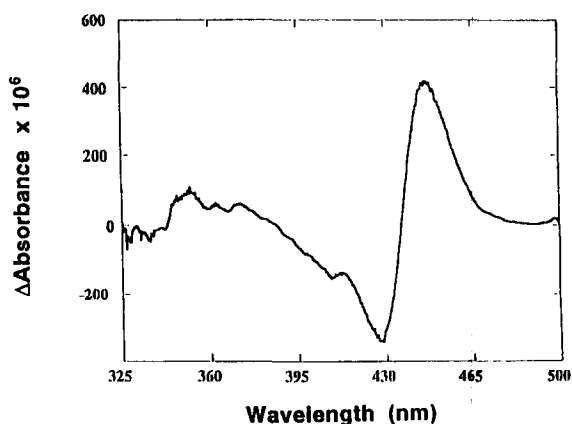
<sup>a</sup> Single mode contribution to  $\chi_{\text{vib}}$ .<sup>b</sup> Interference from solvent scattering ( $\text{CH}_3\text{OH}$ ) precludes exact determination of scattering intensity, normal coordinate displacement and reorganizational energy contribution.

Stokes shift of  $7000 \text{ cm}^{-1}$  (compare Figs. 1 and 5)<sup>3</sup>. Time resolved measurements yielded an upper limit estimate of 200 ps for excited state decay. The measured quantum yield of 0.004, however, clearly is small. It follows that the decay kinetics must be dominated by a non-radiative process – presumably back electron transfer. On that basis,  $k_{\text{ET}}$  (Eq. 1) is  $5 \times 10^9 \text{ s}^{-1}$  or greater.

Electrochemical studies of **1** (cyclic voltammetry) reveal an irreversible oxidation at ca. 390 mV and an irreversible reduction at ca. –880 mV. These are assigned, respectively, as coordinated thiolate oxidation and nitrobenzene reduction. Corresponding measurements for **2** yield only the oxidation wave. For both **1** and **2** the expected  $\text{Cd(II)}$  reduction is evidently obscured by solvent reduction.

Finally, an alternative view of reaction 1 would be an intraligand CT transition that is simply perturbed by the replacement of the thiol proton by a cadmium ion. Indeed, the free thiol (protonated) also exhibits a broad and relatively intense near-UV ab-

sorbance ( $\lambda_{\text{max}} = 412 \text{ nm}$ ). On the other hand, for small species such as **1** – where the same atoms play the roles of core (cluster) and surface (capping) chalcogenide – the distinction between the two descriptions may not be particularly instructive. Clearly, however, for larger clusters of the type  $\text{Cd}_x\text{S}_y(\text{S-R})_z^{n-}$  a differentiation between core (quantum confined donor) and surface (isolated ligand like) CT behavior is significant. For  $\text{R} = \text{benzene}$ , several well defined clusters of larger size are known [12–16]. For  $\text{R} = 4\text{-nitrobenzene}$ , however, we have thus far

Fig. 2. Uncorrected electronic Stark effect spectrum of **1** at 77 K.

<sup>3</sup> Careful emission and excitation lineshape and energy measurements, together with multiple control experiments, were used to establish unambiguously that **1** – rather than a decomposition product – was the emitting species.

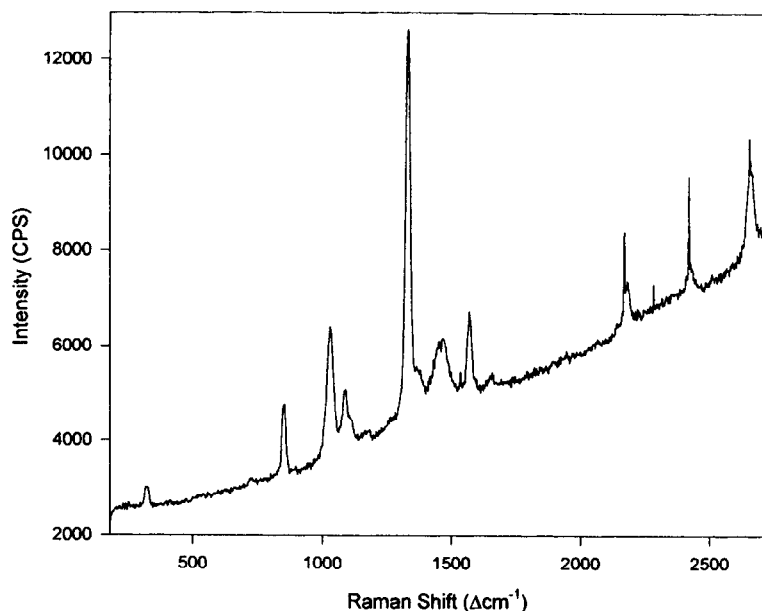


Fig. 3. Uncorrected resonance Raman spectrum for **1** based on 351 nm excitation. Asterisks denote scattering from solvent.

been unable to obtain the next two members of the adamantoid cluster series, i.e.  $\text{Cd}_{10}\text{S}_4(\text{S-NB})_{16}^{4-}$  and  $\text{Cd}_{20}\text{S}_{13}(\text{S-NB})_{22}^{8-}$  (although a somewhat larger cluster, as yet incompletely characterized, has been obtained [35]). The synthetic difficulties are probably related to the diminished Lewis basicity of 4-nitrothiophenolate in comparison to thiophenolate. Decreased basicity could lead to incomplete capping

(say, for the  $\text{Cd}_{10}$  entity), thereby providing a thermodynamic incentive for aggregation and creation of clusters larger than those expected from the stoichiometries of the starting materials [16]. In any case, preliminary experiments with the larger cluster reveal an apparent cluster-to-nitrobenzene CT transition, but at nearly the same energy as found for **1**.

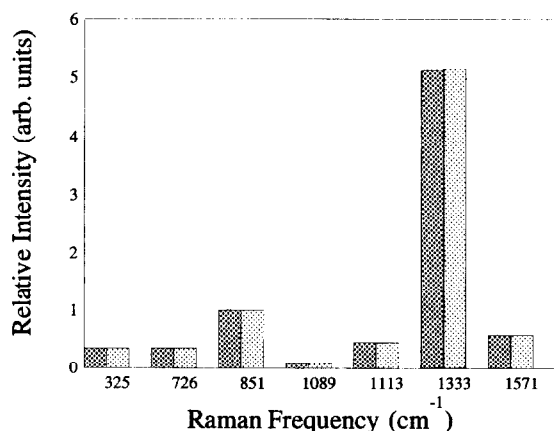


Fig. 4. Instrument-response-corrected Raman scattering intensities (shaded bars) and calculated Raman scattering intensities (solid bars) for **1** based on 351 nm excitation.

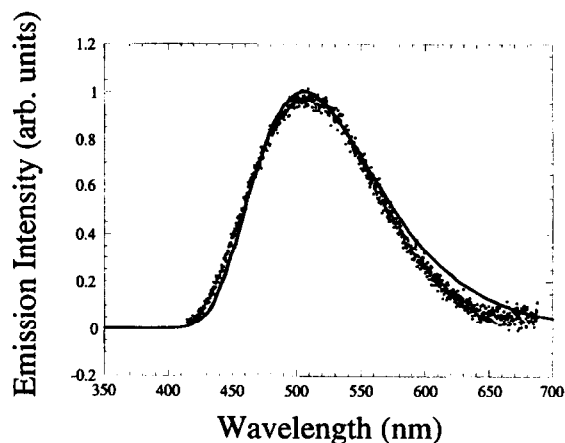


Fig. 5. Instrument- and background-corrected emission spectrum for **1** in methanol as solvent. Solid line is a calculated fit based on energetic and reorganizational parameters given in the text and in Table 1.

This suggests that the observed transition, while clearly coupled to Cd–S bond activation, likely involves primarily *surface* sulfur atoms as electron donors. Further characterization of the large system and more detailed analysis of the small system are in progress.

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