Host to Guest Energy Transfer in a Self-assembled Supramolecular Nanocage Observed by Picosecond Fluorescence Quenching

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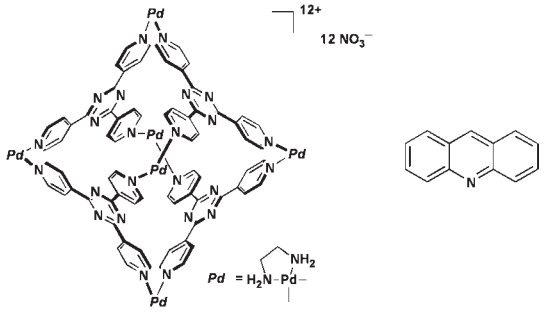
(Received December 24, 2004; CL-041601)

The host–guest energy transfer process in a self-assembled system was investigated by picosecond time-resolved fluorescence spectroscopy. A self-assembled coordination nanocage (Pd_6L_4) was photoexcited and the appearance of the fluorescence from an encapsulated guest acridine dye molecule was observed. The time constant (1.3 ns) as well as the efficiency (9%) of the energy transfer from the nanocage to the guest molecule was determined.

Supramolecular systems have been receiving great attention in wide fields of materials science.[1] Especially, photoinduced energy transfer in complex molecular assemblies has been studied extensively toward realization of artificial light-energy conversion systems that mimic photosynthesis.[2] Very recently, it was reported that a self-assembled host–guest complex can act as a special photochemical reactor of nanometer dimension,[3] where energy transfer in the complex is essentially important as the primary process of the photochemistry. For the better application of supramolecular complexes to artificial photosynthesis or nanoreactors, fundamental knowledge of energy-transfer dynamics in the complexes is indispensable. In this letter, we report the first observation of photoinduced energy transfer from a self-assembled host molecule to a guest dye molecule using the picosecond time-resolved fluorescence quenching technique.[4]



Pd_6L_4 acridine

We chose the self-assembled palladium coordination nanocage (Pd_6L_4) as the host molecule. Pd_6L_4 self-assembles from six Pd^{2+} coordination blocks and four pyridine-based bridging ligands.[5] Acridine, which we chose as the guest molecule, is encapsulated by Pd_6L_4 into its hydrophobic nanospace. This was assured by the broadening and higher-field chemical shift of acridine signals in a ^{1}H NMR spectrum of an aqueous solution of 1:1 mixture of Pd_6L_4 and acridine (the concentration of each solute is 1×10^{-3} mol dm^{-3}).[5] The ^{1}H NMR signal integration ratio of acridine to the nanocage indicates the formation of a 1:1 host–guest complex, which eliminates the effect of interactions between plural guest molecules in the nanocage. Figure 1 shows the UV absorption spectrum of Pd_6L_4 (line) and that of acridine (dotted line) in water in the wavelength region of 260–400 nm. The spectrum of the host–guest complex in the same region can be basically reproduced by the sum of the host and the guest spectra. It indicates that the electronic structure of Pd_6L_4 and that of acridine are not drastically changed upon the complex formation.

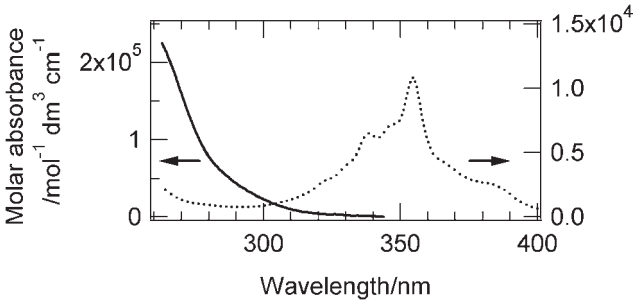


Figure 1. Molar absorption spectra of Pd_6L_4 (line) and acridine (dotted line) in aqueous solution.

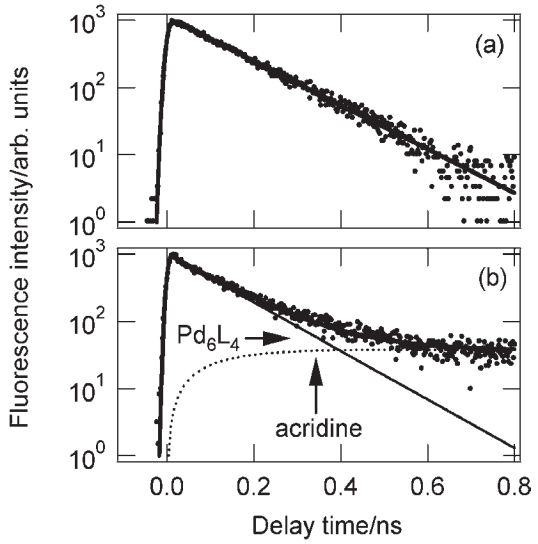


Figure 2. Fluorescence decay curves of (a) Pd_6L_4 and (b) Pd_6L_4–acridine complex (dots: data, bold lines: fitting). In (b), the contribution of Pd_6L_4 (thin line) and acridine (dotted line) are drawn separately.

Picosecond time-resolved measurements were performed to observe the fluorescence dynamics of Pd_6L_4 and Pd_6L_4–acridine complex. The excitation wavelength was 267 nm, which made it possible to excite Pd_6L_4 selectively, because the molar absorption coefficient (ε) of Pd_6L_4 is 80 times larger than ε of acridine.

The fluorescence was spectrally dispersed by a polychromator and detected by a streak camera in the time range of 1 and 50 ns with the time resolution of 20 and 600 ps, respectively. The streak camera was operated in the photon counting mode.

Figure 2a shows the fluorescence decay curve of Pd_6L_4 in water measured in the time range of 1 ns. The signal was integrated in the wavelength region of 400–480 nm. The decay curve can be perfectly reproduced by a single exponential function ($A_1 \exp(-t/\tau_1)$) with the time constant (τ_1) of 133 ps. The observed fluorescence is readily ascribed to the lowest excited singlet (S_1) state of Pd_6L_4, and τ_1 corresponds to the S_1 lifetime. Figure 2b depicts the fluorescence decay curve of the Pd_6L_4–acridine complex obtained under the same experimental condition as for Pd_6L_4. The decay curve of the complex was not fitted to a single exponential function but was well reproduced by a double exponential function ($A'_1 \exp(-t/\tau'_1) + A'_2 \exp(-t/\tau'_2)$). The fitting analysis showed that the shorter time constant (τ'_1) is 120 ps. The longer one (τ'_2) was determined to be 9.7 ns by a separate experiment for the wide time range of 50 ns. Since we selectively photoexcite the host Pd_6L_4, the contribution of Pd_6L_4 is expected to be predominant in the fluorescence in early time. As seen in Figure 2b, the shorter lifetime component predominates in the time range of 0–200 ps after photoexcitation. This 120-ps component is undoubtedly assigned to the S_1 fluorescence of Pd_6L_4 in the complex. For the assignment of the slow 9.7 ns component, we performed a measurement with excitation at 400 nm for the Pd_6L_4–acridine complex. Because ε of acridine is 23 times larger than ε of Pd_6L_4 at 400 nm, acridine is selectively photoexcited in the complex. The decay curve observed with the 400-nm photoexcitation (data not shown) showed a lifetime of 9.7 ns that is in perfect agreement with τ'_2. It indicates that the longer lifetime component of the complex fluorescence is due to acridine encapsulated in the nanocage. τ'_2 is the S_1 lifetime of acridine in the complex.

The 267-nm photoexcitation of the complex directly induces the fluorescence of the host molecule Pd_6L_4, which was identified as the shorter lifetime component. The fluorescence of the guest molecule acridine is not supposed to be induced directly, because of small ε at the excitation wavelength. The S_1 state of acridine in the complex is generated through energy transfer from the photoexcited nanocage.

We can rewrite the double exponential function to properly describe the energy transfer from the host to the guest in the following way:

$$A'_1 \exp(-t/\tau'_1) + A'_2 \exp(-t/\tau'_2) = (A'_1 + A'_2) \exp(-t/\tau'_1) + A'_2[\exp(-t/\tau'_2) - \exp(-t/\tau'_1)], \quad (1)$$

where the second term on the right hand side describes the rise and decay of the acridine fluorescence. As observed, τ'_1 (= 120 ps) is shorter than τ_1 (= 133 ps): the S_1 lifetime of Pd_6L_4 becomes shorter upon the complex formation (i.e. rate quenching). This lifetime shortening manifests the opening of a new decay pathway from the S_1 state of Pd_6L_4, i.e., the energy transfer to acridine. Moreover, the time-resolved fluorescence data provide quantitative information about the energy transfer process. The lifetime shortening caused by the energy transfer can be written as

$$\tau'^{-1}_1 = \tau_1^{-1} + \tau_{ET}^{-1}, \quad (2)$$

where τ_{ET} is the time constant of the energy-transfer process. (It is assumed that the fluorescence rate quenching is brought about only by the energy transfer to the guest molecule.) From Eq 2, we obtain τ_{ET} as 1.3 ns. The ratio of S_1 Pd_6L_4 that decays through the energy transfer is τ'_1/τ_{ET}, which is calculated to be 0.09. Thus, 9% of S_1 Pd_6L_4 transfers its energy to acridine inside.

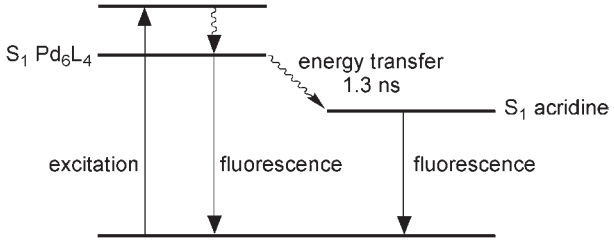


Figure 3. Schematic illustration of energy transfer in Pd_6L_4–acridine complex.

In Figure 3, the result of the present study is summarized. After the photoexcitation, the energy stored in S_1 nanocage is transferred to the guest dye molecule, which gives rise to the long-lifetime fluorescence from the dye. The present experiment directly elucidates the energy transfer in the host–guest complex. We can exploit the obtained information to develop new and promising supramolecular systems for light-energy conversion or nanoreactors.

We thank Professor Makoto Fujita of The University of Tokyo for the supply of Pd_6L_4 and valuable advice.

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Published on the web (Advance View) March 25, 2005; DOI 10.1246/cl.2005.618