Cation–π-driven Fluorescence Signalling of Ammonium Cations by Naphthyl-substituted $Zn_{10}S_{16}$ and $Cd_{10}S_{16}$ Clusters

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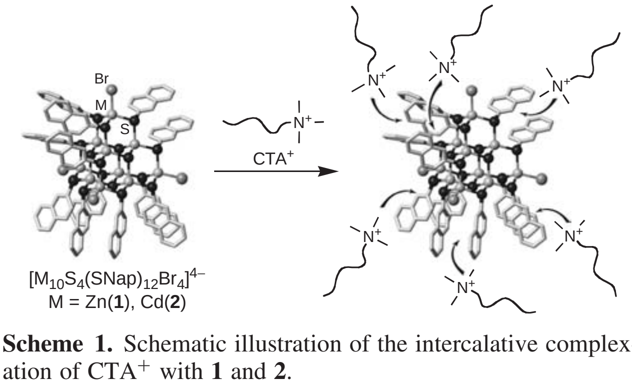
$Zn_{10}S_{16}$ and $Cd_{10}S_{16}$ clusters bearing twelve naphthalene units on the surface showed characteristic blue emission in response to the cation–π-mediated intercalative binding of quaternary ammonium cations that allows the formation of ground-state naphthalene aggregates.

Ensembles of several aromatic units arranged in a particular orientation have been of great interest because of the unique optical properties arising from the electronic interaction of the proximal π-chromophores.[1] Molecular clusters of ZnS and CdS are attractive platforms for the construction of well-defined aromatic ensembles since they can accommodate multiple S-substituents on the surface. Herein, we report that the naphthalene chromophores attached on $M_{10}S_{16}$ type anionic clusters ($[Zn_{10}S_4(SNap)_{12}Br_4]^{4-}$ (**1**), $[Cd_{10}S_4(SNap)_{12}Br_4]^{4-}$ (**2**))[2] form blue-emitting aggregates in response to the intercalative binding of unhindered quaternary ammonium cation.

Recently, we have shown that cetyltrimethylammonium ion (CTA^+) interacts with the surface phenyl groups of $[Cd_{10}S_4(SPh)_{12}Br_4]^{4-}$ (**3**) via cation–π interaction to accumulate near the cluster core, while such intercalative binding hardly occurred with sterically hindered tetraoctylammonium ion (TOA^+).[3] A similar intercalative binding (Scheme 1) and preference for CTA^+ were observed in the case of naphthyl-substituted clusters (**1** and **2**). For example, when the bromide salt of CTA^+ (CTAB) was added to **2**$(TOA)_4$ in $CDCl_3$, the ^{1}H NMR spectrum exhibited notable upfield shifts of the CTA^+ signals, whereas the TOA^+ signals were observed at the nearly same positions as those of TOAB alone.[4] However, with respect to the intercalation stoichiometry, **2** was evidently different from **3** for which the surface phenyl groups interact with cations in a 1:1 molar ratio:[3] Job diagram for the complexation of **2**$(TOA)_4$ with CTAB, where the sum of $[SNap]_0$ ($= 12 \times [\mathbf{2}]_0$) and $[CTAB]_0$ was kept constant, gave a maximum at $[SNap]_0/([SNap]_0 + [CTAB]_0) = 0.66$, indicating the 2:1 interaction of the naphthalene units and CTA^+ cations. This stoichiometry indicates that the cation intercalation induces the formation of assemblies consisting of multiple, at least two, naphthalene units. The association constant, assuming that two naphthalene units provide a single binding site, was estimated to be 337 M^{-1} from the titration data. The binding profile of the ZnS cluster **1** towards CTA^+ was virtually identical to that of **2**.



Scheme 1. Schematic illustration of the intercalative complexation of CTA^+ with **1** and **2**.

Upon excitation at 340 nm in $CHCl_3$ at 25 °C under air, the nonintercalative form of the ZnS cluster $[\mathbf{1}(TOA)_4]^4$ showed an emission band at 400 nm (Figure 1a). Since neither hexyl- nor phenyl-capped analogues of the ZnS cluster showed any photoluminescence, the $Zn_{10}S_{16}$ core itself is essentially nonluminescent so that the observed emission of **1**$(TOA)_4$ appears to be associated with the surface naphthalene chromophores. Actually, the excitation spectrum ($\lambda_{em} = 420$ nm) of **1**$(TOA)_4$ (Figure 1d) was similar to that of 2-naphthalenethiol (Figure 1f).[5] On the other hand, such an emission was not observed for the CdS cluster **2**$(TOA)_4$, which, however, showed a broad band at ≈600 nm assignable to the trap emission of the semiconductor CdS core (Figure 2a). The lack of the 400-nm emission in **2**$(TOA)_4$ suggests that the electron/energy transfer takes place from the excited states of the naphthalene chromophore to the CdS moiety.

The intercalative binding of CTA^+ caused notable changes of the fluorescence profiles of **1** and **2**. For example, when **1**$(TOA)_4$ was mixed with CTAB, the 400-nm emission band was enhanced with a shift to 420 nm (Figure 1b). On the other hand, with **2**$(TOA)_4$, the cluster emission at 600 nm was quenched but a new band at 420 nm was emerged and developed as the progress of the intercalation (Figure 2b),[6] where the final spectrum was similar to that observed for the ZnS cluster system (Figure 1b). Accordingly, the emission color changed from weak orange to blue. Titration experiments indicated that the plots of the 420-nm emission intensity versus $[CTAB]_0/[\mathbf{2}]_0$ reached a

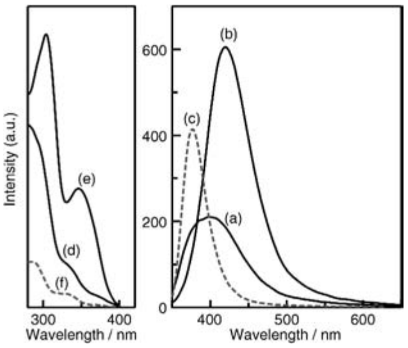


Figure 1. Photoluminescence (right, $\lambda_{ex} = 340$ nm) and excitation (left, $\lambda_{em} = 420$ nm) spectra of **1**$(TOA)_4$ (6.7 μM) (a and d) and **1**$(TOA)_4$/CTAB (6.7 μM/20 mM) (b and e), and 2-naphthalenethiol (80 μM) (c and f) in $CHCl_3$ at 25 °C under air.

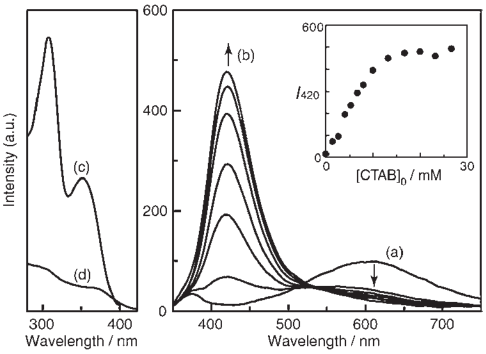


Figure 2. Photoluminescence spectrum ($\lambda_{ex} = 340$ nm) of **2**$(TOA)_4$ (6.7 μM) (a) and spectral changes upon titration with CTAB (b) (inset: plots of the emission intensities at 420 nm versus $[CTAB]_0$), and excitation spectra of **2**$(TOA)_4$/CTAB (6.7 μM/20 mM, $\lambda_{em} = 420$ nm) (c) and **2**$(TOA)_4$ (6.7 μM, $\lambda_{em} = 600$ nm) (d) in $CHCl_3$ at 25 °C under air.

plateau at $[CTAB]_0/[\mathbf{2}]_0 \approx 3000$ (Figure 2, inset). At this molar ratio, the six intercalation sites are almost fully occupied by CTA^+ from the association constant. Thus, the evolution of the 420-nm band appears closely correlated with the π-complex formation.

A further insight was provided from the excitation spectra of the intercalative complexes **1**/CTA^+ and **2**/CTA^+. When monitored at 420 nm, they showed similar profiles to each other with two bands at 300–400 nm (Figures 1e and 2c).[7] Considering the well-known difference in the optical properties of ZnS and CdS clusters,[8] the observed similarity suggests that the cluster and naphthalene chromophores are isolated from each other. Actually, the absorption associated with the excitation of the CdS moiety (Figure 2d) is different from the two-band excitation spectra of the intercalative complexes. Since these excitation spectra were also different from that of 2-naphthalenethiol (Figure 1f), it is likely that the 420-nm emission is not due to the excimer from the excited naphthalene monomers but is from the naphthalene aggregates formed at the ground state by the cation intercalation. As the emitting species, cation-sandwiched dimers (Figure 3a) is one of the possible candidates, but recent theoretical studies on Ph–NMe_4^+–Ph sandwich complexes have claimed that there are no electronic interactions between two facing aromatic systems because of the long distance.[9] In this respect, another possibility is that the cation–naphthalene complexation, including the sandwich type, promotes the formation of π-stacks with the adjacent naphthalene units (Figure 3b), thereby showing the dimer emission at 420 nm.

As we have seen, the evolution of the 420-nm emission is firmly associated with the cation penetration into the sterically restricted aromatic concave. Therefore, the fluorescence responses towards ammonium cations are expected to reflect the guest cation sizes. Actually, the emission intensities of **2**$(TOA)_4$ (6.7 μM) in the presence of a given amount of CTAB, NEt_4Br, NBu_4Br, and TOAB (6.7 mM) gave a clear correlation with the steric bulks of the cations, where the emission intensities relative to the **2**/TOAB system were 5.7, 4.8, and 3.3 for the **2**/CTAB, **2**/NEt_4Br, and **2**/NBu_4Br systems, respectively. The observed selectivity is only moderate but may be enhanced by the elaborate design of the surface units.

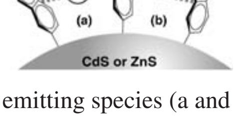


Figure 3. Possible emitting species (a and b) for the blue emission.

The cation–π interaction is a general and important nonbonding force,[10] but there have been limited examples of the utilization of cations as mediators for the construction of aromatic ensembles.[11] In the present paper, we have demonstrated fluorescence signalling of quaternary ammonium cations driven by cation–π interaction, where the guest cations promote the aggregation of the naphthalene chromophores on the cluster surface, allowing unique optical response.

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References and Notes

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4 In contrast to **3**, **1**, and **2** showed some degree of intercalation activities towards TOA^+ in the absence of CTA^+, but its affinity was very low. At the low concentration used for the fluorescence study, the cations in the TOA salts should be located mostly outside the cluster periphery, and, therefore, they are regarded as "nonintercalative" complexes.
5 Since the excitation of **1**$(TOA)_4$ with a higher-energy light resulted in a blue shift of the fluorescence (e.g., $\lambda_{max} = 385$ nm with $\lambda_{ex} = 310$ nm), the excitation spectrum (Figure 1d) appears to be binary consisting of naphthalene monomer and dimer components. Considering also the emission spectrum of 2-naphthalenethiol monomer (Figure 1c), the 400-nm band of Figure 1a is likely to be a mixture of monomer/excimer and dimer emissions. No such dependency on the excitation wavelength was observed after the cation intercalation.
6 Under *anaerobic* conditions (argon), the growth of the 420-nm band showed an almost identical profile, while the cluster emission (600 nm) was contrary enhanced similarly to the phenyl-capped cluster **3** (Ref. 3).
7 The absorption spectral changes upon CTA^+ intercalation were, though little, very similar to the excitation spectra.
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