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Photoinduced Electron Transfer in Host-Guest Complexes of α- and β-Substituted Naphthalene Derivatives with Mono-6-*O*-*m*-Nitrobenzoyl-β-Cyclodextrin

QI-HUA WU, MAN-ZHOU ZHU, SU-JUN WEI, KE-SHENG SONG, LEI LIU* and QING-XIANG GUO*
Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

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Key words: binding constant, fluorescence quenching, monosubstituted cyclodextrin, photoinduced electron transfer, Sterm–Volmer relationship

Abstract

Mono-6-*O*-*m*-nitrobenzoyl-β-cyclodextrin (mNBCD) was synthesized as a novel supramolecular electron acceptor. Both the theoretical and experimental analyses suggested that mNBCD should possess a self-inclusion conformation. Fluorescence quenching experiments revealed efficient photoinduced electron transfers (PET) between mNBCD and naphthalene compounds in aqueous solution. 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. Both the dynamic Stern–Volmer constants and static binding constants were determined. It was found that the binding constants of mNBCD complexes were higher than those of β-cyclodextrin complexes.

Introduction

Photosynthesis, a vital process in biochemistry, has evolved over time to achieve ultrafast photoinduced electron transfer (PET) from electronically excited chlorophylls to quinone receptors [1]. Model studies of this process not only provide important insights into the mechanisms of photosynthesis [2], but also may enable us to construct artificial systems for the conversion of solar energy into chemical potential [3].

The simplest model for PET is composed of an electron donor and acceptor covalently linked to each other [4]. Although studies on these donor–acceptor dyads are very important, the covalent systems cannot fully mimic the biological processes in which the donor and acceptor are held together by proteins without any covalent linkage. A better model for biological PET should be constructed using non-covalent interactions, which could be hydrogen bonding [5], π-stacking [6], and metal–ligand coordination [7]. Nevertheless, the most ideal approach to mimic the biological PET is to build the donor–acceptor dyad in aqueous solution using the hydrophobic interaction. For this reason, the aqueous PET in peptide [8], nucleic acid [9], micelle [10], and certain water-soluble host–guest systems have been intensively studied.

Cyclodextrins (CDs) are important water-soluble host molecules. They are cyclic oligosaccharides with six (α), seven (β), or eight (γ) glucose units. The internal wall of CD is hydrophobic, whereas the two rims of CD are hydrophilic. Thus CDs can form inclusion complexes with diverse organic compounds in aqueous solution [11]. This binding property has been used in the construction of artificial enzymes [12], drug delivery systems [13], and molecular machines [14]. The same binding property is also expected to be useful in the assembly of supramolecular PET systems.

It is worthy noting that the effects of native CDs on PET reactions in water have been studied by many groups [15]. However, much less effort has been devoted to the utilization of CDs in constructing PET systems [16]. Very recently, De Cola *et al.* synthesized metal-coordinated CDs and studied their PET with viologens [17]. Park *et al.* synthesized naphthalene-substituted β-CD and studied its PET with adamantylmethyl viologen [18]. We synthesized a CD electron acceptor, mono-6-*O*-*p*-nitrobenzoyl-β-CD (pNBCD) and studied its PET with naphthalene derivatives [19]. In agreement with De Cola and Park's work, we observed very efficient PET in the pNBCD-naphthalene system. Since no chemical bond is available between pNBCD and naphthalene, this PET must occur through space but not through bond. Thus we proposed that pNBCD should form inclusion complexes with naphthalene derivatives and the efficient fluorescence quenching should be caused by

* Authors for correspondence. E-mail: leiliu@chemist.com, qxguo@ustc.edu.cn

the static quenching within the pNBCD–naphthalene complexes.

On the basis of our experimental and theoretical analyses, the *p*-nitrobenzoyl moiety in pNBCD was proposed to stay outside the CD cavity. Interestingly, our theoretical analyses also predicted that if we move the *para*-nitro group to the *meta* position, the resulting compound, mono-6-*O*-*m*-nitrobenzoyl-*β*-CD (mNBCD) should have its *m*-nitrobenzoyl group self-included in the CD cavity. Clearly it would be very interesting and important to know the effects of this intriguing self-inclusion on the PET reactions. Therefore, we synthesized mNBCD and performed a detailed study on its PET with various naphthalene compounds.

Experimental

Materials

β-Cyclodextrin (*β*-CD) was recrystallized three times and dried in vacuum at 100 °C for 12 h before use. Compounds **1–4** and **7** was obtained commercially and used without further purification. Compound 5 and 6 were recrystallized three times in ethanol before use. Tetrabutylammonium perchlorate (TBAP) was dried in vacuum prior to use. Deionized water was used in the measurements.

Measurement

One-dimensional ^{1}H NMR and two-dimensional ^{1}H–^{1}H NOESY was recorded on a Bruker DMX-300 spectrometer. IR spectra were recorded using a Bruker Vector 220 Infrared Spectrometer. Mass spectrum of mNBCD was performed on a BIFLEX III MALDI-TOF spectrometer. Fluorescence spectra were measured using a CRT-970 spectrometer in aqueous solution at room temperature. Elemental analysis was performed on an Elementar Vario EL-III instrument. Oxidation potential ($E_{A/A-}$) of mNBCD in acetonitrile was measured by cyclic voltammetry with an Ag/AgCl reference electrode at scan rates of 100 mv/s.

Synthesis

Mono-6-O-m-Nitrobenzoyl-β-cyclodextrin
β-CD (34 g, 0.03 mol) was dissolved in 300 ml of freshly distilled pyridine, into which 50 ml of pyridine solution of *m*-nitrobenzoyl chloride (1.9 g, 0.01 mol) was added dropwise at 0 °C. The mixture was stirred for 24 h under nitrogen. The reaction was quenched by addition of 5 ml of water. After removal of the solvent, the product was collected and purified by Sephadex G-25 column. MS: $[M + Na]^+ = 1306.7$. UV–vis (H_2O) λ_{max}: 220, 264 nm. IR (KBr) $v = 3375$, 1725, 1080, 1029 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) $\delta = 8.63$ (s, 1H, H-3′), 8.51 (d, 1H, H-5′), 8.41 (d, 1H, H-7′), 7.83 (t, J = 8 Hz, H-6′), 5.65–5.81 (m, 14H, -OH), 4.82–4.92 (m, 7H, H-1), 4.65 (d, 1H, H-5), 4.42 (s, broad, 6H, -OH), 4.33 (m, 1H, H-3), 4.03 (m, 1H, H-6), 3.32–3.65 (m, 39H, CH and CH_2). ^{13}C NMR (300 Hz, D_2O): 167.4 (C-1′), 149.9 (C-4′), 137.6 (C-7′), 132.8 (C-2′), 132.6 (C-6′), 130.2 (C-5′), 126.0 (C-3′), 104.5, 104.3, 104.1, 104.0, 103.6, 84.0, 83.3, 82.9, 82.5, 75.7, 75.2, 75.1, 75.0, 74.3, 74.1, 74.0, 73.9, 67.6, 61.8, 61.4, 56.3.

3-Nitrobenzoic acid 2-hydroxyethyl ester
Synthesized using the same method as that utilized for mNBCD. m.p. 49–50 °C. MS: 212.0554. UV–vis (H_2O): 220, 262 nm. IR (KBr) $v = 3529$, 3090, 2952, 1726, 1532, 1145, 1074, 892, 826, 719 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 8.89$ (m, 1H), 8.38–8.45 (m, 2H), 7.67 (m, 1H), 4.53 (m, 2H), 4.01 (t, J = 4.5 Hz, 2H), 1.89 (s, 1H). ^{13}C NMR (300 Hz, $CDCl_3$): 164.9, 148.4, 135.5, 131.8, 129.8, 127.7, 124.8, 67.5, 61.2. Elemental analysis ($C_9H_9NO_5$): Found: C 51.14, H 4.31, N 6.64, Calculated: C 51.18, H 4.27, N 6.64.

Theoretical method

Theoretical calculations were performed using Gaussian 98 software packages [20]. Crystalline structure of *β*-CD was utilized in the construction of mNBCD [21], to which the 6-*O*-*m*-nitrophenyl moiety was attached using all the possible conformations (See the Appendix). All these different conformers were then subjected to full geometry optimization by the PM3 method [22]. In this way we obtained a conformer of mNBCD with the lowest electronic energy.

Results and discussions

Conformation of mNBCD

The conformation of mono-substituted cyclodextrin is an interesting problem [23]. The central question is whether the whole molecule is locked in a self-inclusion conformation in which the substituent enters the hydrophobic cavity of cyclodextrin. Our previous experimental study on pNBCD suggested that pNBCD should not have any self-inclusion [19]. This observation is in good agreement with the results from our theoretical study at the PM3 level [24], which predicts that the rim-covering conformation has a low energy than the self-inclusion and out-stretching conformations.

Detailed analyses revealed that in order to achieve the self-inclusion conformation pNBCD has to adopt an *endo*-conformation in the ester bond, which is highly unfavorable in energy (See Figure 2). On the other hand, when an *exo*-ester bond is present, *p*-nitrophenyl group cannot enter the cyclodextrin cavity. This is simply caused by the length of the *p*-nitrophenyl moiety, which leads to significant steric repulsion when the *p*-nitrophenyl moiety is inside the cavity (See Figure 2). It is worthy to note that with an *endo*-ester bond,

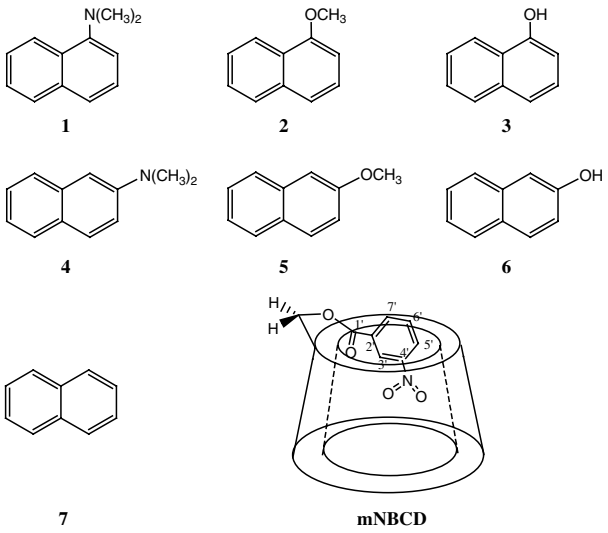


Figure 1. Electron donors (**1–7**) and electron acceptor (mNBCD).

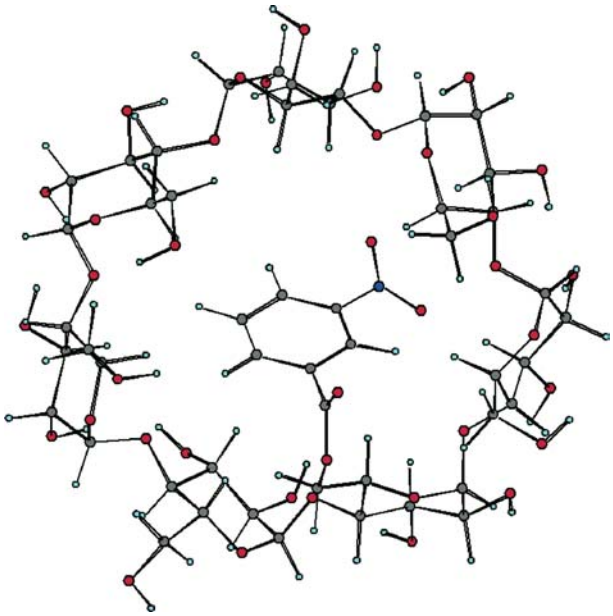


Figure 3. The most stable conformation of mNBCD predicted by the PM3 method.

pNBCD can also adopt an out-stretching conformation, in which the *p*-nitrophenyl moiety stays far away from the cyclodextrin cavity. This out-stretching conformation is less favored than the rim-covering conformation according to PM3, presumably because of the van der Waals attractions between the *p*-nitrophenyl and cyclodextrin moieties.

In comparison to *p*-nitrophenyl group, *m*-nitrophenyl group is much shorter in length (See Figure 2). Therefore, with an *endo*-ester bond *m*-nitrophenyl group can enter the cyclodextrin cavity without causing much steric repulsion. This prediction is verified by the PM3 geometry optimization in vacuum. PM3 calculations also indicate that the self-inclusion conformation of mNBCD has a lower energy than the out-stretching conformation (See Figure 3), possibly due to the van der Waals interactions between the *m*-nitrophenyl moiety and cyclodextrin cavity. We have not attempted to use the PM3 method to optimize the geometry of mNBCD in water. However, we anticipate that mNBCD should more likely adopt the self-inclusion conformation in aqueous solution because the hydrophobic effect can enhance the packing between the *m*-nitrophenyl and cyclodextrin moieties.

Our theoretical prediction is supported by the experimental study using the NOE method. As shown in Figure 4, the ^1H–^1H NOESY spectrum of mNBCD in D_2O shows significant NOE correlations between the protons on the nitrophenyl moiety and the protons (H-3, H-5, and H-6) on cyclodextrin. Since these NOE correlations indicate that the spatial distances between

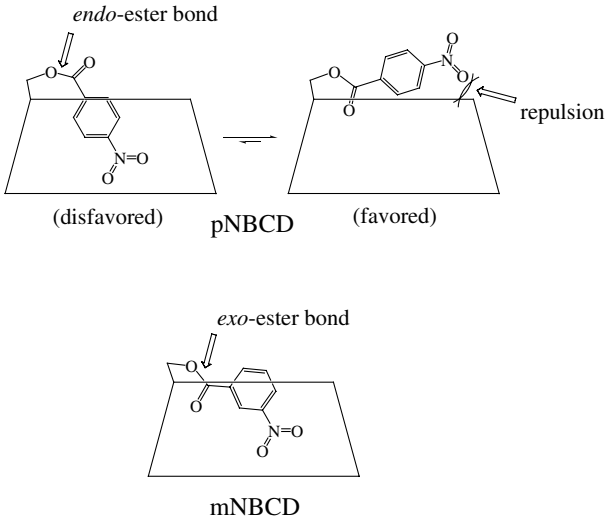


Figure 2. Comparing the conformations of pNBCD and mNBCD.

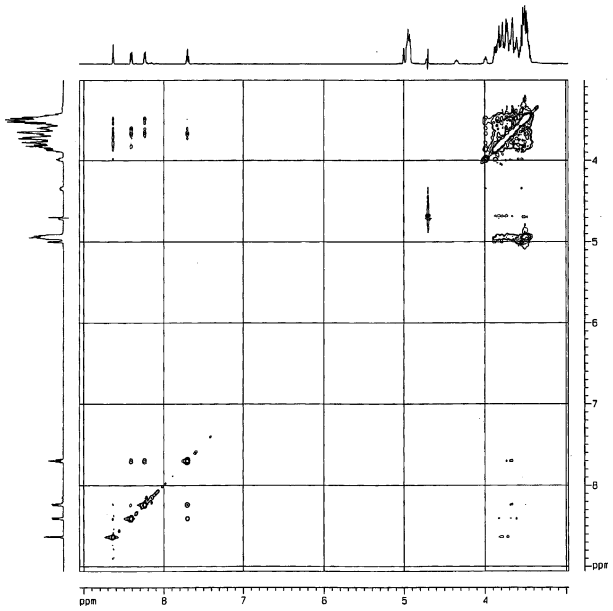


Figure 4. ^1H–^1H NOESY spectrum of mNBCD in D_2O.

these protons should be less than 5 Å, it can be concluded that mNBCD must adopt the self-inclusion conformation.

Fluorescence quenching of mNBCD complexes

Fluorescence spectra of the inclusion complexes between mNBCD and naphthalene derivatives (**1–7**) were studied at room temperature in aqueous solution. It was found that the fluorescence emission of the naphthalene derivatives were dramatically quenched when mNBCD was added into the solution (See Figure 5).

The fluorescence quenching can be explained by two reasons, i.e. photoinduced energy transfer or photoinduced electron transfer. Photoinduced energy transfer requires that the excited singlet energy of the donor should be higher than that of the acceptor. However, it is clear that the energy of the excited singlet naphthalene derivatives is much lower than the energy of the excited singlet of mNBCD. Thus we can rule out the possibility that the fluorescence quenching is caused by the energy transfer from the naphthalene derivatives to mNBCD.

On the other hand, whether the photoinduced electron transfer can take place is dictated by the Rehm–Weller relationship [25].

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

($E_{\mathrm{D}+\cdot/\mathrm{D}}$ and $E_{\mathrm{A}/\mathrm{A}-\cdot}$ 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 ground-state electron acceptor. If $\Delta G_{\mathrm{PET}} > 0$, no photoinduced electron transfer can take place.

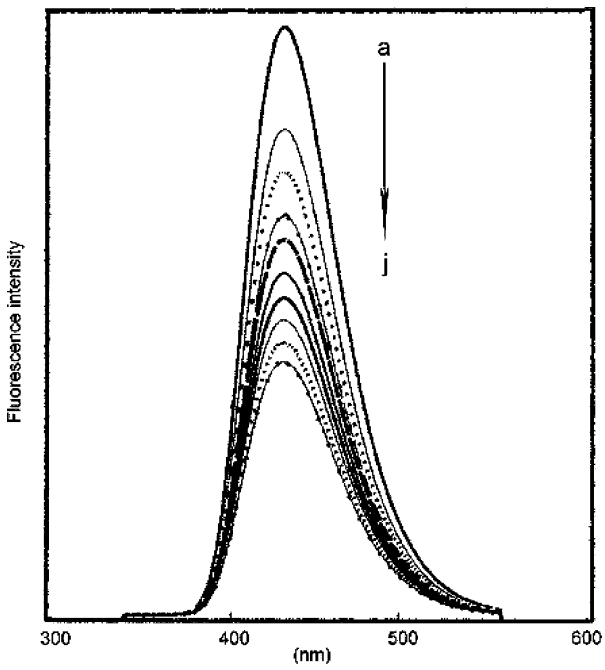


Figure 5. The fluorescence spectra of **4** (2.0×10^{-6} M) in the presence of different concentration of mNBCD in water: 0; 2.0×10^{-5} M; 3.0×10^{-5} M; 4.0×10^{-5} M; 5.0×10^{-5} M; 6.0×10^{-5} M; 7.0×10^{-5} M; 8.0×10^{-5} M; 9.0×10^{-5} M; 1.0×10^{-4} M.

Table 1. Redox potentials of the naphthalene compounds and ΔG_{PET} between the naphthalene compounds and mNBCD

Donors	1	2	3	4	5	6	7
ΔG_{PET} (eV)	−0.88	−0.93	−0.53	−1.06	−0.97	−0.30	−1.07

Note: ΔG_{PET} calculated from the simplified Rehm-Weller equation, $\Delta G_{\mathrm{PET}} = E_{\mathrm{D}+\cdot/\mathrm{D}\cdot} - E_{\mathrm{A}/\mathrm{A}-\cdot} - E_{00\cdot}$, $E_{\mathrm{A}/\mathrm{A}-\cdot} = -1.15$ eV. Values of $E_{\mathrm{D}+\cdot/\mathrm{D}}$ and E_{00} are from reference 19.

Herein the simplified Rehm–Weller relationship (i.e., $\Delta G_{\mathrm{PET}} = E_{\mathrm{D}+\cdot/\mathrm{D}} - E_{\mathrm{A}/\mathrm{A}-\cdot} - E_{00}$) is used to estimate the driving force for electron transfer [19]. E_{00} is estimated by the emission energy of the naphthalene derivatives. The redox potentials are measured using the cyclic voltammetry. The results are listed in Table 1, which basically indicate that ΔG_{PET} is negative for all the naphthalene derivatives. It is worthy noting that in the full Rehm–Weller relationship, the term $-\frac{e^2}{4\pi\varepsilon_s\varepsilon_0 R_{\mathrm{cc}}}$ is always negative. The term $\frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{r^+}+\frac{1}{r^-}\right)\left(\frac{1}{\varepsilon_{\mathrm{ref}}}-\frac{1}{\varepsilon_s}\right)$ is also always negative because in water $\varepsilon_s > \varepsilon_{\mathrm{ref}}$. Therefore, if the estimated ΔG_{PET} from the simplified Rehm–Weller relationship is negative, the real ΔG_{PET} should actually be more negative. Therefore, photo-induced electron transfer is able to take place between the naphthalene derivatives and mNBCD.

Stern–Volmer relationship

Two pathways of photoinduced electron transfer can take place between the excited naphthalene compounds and mNBCD. The first is dynamic quenching, which corresponds to the bimolecular electron transfer between mNBCD and free excited naphthalene in solution. The second is static quenching, which refers to the intra-supramolecular electron transfer between mNBCD and naphthalene included in mNBCD cavity (See Figure 6).

The Stern–Volmer relationship Equation (2) for a system with both dynamic and static components has been derived previously [26].

$$I_0/I = 1 + (K_{\mathrm{sv}} + K + K \cdot K_{\mathrm{sv}} \cdot [\mathrm{Q}]) \cdot [\mathrm{Q}] \quad (2)$$

In Equation (2), I_0 and I are the fluorescence intensities of the guest molecule in the absence and presence of quencher (Q). K_{sv} is the dynamic Stern–Volmer constant, which equals to the product of the fluorescence lifetime and the dynamic quenching rate constant, $\tau_f \cdot k_q$. K is the binding constant between the

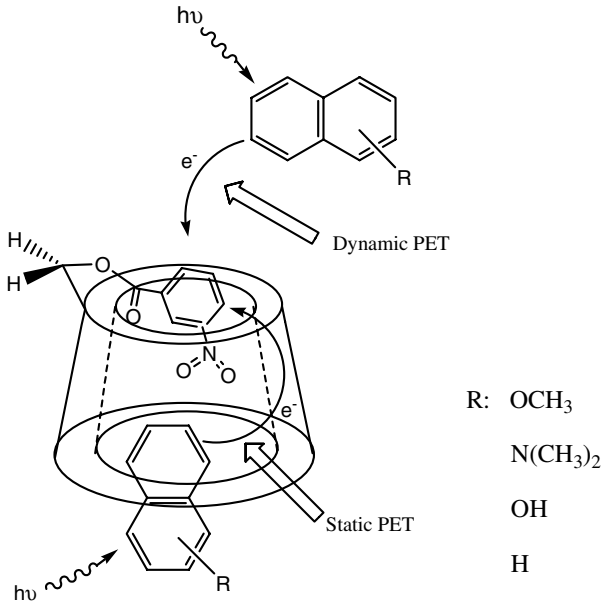


Figure 6. Dynamic and static PET in the host–guest complexes between naphthalene derivatives and mNBCD.

fluorescence compound and the quencher. If [Q] approaches zero, Equation (2) changes into Equation (3).

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

This means that the limiting slope of the Stern–Volmer relationship is (K_{sv} + K).

In the present study, we studied the Stern–Volmer relationships in the fluorescence quenching of compound **1–7** by mNBCD. It was found that all the guest compounds exhibit nice linear correlations between I_0/I and [Q] (See Figure 7). Therefore, from the slopes of the correlations we could easily determine the value of

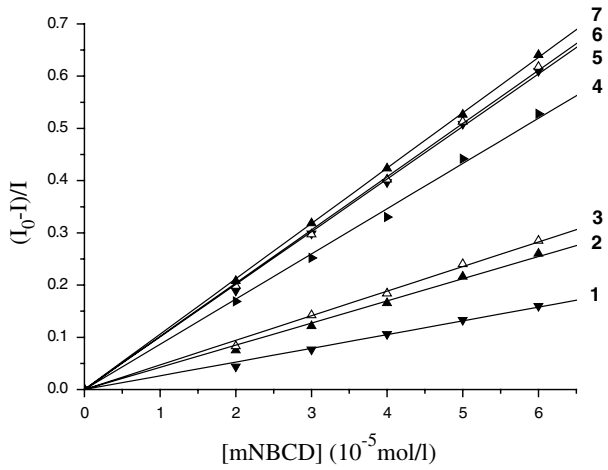


Figure 7. Stern–Volmer plots for the fluorescence quenching of naphthalene derivatives (**1–7**) by mNBCD in water at room temperature (I_0 is the fluorescence intensity of the naphthalene derivatives in the absence of mNBCD, I is the fluorescence intensity in the presence of mNBCD at the different concentrations ranging from 2.0×10^{-5} mol/l to 6.0×10^{-5} mol/l).

Table 2. Stern–Volmer constants measured from the fluorescence quenching experiments between naphthalene compounds and mNBCD

Donors	K + K_{sv} ($\times 10^{-4}$ M^{-1})	K_{sv} ($\times 10^{-4}$ M^{-1})	K (M^{-1})
1	0.263 ± 0.042	0.188 ± 0.028	0.075×10^4
2	0.424 ± 0.063	0.241 ± 0.036	0.183×10^4
3	0.471 ± 0.059	0.206 ± 0.015	0.265×10^4
4	0.866 ± 0.098	0.407 ± 0.058	0.459×10^4
5	1.007 ± 0.069	0.750 ± 0.111	0.257×10^4
6	1.018 ± 0.061	0.655 ± 0.065	0.363×10^4
7	1.060 ± 0.033	0.702 ± 0.070	0.358×10^4

Note: (K + K_{sv}) is the slope of the plot between $(I_0-I)/I$ and [mNBCD] measured from the fluorescence quenching experiments using mNBCD. K_{sv} is the slope of the plot between $(I_0-I)/I$ and [3-nitrobenzoic acid 2-hydroxyethyl ester] measured from the fluorescence quenching experiments using 3-nitrobenzoic acid 2-hydroxyethyl ester. K is the calculated binding constant between the naphthalene compound and [mNBCD] from (K + K_{sv}) and K_{sv}.

(K_{sv} + K) for each guest compound. These results are summarized in Table 2. From both Figure 7 and Table 2 it can be seen that the fluorescence quenching efficiency of the donor-acceptor systems decreases in the order **7** > **6** > **5** > **4** > **3** > **2** > **1**.

Dynamic Stern–Volmer constants and binding constants

The above measurements revealed an interesting trend of fluorescence quenching efficiency in different host–guest systems. In order to understand this trend we need to separate the dynamic Stern–Volmer constant K_{sv} from the host–guest binding constant K. For this purpose we synthesized a model compound, 3-nitrobenzoic acid 2-hydroxyethyl ester (mNBHE). It is expected that the redox property of mNBHE should be very close to that of mNBCD because they have very similar chemical structures. Therefore, it is reasonable to assume that the dynamic Stern–Volmer constant of mNBHE is very close to that of mNBCD. On the other hand, being a small molecule mNBHE should not be able to form any noncovalent complex with naphthalene compounds in water [27]. Thus if mNBHE can quench the fluorescence of the naphthalene compounds, this quenching should completely be a bimolecular, dynamic quenching.

On the basis of the above analysis, we studied the Stern–Volmer relationships in the fluorescence quenching of compounds **1–7** by mNBHE in aqueous solution (See Figure 8). As the fluorescence quenching in these systems are completely dynamic in nature, the slopes of the regression lines equal to the dynamic Stern–Volmer constants of mNBHE, and then, corresponding K_{sv} values for mNBCD. These results are listed in Table 2.

From Figure 8 and Table 2, it is clear that the K_{sv} values decrease in the order **5** > **7** > **6** > **4** > **2** > **3** > **1**. This order is not fully consistent with the order for the total fluorescence quenching efficiency of mNBCD. At present, we have not fully understood why the dynamic quenching efficiency

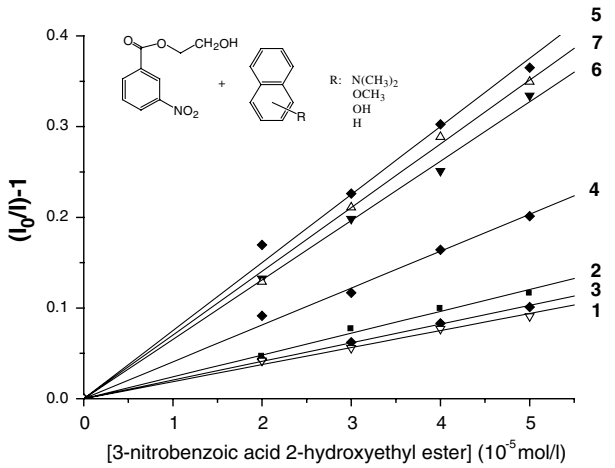


Figure 8. Stern–Volmer plots for the fluorescence quenching of naphthalene derivatives (**1–7**) by mNBHE in water at room temperature (I_0 is the fluorescence intensity of the naphthalene derivatives in the absence of 3-nitrobenzoic acid 2-hydroxyethyl ester, I is the fluorescence intensity in the presence of 3-nitrobenzoic acid 2-hydroxyethyl ester at the different concentrations ranging from 2.0×10^{-5} mol/l to 5.0×10^{-5} mol/l).

between a naphthalene donor and a *meta*-nitrobenzoyl ester follows the above order. Nonetheless, it is worthy mentioning that the dynamic quenching constant is dependent both on the fluorescence lifetime of the donor and on the electron-transfer rate between the donor and acceptor.

Using the K_{sv} values we can calculate the binding constants between mNBCD and the naphthalene compounds (See Table 2). It is found that the binding constants between mNBCD and naphthalene compounds are about 750–3500. Therefore, under the experimental conditions (i.e. [naphthalene compound] $= 2 \times 10^{-6}$ M, [mNBCD] $= 2$–6×10^{-5} M), there is about 2–20% of the naphthalene compound included in the mNBCD cavities. This is the reason why both the dynamic and static quenchings are significant in the mNBCD–naphthalene compound systems.

Comparing the present results with our previous data for pNBCD [19], we find that for α-substituted naphthalene substrates the K_{sv} values with pNBCD are higher than the K_{sv} values with mNBCD. For example, K_{sv} (pNBCD-**2**) $= 6152$ M^{-1} is higher than K_{sv} (mNBCD-**2**) $= 2410$ M^{-1}. On the other hand, for β-substituted naphthalene substrates the K_{sv} values with mNBCD are higher than the K_{sv} values with pNBCD. For example, K_{sv} (mNBCD-**5**) $= 7500$ M^{-1} is higher than K_{sv} (pNBCD-**5**) $= 1357$ M^{-1}. These interesting differences are possibly due to the fact that mNBCD can adopt a self-inclusion conformation but pNBCD cannot.

Comparing the binding constants of mNBCD and β-CD

In order to get a better understanding on the binding constants of mNBCD, we also measured the binding constants of the naphthalene compounds with native β-CD (See Table 3). Comparing the two sets of binding

Table 3. Comparing the binding constants (K) of naphthalene compounds with mNBCD and β-CD.

Guest compound	β-CD	mNBCD
1	348[a]	750[a]
2	1381[b]	1830[a]
3	1219[b]	2650[a]
4	530[a]	4590[a]
5	526[a]	2570[a]
6	590[c]	3630[a]
7	678[b]	3580[a]

Note: [a] Determined in the present study. [b] Taken from Ref. 28. [c] Taken from Ref. 29.

constants, we have the following interesting observations.

(1) The binding constant of α-*N*,*N*-dimethylamino-naphthalene is significantly smaller than those of the other naphthalene compounds in both mNBCD and β-CD complexation. CPK models suggest that there is a serious steric problem between the NMe_2 group and the CD rim when the naphthalene moiety enters the CD cavity.

(2) The binding constants of α-hydroxy-naphthalene and α-methoxy-naphthalene are much higher than that of α-*N*,*N*-dimethylamino-naphthalene in both the mNBCD and β-CD cases. This is partly due to the smaller steric effect caused by the OH and OCH_3 groups. An additional reason might be the hydrogen bonding interactions between the OH groups of CDs and the oxygen atom in OH and OCH_3.

(3) The binding constants for mNBCD are significantly higher than those for β-CD. This behavior can be explained by two factors. First, the *m*-nitrophenyl moiety is hydrophobic and therefore, there might be enhanced hydrophobic packing in the mNBCD complexes than in the β-CD complexes. Second, charge transfer interaction may occur between the electron-deficient *m*-nitrophenyl moiety and the electron-rich naphthalene guest compounds.

Conclusions

In the present study, we synthesized a new cyclodextrin host molecule (i.e. mNBCD) as an electron acceptor. Both the theoretical and experimental analyses suggested that this host molecule should possess a self-inclusion conformation. Fluorescence quenching experiments revealed that efficient photoinduced electron transfer could take place between mNBCD and naphthalene compounds in aqueous solution. 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. Both the dynamic Stern–Volmer constants and static

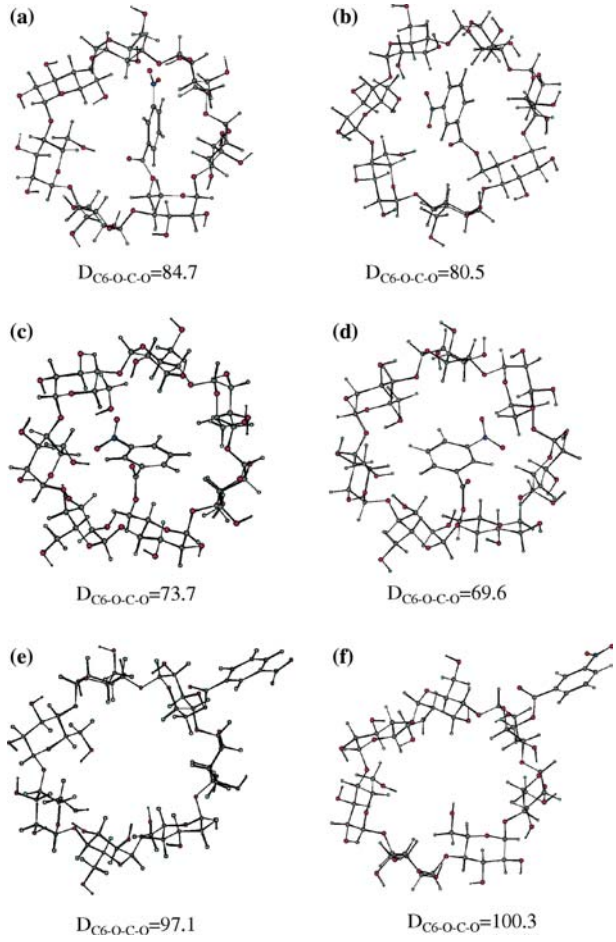
binding constants were determined. We also compared the binding constants of mNBCD complexes with those of β-CD complexes.

Acknowledgement

We thank NSFC, CAS, and MOST for the financial support.

Appendix

The initial geometries utilized in the theoretical study on mNBCD:



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