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COMMUNICATION

Room Temperature Phosphorescence from a Guest Molecule Confined in Restrictive Space of an Organic–Inorganic Supramolecular Assembly

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Stable room-temperature phosphorescence of guest aromatic molecules was achieved by the effective suppression of oxygen quenching. The organic capsule (first wall) suppressed static oxygen quenching by enclosing a guest molecule, and dynamic quenching via the capsule opening–closing process was well suppressed and manipulated by the intercalation of this capsule into the restrictive space between clay nanosheets (second wall).

The use of supramolecular assemblies in controlling the ground and excited-state phenomena of organic molecules has attracted much attention since Lehn's pioneering work in supramolecular chemistry¹. Huge contributions in this field have contributed to an increased understanding of the behavior of molecules in a wide variety of supramolecular assemblies such as micelles, polymers, gels, crystals, and metal-organic frameworks (MOF); and inside organic and inorganic hosts such as cyclodextrins (CD), calixarenes (CA), cavitands, clay minerals, or other types of nanosheets, zeolites, and mesoporous materials.^{1–9}

Ramamurthy's group has focused on exploiting the photophysical and photochemical properties such as electron, energy, and spin transfers as well as the conformational restriction of organic molecules included within the restrictive space of an organic capsule comprising octa-acid (OA) or octa-amine (OAm) molecules (Figure 1).² The diffusion-limited rates of triplet–triplet energy transfer between the excited triplet state of donor and acceptor (triplet oxygen) in water decreased to less than $10^8 \text{ M}^{-1} \text{ s}^{-1}$ when the guest was encapsulated.^{10,11} The mechanism of energy transfer was found to be dependent on the rate of the capsule opening and closing on the microsecond time scale. Capsule opening occurs

when the hydrophobic interactions between the two constituent cavitand molecules become sufficiently weak to allow a quencher oxygen molecule to access the encapsulated guest molecule. Thus, quenching of the excited triplet state of the molecules inside the capsule is a dynamic process. These results clearly indicated that Dexter type triplet–triplet energy transfer occurs between the excited triplet donor and the ground-state oxygen via the capsule opening process. If capsule opening could be suppressed by the induction of another force, strong, stable room-temperature phosphorescence can be easily realized.

To this end, our approach is to introduce additional Coulombic interaction into the original hydrophobic interactions that form the capsuleplex, through the use of inorganic nanosheets. Our group recently reported that a cationically charged organic capsule, composed of two cavitand molecules with eight ammonium groups (octa amine¹² (OAM, Figure 1)) could be anchored on an anionically charged saponite clay nanosheet. Guest@OAM₂¹⁶⁺ represents a protonated capsular assembly having 16 positive charges enclosing aromatic guest molecule. As Takagi's group has already established for porphyrins or other dyes^{13,14}, capsules have the ability to be stably arranged on a saponite surface (Figure 1b) without any unfavorable ground-state interactions such as aggregation and self-quenching^{15–17}. Although guest@OAM₂¹⁶⁺ has 16 positive charges, it behaves like a tetra-cationic porphyrin, with only the 4 cationic charges at the bottom anchored to the clay surface. Furthermore, we have reported that the center-to-center distance between the guest@OAM₂¹⁶⁺ under the highest density conditions is 2.4 nm, which is identical to that for tetra-cationic porphyrins (see Figure 1b for schematic illustration). Our hypothesis is that the addition of a second saponite nanosheet into the structure shown in Figure 1b would yield a sandwich structure (Figure 1c) due to Coulombic interactions between the cationic charges on the capsule and the anionic charges on saponite. Thus, opening of the capsule, which allows for phosphorescence quenching by oxygen molecules in solution, is expected to be highly regulated. The combination of two

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supramolecular systems toward highly organized photophysical phenomena of the enclosed guest is presented in this paper.

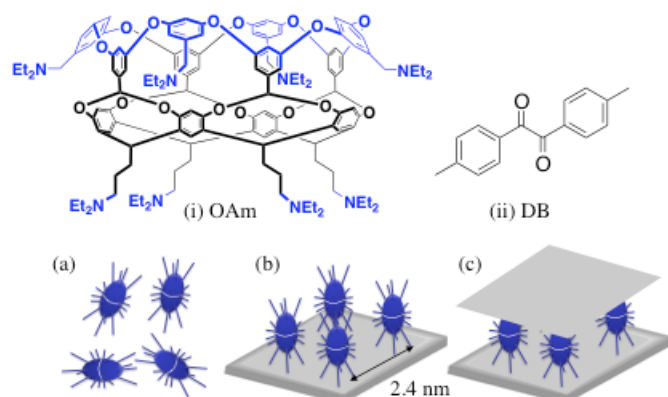


Figure 1. Structures of (i) octa amine (OAm⁸⁺) and (ii) 4,4'-dimethylbenzil (DB). Schematic illustrations of samples used in this study: (a) free DB@OAm₂¹⁶⁺ in water, (b) DB@OAm₂¹⁶⁺ anchored on exfoliated saponite nanosheet in aqueous suspension, and (c) DB@OAm₂¹⁶⁺ intercalated in two saponite nanosheets in aqueous suspension.

In this study, we selected 4,4'-dimethylbenzil (DB, Figure 1) as a phosphorescent guest molecule. DB has very high rate constants of intersystem crossing (ISC) from S₁ to T₁, and thus phosphoresces. In the absence of OAm, the T₁ state of DB is quenched by molecular oxygen via energy transfer in acetonitrile, with rate constant of $8.2 \times 10^8 \text{ (mol/L)}^{-1} \text{ s}^{-1}$.¹⁰ Our group has reported that the T₁ state of DB@OAm₂¹⁸⁺ is sensitively quenched by oxygen compared with other molecules such as pyrene.¹⁰ By detailed photophysical measurements and 2D NMR studies, the mechanism of quenching by molecular oxygen has been revealed as follows. The triplet state of n-π* is localized at the C=O chromophore, which is located at capsule entrance for DB that is the joint of two cavitand molecules, and is therefore, more accessible to oxygen. On the other hand, the pyrene triplet states (π-π*) are delocalized over the entire molecule, which makes them less accessible to oxygen quenching at the capsule entrance. Thus, the T₁ state of DB is sensitively quenched oxygen molecule through capsule opening, and this is suitable to reveal the effect of sandwiching between two saponite nanosheets on the opening-closing process of the capsuleplex.

The saponite clay mineral used in this study was prepared by hydrothermal synthesis according to the literature,¹⁸ and analyzed by XRD, XRF, ²⁷Al-NMR, FT-IR, AFM, and TG/DTA methods. The cation-exchange capacity (CEC) was 1.0 meq g⁻¹, and the average distance between the anionic charges was 1.2 nm on the basis of a hexagonal array. OAm was synthesized according to the literature procedure.¹² A solution of DB included within OAm₂¹⁶⁺ was prepared under acidic conditions (pH 1.0) according to the literature. The inclusion of DB within OAm₂¹⁶⁺ and the ratio of the host-to-guest complex were checked by ¹H NMR measurements and NMR titration experiments in water under acidic conditions (pH = 1.0).^{12,15}

Under the present experimental conditions, all eight triethylamine groups of OAm should remain protonated. For spectral measurements, the stock solution of DB@OAm₂¹⁶⁺ was diluted with aqueous HCl to maintain a pH of 1.0. Absorption and fluorescence spectra were measured with UV-3150 spectrophotometer (Shimadzu) and FS920CDT fluorometer (Edinburgh Instruments). Phosphorescence lifetimes were measured on an OB920 fluorometer (Edinburgh Instruments) using a pulsed microsecond xenon lamp as excitation source and multi-channel scaling for data acquisition.

In this study, we compare three systems: (a) free DB@OAm₂¹⁶⁺ in water, (b) DB@OAm₂¹⁶⁺ anchored on exfoliated clay nanosheet in aqueous suspension, and (c) DB@OAm₂¹⁶⁺ intercalated between two clay nanosheets in aqueous suspension (Figure 1). Sample (a) was prepared by diluting a stock solution of DB@OAm₂¹⁶⁺ with aqueous HCl solution. DB@OAm₂¹⁶⁺-clay complexes (samples (b) and (c)) were prepared by mixing stock solutions of DB@OAm₂¹⁶⁺ and an aqueous saponite dispersion at pH 1.0 (adjusted by using aqueous HCl solution). Sample (b) was prepared by mixing DB@OAm₂¹⁶⁺ with an aqueous dispersion of saponite clay at the maximum adsorption amount with an average intercapsule distance of 2.4 nm, as determined in our previous study¹⁵. This high density adsorption aims to suppress the formation of a partially sandwiched structure (Figure 1c) resulting from the presence of free anionic charges on free clay.¹³ Sample (c) was prepared by the addition of a fourfold amount of saponite clay into sample (b), followed by three freeze-thaw cycles. Free saponite clay attracts the upper free cationic charges of DB@OAm₂¹⁶⁺ to form an intercalation structure (Figure 1c), and the repeated freeze-thaw process may enhance the formation.

In this study, we probed the opening-closing of DB@OAm₂¹⁶⁺ by monitoring the quenching of the excited triplet state of the guest DB molecule present inside a capsule (and further inside the nanosheets for samples (b) and (c)) by molecular oxygen present in solution. The rate of quenching was estimated by monitoring the intensity of phosphorescence or the lifetime of the T₁ state of DB in the presence of different concentrations of oxygen in water. The concentration of oxygen in the aqueous solution was controlled by bubbling O₂/N₂ gas (O₂ concentration of 0%, 21%, 50%, and 100%) for 30 min before the measurement. It was found that 30 min was sufficient to reach equilibrium.

Room-temperature steady-state emission spectra are shown in Figure 2. The excitation wavelength was set at 355 nm. The concentration of DB@OAm₂¹⁶⁺ was kept constant at $1.0 \times 10^{-6} \text{ M}$ for all samples. The emission from DB consists of fluorescence (λ_{max} = 495 nm) and phosphorescence (λ_{max} = 560 nm). In the absence of oxygen (0%), all three samples showed similar emission intensities, suggesting that DB@OAm₂¹⁶⁺ did not decompose or induce any change in the capsuleplex structure upon complexation with the saponite nanosheets, since free DB does not dissolve in water and the emission should be largely quenched. In the presence of oxygen in a solution, the phosphorescence was significantly quenched by oxygen, whereas the fluorescence showed only minor changes

with the oxygen concentration. Most interestingly, the tendency of phosphorescence quenching was completely different between free DB (Figure 2a) and DB@OAm₂¹⁶⁺ (Figure 2b and c). This observation clearly suggests that the energy transfer from the T₁ state of DB to the ground state of molecular oxygen was inefficient when the capsule was anchored on or intercalated with saponite nanosheets. Moreover, the phosphorescence quenching observed for intercalated system (Figure 2c) saw an increase in reduction from the capsule anchored on a single saponite nanosheet (Figure 2b). Thus, we concluded that the opening–closing behavior of DB@OAm₂¹⁶⁺ was strongly suppressed inside the space between the two saponite nanosheets. The mechanism for the phosphorescence enhancement for sample (b) can be considered as follows: the Coulombic interaction between the capsule's upper cationic charges (those not attached to the saponite nanosheet) and the anionic charges of the saponite nanosheet strongly suppresses the opening–closing of the capsule. Moreover, the exfoliated saponite nanosheet provides a hydrophilic surface for guest molecules, allowing them to form aggregates on the surface.¹⁹ Hence, DB@OAm₂¹⁶⁺ is strongly stabilized not only by the Coulombic interaction between the cationic charges of the capsule and the anionic charges of the saponite nanosheets, but also by the hydrophobic interaction between DB@OAm₂¹⁶⁺ and the surrounding water that influences to the entire capsule being on the surface. Our previous photophysical measurements have revealed that the hydrophobicity of the saponite nanosheet surface is considerable even for a highly charged species such as 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin (TMPyP) and that the hydrophobic force acts as one of the dominant mechanisms for the stabilization of the guest molecule on the nanosheet surface;^{20,21} this is the presumable mechanism for the suppression of opening–closing process of the capsule when anchored on a saponite nanosheet. It is also important to note that the oxygen diffusion rate in a bulk aqueous solution and in the space of clay nanosheets (sample (c)) might be different. This could be one of the reasons for the phosphorescence enhancement observed for sample (c). However, the large enhancement of phosphorescence intensity observed in sample (b) clearly indicates that the anchoring onto clay nanosheet makes the capsule opening–closing inefficient.

To quantitatively analyze the oxygen quenching process, time-resolved fluorescence measurements were studied. The excitation wavelength was 355 nm. The detection wavelength was set at the phosphorescence maxima of DB (560 nm). Very fast decays observed immediately after the pulse irradiations were due to the contribution of fluorescence from the S₁ state on a nanosecond time scale. The obtained phosphorescence decays were analyzed as mono-exponential decays except for the sample (c) at higher oxygen concentrations. In the absence of oxygen (0% O₂) all three samples (a–c) showed similar

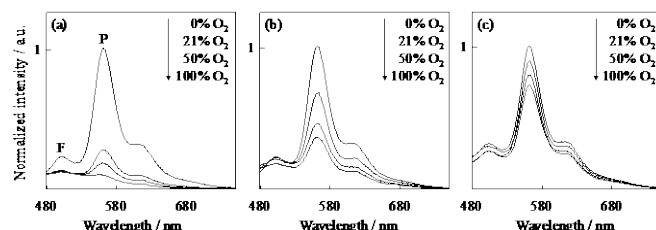


Figure 2. Emission spectra of (a) free DB@OAm₂¹⁶⁺, (b) DB@OAm₂¹⁶⁺ anchored on exfoliated clay nanosheet, and (c) DB@OAm₂¹⁶⁺ intercalated in two clay nanosheets, observed at various concentrations of O₂ in water. The excitation wavelength was set at 355 nm. The concentration of DB@OAm₂¹⁶⁺ was held constant at 1.0×10^{-6} M. F and P denote the fluorescence and phosphorescence maxima of DB.

phosphorescence decay with a lifetime of approximately 610 μ s. Further supporting the conclusions from the steady-state emission spectra (Figure 2), this result indicates the stability of DB@OAm₂¹⁶⁺ sandwiched between saponite nanosheets. A large decrease in the phosphorescence lifetime was observed for free DB@OAm₂¹⁶⁺ in water (sample (a)), with 90% quenching even in the presence of 21% of oxygen solution (Figure 3a). In contrast, the decrease was very slight (*ca.* 10%) when DB@OAm₂¹⁶⁺ was sandwiched between two saponite nanosheets at the same oxygen concentration (Figure 3c). At high oxygen concentration the decay for sample (c) was fit to a biexponential function where a small contribution (*ca.* 10%) was observed for the shorter lifetime component as shown in Figure S1 in Supporting Information. The origin of this shorter lifetime component is uncertain, however, one possible reason is due to the configuration of capsules. The particle size of clay nanosheet used in this work is around 30 to 50 nm. We can calculate a ratio between capsules those present at the outer side of clay nanosheet and the others present at the inner side of nanosheet surrounded by other capsules. The ratio of capsules between former and latter spatial arrangements is calculated to be 11:89 on a square clay nanosheet with 40 nm of diameter. The outer capsules should be more accessible to molecular oxygen present in solution. Moreover, a passivation of capsule structure sandwiched by two nanosheets is expected to be less stable at the edge of nanosheet, resulting in a larger phosphorescence quenching. This spatial arrangement of the capsules is the most likely reason for the observation of shorter lifetime components for sample (c).

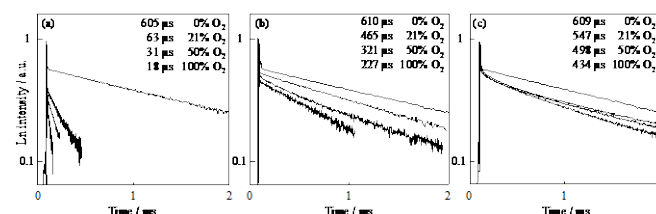


Figure 3. Time-resolved emission decays for (a) free DB@OAm₂¹⁶⁺, (b) DB@OAm₂¹⁶⁺ anchored on exfoliated clay nanosheet, and (c) DB@OAm₂¹⁶⁺ intercalated in two clay nanosheets, observed at various concentrations of O₂ in water.

The excitation wavelength was 355 nm. The concentration of DB@OAm₂¹⁶⁺ was set at 1.0×10^{-6} M.

The rate constants for the T₁ state oxygen quenching were obtained from the slope of Stern-Volmer plots of τ_0/τ versus the oxygen concentration in water (Figure 4). From the slope, the quenching rate constants (k_q) were determined to be 4.7×10^7 , 2.3×10^6 , and 5.4×10^5 s⁻¹ M⁻¹ for samples a, b, and c, respectively. These data suggest that oxygen is still able to quench the triplet state of DB in these tested samples; however, the rate constants are significantly lower than that for the diffusion-limited quenching of free DB without OAm in acetonitrile (8.2×10^8 s⁻¹ M⁻¹)¹⁰. The encapsulation by OAm₂¹⁶⁺ resulted in a significant reduction in the rate constant, in agreement with previous studies using an octa acid cavitand¹⁰. Moreover, the intercalation into the inter-layer space of the saponite nanosheets (sample c) resulted in the further reduction of k_q . These results clearly suggest that the accessibility of oxygen to the DB enclosed within the OAm capsuleplex was strongly suppressed inside the restrictive space of the saponite nanosheets. Thus, we concluded that the opening-closing of the capsuleplex can be well manipulated through the introduction of saponite nanosheets (second wall) as part of an organic-inorganic supramolecular system for the guest DB molecule inside the capsule (first wall). The results presented in this report therefore suggest that a combination of supramolecular systems is promising for progressive future technologies with highly controllable structures and properties, which are difficult to achieve with our present molecular and supramolecular techniques.

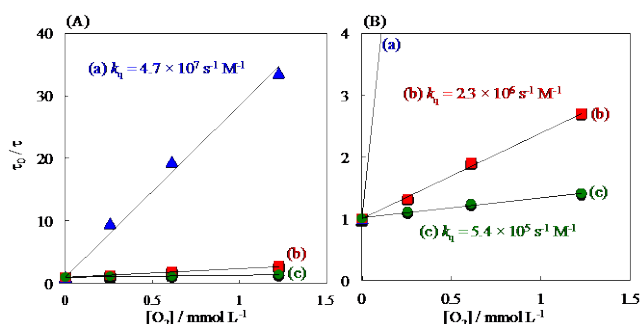


Figure 4. (A) τ_0/τ plot as a function of O₂ concentration for (a) free DB@OAm₂¹⁶⁺, (b) DB@OAm₂¹⁶⁺ anchored on exfoliated clay nanosheet, and (c) DB@OAm₂¹⁶⁺ intercalated in two clay nanosheets in water. Quenching rate constants (k_q) are shown inside. (B) is an enlarged graph.

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