Photoinduced Electron Transfer between Mono-6-*p*-nitrobenzoyl-*β*-cyclodextrin and Adamantanamine-C_n-porphyrins

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A series of monotailed porphyrins, zinc 5-{4-[*ω*-(1-adamantaneamino)alkyloxy]phenyl}-10,15,20-triphenyl porphyrinate ($ZnPC_nA$, $n = 4, 5, 6$), were synthesized in which the porphyrin moiety was connected to 1-adamantanamine via a flexible hydrocarbon chain. It was found that photoinduced electron transfer could occur between these porphyrin compounds and mono-6-*p*-nitrobenzoyl-*β*-cyclodextrin (NBCD) in aqueous solution. Detailed steady-state and time-resolved fluorescence measurements revealed two pathways of electron transfer, i.e., the electron transfer between the free donor and free acceptor in solution (dynamic quenching), and the electron transfer between the donor and acceptor bound in a supramolecular complex (static quenching). In these two pathways, the static quenching was found to be highly efficient and dominant in the presence of NBCD. The remarkably large electron-transfer rate (k_{SET}, ca. 1.0×10^9 s^{-1}) of the static quenching was found to be very close to that of a covalently linked porphyrin−nitrobenzene dyad.

1. Introduction

Photosynthesis has evolved over time to prompt ultrafast photoinduced electron transfer from the electronically excited chlorophylls to quinone receptors.[1] Model studies of this process with synthetically derived photosynthetic mimics not only can improve our understanding of the detailed mechanism of biological 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 the photoinduced electron transfer is composed of an electron donor and acceptor covalently linked to each other.[4] Studies on these donor−acceptor dyads have revealed interesting dependency of the electron-transfer rate on the donor−acceptor distance, the donor−acceptor orientation, the nature of the spacer, and the nature of the solvent.[4] Nevertheless, these systems cannot fully mimic the biological electron transfer, because in the biological systems the donor and acceptor are held together by proteins without any covalent linkage.

A better model for the photoinduced electron transfer is composed of an electron donor and acceptor connected via noncovalent interactions. Although such noncovalent interactions as hydrogen bonding,[5] *π*-stacking,[6] and metal−ligand coordination[7] can be used to construct the supramolecular photoinduced electron-transfer system, the most ideal approach to mimic the biological processes is to build the donor−acceptor dyad in aqueous solution by means of hydrophobic interactions. Thus, the aqueous photoinduced electron transfer in peptide,[8] nucleic acid,[9] micelle,[10] and certain water-soluble host−guest systems have been intensively studied.

Cyclodextrin (CD) is one of the most important water-soluble host molecules. It is a cyclic oligosaccharide 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. As a result, CD can form inclusion complexes with many organic compounds in aqueous solution.[11] This binding property of CD has been successfully used in the construction of artificial enzymes,[12] drug delivery systems,[13] and molecular machines.[14] The binding property of CD is also expected to be useful in the assembly of supramolecular photoinduced electron-transfer systems.

It should be mentioned that the effects of the addition of native CDs on the photoinduced electron-transfer reactions in water have been studied by many groups.[15] However, much less effort has been devoted to the use of CDs in constructing photoinduced electron-transfer systems.[16] Recently, De Cola et al. synethsized metal-coordinated CDs and studied their photoinduced electron transfer with viologens.[17] Park et al. synthesized naphthalene-substituted *β*-CD and studied its photoinduced electron transfer with adamantylmethyl viologen.[18] We synthesized a CD electron acceptor, *p*-nitrobenzoyl-*β*-cyclodextrin (NBCD), and studied its photoinduced electron transfer with naphthalene derivatives.[19]

In agreement with what were found by De Cola and Park in their systems, we observed very fast and efficient photoinduced electron transfer in our NBCD−naphthalene system.[19] Since no chemical bond is available between NBCD and naphthalene, this electron transfer must occur through space but not through bond. Nevertheless, in our 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 whose electron-donating moiety and binding moiety 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.

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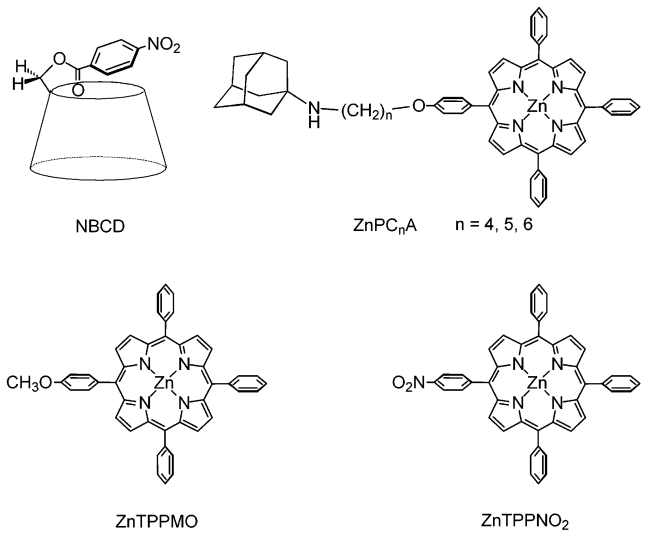

Figure 1. Electron acceptor and electron donors in the supramolecular systems and reference compounds (ZnTPPMO, ZnTPPNO$_2$).

Therefore, in the present study we synthesized a series of monotailed zinc tetraphenylporphyrins in which the zinc porphyrin moiety was connected to 1-adamantanamine via a flexible hydrocarbon chain (Figure 1). We chose metalloporphyrins as the electron donor because of their good biological relevance. We chose 1-admantanamine as the binding site because of its strong complexation with β-CD.[20] We were interested in knowing whether photoinduced electron transfer could occur efficiently between the zinc tetraphenylporphyrins and NBCD. We were also interested in knowing the effect of the length of the hydrocarbon linker on the velocity and efficiency of the electron-transfer reaction.

2. Experimental Section

2.1. Materials. NBCD was synthesized following the reported procedure.[19] Pyrrole, benzaldehyde, 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane, 4-hydroxybenzaldehyde, 4-nitrobenzaldehyde, 1-adamantanamine, and zinc acetate were obtained commercially and used without further purification. Deionized water was used throughout the experiments.

2.2. Instruments. ^{1}H NMR spectra were recorded on a Bruker DMX-500 NMR spectrometer. Absorption spectra were recorded on a Shimadzu UV-2100 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. MALDI-TOF mass spectra were recorded with a BIFLEX III instrument.

2.3. Electrochemical Measurements. Cyclic voltammetry measurements were carried out with a CHI 620A Electrochemical Analyzer. A platinum microsphere was used as the working electrode and the counterelectrode was platinum wire; a Fc^+/Fc (Fc = ferrocene) couple was used as the reference electrode. CH_3CN (spectrophotometric grade) was used as the solvent and 0.1 M Bu_4NClO_4 was used as the supporting electrolyte.

2.4. Syntheses of Reagents. *A. Zinc 5-(4-Hydroxyphenyl)-10,15,20-triphenylporphyrinate (ZnTPPOH).* Freshly distilled pyrrol (26.8 g, 0.4 mol) was added to a solution of 4-hydroxybenzaldehyde (12.2 g, 0.1 mol) and benzaldehyde (31.8 g, 0.3 mol) in 500 mL of propionic acid. The mixture was refluxed for 4 h. After most of the propionic acid was removed by distillation under vacuum, 500 mL of methanol was added. The black solid was collected by filtration and washed with methanol several times. The black solid was then dissolved in 500 mL of chloroform−methanol (7:3 v/v). Zinc acetate (60 g, 0.328 mol) in 300 mL of methanol was added. The solution was refluxed for 3 h. After the solvent was evaporated, the residue was extracted by chloroform. The organic layer was concentrated and purified by using flash chromatograph over silica gel column (eluent: chloroform). The second fraction was collected and concentrated. This method of purification was repeated once more with chloroform as eluent to obtain purple solid porphyrin. Yield 2.47 g (3.56%). ^{1}H NMR ($CDCl_3$) δ 8.92−8.84 (8 H, m), 8.20 (6 H, m), 7.95 (2 H, d), 7.76−7.50 (9 H, m), 7.10 (2 H, d), 5.03 (1 H, s).

B. Zinc 5-(4-(ω-Bromoalkyloxy)phenyl)-10,15,20-triphenylporphyrinate (ZnPC$_n$Br). A typical procedure for the syntheses of ZnPC$_n$Br is as follows (e.g. n = 4): ZnTPPOH (0.5 g 0.72 mmol), 1,4-dibromobutane (2.0 g, 9.26 mmol), and potassium carbonate (2.0 g, 14.5 mmol) were suspended in 50 mL of dry *N*,*N*-dimethylformamide and stirred for 48 h at room temperature. The solvent was evaporated under reduced pressure. The residue was dissolved in chloroform and washed in water. The organic layer was dried over anhydrous sodium sulfate and evaporated to remove the solvent. The residue was purified with flash chromatography over silica gel column (eluent: chloroform). The first fraction was collected and concentrated. This method of purification was repeated two times and purple solid was obtained.

ZnPC$_4$Br: Yield 0.48 g (80.5%). ^{1}H NMR ($CDCl_3$) δ 8.98−8.93 (8 H, m), 8.22−8.20 (6 H, m), 8.10 (2 H, d), 7.76−7.70 (9 H, m), 7.23 (2 H, d), 4.25 (2 H, t), 3.60 (2 H, t), 2.24−2.16-(4 H, m).

ZnPC$_5$Br: Yield 0.36 g (59.4%). ^{1}H NMR ($CDCl_3$) δ 8.95−8.84 (8 H, m), 8.21 (6 H, m), 8.05 (2 H, d), 7.77−7.50 (9 H, m), 7.21 (2 H, d), 4.21 (2 H, t), 3.59 (2 H, t), 2.10−2.04 (4 H, m), 1.84−1.76 (2 H, m).

ZnPC$_6$Br: Yield 0.46 g (74.7%). ^{1}H NMR ($CDCl_3$) δ 8.99−8.93 (8 H, m), 8.22−8.20 (6 H, m), 8.10 (2 H, d), 7.76−7.71 (9 H, m), 7.24 (2 H, d), 4.24 (2 H, t), 3.49 (2 H, t), 2.03−1.96 (4 H, m), 1.64−1.73 (4 H, m).

C. Zinc 5-(4-(ω-(1-Adamantaneamino)alkyloxy)phenyl)-10,15,20-triphenylporphyrinate (ZnPC$_n$A). A typical procedure for the syntheses of ZnPC$_n$A is as follows (e.g. n = 4): A 100-mL sample of an ethanol/chloroform (1:1 v/v) solution of ZnPC$_4$Br (0.3 g, 0.36 mmol) and 1-adamantanamine (0.1 g, 6.62 mmol) in autoclave was heated at 100 °C for 10 h. After the solvent was removed, the residue was extracted with 5% Na_2CO_3 and chloroform. The organic layer was purified over a silica gel column with chloroform/methanol (15:1, v/v). Purple solid was obtained.

ZnPC$_4$A: Yield 0.23 g (71.2%). ^{1}H NMR (CDCl3)δ 8.97−8.90 (8 H, m), 8.20−8.16 (6 H, m), 8.11 (2 H, d), 7.75−7.65 (9 H, m), 7.20 (2 H, d), 4.32 (2 H, m), 3.20 (2 H, m), 2.54 (2 H, m), 2.25 (9 H, m), 2.12 (2 H, m), 1.81−1.73 (4 H, m), 1.52 (2 H, m), 1.26 (1 H, s). IR (KBr) 3421, 3050, 2902, 2847, 1596, 1507, 1484, 1438, 1338, 1244, 1172, 1067, 991, 794, 701 cm^{-1}. Element Anal. Calcd for $C_{58}H_{51}N_5OZn$: C, 77.51; H, 5.68; N, 7.80. Found: C, 77.87; H, 5.74; N, 7.78. MALDI MS (*m*/*z*) 898 (exact mass 897.3).

ZnPC$_5$A: Yield 0.22 g (67.1%). ^{1}H NMR ($CDCl_3$) δ 8.96−8.87 (8 H, m), 8.20−8.14 (6 H, m), 8.08 (2 H, d), 7.74−7.65 (9 H, m), 7.26 (2 H, d), 4.25 (2 H, m), 2.96 (2 H, m), 2.38−1.93 (15 H, m), 1.85−1.52 (6 H, m), 1.25 (1 H, s). IR (KBr) 3431, 3050, 2911, 2848, 1599, 1506, 1480, 1444, 1335, 1241, 1171, 1067, 996, 797, 749, 707 cm^{-1}. Element Anal. Calcd for

TABLE 1: Redox Potentials[a] (mV) of the Porphyrins in CH_3CN and ΔG_{PET} (mV) between the Porphyrins and NBCD Calculated with the Rehm−Weller Equation

compd	$P^{+\bullet}$	P^{2+}	$-NO_2^{-\bullet}$	λ_{em} (nm)	E_{00}[b]	ΔG_{PET}[c]
$ZnPC_4A$	425	705		658	1884	−418
$ZnPC_5A$	431	710		669	1853	−381
$ZnPC_6A$	438	723		659	1881	−402
ZnTPPMO	410	698		645	1922	−571
NBCD			−1041			

[a] The potentials are referenced to Fc^+/Fc at a scan rate of 100 mV/s in 1×10^{-3} M solutions of the compounds in 0.1 M $Bu_4NClO_4-CH_3CN$ at 298 K. [b] E_{00} (meV) = 12398/λ_{em} (Å). Strictly E_{00} should be estimated by the overlap between absorption and emission spectra. The E_{00} value calculated by using the previous equation is therefore slightly underestimated. [c] ΔG_{PET} (mV) was in fact the value in CH_3CN. The corresponding ΔG_{PET} value in aqueous solution should be more negative than ΔG_{PET} in CH_3CN due to the better solvation of the charge-separated species in water.

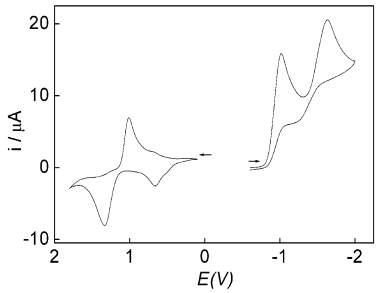

Figure 2. Cyclic voltammogram of $ZnPC_4A$ in acetonitrile.

$C_{59}H_{53}N_5OZn$: C, 77.63; H, 5.81; N, 7.68. Found: C, 77.91; H, 5.77; N, 7.54. MALDI MS (*m*/*z*) 912 (exact mass 911.4).

$ZnPC_6A$: Yield 0.25 g (75.1%). ^1H NMR ($CDCl_3$) δ 8.96−8.87 (8 H, m), 8.20−8.16 (6 H, m), 8.10 (2 H, d), 7.73−7.67 (9 H, m), 7.24 (2 H, d), 4.23 (2 H, m), 2.95 (2 H, m), 2.30−1.93 (15 H, m), 1.74−1.56 (8 H, m), 1.25 (1 H, s). IR (KBr) 3419, 3050, 2902, 2847, 1596, 1507, 1483, 1483, 1439, 1337, 1243, 1172, 1065, 991, 794, 751, 699 cm^{-1}. Element Anal. Calcd for $C_{60}H_{55}N_5OZn$: C, 77.75; H, 5.94; N, 7.56. Found: C, 77.39; H, 6.05; N, 7.49. MALDI MS (*m*/*z*) 926 (exact mass 925.4).

3. Results and Discussion

3.1. Electrochemistry. Using the Rehm−Weller equation (eq 1),[21] we can calculate the free energy change of a photoinduced electron-transfer reaction.

$$\Delta G_{PET} = e[E_{D^{+\bullet}/D} - E_{A/A^{-\bullet}}] - E_{00} - \frac{e^2}{4\pi\epsilon_s\epsilon_0 R_{cc}} - \frac{e^2}{8\pi\epsilon_0}\left(\frac{1}{r^+} + \frac{1}{r^-}\right)\left(\frac{1}{\epsilon_{ref}} - \frac{1}{\epsilon_s}\right) \quad (1)$$

($E_{D^{+\bullet}/D}$ and $E_{A/A^{-\bullet}}$ are the redox potentials of the electron donors and acceptor, respectively. E_{00}[22] 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 $\Delta G_{PET} < 0$, electron transfer can occur between the photoexcited electron donor and ground-state electron acceptor.

The redox potentials of $ZnPC_nA$ and NBCD are measured by using cyclovoltammetry (Table 1). A typical cyclic voltammogram of $ZnPC_4A$ is shown in Figure 2. The excitation energy of $ZnPC_nA$ (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 are calculated to be negative for all the porphyrin compounds. Therefore, photoinduced electron transfer may take place between $ZnPC_nA$ (or ZnTPPMO) and NBCD.

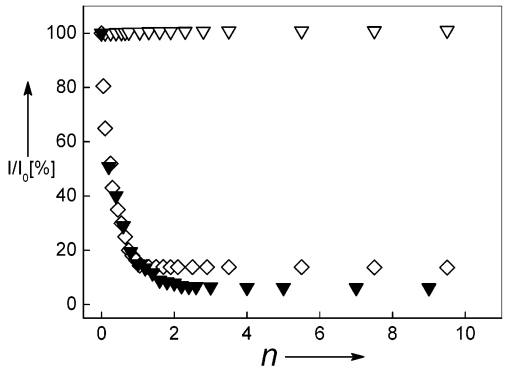

Figure 3. Fluorescence intensity of $ZnPC_4A$ in aqueous solution (4.0 μM) with aqueous solutions of NBCD (bottom), β-CD (upper), and NBCD + β-CD (middle). n = [host]/[guest], host = NBCD, β-CD, or NBCD + β-CD, guest = $ZnPC_4A$.

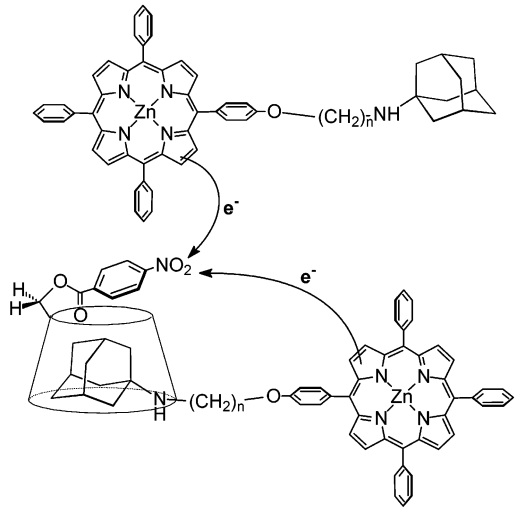

Figure 4. Two pathways of electron-transfer reactions between the excited $ZnPC_nA$ and NBCD.

3.2. Steady-State Fluorescence. The interaction between NBCD and $ZnPC_nA$ in aqueous solution is studied with use of the steady-state fluorescence. When an aqueous solution of $ZnPC_nA$ is titrated with NBCD, the fluorescence intensity from the porphyrin moiety decreases sharply until it is completely quenched (Figure 3). In comparison, when $ZnPC_nA$ is titrated with β-CD, the fluorescence intensity from the porphyrin moiety remains constant.

Since the energy of the excited singlet porphyrin derivatives is much lower than that of NBCD, energy transfer cannot take place from an excited porphyrin species to NBCD. Therefore, the only plausible mechanism for the fluorescence quenching is that photoinduced electron transfer occurs between $ZnPC_nA$ and NBCD.

Two pathways of electron transfer can take place between the excited $ZnPC_nA$ and NBCD. The first is dynamic quenching, which corresponds to the bimolecular electron transfer between NBCD and free excited $ZnPC_nA$ in solution. The second is static quenching, which refers to the intrasupramolecular electron transfer between NBCD and $ZnPC_nA$ included in the NBCD cavity[23] (Figure 4).

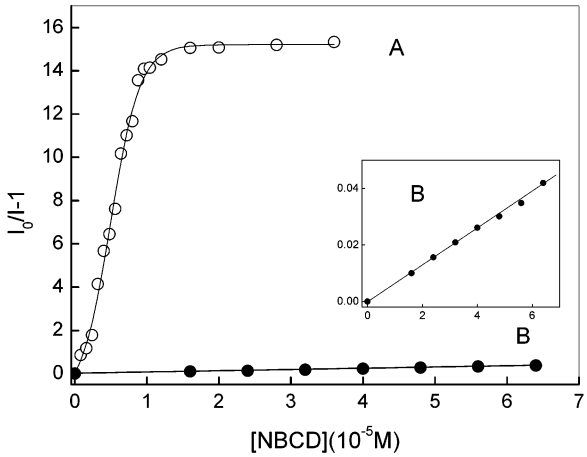

Figure 5. Plot of I_0/I against [NBCD] for the fluorescence quenching of $ZnPC_4A$ (A, ○) and ZnTPPMO (B, ●) in water at room temperature (I_0 is the fluorescence intensity in the absence of NBCD; I is the fluorescence intensity in the presence of NBCD).

3.3. Stern−Volmer Equation. We plot in Figure 5 I_0/I against the concentration of NBCD observed in the titration experiment. Herein, I_0 is the fluorescence intensity of the porphyrin compound (4.0 μM) in the absence of NBCD. I is the fluorescence intensity in the presence of the quencher, NBCD.

According to the Stern−Volmer equation, when there is only dynamic quenching in a fluorescence system we should have the following equation.[24]

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

Herein, k_q is the bimolecular quenching constant. τ_0 is the fluorophore lifetime in the absence of quencher. A good example for eq 2 is the quenching of ZnTPPMO fluorescence by NBCD, for which a straight line is obtained between I_0/I and [NBCD][25] (Figure 5B). It should be noted that Figure 5B also shows that the dynamic quenching of the porphyrin fluorescence by NBCD is not significant.

However, it is clear from Figure 5A that the plot of I_0/I against [NBCD] does not fit eq 2 for $ZnPC_4A$. In this system, I_0/I increases sharply when a tiny amount of NBCD is added. Then the increase of I_0/I slows down slightly as [NBCD] increases. Once [NBCD] is larger than 15 μM, I_0/I reaches its maximum and remains constant despite the further increase of [NBCD]. This I_0/I−[NBCD] curve clearly indicates that in addition to the dynamic quenching, the static quenching (i.e. the intrasupramolcular photoinduced electron transfer) should also exist in the $ZnPC_4A$−NBCD system.

It should be mentioned that the fluorescence property of $ZnPC_4A$ in the presence of NBCD (>15 μM) is similar to that of the reference compound $ZnTPPNO_2$. In $ZnTPPNO_2$, a donor (porphyrin) moiety is connected covalently to an acceptor (*p*-nitrophenyl) moiety. As a result, the fluorescence of the porphyrin moiety of $ZnTPPNO_2$ is almost fully quenched via an intramolecular electron transfer. The fluorescence of $ZnTPPNO_2$ is also independent of the addition of an external quencher (e.g. NBCD).

3.4. Binding Constants. The remarkable quenching of the porphyrin fluorescence by NBCD in the $ZnPC_nA$ system is mainly caused by a highly efficient intrasupramolecular static quenching. There are two distinct species in the $ZnPC_nA$−NBCD solution. One is free $ZnPC_nA$, whose fluorescence intensity is high because of the insignificant dynamic quenching. The other is the inclusion complex between $ZnPC_4A$ and NBCD, whose fluorescence intensity is very low because of the highly efficient static quenching. Using this two-state model[11] and the I_0/I−[NBCD] plots, we can easily calculate the binding constants between $ZnPC_nA$ and NBCD, which are 2.6×10^7, 1.2×10^7, and 1.3×10^7 M^{-1} for $n = 4$, 5, and 6, respectively.

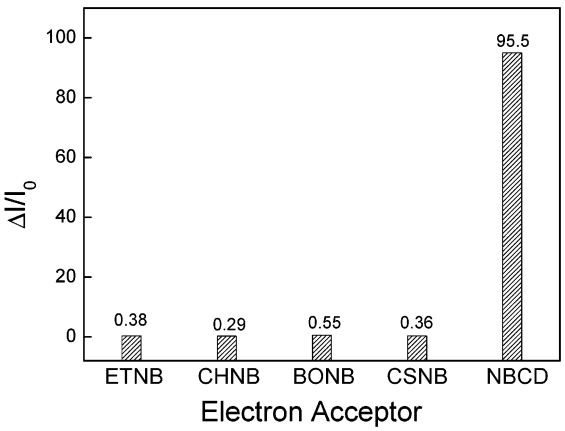

Figure 6. The fluorescence quenching of $ZnPC_4A$ by NBCD and other electron acceptors in aqueous solution ([$ZnPC_4A$] = 4.0 μM).

It is worthy to note that the binding constants between $ZnPC_nA$ and NBCD are much larger than the binding constants ($\sim 10^5$ M^{-1}) determined previously for the complexes between other adamantine derivatives and β-CD.[11] We assume that the charge-transfer interaction between the electron donor and acceptor, in addition to the hydrophobic interactions, may contribute to the extraordinary stability of the $ZnPC_nA$−NBCD complexes.

3.5. Control Experiments. To confirm the intrasupramolecular quenching mechanism, some control experiments have been conducted. In the first control experiment, fluorescence titration is performed with ethyl *p*-nitrobenzoate (ETNB), cyclohexyl *p*-nitrobenzoate (CHNB), bornyl *p*-nitrobenzoate (BONB), or cholesteryl *p*-nitrobenzoate (CSNB) as the quencher. It is found that when 1.0 equiv of a *p*-nitrobenzoyl ester is added to $ZnPC_4A$, the fluorescence intensity of $ZnPC_4A$ decreases by 0.38% for ETNB, 0.29% for CHNB, 0.55% for BONB, and 0.36% for CSNB. In comparison, when 1.0 equiv of NBCD is added to $ZnPC_4A$, the fluorescence intensity of porphyrin decreases by 95.5% (Figure 6). These observations indicate that without a binding site, only the dynamic quenching occurs between $ZnPC_4A$ and a *p*-nitrobenzoyl ester.

3.6. Competition Experiments. β-CD alone does not exert any quenching effect on $ZnPC_4A$ (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 (Figure 3). In fact, the final I_F value is 28.4 for the β-CD−NBCD titration experiment, whereas the final I_F value for the NBCD titration experiment is 12.8. Since the original I_F value of the pure $ZnPC_4A$ solution is 208.9, we can calculate that in the $ZnPC_4A$−β-CD−NBCD system ([β-CD] = [NBCD] ≫ [$ZnPC_4A$]), 8.0% of total $ZnPC_4A$ should stay in β-CD whereas 92.0% of total $ZnPC_4A$ should stay in NBCD. This means that the binding constant of the $ZnPC_4A$−NBCD complex should be about 11 times larger than that of $ZnPC_4A$−β-CD. As the binding constant of $ZnPC_4A$−NBCD is 2.6×10^7 M^{-1}, the binding constant of $ZnPC_4A$−β-CD should be 2.2×10^6 M^{-1}.

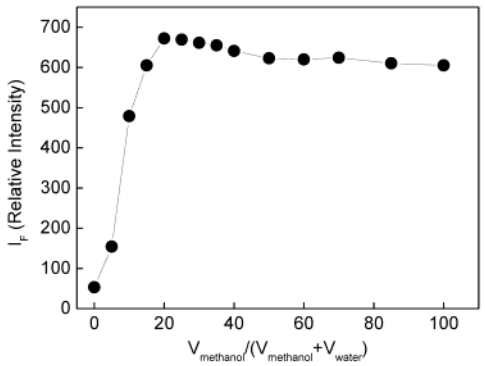

Figure 7. Fluorescence intensity changes of $ZnPC_4A$ with addition of methanol in aqueous solution in the presence of NBCD ([$ZnPC_4A$] = [NBCD] = 4.0 μM).

The binding constant for $ZnPC_4A-$NBCD is larger than that for $ZnPC_4A-\beta$-CD, possibly because of the charge-transfer interaction between the electron donor and acceptor. The binding constant for $ZnPC_4A-\beta$-CD is about four times larger than that for the complex between β-CD and 1-adamantanecarboxylic acid (4.8×10^5 M^{-1}),[26] possibly because the hydrocarbon linker in $ZnPC_4A$ also contributes to the binding. In any case, the β-CD−NBCD titration experiment indicates that β-CD can inhibit the quenching of NBCD to some extent.

3.7. Methanol Co-solvation. When methanol is added to the aqueous $ZnPC_4A-$NBCD solution, the fluorescence intensity of the system increases sharply, until the concentration (v/v) of methanol reaches 20% (Figure 7). After the concentration of methanol reaches 20%, addition of more methanol into the system does not significantly change the fluorescence intensity. Clearly, the role of methanol here is to destroy the hydrophobic interaction between NBCD and $ZnPC_4A$. As less $ZnPC_4A$ is included in NBCD, less static quenching can take place. When the concentration of methanol is higher than 20%, no complex between NBCD and $ZnPC_4A$ can be formed in the solution and therefore the fluorescence quenching under this condition should be completely bimolecular in nature.

3.8. Time-Resolved Fluorescence. The photoinduced electron transfer between NBCD and $ZnPC_nA$ is also studied by using the time-resolved fluorescence. From these experiments, it is found that the decay of the fluorescence intensity of $ZnPC_nA$ in water is monoexponential in the absence of NBCD. In comparison, the decay of the fluorescence intensity of $ZnPC_nA$ in the presence of NBCD obeys a double exponential function.

$$F(t) = A_L \exp(-t/\tau_L) + A_S \exp(-t/\tau_S) \quad (3)$$

Equation 3 means that there are two components in the decay, i.e., a long-lived one (L) and a short-lived one (S). The long-lived component can be attributed to the fluorescence decay of uncomplexed $ZnPC_nA$, whereas the short-lived component should come from the fluorescence decay of $ZnPC_nA$ complexed with NBCD.

It is found that the lifetime (τ_L or τ_S) of the long-lived component or short-lived component is fairly insensitive to the concentration of NBCD in the range $0 \le$ [NBCD] $\le$ [$ZnPC_nA$]. The insensitivity of τ_S indicates that only one type of $ZnPC_nA-$NBCD complex exists in the solution. The insensitivity of τ_L indicates that the bimolecular dynamic quenching between NBCD and free $ZnPC_nA$ molecules is not significant in the presence of a low concentration of NBCD ($\le$4.0 μM).[27]

Interestingly, the lifetime of $ZnTPPNO_2$ fluorescence is measured to be 0.69 ns (see Table 2). This value is close to τ_S of the $ZnPC_nA-$NBCD systems (τ_S = 0.71, 0.52, 0.67 ns for n = 4, 5, 6). Therefore, the fluorescence quenching rate of a $ZnPC_nA-$NBCD complex is close to that of $ZnTPPNO_2$. On the other hand, the lifetime of ZnTPP fluorescence by itself is 3.21 ns. This value is larger than τ_L of $ZnPC_nA$ (i.e. the lifetime of $ZnPC_nA$ by itself) possibly due to the structure difference.

TABLE 2: Intrasupramolecular Electron-Transfer Rates (k_{SET}) and Fluorescence Quenching Quantum Yield ($\Phi_F{}^q$) of the $ZnPC_nA-$NBCD Systems[a] in Aqueous Solution

compd	τ_S/ns	τ_L/ns	$k_{SET}/10^9$ s^{-1}	$\Phi_F{}^q$ (%)[d]
$ZnPC_4A$	0.71 ± 0.05	1.85 ± 0.07	0.87 ± 0.12	61.7
$ZnPC_5A$	0.52 ± 0.04	1.81 ± 0.06	1.37 ± 0.16	71.3
$ZnPC_6A$	0.67 ± 0.06	1.73 ± 0.07	0.91 ± 0.14	61.2
$ZnTPPNO_2$[b]	0.69 ± 0.05		1.14 ± 0.11[c]	
ZnTPP[b]		3.21 ± 0.09		

[a] [NBCD] = [porphyrin] = 4.0 μM. [b] ZnTPP = zinc 5,10,15,20-tetraphenyl porphyrinate. τ_L for ZnTPP was measured in the absence of NBCD. [c] Calculated by using the following: $k_{SET} = 1/\tau_{S(ZnTPPNO_2)} - 1/\tau_{L(ZnTPP)}$. [d] Because τ_L is not sensitive to [NBCD] when [NBCD] is small, we let τ_0 equal τ_L.

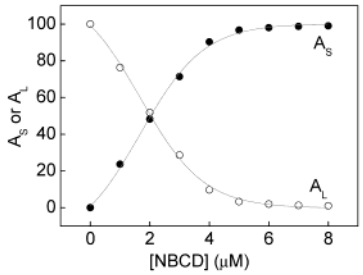

Figure 8. The change of the magnitude of the short-lived (A_S) and long-lived (A_L) component of $ZnPC_4A$ with increasing concentration of NBCD ([$ZnPC_4A$] = 4.0 μM).

It is also found that the magnitude of the short-lived component (A_S) increases sharply with increasing concentration of NBCD, whereas the magnitude of the long-lived component (A_L) decreases sharply at the same time (see Figure 8). This behavior is consistent with the two-state model described in the above discussion.

We are interested in knowing if co-solvation can affect the time-resolved fluorescence. Therefore, we add methanol to an aqueous solution of 1:1 $ZnPC_4A-$NBCD. Interestingly, when the concentration of methanol increases from 0 to 20% (v/v), the fractional contribution of the short-lived component decreases sharply from 90.7% to 0. For the 20% methanol solution, the decay profile is monoexponential with a lifetime about 1.59 ns. When the concentration of methanol increases from 20% to 100%, the decay profile is always monoexponential. This observation is consistent with the fact that in a 20−100% methanol solution the fluorescence decay of the $ZnPC_4A-$ETNB system is monoexponential.

3.9. Electron-Transfer Rates. We can calculate the rate constant of the photoinduced electron transfer using the following equation.

$$k_{SET} = 1/\tau_S - 1/\tau_L \quad (4)$$

It is found that k_{SET} values for the $ZnPC_nA-$NBCD systems are 0.87×10^9, 1.37×10^9, and 0.91×10^9 s^{-1} for n = 4, 5, and 6. These rates are close to the intramolecular electron-transfer rate of $ZnTPPNO_2$ (1.14×10^9 s^{-1}). Therefore, the flexible carbon chain and the cyclodextrin−adamantane interaction do not significantly slow the electron transfer between the porphyrin moiety and nitrobenzene moiety.

It should be noted that the electron transfer between $ZnPC_nA$ and NBCD must occur though space, because there is no bond between $ZnPC_nA$ and NBCD. Compared to the electron transfer in the systems held together by hydrogen bonds or metal coordination, the present electron transfer is more challenging because NBCD and $ZnPC_nA$ are held together by the hydrophobic interaction (a combination of weak van der Waals interactions and solvent entropy effect).

The dependence of the electron transfer rate on the linker length is intriguing. Although currently we cannot provide a good explanation for the slightly higher rate observed for $ZnPC_5A$ compared to those for $ZnPC_4A$ and $ZnPC_6A$, we should mention that in aqueous solution the hydrocarbon linker between adamantane and porphyrin may be highly folded. Therefore, it remains to clarify the actual distance between the *p*-nitrophenyl moiety and porphyrin moiety in a $ZnPC_nA-$NBCD complex. In addition, the different conformations adopted by the $ZnPC_nA-$NBCD complexes may also affect their individual electron-transfer rates in a nonmonotonic way.[28]

3.10. Quantum Yields. We can calculate the fluorescence quenching quantum yield of the electron transfer using the following equation.

$$\Phi_F^{\ q} = k_{SET}/[k_{SET} + (1/\tau_0)] \quad (5)$$

In eq 5 τ_0 stands for the fluorescence lifetime of $ZnPC_nA$ in the absence of NBCD in aqueous solution. According to Table 2, the quantum yields of the $ZnPC_nA-$NBCD systems are 61.7%, 71.3%, and 61.2% for $n = 4$, 5, and 6, respectively. These values are smaller than the quantum yield found in the NBCD−2-*N*,*N*-dimethylaminonaphthalene system (98.9%), mainly because the fluorescence lifetime of the porphyrin compound (∼1.8 ns) is much smaller than that of 2-*N*,*N*-dimethylaminonaphthalene (24.9 ns).

4. Conclusion

A series of monotailed porphyrins were designed and synthesized, in which the porphyrin moiety was connected to 1-adamantanamine via a flexible hydrocarbon chain. It was found that photoinduced electron transfer could occur between these porphyrin compounds and mono-6-*p*-nitrobenzoyl-β-cyclodextrin in aqueous solution. Detailed steady-state and time-resolved fluorescence experiments revealed two pathways of electron transfer, i.e., the electron transfer between the free donor and free acceptor in solution (dynamic quenching), and the electron transfer between the donor and acceptor bound in a supramolecular complex (static quenching). In these two pathways, the static quenching was found to be highly efficient and dominant in the presence of NBCD. The remarkably large electron-transfer rate (k_{SET}, ca. 1.0×10^9 s^{-1}) of the static quenching was also found to be very close to that of a covalently linked porphyrin−nitrobenzene dyad.

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