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Photoinduced Electron Transfer in a Supramolecular Species Building of Mono-6-*p*-nitrobenzoyl-*β*-cyclodextrin with Naphthalene Derivatives

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Photoinduced electron transfer was observed in the supramolecular complexes of *p*-nitrobenzoyl-*β*-cyclodextrin (NBCD) with a number of naphthalene derivatives, which were stabilized clearly via hydrophobic interactions in aqueous solution. Both steady-state and time-resolved fluorescence measurements were conducted, which revealed that there were two routes of electron transfer, i.e., electron transfer between the free donor and free acceptor in solution and electron transfer between the donor and acceptor bound in a supramolecular assembly. The evidence collected demonstrates that the latter route was very efficient. As a result, the rate and quantum yield of the fluorescence quenching in the present supramolecular system were appreciably large.

Introduction

Photoinduced electron-transfer plays a key role in photosynthesis[1] and, hence, has intrigued scientists for many years to look into its detailed mechanism[2] and to synthesize artificial systems for the conversion of solar energy into chemical potential.[3] Toward this goal, many covalently linked electron donor−acceptor dyads[4] have been synthesized and extensively studied experimentally and theoretically. However, these systems cannot fully mimic biological electron transfer,[5] because the latter usually occurs between the donor and acceptor held together by noncovalent interactions. Moreover, in biological systems, the donor and acceptor are organized so well that the electron transfer proceeds very fast and selectively with a characteristic high quantum yield.[6]

Recently, the supramolecular approach has attracted considerable interest[7] in the study of artificial photoinduced electron transfer. Noncovalent interactions, including hydrogen bonding,[8] π-stacking,[9] and metal−ligand coordination[10] have been used to assemble electron donors and acceptors. Modest successes have been achieved in these systems. However, it should be noted that in biological systems, the photoinduced electron transfer usually takes place in aqueous solution, in which hydrophobic interactions[11] play an important role in holding the donor and acceptor together.

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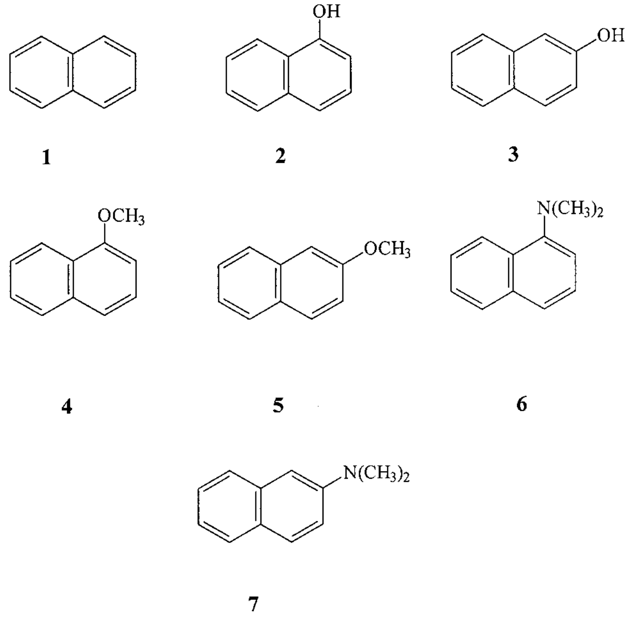
Chart 1. Electron Donors/Guests in Supramolecular Systems



Herein, we designed and synthesized an artificial system of photoinduced electron transfer in which the acceptor (*p*-nitrobenzoyl-β-cyclodextrin, NBCD) and donor (naphthalene derivatives) were clearly held together via hydrophobic interactions. Steady-state and time-resolved fluorescence were employed, and very efficient photoinduced electron transfer has been observed. During the course of our study, some other groups[12] have also used cyclodextrin-related compounds in the study of photoinduced electron transfer. However, in our work no metal ions were involved and the whole system is organic.

Experimental Section

Materials. β-Cyclodextrin (β-CD) was recrystallized three times and dried in vacuo at 100 °C for 12 h before use. *p*-Nitrobenzoyl chloride, **4**−**7** (Chart 1), and 1-adamantanamine (ADMA) were obtained commercially and used without further purification. Compounds **1** and **2** and 1-naphthoic acid (NA) were purified by sublimation at reduced pressure, and **3** was recrystallized three times before use. Deionized water was used throughout the experiments.

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DMX-500 NMR spectrometer and ^{1}H−^{1}H NOESY with a Bruker AM-400 spectrometer. MS spectra were run with a VG ZAB spectrometer. Fluorescence emission spectra were measured with a Hitachi MP850 spectrometer. Fluorescence lifetime was determined with a Horiba NBES-1100 single photon counting instrument. Both the steady-state and time-resolved fluorescence were measured in degassed aqueous solution at room temperature.

Synthesis of NBCD. β-CD (22.7 g, 0.02mol) and 1.9 g (0.01mol) of *p*-nitrobenzoyl chloride were dissolved in 250 and 100 mL of freshly distilled pyridine, respectively. The two solutions were mixed after being cooled in an ice bath. The mixture was stirred for 36 h under argon. The reaction was quenched with the addition of water. The product (4.5 g, 18% yield) was purified by repeated crystallization with 5:1 acetone−water. TLC: $R_f = 0.4$ (5:4:3 butanol−ethanol−water (v/v/v) as eluents). MS: M$^+$ 1284. IR (KBr): 1700 cm^{-1} ($\nu_{C=O}$). UV/vis (H_2O) λ_{max}: 188, 262 nm. ^{1}HNMR (500 MHz, DMSO-d_6, TMS): δ 8.37 (d, 2H), 8.26 (d, 2H), 5.75 (s, broad, 16H), 4.92 (d, 1H), 4.85 (s, 5H), 4.45 (s, broad, 8H), 4.06 (s, broad, 1H), 3.66−3.33 (m, 39H); ^{13}CNMR (125.8 MHz, DMSO-d_6): 168.3, 154.4, 138.9, 135.0, 128.0, 106.6, 106.0, 105.7, 86.4, 85.6, 85.3, 77.5, 77.1, 76.5, 76.1, 72.9, 68.9, 64.0, 63.5. Anal. Calcd for $C_{49}H_{73}NO_{38}\cdot 3H_2O$: C, 44.00; H, 5.91; N, 1.05. Found: C, 44.17; H, 6.19; N, 0.92.

Results and Discussion

Conformation of NBCD. It is well-known that a modified cyclodextrin attached to an aromatic moiety often exhibits a self-inclusion phenomenon.[13] However, in the case of NBCD, both experimental and theoretical studies indicate no self-inclusion.

The ^{1}H−^{1}H NOESY spectrum of NBCD in D_2O (see Supporting Information) shows no signal of correlation between the protons of the *p*-nitrobenzoyl group and those of β-CD. It indicates that the *p*-nitrobenzoyl group is not located inside the β-CD cavity.

Theoretical calculations in a vacuum[14] by the molecular mechanics method using a universal force field (UFF) as well as the density functional theory method support the above conclusion that the rim-covering conformation is the most stable and possesses an energy that is significantly lower than that of the out-stretching or self-inclusion one.

Binding Property of NBCD. In general, the binding force of β-CD with the substrates will be enhanced if the sixth position of the cyclodextrin is modified with a hydrophobic group.[15] However, the measurements of the binding constants of NBCD with naphthalene derivatives **1**−**7** are not feasible with UV and calorimetric methods because of the very low solubility of the substrates. The steady-state fluorescence method is also infeasible since the fluorescence of the substrates is quenched by NBCD. Therefore, we can only measure the binding constants of NBCD with **4**−**7** from lifetime results. As seen, those numbers are truly much larger than the binding constants of natural β-CD with naphthalene derivatives, which are usually below 1.0×10^3 dm^3/mol. Therefore, NBCD can form relatively stable complexes with naphthalene derivatives.

The molecular modeling result of the NBCD complex with β-*N*,*N*-dimethyl-aminonaphthalene (2-DMAN) is shown in Figure 1. From Figure 1, it can be seen that in the NBCD complex, the naphthyl moiety is deeply included in the cavity. Moreover, the *p*-nitrobenzoyl group is very close to 2-DMAN, which is obviously favorable for the electron transfer between them.

Steady-State Fluorescence Study. The interaction between NBCD and naphthalene derivatives (**1**−**7**) and NA in aqueous solution is studied with steady-state fluorescence and absorption spectra. From the absorption spectra, it is concluded that no ground-state complex is formed because no new band of absorption other than those of the host and guest can be detected upon the

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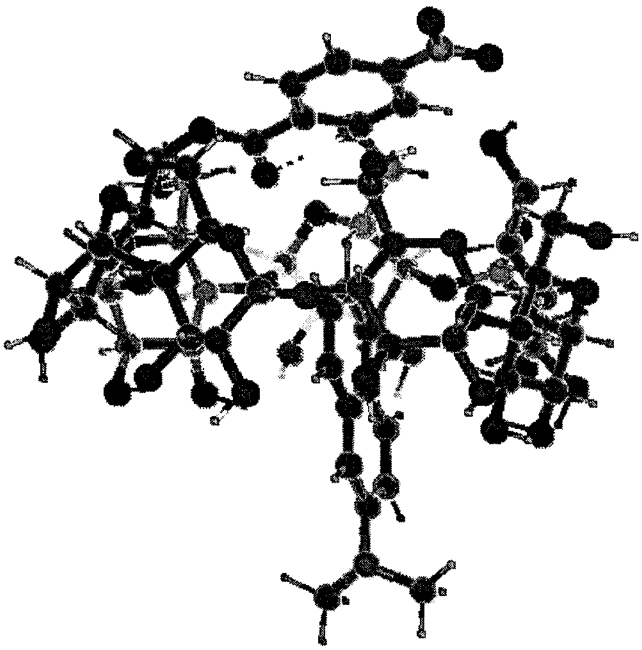

Figure 1. Structure of NBCD−2-DMAN inclusion complex obtained by quantum chemical calculations.

Table 1. ΔG_{ET} Calculated from the Rehm−Weller Equation

guest	λ_{em} (nm)	E_{00} in H_2O (eV)[a]	$E_{D^{+\bullet}/D}$ (eV)	ΔG_{ET} (eV)
1	330	3.76	$1.54^{MeCN\ b}$	−0.95
2	340	3.65	$1.97^{H_2O,\ pH = 0.1\ c}$	−0.38
3	359	3.45	$2.00^{DMF,\ pH = 0.1\ c}$	−0.15
4	356	3.48	$1.36^{MeCN\ d}$	−0.82
5	355	3.49	$1.42^{MeCN\ e}$	−0.77
6	445	2.79	$0.75^{MeCN\ d}$	−0.74
7	430	2.88	$0.67^{MeCN\ d}$	−0.91
NA	330	3.76	$2.60^{MeCN\ d}$	0.14

[a] λ_{em} is the emission wavelength, $E_{00} = h\nu = 12398.1/\lambda_{em}$ (Å),[17] and $E_{A/A^{-\bullet}} = -1.30$ eV.[18] [b] From ref 19. The calculated ΔG_{ET} values refer to the MeCN medium, as $E_{Ox/Red}$ was obtained in MeCN solutions. Corresponding ΔG_{ET} values in an H_2O solution should be even more negative and the ET process more favorable due to the higher solvent polarity. [c] From ref 20. [d] From ref 21. [e] From ref 16.

addition of naphthalene derivatives to NBCD. Since the energies of the singlet excited states of naphthalene derivatives are all much lower than that of NBCD, the energy transfer from the naphthalene derivatives to NBCD is impossible.

On the other hand, according to the Rehm−Weller equation,[16]

$$\Delta G_{ET} = E_{D^{+\bullet}/D} - E_{A/A^{-\bullet}} - E_{00}$$

if $\Delta G_{ET} < 0$, electron transfer can take place between the excited naphthalene and NBCD. Here, $E_{D^{+\bullet}/D}$ and $E_{A/A^{-\bullet}}$ are the redox potentials of the electron donors and electron acceptor, respectively, and E_{00}[17] is the excited-state energy of the naphthalene derivatives.

In Table 1 are listed the values of ΔG_{ET} for the naphthalene derivatives **1**−**7** and NA. From Table 1, it can be seen that photoinduced electron transfer can take place between **1**−**7** and NBCD, as their ΔG_{ET} values are negative. In fact, significant fluorescence quenching is observed for these naphthalene derivatives when NBCD is added, which indicates the occurrence of electron transfer. However, ΔG_{ET} is positive for NA. Accordingly, the fluorescence of NA is enhanced upon the addition of NBCD. This fluorescence enhancement is probably due to the change of the polarity of the molecular environments.[15]

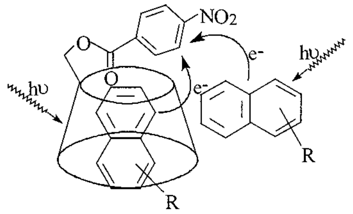

Figure 2. Two pathways of photoinduced electron-transfer reactions between naphthalene derivatives and NBCD.

As mentioned above, NBCD should adopt the rim-covering conformation.[14] As a result, electron transfer can take place either between NBCD and the free excited guest molecule in solution (dynamic quenching) or between NBCD and the guest molecule complexed inside the NBCD cavity (static quenching) (Figure 2).

For steady-state fluorescence, the Stern−Volmer (SV) relationship for a system with dynamic and static quenching components has been derived previously:[22]

$$\frac{I_0}{I} = (1 + K_b[Q])(1 + \tau_0 k_q[Q]) = 1 + (K_b + \tau_0 k_q)[Q] + K_b \tau_0 k_q [Q]^2 \quad (1)$$

where I_0 and I are the fluorescence intensities in the absence and presence of quencher (Q), respectively, k_q is the bimolecular quenching constant, τ_0 is the lifetime of the fluorophore in the absence of quencher, and K_b is the supramolecular binding constant.

The above expression predicts that the limiting slope as [Q] approaches zero is the sum of the binding constant (K_b) and the dynamic Stern−Volmer constant ($\tau_0 k_q$), and at large [Q], the plot should deviate upward from the line. For small [Q], the Stern−Volmer curve will be a straight line with a slope of $K_b + \tau_0 k_q$, as shown in eq 2:

$$\frac{I_0}{I} = 1 + (K_b + \tau_0 k_q)[Q] \quad (2)$$

In the present system, the experimental results obtained were fitted with eq 2 (see Figure 3) because the concentration of NBCD is about 10^{-5} mol/dm^3. It is well-known that the fluorescence quenching is usually described by the following Stern−Volmer relationship (eq 3) when there is only dynamic quenching:

$$\frac{I_0}{I} = 1 + \tau_0 k_q [Q] \quad (3)$$

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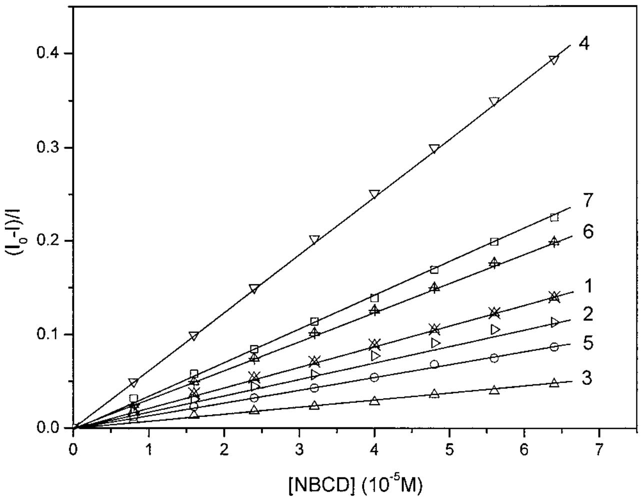

Figure 3. Stern−Volmer plots for the fluorescence quenching of naphthalene derivatives with NBCD in water at room temperature (I_0 is the fluorescence intensity in the absence of NBCD and I is the fluorescence intensity in the presence of NBCD with the concentration varying from 0.8×10^{-5} to 6.4×10^{-5} mol/dm^3).

Table 2. Apparent Stern−Volmer Constants (K_{SV}^{h}),[a] Fluorescence Lifetime in the Absence of Quencher (τ_0),[b] Reduction Potentials of Excited Donors (E_{ox}^{*}),[c] and Hypothetical Fluorescence Quenching Constants (K_q^h)[d] of Donors

donors	K_{SV}^{h} (M^{-1})	τ_0 (ns)	E_{ox}^{*} (eV)	K_q^h (M^{-1} s^{-1})
1	2187	96.0	−2.22	2.278×10^{10}
2	1767	43.9	−1.68	4.025×10^{10}
3	742	11.3	−1.45	6.566×10^{10}
4	6152	19.6	−2.12	31.39×10^{10}
5	1357	32.2	−2.07	4.214×10^{10}
6	3105	26.1	−2.04	11.90×10^{10}
7	3515	24.9	−2.21	14.12×10^{10}

[a] K_{SV}^{h} is the slope of the plot of $(I_0 - I)/I$ vs [NBCD]. [b] Obtained by the time-resolved fluorescence or from reference. [c] $E_{ox}^{*} = E_{ox} - E_{00}$ (eV), and $E_{ox}(E_{D^{+\bullet}/D})$ and E_{00} came from Table 1. [d] $K_q^h = K_{SV}^h/\tau_0$.

From Figure 3, if we suppose that there was only dynamic quenching in the studied system, the hypothetic fluorescence quenching constants k_q^h in the dynamic process are calculated from the apparent Stern−Volmer constants (K_{SV}^h, $K_{SV}^h = \tau_0 k_q + K_b$), which are summarized in Table 2. The diffusion rate constants of the studied solvent systems are taken into consideration, which are estimated to be $k_{diff} = 8kT/3\eta \approx 6.6 \times 10^9$ M^{-1} s^{-1}.[23] From Table 2, every value of k_q^h is much larger than k_{diff}. Thus, the electron transfer should proceed not only through diffusion but also within the supramolecular system. According to Figure 3, as the concentration of NBCD increases, the value of $(I_0 - I)/I$ is enhanced, which means that, the more donor−acceptor complexes formed, the more efficient the electron transfer. In fact, according to Abelt et al.,[24] a linear Stern−Volmer plot indicates that the static quenching within a supramolecular system is nearly complete. Therefore, the efficiency of the intrasupermolecule static quenching is quite high because of the more effective overlap of molecular orbital between the electron donor and acceptor.

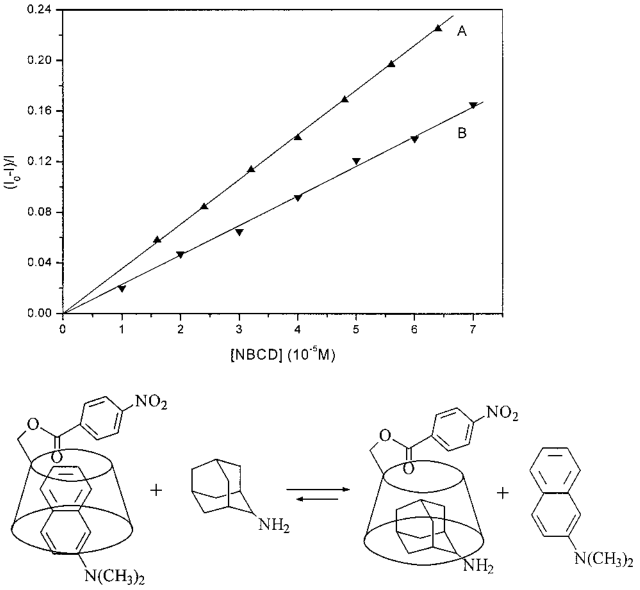

Figure 4. Fluorescence quenching of 2-DMAN with NBCD in aqueous solution without 1-adamantanamine (A) and with 1-adamantanamine (B).

Notably, the rule established by Marcus and Rehm and Weller that k_q should rely on E_{ox}^{*} (the same electron acceptor) cannot be applied in the present systems. This is because NBCD and the naphthalene derivatives form complexes, in which the guest compounds with different substituents have different volumes, hydrophobicity, and dipole moments. As these differences can significantly affect the binding constants and conformations of the complexes, the fluorescence quenching constant does not rely on the single factor (E_{ox}^{*}).

To further support the above mechanism, the complex of NBCD with 2-DMAN is analyzed in detail with the steady-state fluorescence. Its fluorescence quenching constant in aqueous solution decreases when ADMA (1×10^{-6} M) is added into the system (Figure 4). Apparently, 2-DMAN (2×10^{-6} M) included in NBCD will be partially excluded from the cavity of the latter by the addition of ADMA, which is a much better substrate of β-CD (the binding constant is about 9200 M^{-1}). Thus, the electron transfer can partially take place between NBCD and free 2-DMAN in the solution. The absence of the partial intrasupramolecular electron-transfer pathway results in the decrease of the observed apparent fluorescence quenching constant.

The decrease in the fluorescence quenching constant of 2-DMAN with NBCD is also observed when methanol is added into the solution (Figure 5). The apparent reason for the decrease in the quenching constant of the 2-DMAN−NBCD system by methanol is attributed to the fact that when methanol is added, the hydrophobic 2-DMAN in the cyclodextrin cavity will be replaced by and enter into the bulk solution.

In short, all the results from the steady-state fluorescence measurements show that in the present systems, the photoinduced electron transfer takes place between NBCD and the guest molecule included inside the NBCD cavity.

Time-Resolved Fluorescence. Herein, the systems of NBCD with **4**−**7** are investigated in detail with the time-resolved fluorescence. First, the decay of the singlet

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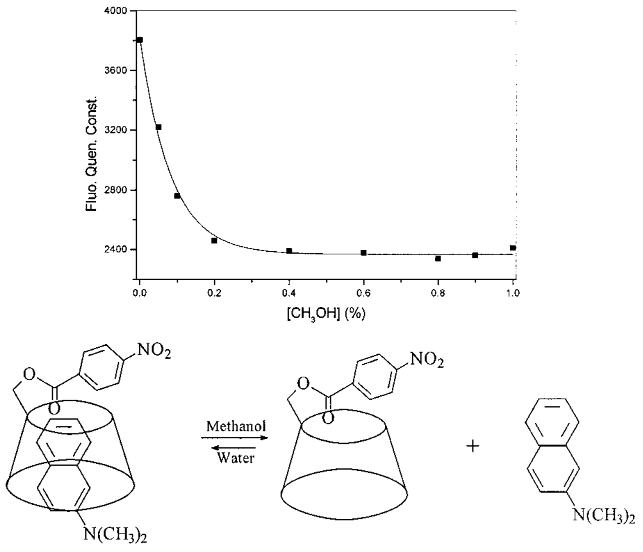

Figure 5. Solvent effect on the fluorescence quenching of 2-DMAN with NBCD in water–methanol binary solvents.

excited guests in water (2.0, 4.0, 4.0, 5.0 × 10^{-6} mol/dm^3, respectively) is found to be monoexponential in the absence of NBCD. However, the decay of the fluorescence intensity for the systems with NBCD as a quencher obeyed a double-exponential function:

$$F(t) = A_L \exp(-t/\tau_L) + A_S \exp(-t/\tau_S)$$

a long-lived component with a variable lifetime depending on the concentration of NBCD and a short-lived one with a constant lifetime within the experimental error. The amplitude of the exponential component with the shorter lifetime (A_S) increased with an increase in the concentration of NBCD; the amplitude of the component with the longer lifetime (A_L) decreased with it (Table 3). The short-lived component can be attributed to the fluorescence from the naphthalenes bound within NBCD. The long-lived component is ascribed to normal deactivation of the excited state of the uncomplexed guests. Apparently, both routes of electron transfer are present in the system. The monoexponential decay profile of the guests is unchanged even when 0.40 mM of ADMA is present when an increasing amount of NBCD is added (Table 3). It can be interpreted that when the ADMA is present in the solution, because of its better fit to the cyclodextrin cavity, the complexed naphthalene derivatives are excluded from the NBCD cavity, resulting in the decrease in the intrasupramolecular electron transfer.

The linearity of Stern–Volmer plots has been tested for the long-lived component and is shown in Figure 6; K_{SV}^T and k_q^T were calculated and are summarized in Table 4. From Table 4, every value of k_q^T similar to k_{diff} shows that the long-lived component was dynamically quenched by NBCD. On the other hand, the binding constants for the complexation of NBCD with naphthalene derivatives were obtained from the difference between K_{SV}^h (eq 2) from the steady-state fluorescence and K_{SV}^T from time-resolved results (Table 4).[25]

Table 3. Time-Resolved Fluorescence Parameters for the Electron Donors in the Absence and in the Presence of NBCD and Inhibitor ADMA[a]

guest	[NBCD] ([ADMA]), mM	τ_L, ns	A_L	τ_S, ns	A_S
4	0	19.6	1.0		
	0.24	18.8	0.41	0.978	0.59
	0.32	18.5	0.34	0.922	0.66
	0.40	18.3	0.29	0.892	0.71
	0.48	18.1	0.26	0.891	0.74
	0.56	17.8	0.22	0.882	0.78
4 + ADMA	0.40 (0.40)	19.5	1.0		
5	0	32.2	1.0		
	0.24	31.5	0.78	1.10	0.22
	0.32	31.2	0.73	1.10	0.27
	0.40	31.0	0.68	1.05	0.32
	0.48	30.7	0.63	1.04	0.37
	0.56	30.4	0.60	1.04	0.40
5 + ADMA	0.40 (0.40)	32.1	1.0		
6	0	26.1	1.0		
	0.24	25.5	0.58	0.599	0.42
	0.32	25.3	0.52	0.601	0.48
	0.40	25.1	0.46	0.587	0.54
	0.48	24.8	0.41	0.587	0.59
	0.56	24.6	0.38	0.589	0.62
6 + ADMA	0.40 (0.40)	26.1			
7	0	24.9	1.0		
	0.24	24.0	0.54	0.280	0.46
	0.32	23.7	0.47	0.275	0.53
	0.40	23.5	0.42	0.269	0.58
	0.48	23.2	0.38	0.270	0.62
	0.56	22.8	0.34	0.258	0.66
7 + ADMA	0.40 (0.40)	24.5	1.0		

[a] τ_L and τ_S are lifetimes for the long-lived exponential decay component and the short-lived one, respectively. A_L and A_S are fractional amplitudes for the long-lived component and the short-lived one, respectively.

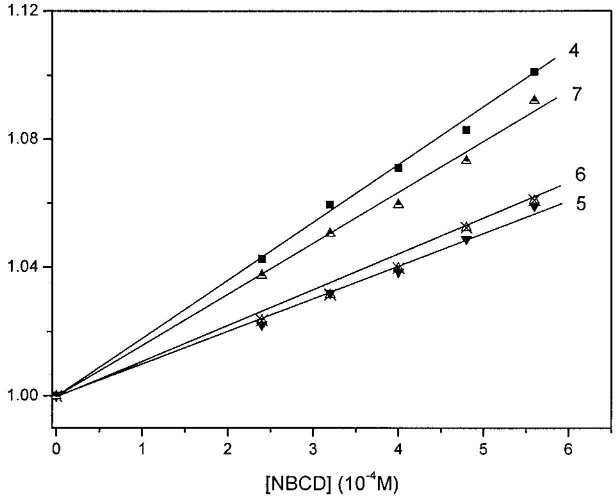

Figure 6. Stern–Volmer plots for the quenching of the long-lived component (τ_L) of the fluorescence of **4**–**7** by NBCD.

The decay of 2-DMAN was also monitored in methanol solution. In the absence of NBCD, the lifetime profile of 2-DMAN in methanol solution is monoexponential with a lifetime of 12.7 ns. When NBCD is added to the solution, the lifetime profile remains monoexponential, although the lifetime becomes somewhat shorter (Table 5). Apparently, because the hydrophobic interaction is not significant in a methanol solution, only intermolecular quenching occurs in the NBCD–2-DMAN methanol solution. The time-resolved fluorescence study is also performed in a control system of 2-DMAN and ethyl *p*-nitrobenzoate (ETNB) in aqueous solution, in which only intermolecular electron transfer can occur. As the concentration of ETNB increases, the fluorescence decay

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[25] Sukhendu, N.; Avinash, V. S. *Chem. Phys. Lett.* **2001**, *344*, 138.

Table 4. Stern–Volmer Constants ($K^{\mathrm{T}}_{\mathrm{SV}}$, M^{-1}), Dynamic Quenching Constants ($k^{\mathrm{T}}_{\mathrm{q}}$, M^{-1} s^{-1}), and Binding Constants (K_{b}, M^{-1}) Obtained from Time-Resolved Fluorescence Measurements

donors	τ_0 (ns)	$K^{\mathrm{T}}_{\mathrm{SV}}$ (M^{-1})	$k^{\mathrm{T}}_{\mathrm{q}}$ (10^9 M^{-1} s^{-1})	K_{b}[a] (M^{-1})
4	19.6	180	9.18	5972
5	32.2	105	3.26	1252
6	26.1	109	4.17	2996
7	24.9	164	6.58	3351

[a] $K^{\mathrm{h}}_{\mathrm{SV}} - K^{\mathrm{T}}_{\mathrm{SV}}$.

Table 5. Lifetime of 2-DMAN Changed with the Concentration of NBCD in a Methanol Solution and Changed with the Concentration of ETNB

[NBCD] (M)	τ (ns)	[ETNB] (M)	τ (ns)
0	12.7	0	24.9
4.8×10^{-5}	12.7	4.8×10^{-5}	24.3
6.4×10^{-5}	12.6	6.4×10^{-5}	24.1

profile remains monoexponential in character. However, the lifetime becomes smaller because the bimolecular quenching process is concentration dependent (Table 5).

From the above results, it can be seen that the time-resolved fluorescence measurements also show that in the present supramolecular system, the photoinduced electron transfer occurs mainly between NBCD and guest molecules located inside the NBCD cavity.

Several data in the present systems are of special interest. First, the photoinduced electron-transfer rate constant from 2-DMAN to NBCD in the supramolecular assembly is

$$k_{\mathrm{SET}} = 1/\tau_1 - 1/\tau_2 = 3.8 \times 10^9\ \mathrm{s}^{-1}$$

Herein, τ_1 is the lifetime of the short-lived component, and τ_2 is the long-lived one.

Second, the fluorescence quenching quantum yield of the intramolecular electron transfer in the supramolecular assembly is defined as $\Phi^{\mathrm{q}}_{\mathrm{F}} = k_{\mathrm{SET}}/[k_{\mathrm{SET}} + (1/\tau_0)] = 0.989$. Here, τ_0 stands for the fluorescence lifetime of 2-DMAN in the absence of quencher in aqueous solution, which equals 24.9 ns. Obviously, these data indicate that the photoinduced electron transfer in the supramolecular assembly is very efficient and its high rate constant can mimic the electron transfer in biological systems such as photosynthesis.

Conclusion

In the present study, we synthesized *p*-nitrobenzoyl-β-cyclodextrin and studied its inclusion complexes with a number of naphthalene derivatives. Conformational analysis indicated that the *p*-nitrobenzoyl group is covering the narrower ring of the cyclodextrin cavity, and intramolecular electron transfer could effectively take place between this electron-withdrawing group and the included electron donors. Thus, the present system represents a supramolecular electron-transfer system held together by hydrophobic interactions.

Steady-state and time-resolved fluorescence measurements indicate that there are two routes of electron transfer, i.e., electron transfer between the free donor and free acceptor in solution and electron transfer between the donor and acceptor bound in a supramolecular assembly.

On the basis of the control studies, it was found that the intrasupramolecular electron transfer was very efficient. Notably, the rate and quantum yield of the fluorescence quenching in the present supramolecular system are appreciably large.

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Supporting Information Available: Three reasonable conformations of NBCD constructed by MOLDEN, a table giving the energies of three possible NBCD conformations from theoretical calculations in a vacuum, and the ^{1}H–^{1}H NOESY spectrum of NBCD in D$_2$O. This material is available free of charge via the Internet at http://pubs.acs.org.

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