

Selective Photoinduced Energy Transfer from a Thiophene Rotaxane to Acceptor

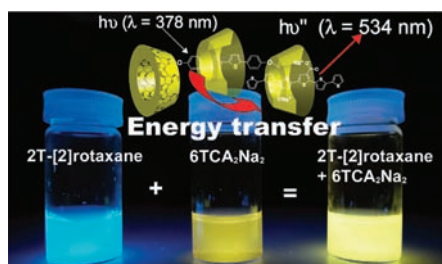
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ABSTRACT



An energy transfer process was investigated using cyclodextrin–oligothiophene rotaxanes (2T-[2]rotaxane). The excited energy of 2T-[2]rotaxane is transferred to the sexithiophene derivative which is included in the cavity of β -CD stoppers of 2T-[2]rotaxane.

Natural light harvesting systems are precisely designed in photosynthetic proteins where light is converted into chemical energy.^{1–3} Biologists and chemists are familiar with molecular electronics based on electron transfer and energy transfer processes. Recently, electron and energy transfer systems, which have been used in either covalent or noncovalent molecular devices, have attracted much attention.^{4–16} Covalent molecular devices, such as molecular wires and artificial light-harvesting antennae, effectively

provide suitable orientations and distances between donors and acceptors for efficient electron and energy transfers. Supramolecular assemblies provide more complex and sophisticated structures and functions. There have already been a variety of fluorescence molecular sensors for cations, anions, and neutral molecules.^{4b} Supramolecular

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approaches provide an effective and selective energy transfer system by the suitably organized space and an affinity between host and guest molecules. Modified cyclodextrins are of major interest as molecular fluorescence sensors, which have selective binding for guest molecules, as a typical example of chromophores bound to CD for energy harvesting purposes.¹⁷

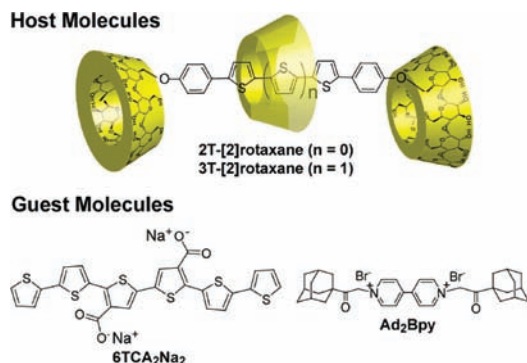


Figure 1. Chemical structures of [2]rotaxanes as donor and guest acceptor molecules.

Previously, we have prepared dimethyl- β -cyclodextrin (DM- β -CD)—rotaxanes with oligothiophenes as an axis molecule and β -cyclodextrin (β -CD) as stoppers, such as bithiophene-[2]rotaxane (2T-[2]rotaxane) and terthiophene-[2]rotaxane (3T-[2]rotaxane). β -CD stoppers have the ability to bind guest molecules selectively in aqueous solutions.¹⁸ The findings led us to hypothesize that there is energy transfer between [2]rotaxanes as a donor molecule and some acceptor molecules. Thus two guest molecules were added onto [2]rotaxanes to see whether selective energy transfer would take place between hosts and guests. Figure 1 shows the chemical structures of [2]rotaxanes and guest molecules. We chose 2,2':5',2''':5'',2''':5''',2''''':5''''',2''''':5''''''-sexithiophene-3'',4''''-dicarboxylic acid disodium salt (6TCA₂Na₂), which has six thiophene rings as energy acceptor guest molecules. 6TCA₂Na₂ has been designed to

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meet requirements for the absorption overlap for 2T-[2]rotaxane and solubility in water. As an electron acceptor molecule, an adamantane bipyridinium guest dimer (Ad₂Bpy) was also chosen. These guest molecules showed relatively high affinities to β -CD, such as 6TCA₂Na₂ ($K_1 = 9.2 \times 10^3 \text{ M}^{-1}$ and $K_2 = 1.8 \times 10^5 \text{ M}^{-1}$)¹⁹ and Ad₂Bpy ($K = 3.2 \times 10^4 \text{ M}^{-1}$).²⁰ These results indicate that inclusion complexes are formed between the guest molecules and β -CD stopper groups of [2]rotaxanes in aqueous solutions.

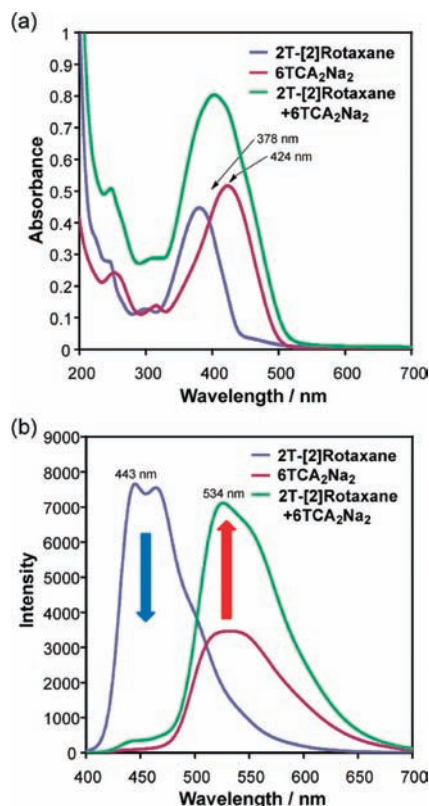


Figure 2. Absorption (a) and fluorescence (b) spectra of 2T-[2]rotaxane, 6TCA₂Na₂, and the mixture of 2T-[2]rotaxane and 6TCA₂Na₂ in aqueous solutions. Concentrations were adjusted to 15 μM , and samples were excited at $\lambda_{\text{ex}} = 378 \text{ nm}$.

Figure 2 shows the absorption and fluorescence spectra of 2T-[2]rotaxane, 6TCA₂Na₂, and a mixture of 2T-[2]rotaxane and 6TCA₂Na₂ in aqueous solutions. Excitation spectra of these compounds are shown in Figure S18. The absorption maximum of 2T-[2]rotaxane and 6TCA₂Na₂ appears at 378 and 424 nm, respectively. When the solutions were irradiated with light at a wavelength of 378 nm, the emission spectra of 2T-[2]rotaxane and 6TCA₂Na₂ showed the maximum at 443 and 534 nm, respectively. When 2T-[2]rotaxane was excited by irradiation at 378 nm in the presence of 6TCA₂Na₂, 99% of emission from 2T-[2]rotaxane at 443 nm was quenched. Simultaneously,

(19) See experimental section and Figures S12–S13 in the Supporting Information.

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Table 1. Photophysical Properties of 2T-[2]Rotaxane, 6TCA₂Na₂, 2T-[2]Rotaxane–6TCA₂Na₂, Respectively, Excited at 390 nm^a

Compound	λ_{em}/nm^b	λ_{obs}/nm^c	Φ_{em}^d	Rate constant k_r/ps^{-1e}	Lifetime/ps τ_1, τ_2	χ^2
2T-[2]rotaxane	443	495	0.10	2.9×10^{-4}	1200 (5.4%), 339 (95%) ^f	1.30
6TCA ₂ Na ₂	534	540	0.11	1.7×10^{-4}	641 ^g	1.06
2T-[2]rotaxane + 6TCA ₂ Na ₂	534	540	0.13	1.0×10^{-4}	1300 ^g	1.21
β -CD + 6TCA ₂ Na ₂	534	540	0.10	5.9×10^{-3}	1120 ^g	1.18

^a Measured in a degassed aqueous solution at 25 °C. ^b Emission maximum. ^c Fluorescence spectra were analyzed by a streak-camera system attached to a 15-cm spectrometer. ^d Absolute fluorescence quantum yield of emission. ^e Rate constant k_r can be calculated as the following equation: $k_r = \Phi_{em}/\tau$. ^f Fluorescence decay of 2T-[2]rotaxane was fitted by two-component model. ^g Fluorescence decay was fitted by single-component model.

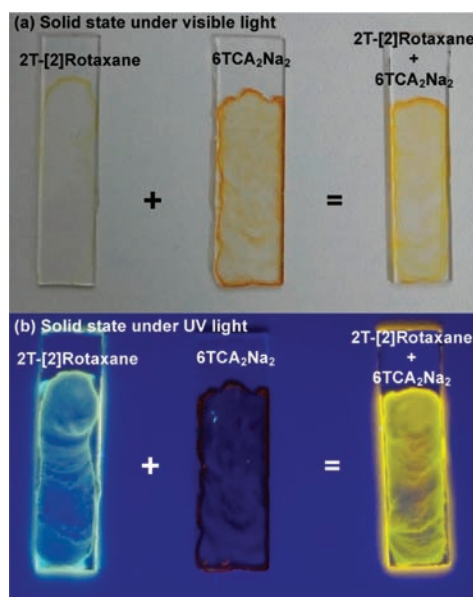
the emission intensity from 6TCA₂Na₂ with 2T-[2]-rotaxane at 534 nm was twice that of 6TCA₂Na₂ without 2T-[2]rotaxane. On the other hand, when 3T-[2]rotaxane was excited by irradiation at 407 nm in the presence of 6TCA₂Na₂, the emission of 6TCA₂Na₂ with 3T-[2]-rotaxane caused a slightly increase (20%) at 534 nm (Figure S14). The reason that the emission from 2T-[2]-rotaxane effectively quenched rather than that from 3T-[2]-rotaxane is related to the fact that the absorption band of 6TCA₂Na₂ overlaps the fluorescence band of 2T-[2]rotaxane, whereas the fluorescence band of 3T-[2]rotaxane slightly overlaps the absorption band of 6TCA₂Na₂ (Figure S15). This poor overlap may be the reason for the weak energy transfer in the 3T-[2]rotaxane–6TCA₂Na₂ system. These results provide clear evidence that the 2T-[2]rotaxane–6TCA₂Na₂ system effectively demonstrates Förster energy transfer.^{21–24}

The addition of an excess amount of adamantane carboxylic acid sodium salt (AdCANA)^{25–27} into an aqueous solution of 2T-[2]rotaxane in the presence of 6TCA₂Na₂ caused a marked decrease (54%) in the fluorescence intensity at 534 nm from 6TCA₂Na₂ (Figure S16). However, the emission intensity from 2T-[2]rotaxane recovered 50% based on the emission of 2T-[2]rotaxane alone. These results prove that the formation of inclusion complexes of 6TCA₂Na₂ in the cavity of the β -CD stoppers is important to perform the Förster energy transfer.

We considered the Förster mechanism of energy transfer from [2]rotaxane to 6TCA₂Na₂. The Förster energy transfer

depends on distance, orientation factor, and overlap integration between an emission band of the donor and an absorption band of the acceptor. It is important to note that donor molecules are within close proximity, i.e., the Förster critical radius (R_0) (15–60 Å)^{21–24} of acceptor molecules. R_0 values between the center of 2T-[2]rotaxane and 6TCA₂Na₂ were obtained as 31.8 Å for 2T-[2]rotaxane–6TCA₂Na₂ and 23.5 Å for 3T-[2]rotaxane–6TCA₂Na₂, respectively. These results indicate that the energy transfer of the 2T-[2]rotaxane–6TCA₂Na₂ complex effectively performed rather than the energy transfer of the 3T-[2]rotaxane–6TCA₂Na₂ complex even with the long distance between the donor and acceptor.

The fluorescence decays of 2T-[2]rotaxane, 6TCA₂Na₂, and 2T-[2]rotaxane–6TCA₂Na₂ were recorded in water at room temperature by using a streak camera system, respectively. These compounds at 15 μ M were excited by a picoseconds laser pulse at 390 nm; the pulse duration is

**Figure 3.** Emission properties of 2T-[2]rotaxane, 6TCA₂Na₂, and 2T-[2]rotaxane–6TCA₂Na₂ in the solid state on glass plates, respectively. (a) Under visible light and (b) under UV light ($\lambda_{ex} = 365$ nm).

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(27) The absorbance intensity of 2T-[2]rotaxane was not subject to the addition of AdCANA. The fluorescence intensity of 2T-[2]rotaxane was slightly increased when the excess amount of AdCANA was added to 2T-[2]rotaxane, indicating that AdCANA does not function as a quencher for 2T-[2]rotaxane. See Figure S17.

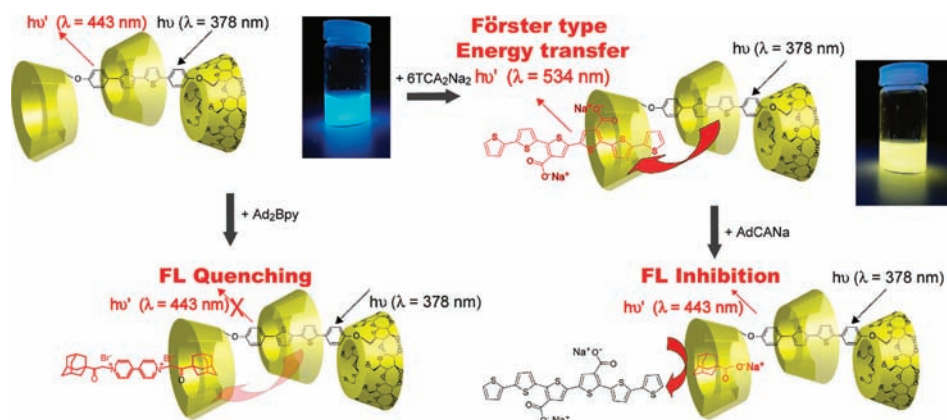


Figure 4. Schematic illustration of the photophysical property of 2T-[2]rotaxane with 6TCA₂Na₂ or Ad₂Bpy in aqueous solutions.

~0.2 ps. Table 1 shows photophysical properties of 2T-[2]rotaxane, 6TCA₂Na₂, and 2T-[2]rotaxane–6TCA₂Na₂, respectively. At 495 nm, the fluorescence decay of 2T-[2]rotaxane showed that the major component of 339 ps (95%) and a longer component of 1200 ps (5.4%) were observed, where analysis of the data using a nonlinear least-squares deconvolution method shows that a sum of double exponentials is sufficient to gain a satisfactory fit. The fluorescence decay of 6TCA₂Na₂ showed a single component of 641 ps at 540 nm, which was fitted by a single exponential. The same experiment was carried out with 2T-[2]rotaxane–6TCA₂Na₂ upon excitation at 390 nm and observation at 495 and 540 nm, respectively. When the fluorescence decay was observed at 540 nm, which is close to the emission maximum, a single component of 1300 ps was observed. The fact that the fluorescence decay derived from 6TCA₂Na₂ in 2T-[2]rotaxane–6TCA₂Na₂ was longer than that of stand-alone 6TCA₂Na₂ is related to the formation of the inclusion complex between the β -CD unit and 6TCA₂Na₂. The fluorescence decay of 6TCA₂Na₂ in the presence of β -CD showed 1120 ps, which is close to the long lifetime component in the 2T-[2]rotaxane–6TCA₂Na₂ system. Unfortunately, we could not observe a fast initial rise component less than 50 ps as it would be too fast to detect with our equipment.

Bipyridinium compounds are well-known as electron acceptor molecules.²⁸ When Ad₂Bpy was used as an electron acceptor molecule, the emission from 2T-[2]rotaxane was significantly quenched by Ad₂Bpy, although the absorption maximum of 2T-[2]rotaxane was largely unresponsive. These results suggest that the excited state of 2T-[2]rotaxane deactivates nonradiatively by energy transfer to Ad₂Bpy.

Figure 3 shows emission properties of 2T-[2]rotaxane, 6TCA₂Na₂, and 2T-[2]rotaxane–6TCA₂Na₂ in the solid state on glass plates, respectively. Aqueous solutions (1 mM, 45 μ L) of these compounds were dropped onto the glass plates, respectively, and then dried in air. Under visible light, 2T-[2]rotaxane, 6TCA₂Na₂, and the 2T-[2]rotaxane–6TCA₂Na₂ complex appeared pale yellow, orange, and light orange, respectively. Under UV irradiation

($\lambda_{\text{ex}} = 365$ nm), 2T-[2]rotaxane and the 2T-[2]rotaxane–6TCA₂Na₂ complex showed blue and bright yellow emission, whereas 6TCA₂Na₂ emitted a significantly weak orange light (Figure 3b). 6TCA₂Na₂ self-quenched in the solid state due to self-aggregation through a π - π stacking interaction. These results indicate that Förster energy transfer of the 2T-[2]rotaxane–6TCA₂Na₂ complex was clearly observed in the solid state.

We successfully observed Förster energy transfer between a bithiophene axis of the rotaxane (2T-[2]rotaxane) and an oligothiophene guest (6TCA₂Na₂) through the host–guest interaction. Figure 4 shows the emission behavior of 6TCA₂Na₂ or Ad₂Bpy in the presence of 2T-[2]rotaxane. There was a weak energy transfer in the 3T-[2]rotaxane–6TCA₂Na₂ system even though the absorption band of 6TCA₂Na₂ overlapped the emission band of 3T-[2]rotaxane. When Ad₂Bpy was used as a guest, the electron transfer took place and marked fluorescence quenching was observed. The energy transfer of the 2T-[2]rotaxane–6TCA₂Na₂ complex was clearly observed in the solid state. The excitation energy of the bithiophene axle of 2T-[2]rotaxane was selectively transferred to an acceptor guest included in the β -CD cavity. Currently, we are investigating the combination of rotaxanes and fluorescent materials as effective triggers for energy and electron transfer.

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Supporting Information Available. Experimental procedures and spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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