Luminescent Cluster Compounds

Surface-Cap-Mediated Host–Guest Chemistry of Semiconductor CdS: Intercalative Cation Accumulation around a Phenyl-Capped CdS Cluster and Its Notable Effects on the Cluster Photoluminescence**

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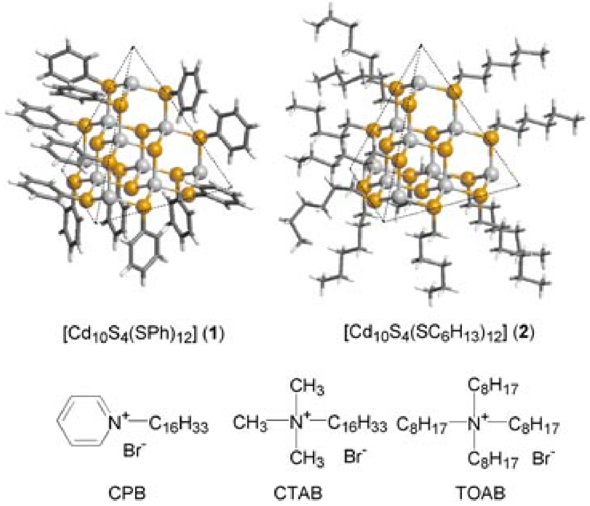
Semiconductor nanoclusters of cadmium chalcogenides have attracted continuing attention in relation to their unique optical and electronic properties.[1] These small clusters usually bear multiple surface organic ligands, which are utilized not only for stabilizing the cluster core but also for the construction of conjugates with chemical and biochemical reagents.[2,3] Although a variety of ligands with covalently appended functionalities have been designed to date,[3] there have been few examples of the host–guest-type conjugation involving guest penetration into the surface organic shell. Herein we show that simple aromatic groups at the cluster surface are capable of trapping organic cations in an intercalative fashion, allowing guest penetration close to the cluster core without direct bonding interactions. We also report the notable effects of this guest penetration on the cluster photoluminescence.

Aryl- and alkyl-capped molecular clusters of cadmium chalcogenides have been of interest as models and precursors of colloidal particles.[4,5] The clusters we use in this case are neutral $[Cd_{10}S_4(SPh)_{12}]$ (**1**) and $[Cd_{10}S_4(SC_6H_{13})_{12}]$ (**2**) bearing a truncated tetrahedral $\{Cd_{10}S_{16}\}$ core and twelve surface substituents.[5] The four unsaturated cadmium atoms at the apexes serve as coordination sites for donating ligands. Accordingly, these clusters easily formed ionic complexes with organic bromide salts by coordination of bromide anions to the apex cadmium atoms.[5b] When the cation moiety has a long alkyl chain, such as cetyltrimethylammonium (CTA^+), 1-cetylpyridinium (CP^+), or tetraoctylammonium (TOA^+), the resulting complexes were very soluble in chloroform, in contrast to the original clusters (**1**, **2**).



^{1}H NMR spectroscopic studies of the phenyl-capped cluster **1** upon complexation with the bromide salts of CTA^+ and CP^+ (CTAB and CPB, respectively) indicated the close cation proximity to the surface phenyl groups. For example, when CTAB (9.2 mM) was mixed with **1** (2.3 mM) in $CDCl_3$, clear upfield shifts were observed for the signals arising from the N-CH_3 ($\delta = 3.48 \rightarrow \delta = 3.04$ ppm) and N-CH_2 ($\delta = 3.57 \rightarrow \delta = 3.17$ ppm) of the cation (Figure 1a: 1, 3). Similar upfield shifts were observed when CPB was used in place of CTAB. These upfield shifts indicate that the cations are bound to **1** in an intercalative fashion (Figure 2), where the cationic center is located in close proximity to the SPh

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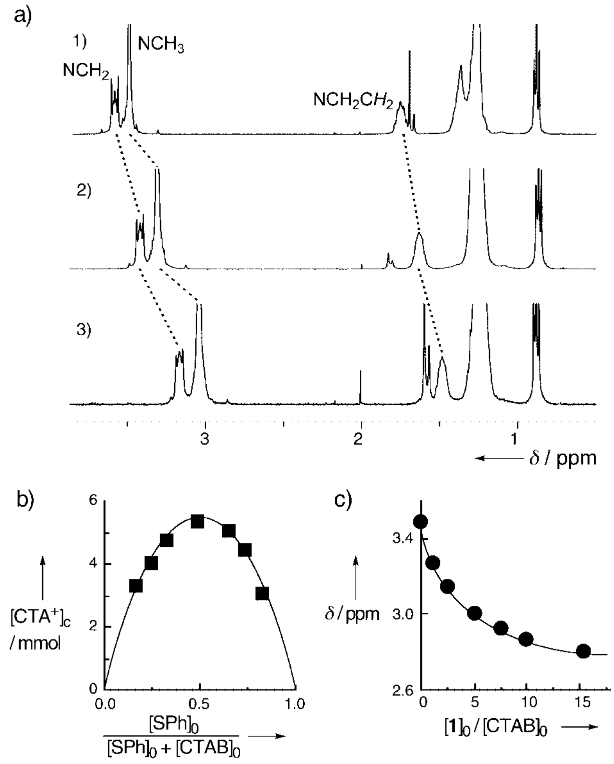

Figure 1. a) ^{1}H NMR spectra of 1) CTAB (9.2 mM), 2) **1**/CTAB (2.3/46.0 mM), and 3) **1**/CTAB (2.3/9.2 mM) in $CDCl_3$ at 25 °C; b) Job plots for the intercalative complexation between SPh of **1** and CTAB. Plots of [complexed CTA^+] versus $[SPh]_0/([SPh]_0+[CTAB]_0)$ with $[SPh]_0+[CTAB]_0$ kept constant (38 mM); c) ^{1}H NMR titration of CTAB (4.3 mM) with **1**/TOAB (1:4 molar ratio) in $CDCl_3$ at 25 °C. Plots of δ values for *N*-CH_3 protons versus $[\mathbf{1}]_0/[CTAB]_0$.

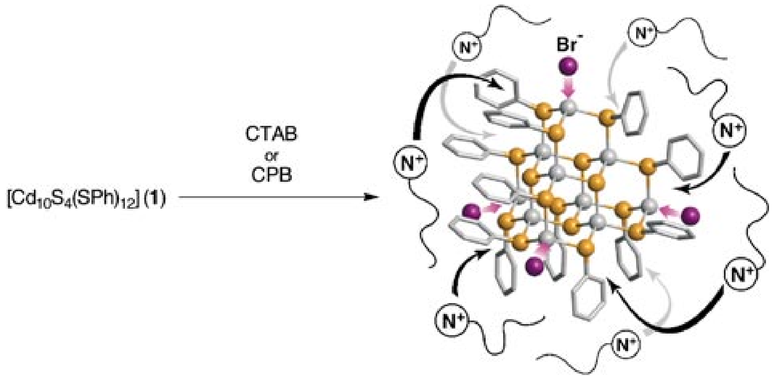

Figure 2. Schematic illustration of the complexation between **1** and CTAB or CPB showing cation intercalation among the surface phenyl groups.

groups and thus near the cluster core, while the C_{16} chain is extended away from the cluster surface.

On the other hand, when sterically hindered TOAB was used for the complexation with **1**, only very small shifts of the signals arising from the cation were observed. Owing to the severe steric bulk around the cationic center, TOA^+ seems reluctant to intercalate into the interstitial space and is therefore located outside the cluster periphery. This "outside-cation" complex still has vacant intercalation sites that can accommodate small cations. The intercalative binding of CTA^+ and CP^+ towards the preformed **1**/TOAB complex occurred similarly to that towards **1** alone. Job plots for the complexation with CTAB in the presence of TOAB,[6] where the sum of $[SPh]_0(=12\times[\mathbf{1}]_0)$ and $[CTAB]_0$ was kept constant, exhibited a maximum at a $[SPh]_0$:$[CTAB]_0$ ratio of unity (Figure 1 b), indicating the 1:1 stoichiometry of SPh and CTA^+ ions. Likewise, CPB gave a similar Job diagram to show a 1:1 complexation with SPh. Thus, considering twelve SPh groups at the surface of **1**, multiple, up to twelve, cations participate in the complexation with a single cluster molecule. From the NMR spectroscopy titration data (Figure 1 c),[6] the association constants for the 1:1 complexation were estimated to be 94 M^{-1} for CPB and 70 M^{-1} for CTAB.[7]

The cation accumulation near the CdS core of **1**, thus observed, is considered to be the results of cation–π interaction with the surface phenyl groups and/or direct cation adsorption on the polar sites of the anionic cluster $[Cd_{10}Br_4S_4(SPh)_{12}]^{4-}$ (e.g., the Br, S sites). The latter has been claimed as a possible driving force in surfactant-stabilized colloid systems,[8] but seems not dominant in the present case. This assumption was supported from the photoluminescence quenching profiles of **1** and the alkyl-substituted control **2** by using CP^+ ion as the electron acceptor: Upon excitation of the cluster moieties at 360 nm, **1** and **2**, in the presence of TOAB in $CHCl_3$, showed trap emissions at 560 and 530 nm, respectively. Both emissions were quenched by the addition of CPB, but the Stern–Volmer plots of the two systems were different. As expected from the intercalative binding of the quencher CP^+ near the cluster core, **1** gave a clear saturation behavior (Figure 3). On the other hand, **2** showed a less efficient luminescence quenching with a linear Stern–Volmer correlation ($r=0.996$; Figure 3) characteristic of a dynamic process. This situation indicates there exists no particular static interaction leading to the close proximity of the quencher to the cluster-anion moiety of **2**.[9] Therefore, a π-mediated force associated with the surface phenyl groups is most likely to be responsible for the cation intercalation towards the phenyl-capped cluster **1**.

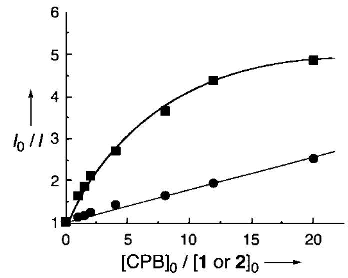

Figure 3. Stern–Volmer plots for the photoluminescence quenching of CdS clusters (**1** (■), **2** (●); 6.7 μM) by CPB in the presence of TOAB (3.3 mM) in $CHCl_3$ at 25 °C. The fluorescence intensities (*I*, $\lambda_{ex}=360$ nm) were monitored at 560 nm for **1** and 530 nm for **2**.

The photoluminescence changes upon complexation with CTAB were also investigated. In colloidal systems, the addition of tetraalkylammonium salts induces some degree of dynamic quenching.[10] In contrast, the intercalative binding of CTA$^+$ ions with **1** caused notable luminescence enhancement. For example, when CTAB (2.0 mM) was added to a mixture of **1** and TOAB in $CHCl_3$ under Ar, the emission intensity was drastically increased with a shift to a longer wavelength (570 nm; Figure 4(b)),[11] whereas the absorption spectrum showed a small change (Figure 4a). Excitation spectra before and after the addition of CTAB were similar in shape with a maximum at approximately 360 nm (Figure 4c), which indicates that the strong luminescence of the CTAB complex arises from the cluster core. On the other hand, alkyl-substituted **2** under similar conditions showed a small decrease of the luminescence intensity, which is similar to that reported for colloidal system.[10] Thus, the large luminescence enhancement with **1** is not due to simple salt effects, but is caused by the intercalative cation binding near the cluster core.

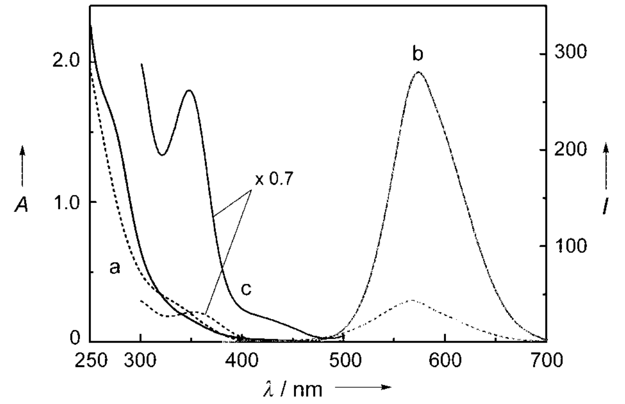

Figure 4. Absorption (a), photoluminescence ($\lambda_{ex}=360$ nm; (b)), and excitation ($\lambda_{em}=570$ nm (c)) spectra of **1**/TOAB (6.7/26.8 μM) before (dotted line) and after (solid line) the addition of CTAB (2.0 mM) in degassed $CHCl_3$ at 25 °C.

The luminescence enhancement reported above appears to be correlated to the structural changes of the phenyl-group shell surrounding the cluster core upon intercalation. In connection with this, in the ^{1}H NMR spectrum the SPh signals showed a significant change upon cation intercalation: The nonintercalative complex **1**/TOAB showed broad and complicated pattern of signals at $\delta = 6.0$–7.8 ppm (Figure 5a), which reflects the disordered orientation of the SPh groups arising from S–C bond rotation. On the other hand, upon addition of 20 equivalents of CTAB to this solution, the SPh signals converged into three major signals assignable to the *ortho*, *meta*, and *para* protons (Figure 5b), which suggests that the cation intercalation restricts the phenyl-ring rotation and so induces a uniform arrangement. Such ordered orientation and/or enhanced conformational rigidity of the surface substituents may suppress the quenching path to the medium by effective core protection and thus increase the luminescence intensity.[11,12]

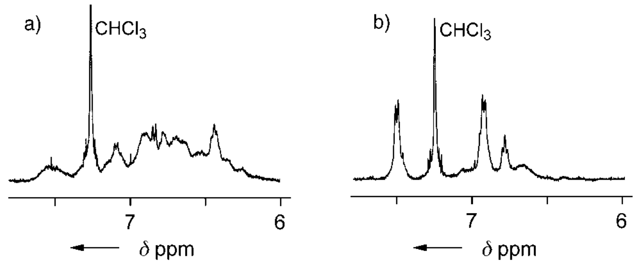

Figure 5. Aromatic region of the ^{1}H NMR spectra of a) **1** (2.3 mM) and b) **1**/CTAB (2.3/46 mM) in the presence of TOAB (9.2 mM) in $CDCl_3$ at 25 °C.

In conclusion, we have demonstrated π-interaction mediated cation accumulation around a phenyl-capped CdS cluster and the guest-responsive photoluminescence properties of this cluster. Application to sensing systems by rational tuning of the π-functionalities as well as the sizes and structures of the clusters is worthy of further investigations.

Experimental Section

1: $[Cd_{10}S_4(SPh)_{16}](NMe_4)_4$[4b] (1.16 g, 0.35 mmol) was heated under vacuum at 180 °C for 6 h, and the resulting solid was washed with hexane and chloroform to give **1** as a pale-yellow solid (0.87 g, 97 %), which gave satisfactory IR and ^{1}H NMR spectra. Elemental analysis calcd (%) for $C_{72}H_{60}Cd_{10}S_{16}$: 33.75, H 2.36, S 20.02; found: C 33.56, H 2.37, S 19.87; no nitrogen was found.

2: Compound **2** was prepared by the thiolate-exchange reaction of **1** with $C_6H_{13}SH$ in the presence of TOAB. 1-hexanethiol (21 mmol) was added to an MeCN solution of **1** (100 mg, 0.039 mmol/5 mL) containing TOAB (0.16 mmol), and the mixture was stirred at RT for 12 h. The mixture was evaporated to dryness and the residue was washed copiously with MeOH to give **2** as a white solid (81 mg, 78 %), which gave satisfactory IR and ^{1}H NMR spectra. Elemental analysis calcd (%) for $C_{72}H_{156}Cd_{10}S_{16}$: C 32.52, H 5.91, S 19.29; found C 32.27, H 5.47, S 18.89; no nitrogen was found.

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[6] The cluster/CTAB (CPB) mixtures at a low salt concentration gave emulsion-like suspensions in $CDCl_3$, so that the titration experiments were carried out in the presence of TOAB since this combination gave a homogeneous mixture at a wide range of concentration ratios.

[7] The association constants were determined by using a nonlinear curve-fitting method, assuming that each binding site works independently.

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[9] Other weak interactions, such as van der Waals forces also seem not to be dominant. No signs of guest (cation)–cluster close proximity were detected in the ^{1}H NMR spectra of the **2**/CTAB(CPB) and **1**/dimethylhexadecylamine systems in the presence of TOAB.

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[11] Titration of **1** with CTAB under the conditions given in Figure 4 showed saturation of the emission intensities at $[\mathrm{CTAB}]_0/[\mathbf{1}]_0 \approx 400$. At this molar ratio, it is estimated that, from the NMR-spectroscopy-determined association constant, at most, two of twelve intercalation sites were occupied by the CTA^+ ions, which suggests that steric isolation of the core by the intercalated cations is not a critical factor for the photoluminescence enhancement. When the $[\mathrm{CTAB}]_0/[\mathbf{1}]_0$ ratio was increased over 600, the intensity was inversely decreased probably a result of the reverse-micelle formation of CTAB.

[12] For an analogous phenyl-capped CdS cluster, increase of the luminescence intensities upon lowering temperature has been reported: N. Herron, A. Suna, Y. Wang, *J. Chem. Soc. Dalton Trans.* **1992**, 2329.