Synthesis of perylene-bridged bis(dibenzo-24-crown-8) and its assembly behavior with a fullerene-based secondary dibenzylammonium salt

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This paper reports the synthesis of a perylene-bridged bis(crown ether) through the condensation reaction between primary amine-armed dibenzo-24-crown-8 and 3,4,9,10-perylenetetracarboxylic dianhydride. Pseudorotaxane with a perylene moiety at the wheel and a fullerene unit in the middle of the axle was prepared, which was evidenced by ^{1}H NMR and fluorescence experiments. Subsequent investigations show that the formation and disassociation of the pseudorotaxane can be controlled by the alternating addition of KPF_6 and 18-crown-6, following the change of the florescence intensity of perylene.

crown ether, perylene, fullerene, pseudorotaxane

1 Introduction

Since 1950, perylene bisimide derivatives have found high grade industrial applications [1] as pigments due to their favorable combination of insolubility and migrational stability, light- and weather-fastness, thermal stability and chemical inertness. Recently, perylene derivatives as n-type semiconductors are also found to be promising compounds for applications in optical [2] and electronic devices [3], such as electrophotography [4], organic field effect transistors [5], photovoltaic devices [6], and organic solar cells [7]. The intrinsic insolubility of perylene bisimides is the main barrier for synthesis, purification and application. To prepare soluble perylene bisimide dyes, Langhals [8] and Seybold *et al*. [9] provided two successful strategies. The first way is to introduce solubilizing substituents at the imide nitrogen, and the other way is to introduce substituents at the carbocyclic scaffold in the so-called bay-area.

Fullerene C_{60} possesses unique and attractive electronic and optical properties owing to the ability of remarkable acceleration of photoinduced charge separation and deceleration of charge recombination in donor-fullerene systems [10]. In order to construct fullerene-containing supramolecular assemblies and advanced materials, fullerene has been incorporated into various systems such as porphyrins [11], ferrocene [12], and hydroquinone [13]. The self-assembly of fullerene-based molecules has aroused much interest in the construction of more complex two- and three-dimensional systems [14].

Dibenzo-24-crown-8 (DB24C8) can form 1:1 complexes with the dialkylammonium cations. This unique binding model has been utilized to construct various supramolecular assemblies containing DB24C8 and dialkylammonium salts [15]. Recently, we reported a reversible luminescent lanthanide switch based on this binding model [16] and a bistable [3] rotaxane with intramolecular charge-transfer behavior [17]. Herein, we synthesized a new perylene-bridged bis-(DB24C8) host molecule (**1**), and constructed a pseudorotaxane system including **1** and a fullerene-based secondary dibenzylammonium cation (**2**) (Figure 1). The reversible fluorescence process of the pseudorotaxane can be modulated

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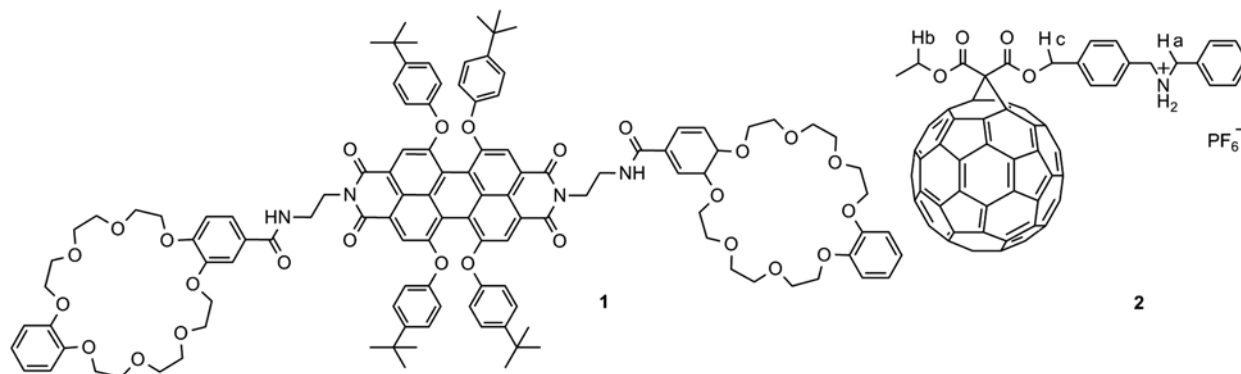*Corresponding author (email: yuliu@nankai.edu.cn)

Figure 1 Structure of host **1** and guest **2**.

by controlling the binding and release of the guest molecule **2**.

2 Experimental

2.1 Materials and apparatus

3,4,9,10-Perylene dianhydride (Sigma-Aldrich company), 4-carboxylic-aciddibenzo-24-crown-8 (**3**) [18], compounds **6** [19], **7** [19] and the fullerene-based secondary dibenzylammonium salt (**2**) [20] were prepared according to the previously reported procedure. Chloroform and dichloromethane were redistilled and kept with 4 Å molecular sieve. Acetonitrile is refluxed for 10 h in the presence of K_2CO_3 and $KMNO_4$, stirred with a proper amount of P_2O_5 overnight, and then distilled at 81–82 °C. All the other chemicals were commercially available.

^{1}H NMR spectra were recorded on a Varian Mercury VX400 spectrometer. Fluorescence spectra were measured with JASCO FP-750 spectrometer. ESI-MS was performed on Thermofinnigan LCQ Advantage LC-MS. MALDI-TOF was performed on Bruker Autoflex III.

2.2 Synthesis of host 1

tert-Butyl 2-(6,7,9,10,12,13,20,21,23,24,26,27-dodecahydro-dibenzo[b,n] [1,4,7,10,13,16,19,22] octaoxacyclotetracosine-2-carboxamido)ethylcarbamate (4)

4-Carboxylic-aciddibenzo-24-crown-8 (**3**) (2.0 g, 4.1 mmol), *tert*-butyl-2-aminoethyl carbamate (0.7 g, 4.6 mmol), *N,N'*-dicyclohexylcarbodiimide (1.4 g, 6.8 mmol) and a little of *N,N*-dimethylamino pyridine were dissolved in dry $CHCl_3$ and the mixture was stirred in an ice bath for 12 h. The reaction mixture was filtered. The filtrate was washed with water twice, and dried over anhydrous sodium sulfate. Then the solvent was removed at reduced pressure to give a white residue. The residue was purified by silica-gel column chromatography using $CHCl_3/CH_3OH$ (20/1) (*v/v*) as the eluent to give product **4** (1.4 g, 50%); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 1.42 (s, 9H), 3.40 (t, 2H), 3.52 (t, 2H),

3.83 (m, 8H), 3.92 (m, 8H), 4.18 (m, 8H), 6.88 (d, 1H), 6.88 (m, 4H), 7.33 (dd, 1H), 7.42 (d, 1H), *m/z* 657 [M+Na]$^+$.

N-(2-Aminoethyl)-6,7,9,10,12,13,20,21,23,24,26,27-dodecahydro-drodibenzo[b,n][1,4,7,10,13,16,19,22]octaoxacyclo-tetracosine-2-carboxamide (5)

Compound **4** was dissolved in 10 mL $CHCl_3$, and the mixture was stirred at room temperature. 4 mL of CF_3COOH was added dropwise. The stirring was continued overnight and followed by evaporation of the solvent. The residue was washed with hexane for three times. The crude product was dissolved in CH_3OH and the pH of the solution was adjusted to 8 by NaOH solution. The crude product was purified by silica-gel column chromatography using $CHCl_3/CH_3OH$ (5/1) (*v/v*) as the eluent to give product **5** (0.5 g, 90%); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 2.95 (t, 2H), 3.48 (t, 2H), 3.82 (m, 8H), 3.92 (m, 8H), 4.17 (m, 8H), 6.83 (d, 1H), 6.88 (m, 4H), 7.30 (dd, 1H), 7.41 (d, 1H), *m/z* 557 [M+Na]$^+$.

Compound 1

Compounds **7** (300 mg, 0.3 mmol) and **5** (500 mg, 0.9 mmol) were dissolved in 6 mL isopropanol, and then 0.1 mL triethylamine was added. The mixture was refluxed under N_2 atmosphere for two days. The mixture was cooled to room temperature and followed by evaporation of the solvent. The crude product was purified by silica-gel column chromatography using $CHCl_3/CH_3OH$ (20/1) (*v/v*) as the eluent to give red powder **1** (300 mg, 50%); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 1.28 (s, 36H), 3.67 (m, 12H), 3.72 (m, 12H), 3.82 (m, 12H), 4.02 (m, 12H), 4.28 (m, 4H), 6.78 (d, 8H) 6.85 (m, 8H), 7.18 (m, 4H), 7.25 (d, 8H), 7.50 (s, 4H), 7.99 (s, 4H) ^{13}C NMR (400 MHz, $CDCl_3$, 298 K) δ 167.11, 164.16, 155.92, 152.89, 151.35, 148.85, 148.55, 147.34, 132.85, 127.17, 126.68, 122.09, 121.41, 120.90, 120.30, 119.62, 119.53, 119.39, 119.17, 114.01, 112.59, 71.35, 71.22, 71.16, 69.90, 69.68, 69.32, 69.23, 69.12, 34.38, 31.46. MS (MALDI-TOF) *m/z*: Anal. calcd $C_{118}H_{128}O_{26}N_4$: [M+Na]$^+$: 2040.8743, found [M+Na]$^+$: 2040.8766.

3   Results and discussion

3.1   Synthesis

The synthetic pathway of **1** is shown in Figure 2. Compound **5** was obtained by DCC condensation of 4-carboxylic-ciddibenzo-24-crown-8 (**3**) with tert-butyl-2-aminoethyl carbamate, followed by CF_3COOH reduction of the Boc-protected group. 3,4,9,10-Perylene tetracarboxylic dianhy-dride is insoluble in organic solvent. To improve its solubil-ity, its bay-area was substituted by four chlorine atoms by reacting with HSO_3Cl, the propyl substituents were intro-duced through reaction with propylamine. Compound **6** was obtained by introducing four *tert*-butyl phenols at the bay-area. Subsequent hydrolyzation of **6** with a base produced compound **7**. Finally, the target compound **1** was obtained by the reaction of **5** with **7** in isopropanol using triethyl-amine as the base. Owing to those soluble substitutions, compound **1** possesses very good solubility in organic solvent.

3.2 ^{1}H NMR spectra of the complex of 1 with 2

To obtain in-depth mechanistic insight into the complexa-tion between host **1** and guest **2**, we performed ^{1}H NMR experiments. Figure 3 shows the signals of some pro-tons moved apparently upon complexation. The Ha proton in **2** shifted downfield from 3.90 to 4.62 ppm. This may be attributed to the hydrogen bond interaction between Ha and oxygen atoms of the crown ether. The resonances of the Hc proton in **2** split into two equal parts. A half of them shifted upfield, while the other remained unchanged. This means that a half of **2** was located in the ring of the crown ether, while the other did not bind with **1**. In addition, the signals of protons in crown ethers (3.4–4.5 ppm) and perylene (8.06 ppm) split apparently, indicating that the distance between C_{60} and the perylene unit became close after complexation. These spectral changes validate the formation of the pseu-dorotaxane [**1**+**2**].

3.3   Fluorescence spectra of the interaction of 1 with 2

Benefiting from the fascinating fluorescence property of perylene, the host **1** displays satisfactory luminescent emis-sion in a $CHCl_3:CH_3CN = 2:1$ (*v/v*) solution (Figure 4). When excited at 510 nm, **1** showed two emission peaks at 620 nm (0→0) and a shoulder peak at 675 nm (0→1) [21]. When 22 equiv of the guest **2** was added to the solution, the fluorescence emission at 620 nm of **1** was significantly quenched to 75% of its original intensity. Instead of **2** with a compound bearing the C_{60} moiety but without secondary dibenzyl-ammonium unit, the luminescence of **1** slightly decreased, which is attributed to the absorption of C_{60} ex-isting at 450–750 nm. In addition, dibenzylammonium hexafluorophosphate does not influence the luminescence of **1**. These combined observations suggest that both the C_{60} unit and the dibenzylammonium cation are two prerequi-sites to quench the fluorescence emission of **1**. That indi-cates the interaction of **1** with **2** leads to the formation of the pseudorotaxane [**1**+**2**], so a PET process from perylene of **1** to the C_{60} moiety of **2** occurs due to the adjacence of C_{60} with perylene.

3.4   Reversible fluorescence switch

The binding behavior of 24C8 and the dialkylammonium cation can be switched reversibly by various external stim-uli, such as pH changes and competition binding. The asso-ciation constants of DB24C8 with K^+ and dialkylammonium cations are 7.6×10^3 and 1.2×10^3 M^{-1}, respectively, while that of 18-crown-6 (18C6) with K^+ is 1.3×10^6 M^{-1} [21]. From those data, we might deduce reasonably that the dial-kylammonium cation in DB24C8 could be replaced by K^+ upon the addition of KPF_6 to the solution of the pseudoro-taxane [**1**+**2**], and then the supramolecular assembly could be reproduced upon the addition of 18-crown-6. To evi-dence this assumption, we performed the fluorescent ex-periments of the pseudorotaxane [**1**+**2**] in the absence and
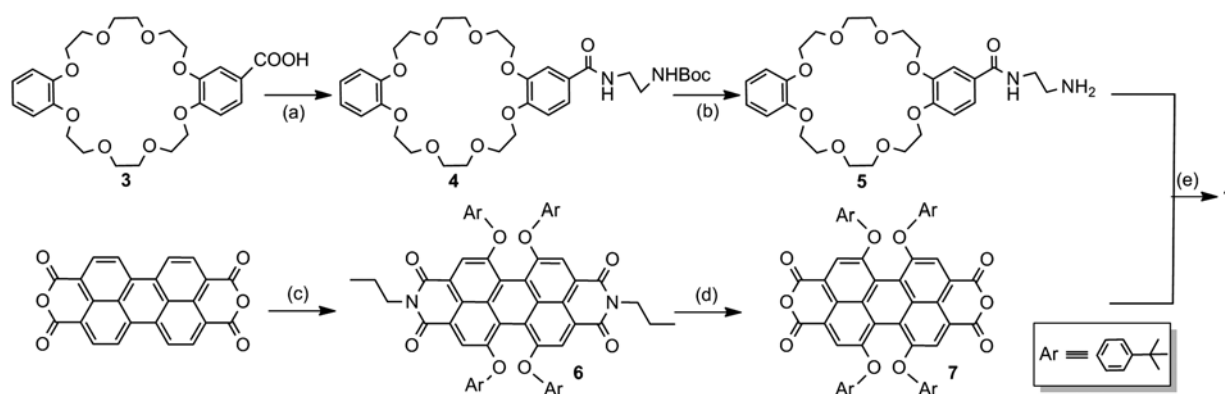

Figure 2   Synthetic routes to host **1**. (a) DCC, DMAP, BocNHCH₂CH₂NH₂,CHCl₃, 12 h, 50%. (b) TFA, 12 h, 90%. (c) (1) HSO₃Cl, I₂, 20 h, 40%,; (2) CH₃CH₂CH₂NH₂, H₂O/CH₃CH₂CH₂OH, 8 h, 99%. (3) ArOH, KCO₃, NMP, 8 h, 90%. (d) KOH/H₂O, CH₃CHOHCH₃, 12 h, 78%. (e) N(Et)₃, CH₃CHOHCH₃, 2 d, 50%.
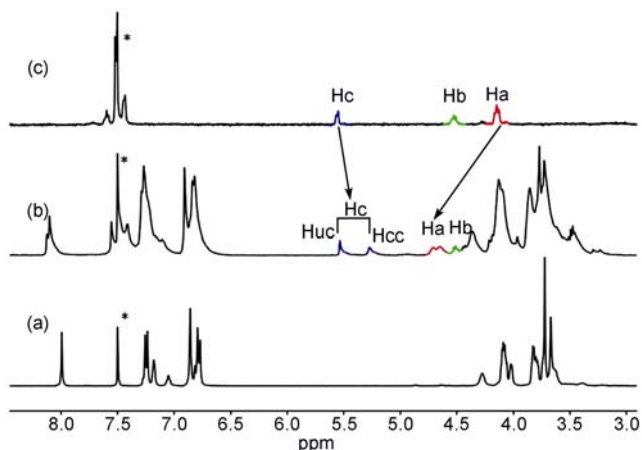
Figure 3   Partial ^{1}H NMR spectra of (400 MHz, CD$_3$CN/CDCl$_3$ = 1/2, 298 K, [**1**]$_0$ = 3 mM) (a) **1**, (b) **1** and 2.0 equiv of **2**, and (c) **2** (Hcu: peak of the uncomplex; Hcc: peak of the complex; *: peak of CDCl$_3$).
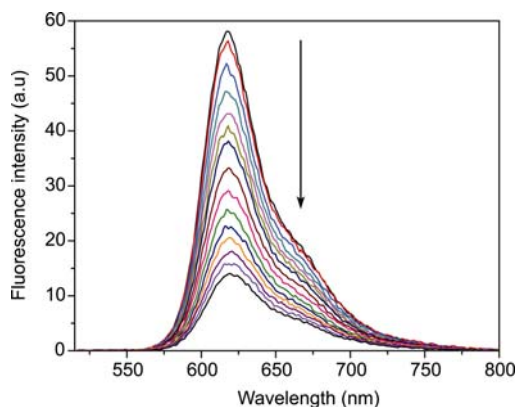
Figure 4   The fluorescence spectra of compound **1** with increasing concentration of **2** (CHCl$_3$:CH$_3$CN = 2:1, 295 K); [**1**] = 1 × 10^{-5} M and [**2**] = 1 × 10^{-5} to 2.2 × 10^{-4} M. λ_{ex} = 510 nm.
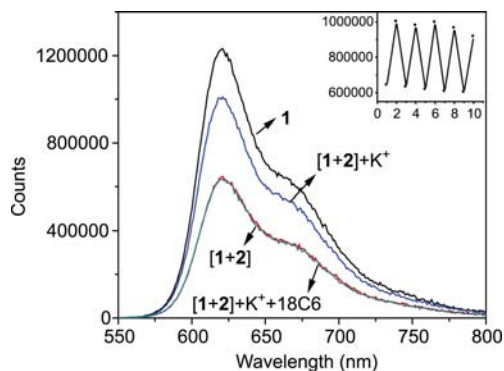
Figure 5   Emission spectral changes observed for **1**, [**1+2**], [**1+2**] + K$^+$, and [**1+2**] + K$^+$ + 18-crown-6. The emission changes of **1** at 620 nm (inset) in the presence (**1**) of **2** and added KPF$_6$ (4, 6, 8, 10) and 18-crown-6 (3, 5, 7, 9) in CH$_3$CN/CHCl$_3$ solution (1:2).

presence of KPF$_6$ and 18-crown-6.

As shown in Figure 5, when KPF$_6$ was added to the solution of the pseudorotaxane [**1+2**], the quenched perylene

emission was restored (91%). This observation suggests that the dialkylammonium cation in DB24C8 was replaced by K$^+$ and the PET process from the perylene moiety to C$_{60}$ was suppressed. To check the reversibility of this process, 18-crown-6 was added to the solution. The luminescence quenching was reproduced again as a proof of regeneration of the pseudorotaxane supramolecular assembly. The process can be repeated several times. These experiments demonstrate that the fluorescence of the pseudorotaxane [**1+2**] can be switched in a reversible manner by external chemical stimuli.

4   Conclusions

In conclusion, a perylene-bridged bis(dibenzo-24-crown-8) **1** and a guest molecule **2** containing C$_{60}$ unit have been synthesized. The binding behavior and the photophysical behavior of the resultant pseudorotaxane between **1** and **2** have been investigated through ^{1}H NMR and fluorescence spectra. The results obtained indicate that the fluorescence of **1** was quenched significantly in the presence of **2**, which is attributed to a PET from perylene of **1** to the C$_{60}$ moiety of **2** in this pseudorotaxane system. The reversible fluorescence process can be modulated by controlling the binding and release of the guest molecules by adding K$^+$ or 18C6, respectively. It is an effective strategy to control the fluorescent behavior of perylene through external chemical stimuli.

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