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Enhancing photostability of cyanine dye by cucurbituril encapsulation

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ABSTRACT

A linear cyanine dye (LDP) guest comprising two binding sites, one 4-[2-[4-(dimethylamino)phenyl] ethenyl]pyridinium group and one *p*-aminophenoxy ethylene group, was synthesized and proved could form inclusion complexes with cucurbit[7]uril (CB[7]) in aqueous solution. A partially encapsulated ([2]pseudorotaxane) state in which one CB[7] ring moved fast between the two binding sites was originally detected and was then transferred into a full encapsulated ([3]pseudorotaxane) state where two CB[7] macrocycles resided on both binding sites with the continuously adding of CB[7] to LDP. The two binding constants K_1 and K_2 were determined as $(6.29 \pm 0.88) \times 10^4\ M^{-1}$ and $(1.58 \pm 0.17) \times 10^4\ M^{-1}$, respectively. Compared with the free LDP, the photostability of the [3]pseudorotaxane is found been distinctively promoted, while that of the [2]pseudorotaxane state is hardly improved.

1. Introduction

The cyanine dyes are undoubtedly one of the most important classes of dyes for their extensive applications, for example, in the area of imaging sensitizer, DNA indicator, ion probe, as well as in data storage and dye-sensitized solar cell [1–7]. It is obvious that photobleaching of cyanine dyes is an undesirable characteristic in most cases. Efforts have been made to improve the stability in regard to the photochemical decomposition by structural modification or adding additives [8–10]. Yet, these methods are somewhat complex or less efficient. Anderson group has also reported a strategy to enhance the photostability of dyes by threading them into the cavity of cyclodextrin [11], but this effective method should be faced with challenging rotaxane construction. Cucurbiturils (CBs) are pumpkin-shaped macrocylic host molecules synthesized from the acid-catalyzed cyclization of glycoluril and formaldehyde. Like cyclodextrins, they are commercially available with good stability, and can form inclusion complexes with a variety of organic guests. Moreover, CBs have higher affinity and better selectivity than cyclodextrins especially for those guests with positive charge, thus could boost stable inclusion complex formation [12]. To the best of our knowledge, reports on slowing down the photobleaching of a dye with cucurbituril are extremely rare [13]. Herein we describe a facile method to reduce the photobleaching of a cyanine dye by simply mixing it with Cucurbit[7]uril (CB[7]) in aqueous solution to form a [3]pseudorotaxane.

2. Experimental

2.1. Chemicals and instruments

Cucurbit[7]uril was synthesized according to reported method [14]. Other reagents were commercially available and used without further purification.

^{1}H NMR spectra were recorded on a Brüker AM 400 spectrometer with tetramethyl silane (TMS) as internal reference. ESI-MS spectra were conducted on Waters LCT Premier XE mass spectroscopy. Absorption spectra and Fluorescence spectra were measured on a Varian Cary100 UV–Vis spectrophotometer and a Varian Cary Eclipse Fluorescence spectrophotometer, respectively. The photobleaching experiments were carried out by using a 500 W xenon lamp emitting visible light with an intensity of 14,000 wcm^{-2}. The photographs were taken by Pentax k–r digital single lens reflex camera.

2.2. Synthesis

2.2.1. Preparation of 1-[2-(4-Nitrophenoxy)ethyl]-4-methyl pyridinium bromide(**1**)

A mixture of 22.0 g (89.8 mmol) 1-(2-bromoethoxy)-4-nitrobenzene [15] and 12.0 g (129 mmol) 4-methylpyridine in

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50 ml DMF was stirred at 100 °C for 10 h, then 60 ml ethyl acetate was added and the resulting mixture was stirred and cooled to room temperature, the precipitate was collected by filtration, washed with 50 ml ethyl acetate and dried to give 21.5 g (71%) **2** as a pale yellow solid. m.p. 240–242 °C; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 8.84$(d, 2H, $J = 6.4$ Hz); 8.15(d, 2H, $J = 9.3$ Hz); 7.33(d, 2H, $J = 6.4$ Hz); 8.25(d, 2H, $J = 9.3$ Hz); 4.78(t, 2H, $J_1 = 4.6$ Hz, $J_2 = 4.8$ Hz); 4.59(t, 2H, $J_1 = 4.8$ Hz, $J_2 = 4.6$ Hz); 2.76(s, 3H)。

*2.2.2. Preparation of 4-[2-[4-(dimethylamino)phenyl]ethenyl]-1-[2-(4-nitrophenoxy)ethyl] pyridinium bromide (**2**)*

A mixture of 11.3 g (33.4 mmol) **1**, 6.0 g (40.3 mmol) 4-(dimethylamino)benzaldehyde and 90 ml ethanol was heated to 60 °C with stirring, then 1.0 ml piperidine was added and the solution was stirred under reflux for 6 h. After cooled to room temperature, the precipitate was collected by filtration, and recrystallized from ethanol to give 10.2 g (65%) **3** as a red solid. m.p. 269–271 °C; ^{1}H NMR(400 MHz, DMSO-d_6): $\delta = 8.82$(d, 2H, $J = 6.7$ Hz); 8.23(d, 2H, $J = 9.2$ Hz); 8.08(d, 2H, $J = 6.9$ Hz); 7.94(d, 1H, $J = 16.0$ Hz); 7.60 (d, 2H, $J = 8.9$ Hz); 7.19(d, 1H, $J = 16.0$ Hz); 7.16(d, 2H, $J = 9.3$ Hz); 6.79(d, 2H, $J = 9.0$ Hz); 4.89(t, 2H, $J = 4.6$ Hz); 4.65(t, 2H, $J = 4.6$ Hz); 3.04(s, 6H).

2.2.3. Preparation of 4-[2-[4-(dimethylamino)phenyl]ethenyl]-1-[2-(4-aminophenoxy)ethyl] pyridinium bromide (LDP)

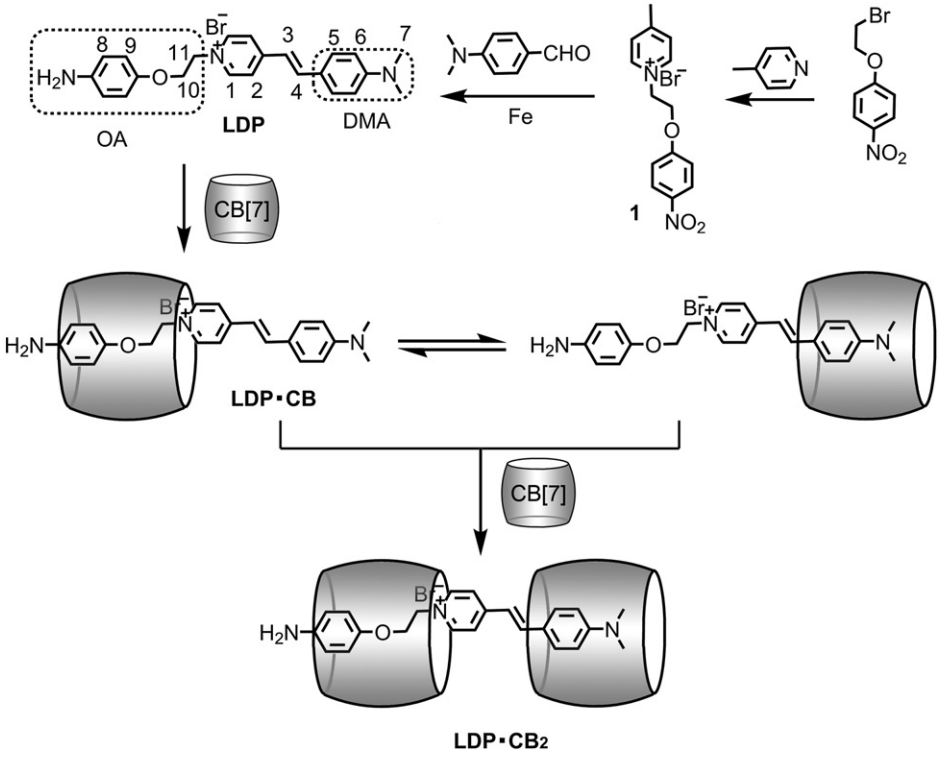
To a solution of 10.0 g (21.3 mmol) **2** in 80 ml hot ethanol, was added 8.0 g (143 mmol) iron powder, 30 ml water and 1.0 ml 45% HBr with stirring. The resulting mixture was heated under refluxed for 4 h and filtered hot, the filtrate was concentrated by rotary evaporation and the resulting solid was recrystallized from ethanol twice to give 4.6 g (51%) LDP as a red powder. m.p. 251–253 °C; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 8.78$(d, 2H, $J = 6.9$ Hz); 8.07(d, 2H, $J = 6.9$ Hz); 7.94(d, 1H, $J = 16.1$ Hz); 7.60(d, 2H, $J = 8.9$ Hz); 7.19 (d, 1H, $J = 16.1$ Hz); 6.79(d, 2H, $J = 9.0$ Hz); 6.63(d, 2H, $J = 8.8$ Hz); 6.49(d, 2H, $J = 8.7$ Hz); 4.77(t, 2H, $J = 4.7$ Hz); 4.31(t, 2H, $J = 4.7$ Hz); 3.03(s, 6H); MS (*m/z*): [M-Br]$^+$ calcd. for $[C_{23}H_{26}N_3O]^+$ 360.21; found: 360.2.

3. Results and discussion

3.1. The formation of inclusion complex

A dimethylamino phenyl moiety (DMA) and a *p*-aminophenoxy ethylene group (OA) were arranged at the two ends of LDP, as shown in Scheme 1. They were both proved as binding sites for CB[7] in our previous study [16], and as a result, a [3]pseudorotaxane might finally be obtained when one LDP molecule binds two CB[7] rings. To confirm the binding ratio, measurements of the fluorescence of a series of LDP solutions with different CB[7] molar fraction were carried out with a total concentration remaining constant. The resulting job plot curve is shown in Fig. 1. The maximum value of the vertical axle corresponds to 0.33 at horizontal axle, and the stoichiometry of LDP and CB[7] is verified to be 1:2.

Although a final [3]pseudorotaxane (abbreviated as LDP·CB_2) would form, LDP may also display as other different architectures when binding to CB[7] at low molar ratio. These are the [2]pseudorotaxanes (abbreviated as LDP·CB) in which one CB[7] macrocycle encircles either of the two binding sites. To investigate the inclusion behaviors of LDP and CB[7], the ^{1}H NMR spectra of LDP aqueous solution titrating with CB[7] were monitored. The ^{1}H NMR technique is a very efficient method to identify the binding site of CBs-based complex. It is a common rule that the protons inside the hydrophobic cucurbituril cavity undergo shielding effect while the outside ones conduct deshielding effects, and those near the carbonyl rim are hardly affected [17,18]. To prevent the protonization of the OA group, the ^{1}H NMR experiments were recorded at a weak base environment (pD = 9.6, and the pK_a of OA



Scheme 1. Synthetic route of cyanine dyes LDP and its complexation behavior with CB[7].