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Energy Transfer in a Mechanically Trapped Exciplex

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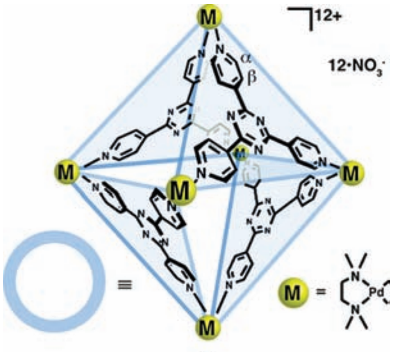
The development of artificial photosynthetic systems requires a fundamental understanding of mechanisms of energy transfer between organic molecules.[1] Covalently tethered donor−acceptor systems often form intramolecular exciplexes and are important for understanding the dependence of energy transfer on donor−acceptor distance, orientation, and electronic coupling. Mechanically linked intramolecular exciplexes, on the other hand, are much less developed and thus relatively unexplored.[2] Recently, some of us reported photoinduced electron transfer (PET) and subsequent photooxidation of alkanes within the self-assembled cage **1**[3] as well as energy transfer within its cavity.[4] Given the reactivity of the photoactive host−guest complexes involving coordination cage **1**,[5] we now report the design, synthesis, and photophysical properties of an emissive, mechanically trapped intramolecular exciplex. We found that selective excitation of the encapsulated guest fluorophore results in efficient energy transfer from the guest to the emissive host−guest exciplex $\mathbf{1}\supset\mathbf{2}$.



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Bisanthracene **2** was chosen as the target guest, as its photophysical properties have been extensively studied[6] and its D_{2d} symmetry should match and fill the cavity of **1**. When excess **2** (10 mol equiv) was suspended in a D_2O solution of cage **1** (7.5 μM) and heated at 100 °C overnight, the solution turned orange. In the ^1H NMR spectra, the two symmetrical doublets of the host split into six doublets, indicating a decrease in the host symmetry from S_4 to D_{2d} upon inclusion of **2**, and a new set of guest signals appeared (Figure 1). All of the signals were sharp and well-defined, indicating a static structure, and the guest protons were shifted far upfield as a result of shielding by the cage panels. Protons **a** and **e** were especially shifted (approximately −3 ppm). ^1H NMR integration indicated ~50% formation of the 1:1 host−guest complex. Longer reaction times increased the yield but also led to degradation. Complex $\mathbf{1}\supset\mathbf{2}$ is quite stable, and aqueous solutions showed no evidence of decomplexation after standing for weeks at room temperature.

Single crystals of pure $\mathbf{1}\supset\mathbf{2}$ were obtained by slow evaporation, and X-ray analysis confirmed the unique structure of the mechanically trapped fluorophore (Figure 2). One anthracene fragment of the bisanthracene guest is sandwiched between two triazine panels and held orthogonal with respect to the other half. The central anthracene rings are 4.6 Å from the triazine cores, and the host and guest π systems are tilted by 36° relative to each other. The origin of the large $-\Delta\delta$ values for hydrogens **a** and **e** becomes apparent, as both of these hydrogens are located above aromatic rings in the triazine panel at distances of 2.7 and 3.4 Å respectively. The extremely large bisanthracene tightly fills the host cavity and thus interacts with each of the four panel π systems.

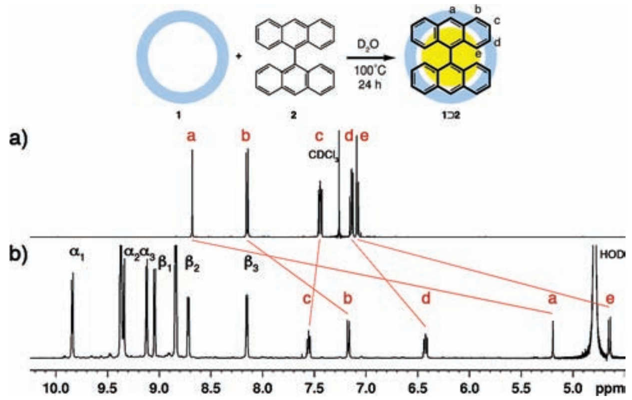

Figure 1. (a) Formation of $\mathbf{1}\supset\mathbf{2}$ and ^1H NMR spectra of (b) bisanthracene **2** in $CDCl_3$ and (c) $\mathbf{1}\supset\mathbf{2}$ in D_2O.

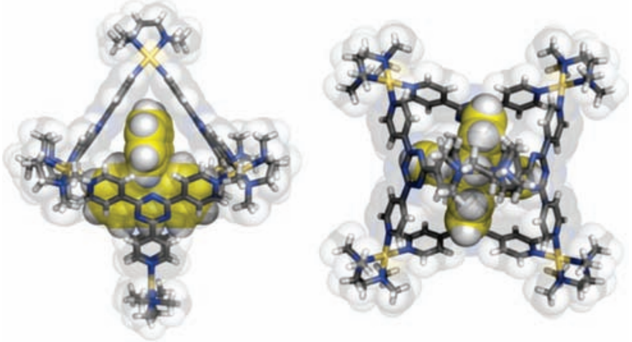

Figure 2. X-ray crystal structure of host−guest complex $\mathbf{1}\supset\mathbf{2}$.

With $\mathbf{1}\supset\mathbf{2}$ in hand, the effects of encapsulation on the photophysical properties were examined. Relative to bisanthracene in EtOH, the 0−0 absorptive transition of encapsulated **2** is blue-shifted by 4 nm. More importantly, a new broad band centered at ~450 nm is indicative of host−guest charge transfer (CT) interactions (Figure 3a). Within the cavity, guest emission is present at

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435 nm ($\Phi_F = 0.0014$), and a new weak, broad emission at ~650 nm appears. The long wavelength and broad, featureless nature of the new peak are characteristic of exciplex formation (Figure 3b).

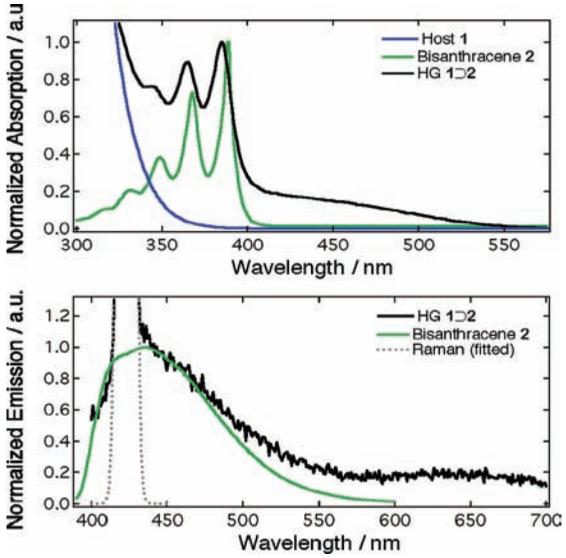


Figure 3. Normalized absorption (upper) and steady-state emission (lower) spectra of host **1** (blue) in H_2O, bisanthracene **2** (green) in EtOH, and $\mathbf{1}\supset\mathbf{2}$ (black) in H_2O with the fitted Raman scattering band (gray dots).

Furthermore, the excitation spectrum of this emission closely resembles the absorption spectrum of $\mathbf{1}\supset\mathbf{2}$,[7] indicating energy transfer from the excited guest **2** to the exciplex state.

Picosecond time-resolved measurements further elucidated the nature of the excited state and revealed that efficient energy-transfer dynamics occur in $\mathbf{1}\supset\mathbf{2}$. Irradiation of $\mathbf{1}\supset\mathbf{2}$ at 370 nm predominantly excites encapsulated guest **2**, and the fluorescence was detected with a streak camera in 1 and 50 ns time ranges with time resolutions of 20 and 600 ps, respectively. The observed fluorescence time profiles were well-fitted with triple-exponential functions having $\tau_1 = 7.4$ ps, $\tau_2 = 113$ ps, and $\tau_3 = 4.4$ ns (Figure 4). Immediately after photoexcitation, the decay with $\tau_1 = 7.4$ ps predominated in the 450−550 nm region and is attributed to the fluorescence from the initially populated excited state of **2** ($\lambda_{max} \approx 430$ nm; band I). Concurrent with the decay of band I, a new emission band appeared at ~650 nm (band II) and decayed with $\tau_2 = 113$ ps. Afterward, a long-lived weak emission (band III) persisted ($\tau_3 = 4.4$ ns) at $\lambda_{max} = 430$ nm.

Irradiation of $\mathbf{1}\supset\mathbf{2}$ at 370 nm selectively excites guest **2**, and band I is assigned to the locally excited state of **2** (G_{LE}). This assignment is supported by the similarity in λ_{max}, picosecond lifetime, and spectral shape of band I and the G_{LE} fluorescence of free **2** in EtOH. Band II is ascribed to emission from host−guest exciplex (HG_{CT}) on the basis of the broad spectral shape and long wavelength. Bisanthracene belongs to a class of biaryls that form emissive twisted charge transfer states (TICTs) upon photoexcitation.[8] Band III is assignable to the TICT state of **2** (G_{TICT}) because the λ_{max}, nanosecond lifetime, and spectral shape are similar to those for the TICT emission of free **2**.

The agreement between the decay of band I and the rise of band II substantiates the energy transfer from G_{LE} to HG_{CT}. This efficient energy transfer significantly shortens the G_{LE} lifetime of encapsulated **2** (7.4 ps) relative to the G_{LE} lifetime of free **2** (41 ps in EtOH). Under the assumption that the time constants of competing nonradiative processes remain similar upon encapsulation, the yield of energy transfer is calculated to be $\phi_{ET} = 0.82$.[7] The emission intensity of G_{TICT} (relative to that of G_{LE}) in the cage is much smaller than that for free **2**. This is reasonable because the yield of G_{TICT} formation is largely reduced in $\mathbf{1}\supset\mathbf{2}$ as a result of the competing energy transfer process from G_{LE} to HG_{CT}. To summarize, excitation of encapsulated **2** generates the initial G_{LE} state (Scheme 1). The majority of excited **2** molecules undergo energy transfer into the weakly emissive HG_{CT} state ($\tau_{ET} = 9$ ps), while the remainder experience structural motion and relax into the G_{TICT} state.

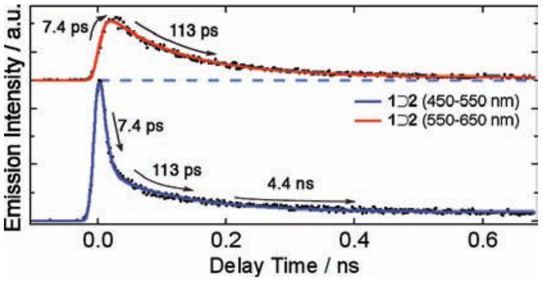
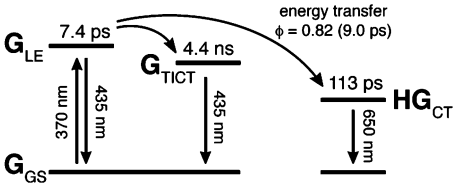


Figure 4. Time-resolved fluorescence traces of $\mathbf{1}\supset\mathbf{2}$ at selected wavelengths.

Scheme 1



In conclusion, the tight fit in the host−guest complex $\mathbf{1}\supset\mathbf{2}$ induces efficient energy transfer from the entrapped fluorophore to the HG_{CT} exciplex. The photophysical processes observed in this unique, mechanically trapped molecular system demonstrate the utility of self-assembled hosts in the design of new supramolecular photochemical and photophysical devices.

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Supporting Information Available: Experimental details, spectroscopic data, and crystallographic data for $\mathbf{1}\supset\mathbf{2}$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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