

Photoinduced Electron Transfer Supramolecular Fluorescent Switch of Mono-6-*p*-nitrobenzoyl- β -cyclodextrin with Porphyrin Derivative

GUO-TAO WEN, MAN-ZHOU ZHU*, MAO-XIANG WANG, YONG-HUI WANG 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 novel supramolecular fluorescence switch system consisted of a perfect host/electron-acceptor mono-6-*p*-nitrobenzoyl- β -cyclodextrin (*p*-NBCD) and an ideal guest/electron-donor (adamantane-C₄-porphyrin) was reported. The 'ON' and 'OFF' states of fluorescence switch were droved by solvent polarity.

Introduction

Photoactive supramolecular systems [1] are very important to use for information gathering [2] and storing [3]. One of the important goals of molecular fluorescent switches is to realize the 'on-off' digital logical function [4]. Many supramolecular fluorescent switches have been synthesized in the past several years [2b, 4b], in general, the 'on-off' states were controlled by transition metal ions [5] or pH values [6].

Cyclodextrin (CD) was widely used to assemble supramolecular systems [7] because of its hydrophobic cavity and hydrophilic surface [8]. We recently synthesized mono-6-*p*-nitrobenzoyl- β -cyclodextrin (*p*-NBCD) and found it to be a perfect electron acceptor and fluorescence quencher for its excited-state guest molecules [9] (Scheme 1).

Our goal in this work was to develop a simple cyclodextrin supramolecular fluorescent switch which 'on-off' states could be controlled by the solvent polarity. We considered that the adamantyl group of adamantamine, compared to other molecules, was a perfect guest for β -cyclodextrin [10] and could be included into its cavity tightly in aqueous solution. On the other hand, porphyrin and its derivatives were good photoactive chromophores in many cases [11] and could be used for fluorescence launchers. In this connection, we first appended an amino-adamantane group to a head of 1,4-dibromo butane and then connected another head to the oxygen atom of [5,10,15-triphenyl-20-(4-hydroxyphenyl)porphyrinato]zinc(II). The resulted

compound **1** has one perfect fluorescence emission center and one strong hydrophobic head.

Experimental

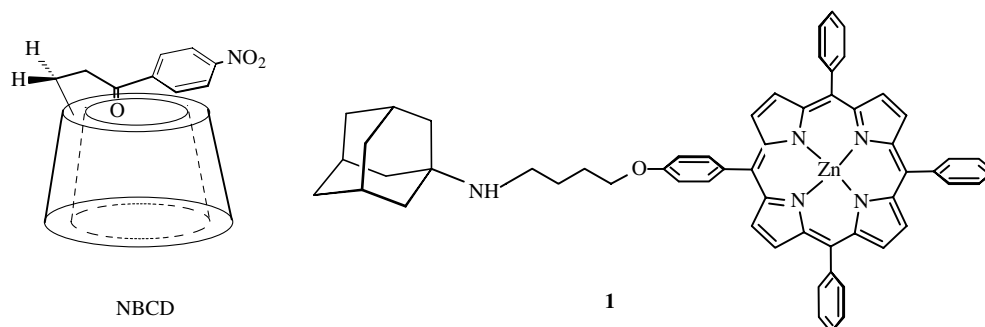
Compound **1** was obtained by the reaction of 1-adamantanamine, 1,4-dibromo butane and [5,10,15-triphenyl-20-(4-hydroxyphenyl)porphyrinato]zinc(II) (ZnTPPOH) in DMF in the presence of dry K₂CO₃. Yield: 48%.

Emission spectra were recorded on a Hitachi MP850 luminescence spectrometer and fluorescence lifetime was determined with a Horiba NBES-1100 single photon counting instrument. Pertinent electrode potentials (of the A/A⁻ and D⁺/D redox couples) for *p*-NBCD and **1** were determined through cyclic voltammetry experiments (versus the Fc⁺/Fc internal reference couple, MeCN, 0.1 M Bu₄NClO₄, Fc = ferrocene). A platinum microsphere was used as the working electrode and the counter electrode was platinum wire. The calculated ΔG_{ET}^0 value refer to the MeCN medium, as $\Delta G_{Ox/Red}^0$ value ($= -FE_{Ox/Red}^0$) was obtained in MeCN solution. Corresponding δG_{ET}^0 value in aqueous solution should be even more negative, and the electron transfer (ET) process more favorable, due to the higher solvent polarity.

Results and discussion

When an aqueous solution of **1** was titrated with *p*-NBCD, the fluorescence intensity of porphyrin unit progressively decreased until complete quenching as the

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

Scheme 1. Structure of NBCD and compound **1**.

equivalents of NBCD equals to 1.0. However, the parallel titration experiments carried out in the spectrofluorimetric cuvette indicate that β -CD binding almost does not interfere with the photophysical activity of relevant porphyrin group of **1**, whose emission spectrum was not altered even after the addition of several equivalents of β -CD (Figure 1). From the UV-vis spectroscopy, it is concluded that no ground-state complex is formed because no new band of absorption other than those of p -NBCD and **1** can be detected upon the addition of p -NBCD to **1**. Since the energy of the singlet excited state of porphyrin unit of **1** is much lower than that of p -NBCD. The energy transfer from the **1** to p -NBCD is impossible. It is suggested that fluorescence quenching is due to an intra-supramolecular ET process within the **1**- p -NBCD adduct by the large including ability of β -CD's cavity for adamantane group. The electron donor tendencies of porphyrin and its derivatives are well recognized [12]. Moreover, the $^*1 \rightarrow p$ -NBCD ET process is thermodynamically feasible, as indicated by the distinctly negative value of $\Delta G_{\text{ET}}^0 = \Delta G_{1+1} - \Delta G_{\text{NBCD}/\text{NBCD}} - E_{0-0} = (425 + 1041 - 1937) \text{ meV} = -471 \text{ meV}$.

To verify the intra-supramolecular quenching mechanism, spectrofluorimetric titration experiments were carried out with the following p -nitrobenzoates: ethyl- p -nitrobenzoate (ETNB), cyclohexyl- p -nitrobenzoate

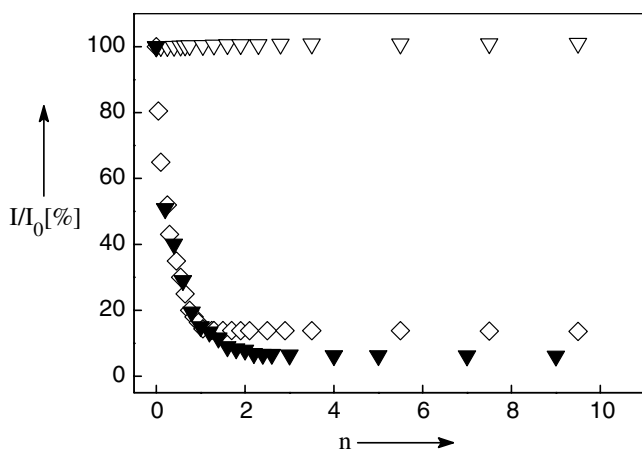


Figure 1. Spectrofluorimetric of **1** in aqueous solution ($4 \times 10^{-6} \text{ M}$) with aqueous solutions of p -NBCD (▼); β -CD (▽); p -NBCD + β -CD (◇); $n = [\text{Host}]/[\text{Guest}]$, Host = p -NBCD and β -CD, Guest = Compound **1**.

(CHNB), borneol- p -nitrobenzoate (BONB) and cheres-terol- p -nitrobenzoate (CSNB). There have only the intermolecular ET routes which were controlled by the diffusion processes in these p -nitrobenzoates and compound **1**. When the equivalent of p -nitrobenzoate equals to 1.0, the porphyrin emission showed a very slight intensity decrease of about 0.38% (ETNB), 0.29% (CHNB), 0.55% (BONB) and 0.36% (CSNB). Competitive titration experiments were also conducted. A $4 \times 10^{-6} \text{ M}$ aqueous solution of **1** was titrated with an aqueous solution containing equimolecular amounts of p -NBCD and the above four p -nitrobenzoates. The I_F titration curves obtained were identical to that with p -NBCD alone, indicating no competition for quenching to the porphyrin unit fluorescence. The β -CD alone does not exert any quenching effect on the porphyrin unit of **1**, however, in a competitive titration experiment (β -CD: p -NBCD = 1:1), I_F was not fully quenched, but decreased to about 90% of the value observed in the titration with NBCD alone (see Figure 1). This indicates that β -CD compete successfully with p -NBCD—binding about 10% of compound **1** and would imply a ratio of the equilibrium constants for the binding formation $K_{\text{NBCD}}/K_{\beta\text{-CD}} \approx 9$. The distinctly higher value of the binding constant observed for p -NBCD may suggest that the connected hydrophobic p -nitrobenzoyl group provides an additional contribution to the stability of p -NBCD adduct [9, 13].

Time-resolved fluorescence studies made with **1** ($4 \times 10^{-6} \text{ M}$) in deaerated aqueous solution indicated monoexponential decay kinetics with a lifetime of $1.85 \pm 0.07 \text{ ns}$ ($\chi^2 = 1.15$). Addition of p -NBCD ($0 \sim 4 \times 10^{-6} \text{ M}$) caused the fluorescence decay profile to become biphasic. Throughout the entire titration, the decay profiles could be analyzed in terms of two exponential components of lifetimes, $1.85 \pm 0.1 \text{ ns}$ and $710 \pm 49 \text{ ps}$. The fractional contribution of short-lived component increased from 0 in the absence p -NBCD to 90.7% at $4 \times 10^{-6} \text{ M}$ p -NBCD. The long-lived component is assigned to non-included **1**, while the short-lived component is attributed to the porphyrin subunit quenched by the p -nitrobenzoyl moiety of the connected host p -NBCD. Since the magnitude of the shorter lifetime remains independent of p -NBCD concentration, we can eliminate diffusional contact as an important mode of fluorescence quenching. Furthermore, the decay

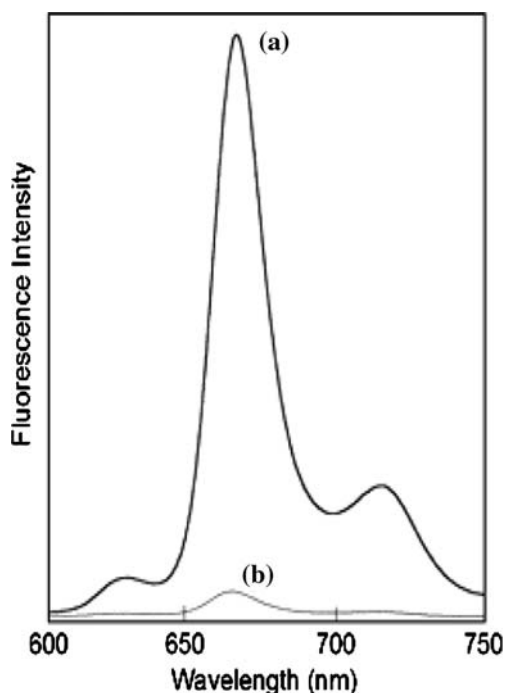


Figure 2. Fluorescence spectra of a 1:1 compound **1**-*p*-NBCD in methanol solution (a) and in aqueous solution (b) at concentration of 4×10^{-6} M; excited at 422 nm.

profile of 1:1 **1**-*p*-NBCD solution was not influenced by the presence of ETNB ($\leq 4 \times 10^{-6}$ M), such that the interaction of **1** and *p*-NBCD is very strong under these conditions. According to the time-resolved fluorescence results, ET rate inside the supramolecular could be calculated: $k_{\text{SET}} = 1/\tau_{\text{S}} - 1/\tau_{\text{L}} = 8.7 \times 10^8 \text{ s}^{-1}$. Analysis of the fractional components [14] in terms of a 1:1 complex between **1** and NBCD gave an association constant of $2.6 \times 10^7 \text{ M}^{-1}$. The unusually large binding-constant makes the supramolecule **1**-*p*-NBCD like ONE covalently linked molecule and fluorescence of fluorophore is almost fully quenched.

Interestingly, when some methanol was added into the aqueous solution of **1**-*p*-NBCD (1:1), fluorescence intensity of porphyrin subunit of **1** increased sharply (Figure 2), compared to compound **1** alone, the fluorescence intensity only quenched about 0.41%, furthermore, the fluorescence intensity keep almost no change when the percent of methanol increase from 20% (v/v) to 100% (v/v). Time-resolved fluorescence was studied at the same conditions, when methanol was added into the **1**-*p*-NBCD (1:1) aqueous solution, the fractional

contribution of short-lived component decreased from 90.7% to 0 when the percent of methanol increase from 0 to 20% (v/v) and then the decay profile became monoexponential with a longer lifetime about $1.59 \pm 0.09 \text{ ns}$. Although the percent of methanol increased from 20 to 100%, the decay profile kept monoexponential. As an inhibition experiment, equimolecular 1-adamantanecarboxylate (Ad), which is known to be a good substrate for cyclodextrin [15], was added into a 4×10^{-6} M [(5,10,15,20-tetraphenyl) porphyrinato]zinc(II) (TPPZn) methanol/water (1:4 (v/v)) solution and then was spectrofluorimetric titrated with *p*-NBCD ($0 \sim 4 \times 10^{-6}$ M). The I_{F} titration curve obtained was identical to that with **1** in the same binary solvent. Because the cavity of *p*-NBCD was taken up by Ad, TPPZn was only quenched by *p*-NBCD via dynamic routes. It is reasonable that the driving force for inclusion decreased when the polarity of solution decreased according to the addition of methanol, and the hydrophobic adamantane moiety of **1** inside the *p*-NBCD's cavity will be replaced by and enter into the bulk solution. The supramolecule consisted of **1** and *p*-NBCD in aqueous solution will be destroyed in 1:4 (v/v) methanol/water or more non-polar pure methanol solution.

The almost fully quenched fluorescence of **1**-*p*-NBCD in aqueous solution was restored in methanol solution. The quenched state is defined as 'off' and restored state is 'on', the supramolecular system of **1**-*p*-NBCD in aqueous solution and methanol solution works as a fluorescent switch (Figure 3), and, the 'on-off' state can be controlled by changing the polarity of solution.

Conclusion

In this paper, we have demonstrated a supramolecular system consisted of a perfect host/electron-acceptor mono-6-*p*-nitrobenzoyl- β -cyclodextrin and an ideal guest/electron-donor (adamantane- C_4 -porphyrin). In aqueous solution, fluorescence of porphyrin subunit of **1** is almost fully quenched by the *p*-nitrobenzoyl group of *p*-NBCD because of the unusual large binding constant and restored in methanol solution due to the non-inclusion ability. The fluorescence quenched/restored supramolecular system can be used as a novel fluorescent switch controlled by solvent polarity.

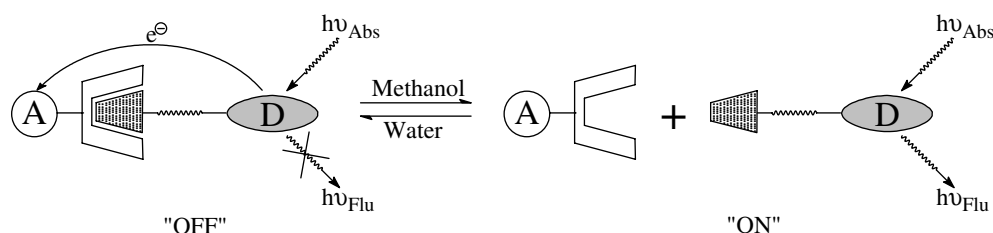


Figure 3. Supramolecular fluorescent switch controlled by the solvent polarity. Larger polarity: 'off', smaller polarity: 'on.'

Acknowledgment

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