ARTICLE

Photoinduced Electron Transfer Between Mono-6-p-nitrobenzoyl-β-cyclodextrin and Adamantanamine-C$_n$-Co/Ni-porphyrins

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Two series monotailed porphyrins, Cobalt-5-{4-[ω-(1-adamantaneamino) alkyloxy]phenyl}-10,15,20-triphenyl porphyrinate (CoPC$_n$A, n=4,5,6) and Nickel-5-{4-[ω-(1-adamantaneamino)alkyloxy]phenyl}-10,15,20-triphenyl porphyrinate (NiPC$_n$A, n=4,5,6), were synthesized, in which the porphyrin moiety was connected to 1-adamantanamine via a flexible hydrocarbon chain. The fluorescence quenching between these donor substrates and mono-6-p-nitrobenzoyl-β-cyclodextrin (NBCD) was studied in detail. Distinct fluorescence quenching occured in these supramolecular systems. This quenching was attributed to the photoinduced electron transfer (PET) inside the supramolecular assembly between the porphyrin donors and cyclodextrin acceptors. Detailed Stern-Volmer constants were measured and they were partitioned into dynamic Stern-Volmer quenching constants and static binding constants. It was demonstrated that the PET interaction between the porphyrin subunits and NBCD is indeed effective.

Key words: Photoinduced electron transfer, Host-guest complex, Cyclodextrin, Supramolecular system, Fluorescence quenching

I. INTRODUCTION

Photoinduced electron-transfer process plays a key role in many biological processes (e.g., photosynthesis [1]), and is also one of the most fundamental and important processes in chemistry. Therefore, it has encouraged scientists to look into the inherent mechanism [2] for years and to design artificial systems for the capture of solar energy and conversion of solar energy into chemical potential [3]. Many covalently linked electron donor-acceptor dyads [4] have been synthesized and extensively studied experimentally and theoretically. However, these systems cannot fully imitate 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 fine that the electron transfer proceeds very fast and selectively with a characteristic of high quantum yield [6].

Currently, the emphases of the relative photoinduced electron transfer research have shifted from small nuclear to supramolecular systems [7], which has the following numerous advantages: absence of diffusional effects, well-defined geometry, distance and orientational effects [8]. Noncovalent interactions, including hydrogen bonding [9], π-stacking [10], and metal-ligand coordination [11] have been used to assemble electron donors and acceptors. Modest successes have been achieved in

these systems. However, it should be pointed out that, in biological systems, the photoinduced electron transfer usually takes place in aqueous solution, in which hydrophobic interactions [12] play an important role in holding the donor and acceptor together.

Cyclodextrins are cyclic oligosaccharides and consist of six, seven, and eight glucopyranose units, which are called α-cyclodextrin (α-CD), β-cyclodextrin (β-CD) and γ-cyclodextrin (γ-CD), respectively [13]. Because the internal wall of CD is hydrophobic, organic molecules of appropriate size can be incorporated into the cavities of CDs to form inclusion complexes in aqueous solutions. The physicochemical properties of the guest molecules vary due to the incorporation into the CD cavities. Taking advantage of this propensity, CDs are used in the construction of artificial enzymes [14], drug delivery system [15] and molecular machines [16].

Many groups have studied the photoinduced electron transfer reaction in aqueous solution with the addtion of native CDs [17]. However, CDs were seldom used in constructing photoinduced electron transfer systems [18]. Recently, Cola *et al.* [19] synthesized metal-coordinated CD and studied their photoinduced electron transfer with viologens. Park *et al.* synthesized naphthalene-substituted β-CD and studied its photoinduced electron transfer with adamantylmethyl viologen [20]. In our previous work [21], we have synthesized a cyclodextrin electron acceptor/supramolecular host mono-6-p-nitrobenzoyl-β-cyclodextrin (NBCD) (Fig.1), and efficient electron transfer in the supramolecular systems consisting of NBCD and naphthalene derivatives were observed.

Porphyrins which have rich redox properties in both

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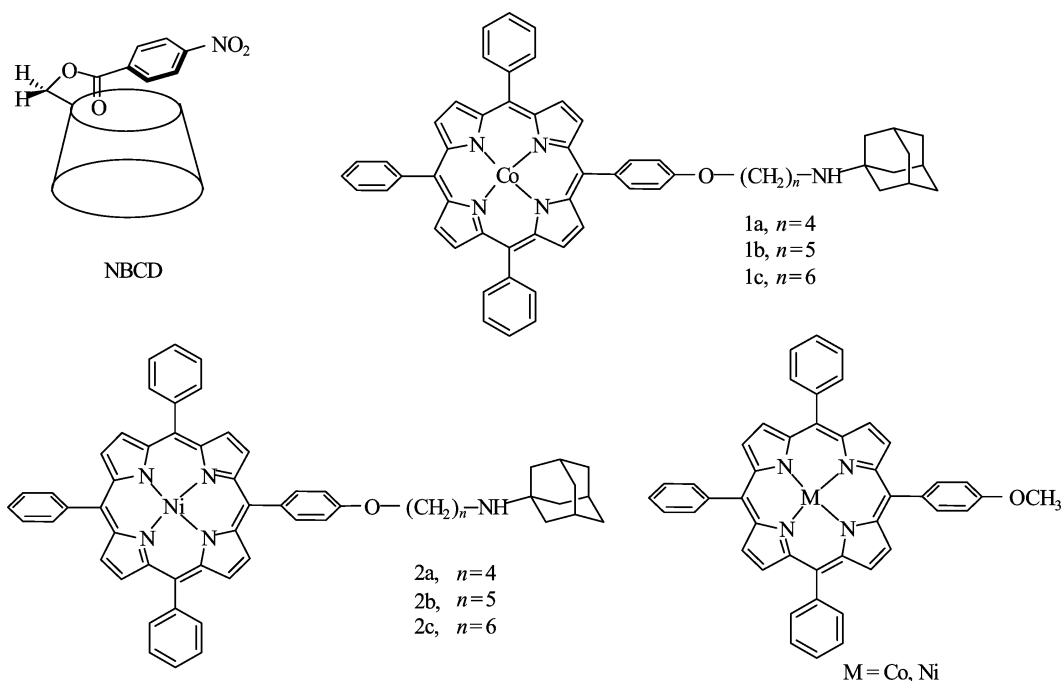
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FIG. 1 Electron acceptor and electron donors in the supramolecular systems and reference compounds (CoTPPMO, NiTPPMO).

the ground and excited states [22] are very useful in the reaction centre of photosynthesis [23], and they have been utilized as important components for design of novel artificial electron transfer systems [24]. In our laboratory we designed a supramolecular system, which is composed of NBCD and Zn-porphyrin derivatives [25], and studied the photoinduced electron transfer process in the system. In this paper, we report the recent experimental results on photoinduced electron transfer in the supramolecular system composed of cobalt or nickel prophyrin derivatives and NBCD.

II. EXPERIMENTAL SECTION

A. Instrument

The ^{1}HNMR spectrum was recorded in CDCl$_3$ on a Bruker DMX-400 MHz spectrometer with tetramethylsilane (TMS) as external standard. Fluorescence spectra were measured using a CRT-970 spectrometer in aqueous solution at room temperature. UV-Vis absorption spectra were detected by Perkin-Elmer Lambda 45 UV/Vis spectraphotometer. Elemental analysis was carried out on a Perkin-Elmer 240C analytical instrument.

B. Materials

Zinc-5-{4-[ω-(1-adamantaneamino)alkyloxy]phenyl} -10,15,20-triphenyl porphyrinate (ZnPC$_n$A, n=4,5,6)

and NBCD were synthesized following the reported procedure [25]. Cobalt acetate and nickel acetate were obtained commercially and used without further purification. Deionized water was used throughout the experiments.

C. Synthesis

5-{4-[ω-(1-adamantaneamino)butyloxy]phenyl}-10,15, 20-triphenyl porphyrinate (HPC$_4$A): A solution of the porphyrin ZnPC$_4$A (0.5 g, 0.44 mmol) in dichloromethane was washed with aqueous hydrochloric acid (2 mol/L) twice, washed with saturated aqueous sodium bicarbonate, dried over Na$_2$SO$_4$, and evaporated to yield the porphyrin HPC$_4$A as a purple solid. Yield: 0.43 g (92.5%). ^{1}HNMR (CDCl$_3$): 8.88-8.80 (8H,m), 8.21-8.16 (6H,m), 8.10 (2H,d), 7.73-7.64 (9H,m), 7.23 (2H,d), 4.25 (2H,m), 2.96 (2H,m), 2.16-1.97 (13H,m), 1.70 (6H,m), 1.25 (1H,s), $-$2.76 (2H,s).

Cobalt-5-{4-[ω-(1-adamantaneamino)alkyloxy]phenyl} -10,15,20-triphenyl porphyrinate (CoPC$_n$A): Typical procedure of syntheses of CoPC$_n$A is as follows (e.g. n=4): Cobalt acetate (194.8 mg, 1 mmol) in 60 mL DMF was added into a DMF solution of HPC$_4$A (0.2 g, 0.24 mmol). The solution was refluxed for 3 h. After evaporation of the solvent, the residue was extracted by chloroform. The organic solution was concentrated and purified by chromatograph on a silica-gel column with chloroform/methanol (15:1), so purple solid was obtained. Yield: 0.19 g (89.2%) ^{1}H NMR (CDCl$_3$):

9.0-8.90 (8H,m), 8.20-8.15 (6H,m), 8.10 (2H,d), 7.75-7.65 (9H,m), 7.18 (2H,d), 4.30 (2H,m), 3.22 (2H,m), 2.57 (2H,m), 2.24 (9H,m) 2.12 (2H,m), 1.80-1.70 (4H,m), 1.52 (2H,m), 1.25 (1H,s). Anal. Calcd for $C_{58}H_{51}N_5OCo$: C 78.01, H 5.71, N 7.84. Found: C 78.18, H 5.72, N 7.81. CoPC$_5$A: Yield: 0.20 g (92.2%). Anal. Calcd for $C_{59}H_{53}N_5OCo$: C 78.12, H 5.84, N 7.72. Found: C 78.14, H 5.85, N 7.69. CoPC$_6$A: Yield: 0.20 g (90.8%). Anal. Calcd for $C_{60}H_{55}N_5OCo$: C 78.24, H 5.97, N 7.60. Found: C 78.21, H 5.99, N 7.58.

Cobalt 5-(4-Methoxyphenyl)-10,15,20-triphenyl porphyrinate (CoTPPMO): CoTPPMO was obtained with the similar procedure mentioned above: A solution of the porphyrin ZnTPPMO (0.1 g, 0.14 mmol) in dichloromethane, was washed with aqueous hydrochloric acid (2 mol/L) twice, washed with saturated aqueous sodium bicarbonate, dried over Na_2SO_4, and evaporated to yield the porphyrin HTPPMO as a purple solid. Then, the solid was dissolved in 20 mL DMF, and Cobalt acetate (116.8 mg, 0.6 mmol) in 40 mL DMF was added. The solution was refluxed for 3 h. After evaporation of the solvent, the residue was extracted by chloroform. The organic solution was concentrated and purified by chromatograph on a silica-gel column with chloroform/methanol (15:1), purple solid was obtained. Yield 85.7 mg (92%). Anal. Calcd for $C_{45}H_{30}N_4OCo$: C 77.02, H 4.28, N 7.98. Found: C 77.41, H 4.30, N 7.94.

The nickel-5-{4-[ω-(1-adamantaneamino)alkyloxy] phenyl}-10,15,20-triphenyl porphyrinate (NiPC$_n$A): NiTPPMO were synthesized with the similar procedure for Cobalt-porphyrin derivatives. NiPC$_4$A: Yield: 0.20 g (93.4%). Anal. Calcd for $C_{58}H_{51}N_5ONi$: C 78.03, H 5.71, N 7.84. Found: C 78.17, H 5.68, N 7.80. NiPC$_5$A: Yield: 0.19 g (87.6%). Anal. Calcd for $C_{59}H_{53}N_5OCo$: C 78.14, H 5.84, N 7.72. Found: C 78.18, H 5.86, N 7.69. NiPC$_6$A: Yield: 0.21 g (95.4%). Anal. Calcd for $C_{60}H_{55}N_5ONi$: C 78.26, H 5.97, N 7.60. Found: C 78.41, H 5.94, N 7.56. NiTPPMO: Yield: 87.9 mg (96.4%). Anal. Calcd for $C_{45}H_{30}N_4ONi$: C 77.05, H 4.28, N 7.98. Found: C 77.36, H 4.30, N 7.96.

III. RESULTS AND DISCUSSION

A. Absorption spectra of porphyrins in the absence and presence of NBCD

The properties of the Co/Ni-porphyrins were studied with the use of absorption spectra. Here Co-porphyrin was chosed as the example to elucidate the observation of UV-Vis spectra. The absorption spectra of CoPC$_n$A ($\sim$1.0 μmol/L, n=4,5,6) were measured by a UV-Vis spectrophotometer in aqueous solution and compared with those of non-tailed reference porphyrin CoTPPMO. The mono-tailed derivatives CoPC$_n$A exhibited normal porphyrin absorption bands in the near

UV and visible regions, very characteristic π-π^* electronic transitions with a strong Soret band in the region of 400-420 nm ($\varepsilon \sim 10^5$ L/(mol cm)) of the allowed S_0-S_2 transition and the less intense Q bands (S_0-S_1 transition) near 550 nm, typical spectra of CoPC$_4$A was showed in Fig.2. However, these were all red shifted by 5-10 nm relative to those of non-tailed reference porphyrins. The small red-shift-property of the tailed porphyrins is quite common and it is the instinctual property of tailed porphyrins.
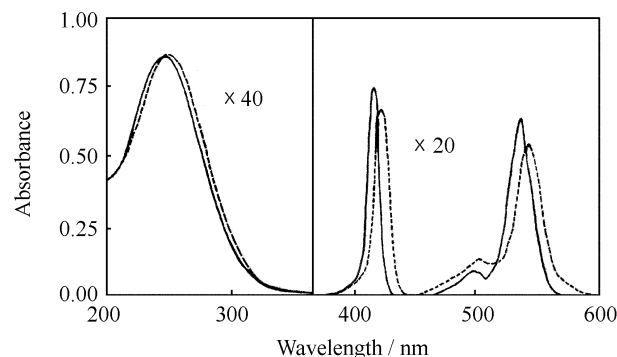

FIG. 2 Left: The absorption spectra of NBCD in the absence (solid line) and presence (dash line) of CoPC$_4$A. Right: UV-Vis absorption spectra of CoPC$_4$A in the absence (solid line) and presence (dash line) of NBCD in water.

To examine interactions between the ground state guest molecules and NBCD in aqueous solutions, the absorption spectra of CoPC$_n$A were recorded in the presence of NBCD (Fig.2). Compared to pure CoPC$_n$A, the Soret and Q bands were all red shifted by 4-8 nm in the presence of NBCD. These phenomena lead to the conclusion that there are interactions between the ground state CoPCnA and NBCD in aqueous solution. It is considered that the adamantyl group of 1-adamantanamine, compared to other molecules, was a perfect guest for β-cyclodextrin [26] and could be included into its cavity tightly in aqueous solution. According to our previous work [21], the binding force of β-CD with the substrates will be enhanced if the sixth position of the cyclodextrin is modified with p-nitrobenzoyl group. It is reasonable to conclude that the change of the absorption spectra was induced by the inclusion of the CoPC$_n$A adamantyl group and NBCD.

B. Fluorescence quenching experiments

The steady-state fluorescence spectra of the NBCD and excited state porphyrins in aqueous solution were studied at room temperature. When an aqueous solution of the mono-tailed porphyrins was titrated with NBCD, the fluorescence intensity of porphyrin subunit decreased sharply as the concentration of NBCD increased, at last the complete quenching was reached (Fig.3).
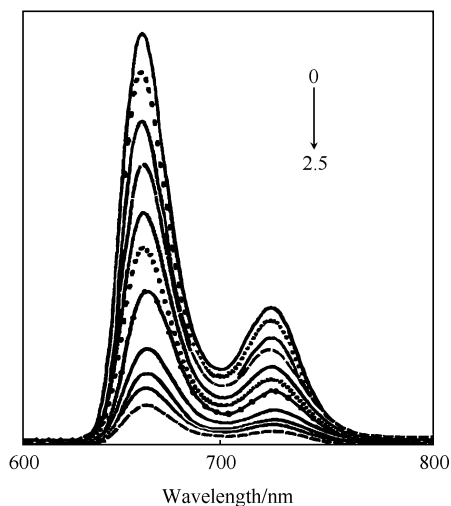
FIG. 3 Fluorescence spectra of **2a** (1.0 μmol/L) in the presence of different concentrations of NBCD in water: 0.0-2.5 μmol/L (λ_{ex}=420 nm).

The fluorescence quenching can be explained by two events, 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 porphyrins derivatives is much lower than the energy of the excited singlet of NBCD [25]. Therefore, it is reasonable that the PET is the mode of the fluorescence quenching in our system.

Two pathways of photoinduced electron transfer can take place between the excited porphyrin compounds and NBCD. The first is dynamic quenching [27], which corresponds to the bimolecular electron transfer between NBCD and free excited porphyrin in solution. The second is static quenching, which refers to the intra-supramolecular electron transfer between NBCD and porphyrin included in NBCD cavity (see Fig.4).

C. Stern-Volmer relationship

The Stern-Volmer relationship (Eq.(1)) for a system with both dynamic and static components has been derived before [28].

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

In Eq.(1), 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 (τ_0) and the dynamic quenching rate constant (k_q), $\tau_0 k_q$. K is the binding constant between the fluorescence compound and the quencher. If [Q] approaches zero, Eq.(1) changes into Eq.(2).
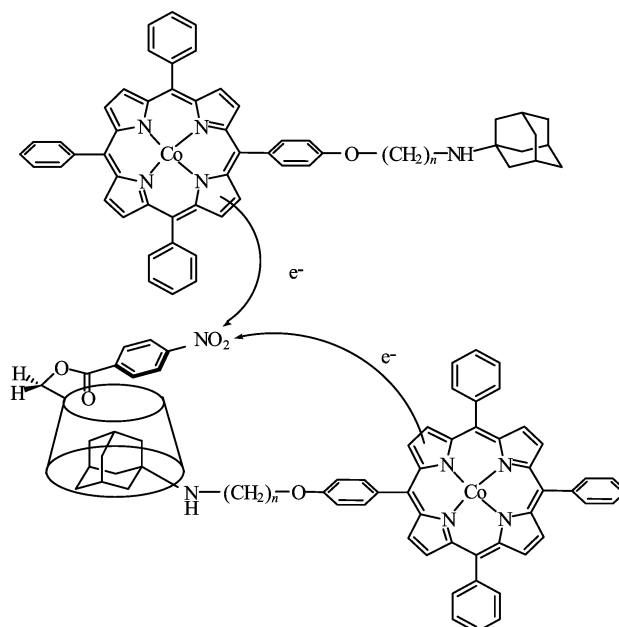
$$I_0/I = 1 + (K_{sv} + K)[Q] \qquad (2)$$

FIG. 4 Two pathways of electron-transfer reactions between the excited CoPC$_n$A and NBCD.

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

In the present study, the Stern-Volmer relationships were studied in the fluorescence quenching of compounds **1a-1c, 2a-2c** by NBCD. All the guest compounds exhibit nice linear correlations between I_0/I and [Q] (see Fig.5). Therefore, from the slopes of the correlations, the value of $(K_{sv} + K)$ for each guest compound could be easily determined. These results are summarized in Table I. From Table I it can be seen that the fluorescence quenching efficiency is higher in the NBCD and Co/Ni-porphyrin systems.
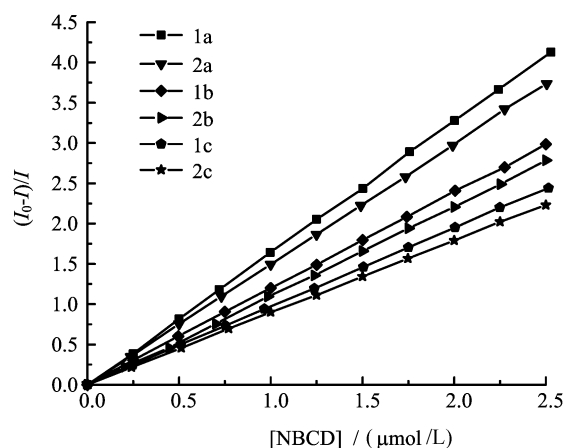

FIG. 5 Stern-Volmer plots for the fluorescence quenching of porphyrin derivatives with NBCD in aqueous solution at the room temperature.

TABLE I Stern-Volmer constants for the quenching between Co/Ni-porphyrin derivatives and NBCD(10^{-6} L/mol)

Compounds	$K + K_{sv}$	K_{sv}	K
1a	1.6355	0.0707	1.5648
1b	1.1941	0.0836	1.1105
1c	0.9742	0.0781	0.8961
2a	1.4943	0.0558	1.4385
2b	1.1060	0.0617	1.0443
2c	0.8952	0.0661	0.8291

D. Dynamic Stern-Volmer constants and binding constants

The above measurements provided the total Stern-Volmer constants. In order to gain more details of the observed behaviors, we separate the total Stern-Volmer constants into dynamic Stern-Volmer constants, K_{sv}, and the host-guest binding constants, K. For this purpose, 4-nitrobenzoic acid 2-hydroxyethyl ester (NBHE), the model compounds, were synthesized. It is expected that the redox property of NBHE should be very close to that of NBCD because they have similar chemical structures. Thus, it is reasonable to assume that the dynamic Stern-Volmer constant of NBHE is very close to that of NBCD. From the other side, being a small molecule, NBHE should not be able to form noncovalent complex with porphyrin compounds in water. Therefore, if NBHE can quench the fluorescence of the porphyrin compounds, the quenching should completely be a bimolecular dynamic quenching.

On the basis of the above analysis, the Stern-Volmer relationships in the fluorescence quenching of compounds **1a-1c, 2a-2c** by NBHE were measured in aqueous solution at room temperature. As the fluorescence quenching in the systems is completely dynamic in nature, the slopes of the regression lines should be equal to the dynamic Stern-Volmer constants of NBHE, and then, corresponding to K_{sv} values for NBCD. By subtracting the total Stern-Volmer constants by K_{sv}, the binding constants were easily calculated. All these results are listed in Table I.

From Table I, it could be seen that the K_{sv}, which stands for the dynamic fluorescence quenching, is quite smaller in comparison with totall Stern-Volmer constants. It means that the remarkable quenching of the porphyrin fluorescence by NBCD in our system is mainly caused by a highly efficient intra-supramolecular static quenching. The efficiency of fluorescence quenching decreased as the length of the hydrocarbon chain increased. It could be observed both in Co-porphyrin and Ni-porphyrin derivatives. This is presumably due to the favourable donor-acceptor distance and orientation of the two components [29]. It is worthy to note that the binding constants between mono-tailed porphyrin derivatives and NBCD are larger than the binding constants ($\sim 10^5$ L/mol) determined previously for the complexes between other adamantine derivatives and β-CD [30]. We assume that the charge-transfer interaction between the electron donor and acceptor, in addition to the hydrophobic interactions, may provide extra stability of the Co/NiPC$_n$A-NBCD complexes.

IV. CONCLUSION

In the present study, we synthesized two series of electron donors−mono-tailed Co/Ni-tetraphenylporphyrins, in which the tetraphenylporphyrin group is linked to the 1-adamantaneamine group by a flexible hydrocarbon chain. Absorption spectra and fluorescence spectra analyses revealed that the adamantyl group of these porphyrin derivatives is tightly included into the cavity of NBCD and assembles supramolecular systems in aqueous solution. Very efficient fluorescence quenching was observed and its occurrence was attributed to the photoinduced electron transfer intra-supramolecular assembly between the porphyrin donors and cyclodextrin acceptors. Detailed Stern-Volmer constants were measured and partitioned into dynamic Stern-Volmer quenching constants and static binding constants. The static binding constants, which are larger than those of the other adamantine derivatives and β-CDs, demonstrated that the binding between all the mono-tailed porphyrin compounds and modified cyclodextrins is more effective.

V. ACKNOWLEDGMENT

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