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Photoinduced Electron Transfer in Host-Guest Complexes of 2-Naphthyl-O$(CH_2)_n$-adamantanamines with Mono-6-*O*-*p*-nitrobenzoyl-*β*-cyclodextrin and Mono-6-*O*-*m*-nitrobenzoyl-*β*-cyclodextrin

HUI-YUAN HU, MAN-ZHOU ZHU*, ZHI-PING ZHANG, GUO-TAO WEN and QING-XIANG GUO
Department of Chemistry, University of Science and Technology of China, 230026, Hefei, P. R. China

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Abstract

A number of naphthalene derivatives containing adamantanamine binding moiety and an $(CH_2)_n$ ($n = 2, 3, 4, 5, 6$) spacer were prepared as the electron donor. A supramolecular assembly was fabricated by the inclusion between the donor substrates and the host molecules, i.e., mono-6-*O*-*p*-nitrobenzoyl-*β*-cyclodextrin (*p*NBCD) and mono-6-O-*m*-nitrobenzoyl-*β*-cyclodextrin (*m*NBCD), in water. The fluorescence quenching in these systems was studied in detail. It revealed efficient photoinduced electron transfers (PET) between the naphthalene donors and the cyclodextrin acceptors. This PET process was partitioned into a dynamic quenching component caused by bimolecule collision reactions and a static quenching component due to hydrophobic binding between the donor and acceptor molecules. Detailed Stern–Volmer constants were measured and they were partitioned into dynamic Stern–Volmer quenching constants (dynamic quenching) and static binding constants (static quenching). In these two pathways, the static quenching was found to be highly efficient and dominant in the presence of NBCD.

Introduction

Life is dependent on energy conversion and energy balance. Photosynthesis plays the most important part for the natural ecosystem as well as for our society. It has evolved over time to prompt ultrafast photoinduced electron transfer from the electronically excited chlorophylls to quinone receptors [1]. Therefore, photoinduced electron transfer has aroused the scientists' interests in looking into its detailed mechanism [2] and in designing laboratory systems for the conversion of solar energy into chemical potential [3]. For this purpose, many covalently linked electron donor-acceptor dyads [4], triads [5], and pentads [6] have been synthesized and studied experimentally and theoretically. But these systems can not fully mimic the biological electron transfer [7], because in the biological systems the donor and acceptor are held together by proteins without any covalent linkage.

So the supramolecular assemblies come into the scientists' sights for the study of artificial photoinduced electron transfer. In these systems, noncovalent forces [8], including van der Waals, hydrophobic, electrostatic, dipole-dipole, and hydrogen-bonding interactions, cooperatively govern the arrangement of the electron donors and acceptors. It should be noticed that the photoinduced electron transfer in biological systems usually takes place in aqueous solution, therefore, in these systems hydrophobic interactions [9] play a key role in holding the donors and acceptors together.

Cyclodextrins (CD), composed of six (α), seven (β), or eight (γ) D-glucopyranose units, possess truncated cone-shaped hydrophobic cavities which are capable of binding various organic, inorganic, and biological molecules to form stable host-guest inclusion complexes in aqueous solution [10]. This feature makes them suitable for an extremely large number of applications from drug delivery devices [11] to enzyme mimics [12]. The same binding property is also expected to be useful in the assembly of supramolecular photoinduced electron transfer systems.

To improve or enhance the original molecular binding abilities of the native cyclodextrins, a great deal of effort has been concentrated on the design and syntheses of novel cyclodextrin derivatives in recent years [13]. In fact, a wide variety of native and chemically modified cyclodextrins have been employed in the studies of the photoinduced electron transfer reactions in water by many groups [14]. However, very little effort has been devoted to the use of CD in constructing photoinduced electron transfer systems. Recently, De Cola *et al.* [15] synthesized metal-coordinated CD and studied their

* Author for correspondence. E-mail: zmz@ustc.edu.cn

photoinduced electron transfer with viologens. Park *et al*. [16] synthesized naphthalene-substituted β-CD and studied its photoinduced electron transfer with adamantylmethyl viologen. We synthesized mono-6-O-*p*-nitrobenzoyl-β-cyclodextrin (pNBCD) and studied its photoinduced electron transfer with naphthalene derivatives [17].

We observed very efficient PET in the pNBCD-naphthalene system [17] which is consistent with De Cola and Park's work. Since no chemical bond is available in this system, this PET must occur through space but not through bond. Thus we proposed that *p*NBCD should form inclusion complexes with naphthalene derivatives and the efficient fluorescence quenching should be caused by the static quenching within the *p*NBCD-naphthalene complexes. Nevertheless, in our *p*NBCD-naphthalene system the electron donating moiety of the electron donor (i.e., the naphthalene ring) is directly included in the cavity of the electron acceptor. It remains interesting to know whether we can use an electron donor the electron donating moiety and binding moiety of which are separated from each other, and whether the distance between the electron donating moiety and binding moiety affects the velocity and efficiency of the electron transfer.

Hence we synthesized a series of novel electron donors **1a**–**1e** that contain naphthalene and 1-adamantanamine connected to each other via a flexible hydrocarbon chain (see Scheme 2). In these donor molecules 1-admantanamine acts as the binding site because of its strong complexation with β-CD [18]. The real donor moiety is naphthalene. We performed a detailed study of their PET with *p*NBCD in aqueous solution. And for the sake of comparison, we also studied the PET course between *m*NBCD and the donors.

Experimental

Materials

β-CD was recrystallized three times and dried in vacuum at 100 (for 12 h before use. 1-Adamantanamine was obtained commercially and used without purification. Tetrabutylammonium perchlorate (TBAP) was obtained from Sigma and dried in vacuum prior to use. Deionized water was used in the measurements. NBCD was prepared using the previously reported method.

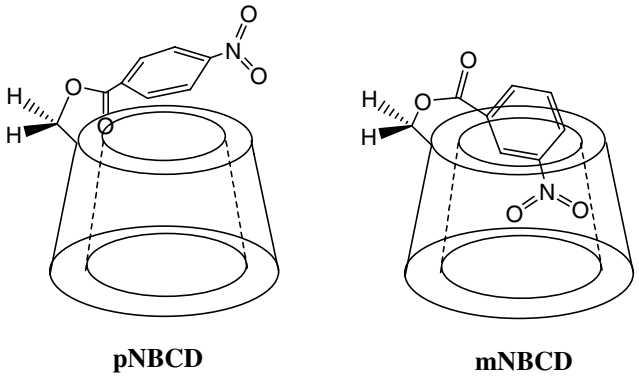
Measurement

^{1}H NMR was recorded with a Bruker DMX-300 spectrometer, $CDCl_3$ as solvent and chemical shift was given in ppm downfield from TMS. IR spectra were recorded at a Bruker Vector 220 infrared spectrometer. Elemental analysis was performed on a Perkin-Elmer 240C analytical instrument. Melting points were determined on a Yanaco melting apparatus and not corrected. The fluorescence and fluorescence emission spectra were measured by a CRT970 fluorescent spectrometer in aqueous solution at room temperature. UV absorption spectra were measured on a Perkin-Elmer lambda 45 UV/vis spectrophotometer. Oxidation potential $E_{D+/D}$ of **1a**–**1e** in acetonitrile was measured by cyclic voltammetry with an Ag/AgCl reference electrode at scan rates of 100 mV/s

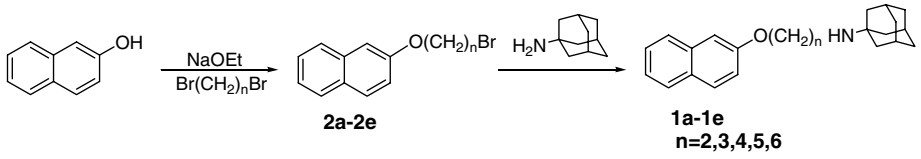
Synthesis

The synthesis method for pNBCD and mNBCD (see Scheme 1) has been reported elsewhere [17]. Compounds **1a**–**1e** were synthesized by the general procedure described below for 1a (see Scheme 2).

Naphthyl-O$(CH_2)_2$-adamantanamine (1a) 2.88 g of 2-naphthanol (0.02 mol) was added to sodium ethoxide [from sodium (0.5 g) and ethanol (20 ml)],and the solution added dropwise during 1 h to a boiling mixture of $Br(CH_2)_2Br$ (3.76 g, 0.02 mol) and ethanol (20 ml). The mixture was refluxed for 4 h. After removal of the solvent, 40 ml of chloroform was added into the residue. The solution was washed with sodium hydroxide and water, and the organic layer was collected and dried over $MgSO_4$. After removal of the solvent the residue was purified by silicon gel column chromatography (eluent: petroleum ether) and obtained pure **2a**. **1a** was



Scheme 1. The structure of two electron donors *p*NBCD and *m*NBCD.



Scheme 2.

then prepared by dissolving **2a** (1.26 g, 0.005 mol) and 1-adamantanamine (0.8 g, 0.005 mol) were dissolved in 50 ml of chloroform containing 1 g Na_2CO_3. The mixture was refluxed overnight. After removal of the solvent, the residue was purified by silica gel column chromatography. The white product 1a was obtained in 40% yield using mixed solvent of CHCl3 and MeOH (50:1, V/V) as eluent. m.p. 97.3–97.6 °C, ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.76–7.69 (m, 3H), 7.42 (m, 1H), 7.33 (m, 1H), 7.17–7.14 (m, 2H), 4.18 (t, 2H), 3.05 (t, 2H), 2.09 (s, 3H), 1.70–1.65 (m, 12H). IR (KBr) *v*: 3054.4, 2940.0, 2887.0, 2848.1, 1625.3, 1597.8, 1255.8, 1217.3, 1179.3, 1029.3, 840.8, 742.7 cm^{-1}; Anal. Calcd for $C_{22}H_{27}NO$: C 82.20, H 8.47, N 4.36; found C 82.52, H 8.10, N 4.35.

Naphthyl-O(CH_2)$_3$ -adamantanamine (1b) ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.76–7.69 (m, 3H), 7.42 (m, 1H), 7.33 (m, 1H), 7.17–7.14 (m, 2H), 4.10 (t, 2H), 2.87 (t, 2H), 2.41 (s, 1H), 2.09 (s, 3H), 1.98 (m, 2H), 1.72–1.63 (m, 12H). IR (KBr) *v*: 3049.4, 2928.0, 2867.0, 2848.1, 1625.3, 1599.8, 1265.8, 1217.3, 1179.7, 1029.3, 840.8, 743.7 cm^{-1}; Anal. Calcd for $C_{23}H_{29}NO$: C 82.34, H 8.71, N 4.18; found C 82.40, H 8.30, N 4.15.

Naphthyl-O(CH_2)$_4$-adamantanamine (1c) ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.76–7.69 (m, 3H), 7.42 (m, 1H), 7.34 (m, 1H), 7.13–7.10 (m, 2H), 4.06 (t, 2H), 2.78 (t, 3H,overlaps with -NH), 2.08 (s, 3H), 1.88 (m, 4H), 1.78-1.64 (m, 12H). IR (KBr) *v*: 3047.4, 2908.1, 2847.9, 1627.0, 1599.1, 1268.2, 1217.9, 1182.8, 1098.4, 833.1, 747.6 cm^{-1}; Anal. Calcd for $C_{24}H_{31}NO$: C 82.47, H 8.94, N 4.01; found C 82.57, H 8.60, N 4.00.

Naphthyl-O(CH_2)$_5$-adamantanamine (1d) ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.12 (s, 1H), 7.75–7.69 (m, 3H), 7.42 (m, 1H), 7.34 (m, 1H), 7.13-7.10 (m, 2H), 4.02 (t, 2H), 2.93 (m, 2H), 2.15 (m, 4H), 2.10 (s, 3H), 1.88 (m, 2H), 1.67–1.58 (m, 12H). IR (KBr) *v*: 3047.4, 2917.5, 2848.5, 2769.3, 1628.5, 1600.9, 1257.4, 1217.3, 1181.2, 1072.1, 832.3, 747.2 cm^{-1}; Anal. Calcd for $C_{25}H_{33}NO$: C 82.60, H 9.15, N 3.85; found C 82.53, H 9.10, N 3.86.

Naphthyl-O(CH_2)$_6$-adamantanamine (1e) ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.06 (s, 1H), 7.75–7.69 (m, 3H), 7.41 (m, 1H), 7.33 (m, 1H), 7.11–7.08 (m, 2H), 4.00 (t, 2H), 2.90 (m, 2H), 2.16 (m, 6H), 2.10 (s, 3H), 1.82 (m, 2H), 1.68-1.46 (m, 12H). IR (KBr) *v*: 3045.7, 2913.0, 2849.2, 2772.2, 1627.8, 1600.5, 1256.7, 1217.2, 1180.8, 1082.3, 830.2, 743.8 cm^{-1}; Anal. Calcd for $C_{26}H_{35}NO$: C 82.71, H 9.34, N 3.71; found C 82.63, H 9.21, N 3.73.

4-Nitro-benzoic acid 2-hydroxy-ethyl ester: 4-nitrobenzoic acid (5.0 g, 0.030 mol) was dissolved in 60 ml of glycol. 0.5 ml of H_2SO_4 was added dropwise under ice bath. After addition, the mixture was heated at 90 °C for 6 h. The mixture was poured into the ice-water and extracted by chloroform three times. The organic layer was washed with water and treated with $MgSO_4$. After removal of the solvent, the crude product was obtained. Pure compound was recrystallized from petroleum ether and chloroform (20:1, V/V). m.p. 74.6–75.9 °C, UV–vis (H_2O) λ_{max}: 264 nm; IR (KBr) *v*: 3331, 2958, 1729, 1287, 1134, 1075, 877, 829, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.29 (m, 2H), 8.23 (m, 2H), 4.53 (m, 2H), 4.01 (m, 2H), 2.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 300Hz): 165.0, 150.6 135.3, 130.8, 123.5, 67.3, 60.9; Anal. Calcd for $C_9H_9NO_5$: C 51.19, H 4.30, N 6.63; found C 51.21, H 4.32, N 6.64.

3-Nitro-benzoic acid 2-hydroxy-ethyl ester: m.p. 52.8–53.8 °C, UV–vis (H_2O) λ_{max}: 220, 261 nm; IR (KBr) *v*: 3530, 2919, 1726, 1267, 1145, 1076, 891, 826, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.89 (s, 1H), 8.43 (m, 2H), 7.68 (t, 1H), 4.53 (m, 2H), 4.02 (m, 2H), 2.07 (s, 1H); ^{13}C NMR ($CDCl_3$, 300Hz): 164.8, 148.2, 135.4, 131.7, 129.8, 127.6, 124.6, 67.4, 60.9; Anal. Calcd for $C_9H_9NO_5$: C 51.19, H 4.30, N 6.63; found C 51.19, H 4.30, N 6.62.

Results and discussion

Steady-state fluorescence study

The interaction between pNBCD or mNBCD with naphthalene derivatives was studied in aqueous solution by steady-state fluorescence and absorption spectra at room temperature. It was found that the fluorescence emission of the naphthalene derivatives was evidently quenched when pNBCD or mNBCD was added into the solution (see Figure 1). In comparison, when naphthalene derivatives are titrated with β-CD, the fluorescence intensity from the naphthalene remains constant (see Figure 3). And from the absorption spectra, it is concluded that no ground-state interactions arise because no new band of absorption other than those of the host and guest can be detected upon the addition of naphthalene derivatives to NBCD.

The fluorescence quench can be explained by two ways. One is the photoinduced energy transfer, the other is photoinduced electron transfer. Since the energy of the singlet naphthalene derivatives is much lower than that of NBCD, energy transfer from an excited naphthalene species to NBCD is impossible. So the only proper mechanism is photoinduced electron transfer between naphthalene derivatives and NBCD.

On the other hand, whether or not the photoinduced electron transfer can take place is dictated by the Rehm-Weller relationship [19].

$$\Delta G_{\mathrm{PET}} = e[E_{\mathrm{D}+/\mathrm{D}} - E_{\mathrm{A}/\mathrm{A}-} - E_{00}] - \frac{e^2}{4\pi\varepsilon_s\varepsilon_0 R_{\mathrm{cc}}} - \frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{r^+}+\frac{1}{r^-}\right)\left(\frac{1}{\varepsilon_{\mathrm{ref}}}-\frac{1}{\varepsilon_s}\right) \quad (1)$$

where $E_{D+/D}$ and $E_{A/A-}$ are the redox potentials of the electron donors and acceptor, respectively. E_{00} is the energy of the excited state from which electron transfer occurs. R_{cc} is the center-to-center distance of the positive and negative charges in the charge separated state. R^+ and r^- are the radii of the positive and negative ions. ε_s is the relative permittivity of the solvent. ε_0 is the vacuum permittivity. If $\Delta G_{\mathrm{PET}} < 0$, electron transfer can occur between the photo-excited electron donor and

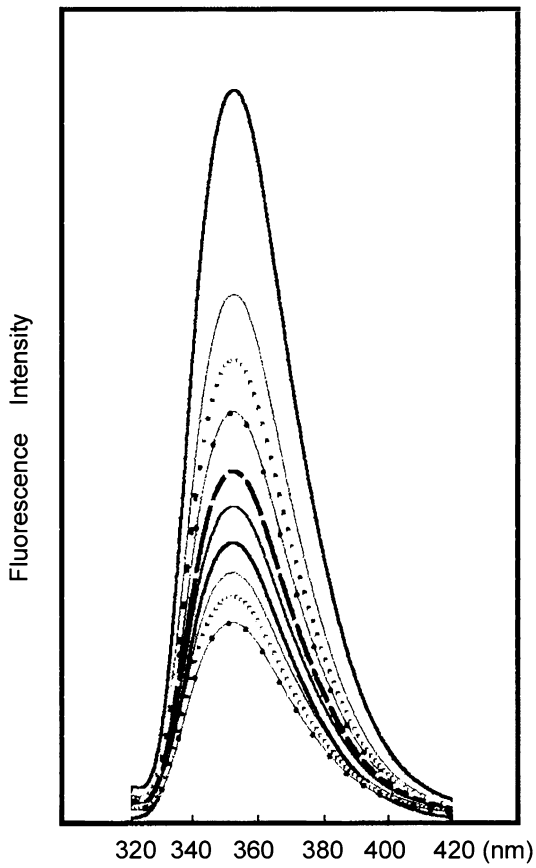


Figure 1. Fluorescence spectra of **1a** (2.0×10.6 mol l^{-1}) in the presence of different concentrations of pNBCD in water: 0, 2.0×10^{-5}, 3.0×10^{-5}, 4.0×10^{-5}, 5.0×10^{-5}, 6.0×10^{-5}, 7.0×10^{-5}, 8.0×10^{-5}, 9.0×10^{-5}, and 1.0×10^{-4} mol l^{-1}.

ground-state electron acceptor. If $\Delta G_{PET} > 0$, no photoinduced electron transfer can take place.

Herein we use the simplified Rehm–Weller relationship [17] [Equation (2)] to calculate the free energy change of a photoinduced electron transfer reaction.

$$\Delta G_{PET} = E_{D+/D} - E_{A/A-} - E_{00} \qquad (2)$$

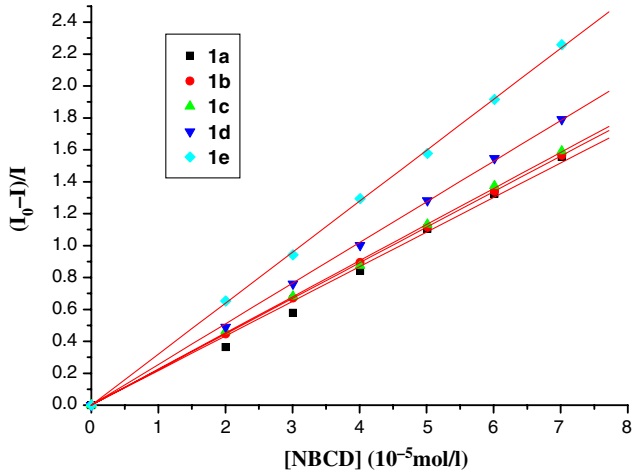


Figure 2. Stern–Volmer plots for the fluorescence quenching of **1a**–**1e** with *p*NBCD in water solution at room temperature. (I_0 is the fluorescence intensity in the absence of *p*NBCD and I is the fluorescence intensity in the presence of *p*NBCD).

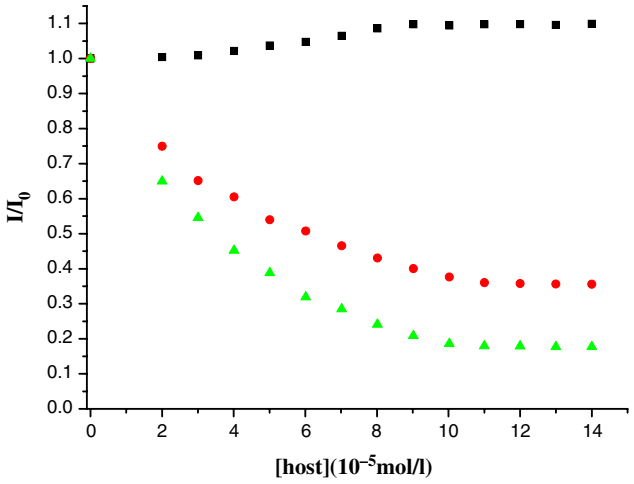


Figure 3. Fluorescence intensity of **1e** in aqueous solution (2×10^{-6} mol l^{-1}) with aqueous solutions of *p*NBCD (bottom), *β*-CD (upper), and *p*NBCD + *β*-CD (middle). host = NBCD, *β*-CD, or *p*NBCD + *β*-CD.

The redox potentials were measured by using cyclic voltammetry, the results are listed in Table 1. The excitation energy of naphthalene derivatives (E_{00}) is estimated by using the wavelength of the emission (λ_{em}). With use of the redox potentials and excitation energy, the ΔG_{PET} values can be calculated to be negative for all the naphthalene derivatives. It is noteworthy that in the full Rehm–Weller relationship, the term $-\frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{r^+}+\frac{1}{r^-}\right)\left(\frac{1}{\varepsilon_{ref}}-\frac{1}{\varepsilon_s}\right)$ is also always negative because in water $\varepsilon_s > \varepsilon_{ref}$. Therefore, if the estimated ΔG_{PET} from the simplified Rehm–Weller relationship is negative, the real ΔG_{PET} should in reality be more negative. Therefore, photoinduced electron transfer may take place between the naphthalene derivatives and NBCD.

Stern–Volmer relationship

For photoinduced electron transfer, two ways can take place between the excited naphthalene derivatives and NBCD. The first is dynamic quenching, which corresponds to the bimolecular electron transfer between the two compounds in solution. The second is static quenching, which refers to the intrasupramolecular electron transfer between excited naphthalene derivatives and NBCD in the cavity of NBCD (see Scheme 3).

We plot in Figure 2 I/I_0 against the concentration of NBCD observed in the titration experiment. Herein, I_0 is the fluorescence intensity of the naphthalene derivatives in the absence of NBCD. I is the fluorescence intensity in the presents of the quencher, NBCD.

For a system with both dynamic and static quench, the Stern–Volmer relationship [20] [Equation (3)] was derived before.

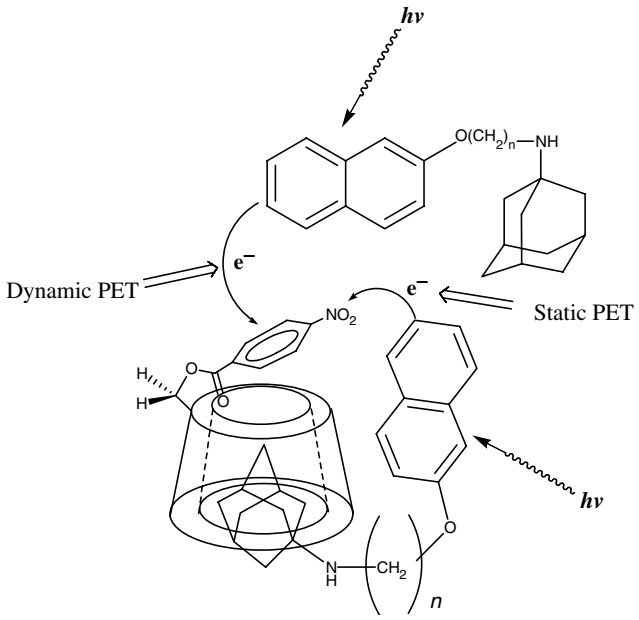
$$I_0/I = 1 + (K_{sv} + K + K \cdot K_{sv} \cdot [Q]) \cdot [Q] \qquad (3)$$

In Equation (3), K_{sv} is the dynamic Stern–Volmer constant, which equals to the product of the fluorescence

Table 1. Redox potentials of the naphthalene compounds and ΔG_{PET} between the naphthalene compounds and *p*NBCD or *m*NBCD

Donors	E_{00} in H_2O/eV	λ_{em}/nm	$E_{D+\cdot/D}$/eV	ΔG_{PET}/eV *p*NBCD	ΔG_{PET}/eV *m*NBCD
1a	3.56	348	1.60	−0.66	−0.81
1b	3.55	349	1.55	−0.70	−0.85
1c	3.53	351	1.52	−0.71	−0.86
1d	3.53	351	1.49	−0.74	−0.89
1e	3.52	352	1.52	−0.70	−0.85
0	3.54	350	1.42 ^{MeCN}	−0.82	−0.97

Note: ΔG_{PET} calculated from the simplified Rehm−Weller equation, $\Delta G_{PET} = E_{D+\cdot/D} - E_{A/A-\cdot} - E_{00}$. λ_{em} is the emission wavelength, $E_{00} = h\nu = 12398.1/\lambda_{em}$ (Å). $E_{A/A-\cdot}$(*p*NBCD) = −1.30 eV. $E_{A/A-\cdot}$(*m*NBCD) = − 1.15 eV. **0** is control compound, 2-methoxylnaphthalene.



Scheme 3.

lifetime and the dynamic quenching rate constant, $\tau_f \cdot k_q$. K is the binding constant between the fluorescence compound and the quencher. If [Q] approaches zero, Equation (3) changes into Equation (4).

$$I_0/I = 1 + (K_{sv} + K) \cdot [Q] \quad (4)$$

In the present research we studied in the fluorescence quenching of compounds **1a**−**1e** by *m*NBCD or *p*NBCD. It found that all the compounds showed nice linear correlations between I_0/I and [Q] (see Figure 2). So we can easily determine the value of $(K_{sv} + K)$ for each guest compound by the slope of the correlations. These results are summarized in Table 2. From Table 2, we can concluded that the fluorescence quenching efficiency is higher in the *m*NBCD system than in the pNBCD system. It is also clear that the fluorescence quenching efficiency for **1a**−**1e** is significantly higher than that for a control compound **0**, 2-methoxylnaphthalene.

Competition experiment

β-CD alone does not exert any quenching effect on naphthalene derivatives. On the contrary, it slightly increased the fluorescence emission of 1e (see Figure 3). However, in a competition experiment with an equal amount of β-CD and NBCD (i.e., [β-CD]:[NBCD]) 1:1), the I_F value cannot be quenched to the same extent as that observed in the titration with NBCD alone (see Figure 3). In fact, the final I_F value is 74.9 for the β-CD-NBCD titration experiment, whereas the final I_F value for the NBCD titration experiment is 37.2. Since the original I_F value of the pure naphthalene solution is 210.5, we can calculate that in the Naphthalene-β-CD-NBCD system ([β-CD] = [NBCD] > > [naphthalene]), 17.9% of total naphthalene should stay in β-CD whereas 82.1% of total naphthalene should stay in NBCD. This means that the binding constant of the naphthalene-NBCD complex should be about 4.6 times larger than that of naphthalene-β-CD. As the binding constant of naphthalene-NBCD is $1.6 \times 10^4\ M^{-1}$, the binding constant of naphthalene-β-CD should be $3.5 \times 10^3\ M^{-1}$.

The binding constant for naphthalene-NBCD is larger than that for naphthalene-β-CD, possibly because of the charge transfer interaction between the electron donor and acceptor. In any case, the β-CD-NBCD titration experiment indicates that the β-CD can inhibit the quenching of NBCD to some extend.

Dynamic Stern−Volmer constants and binding constant

The above measurements provided the total Stern−Volmer constants. In order to gain more insights into the observed behaviors we decided to separate them into dynamic Stern−Volmer constants, K_{sv} and the host-guest binding constants, K. For this purpose, we synthesized two model compounds, i.e., 3-nitrobenzoic acid 2-hydroxyethyl ester (mNBHE) and 4-nitrobenzoic acid 2-hydroxyethyl ester (pNBHE). We can suppose that their redox properties are similar to that of *m*NBCD and *p*NBCD because of the analogous chemical structure. Consequently, it is also reasonable to assume that the dynamic Stern−Volmer constant of *p*NBHE or *m*NBHE is very close to that of *p*NBCD or *m*NBCD. On the other hand, being a small molecule, *p*NBHE or *m*NBHE should not be able to form any noncovalent complex with naphthalene compounds in water. Therefore, if *p*NBHE or *m*NBHE can quench the fluorescence of the naphthalene compounds, the

Table 2. Stern–Volmer constants for the quenching between **1a**–**1f** and *p*NBCD or *m*NBCD ($\times 10^{-4}$ M^{-1})

Donors	*p*NBCD			*m*NBCD		
	$K+K_{sv}$	K_{sv}	K	$K + K_{sv}$	K_{sv}	K
1a	2.169	1.598	0.571	3.033	0.738	2.295
1b	2.230	1.637	0.593	3.098	0.742	2.356
1c	2.263	1.680	0.583	2.901	0.769	2.132
1d	2.548	1.719	0.829	3.972	0.753	3.219
1e	3.195	1.578	1.617	4.672	0.773	3.939
0	1.289	0.958	0.331	1.007	0.768	0.239

Note: $(K+K_{sv})$ is the slope of the plot between $(I_0\text{-}I)/I$ and [NBCD]. K_{sv} is the slope of the plot between $(I_0\text{-}I)/I$ and [nitrobenzoic acid 2-hydroxyethyl ester]. K is the binding constant between the naphthalene compound and [NBCD]. **0** is control compound, 2-methoxylnaphthalene.

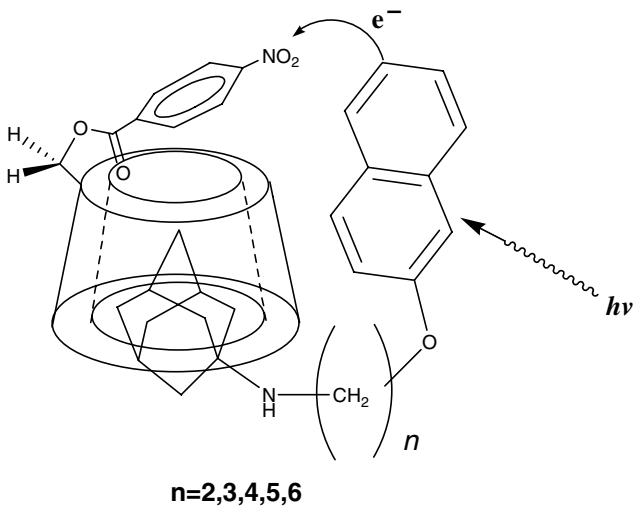


Figure 4. Electron transfer in host-guest complexes of naphthyl-$O(CH_2)_n$-adamantanamine with *p*NBCD.

quenching should completely be a bimolecular, dynamic quenching. So we studied the fluorescence quenching of compounds **1a**–**1e** by *p*NBHE and *m*NBHE in aqueous solution. And from the correlation of I_0/I and [Q] we could easily get the slops of the plot, which equal to the dynamic Stern–Volmer constant (K_{sv}) of *p*NBCD and *m*NBCD. By subtracting the (K_{sv}) from total Stern–Volmer constant, we naturally obtained the binding constant. All these results are listed in Table 2.

According to the Table 2 we can see the binding constant not change much over the different $(CH_2)_n$ chain lengths. It is easy to understand because all the compounds have the same binding moiety, adamantanamine. And we also find that the fluorescence quenching efficiency of the supramolecular system will not be affected by the chain lengths if the binding moiety is fixed (see Figure 4). Furthermore, it is interesting to note that *m*NBCD has higher binding constants than *p*NBCD for the adamantanamine compounds but not **0**.

Conclusions

In the present study we have synthesized a number of naphthalene donor compounds possessing an adamantanamine binding moiety via a flexible hydrocarbon chain. We investigated the fluorescence quenching between these donor substrates and pNBCD and mNBCD. Very efficient fluorescence quenching was observed and its occurrence was attributed to the photoinduced electron transfer inside the supramolecular assembly between the naphthalene donors and cyclodextrin acceptors. Detailed Stern–Volmer constants were measured and they were partitioned into dynamic Stern–Volmer quenching constants (dynamic quenching) and static binding constants (static quenching). In these two pathways, the static quenching was found to be highly efficient and dominant in the presence of NBCD.

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