# Controlled Photophysical Behaviors between Dibenzo-24-crown-8 Bearing Terpyridine Moiety and Fullerene-Containing Ammonium Salt

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Ⓢ *Supporting Information*

ABSTRACT: A novel [2]pseudorotaxane was successfully constructed by the complexation of dibenzo[24]-crown-8 (DB24C8) derivative bearing terpyridine moiety (**1**) with lanthanide ion (Tb^{3+}) and fullerene-containing ammonium salt (**2**), exhibiting the controlled photophysical behaviors as a reversible luminescent lanthanide switch in the presence of K^+ or 18-crown-6 (18C6).
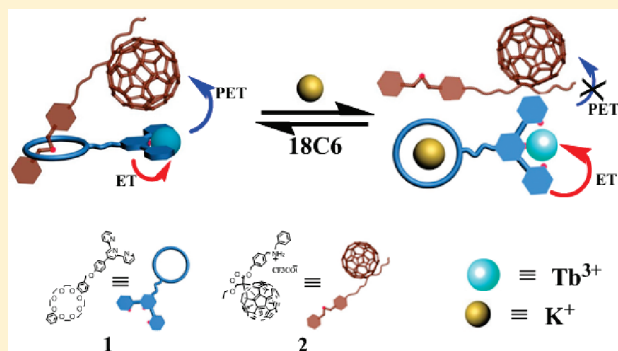
Construction of rotaxanes and pseudorotaxanes[1] has attracted tremendous interest because of not only their mechanically interlocked topologies[2] but also their unique photophysical and electrochemical properties that have potential applications in the field of artificial molecular machinery, such as nanoelectronics,[3] smart surface materials,[4] drug-loading nanoparticles,[5] and non-viral gene-delivery vectors.[6] Triggered by external stimuli,[7] including pH changes, metal ions, temperature or electrochemical redox,[8] these multicomponent assemblies could be modulated in a precisely controlled manner. Recently, Stoddart and co-workers[9] have designed a source−connector−drain nanoarchitectures, where $[Ru(bpy)_3]^{2+}$ (bpy =2,2′-bipyridine)-modified dibenzo-24-crown-8 (DB24C8) could be connected to the viologen by benzonaphtho[36]crown-10 (BN36C10) with a dialkylammonium ion center, displaying a bottom-up construction of the photoinduced electron flow in the self-assembling supramolecular cable. Guldi and Hirsch et al.[10] have reported a series of supramolecular porphyrin−fullerene hybrids through hydrogen-bonding interaction, leading to the long-lived electron-transfer products in the range of tens of nanoseconds. More recently, we have successfully constructed a tris[2]pseudorotaxane[11] and bistable [3]rotaxane,[12] revealing an excellent reversible luminescent lanthanide and pH-controlled intramolecular charge-transfer behaviors, respectively. In the present work, we would like to report the fabrication of a well-defined [2]pseudorotaxane comprised of DB24C8 derivative bearing a terpyridine unit (**1**) as chelators for lanthanide ions and fullerene-containing ammonium salt (**2**), with the aim of comprehensive investigation on the controlled photophysical behaviors of energy transfer (ET) and photoinduced electron transfer (PET) process in the complex of

Scheme 1. Syntheses of 1 and the Molecular Structure of 2
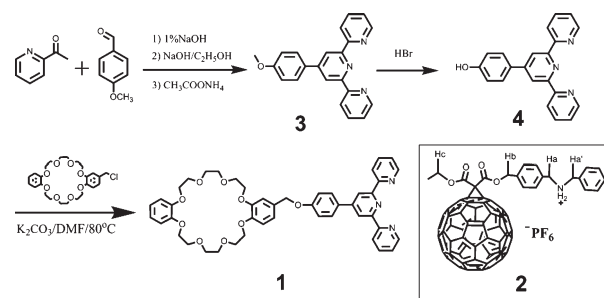
$[\mathbf{1} \cdot Tb]^{3+}$ and $[Tb \cdot \mathbf{1} \cdot \mathbf{2}]^{3+}$, respectively. The results obtained in this work indicate that PET process could be conveniently controlled by the addition of K^+ or 18-crown-6 (18C6).

The synthetic route of **1** and the molecular structure of **2** were described in Scheme 1. 2,6-Bis(2′-pyridyl)-4′-(*p*-hydroxyphenyl)pyridine (**4**) was prepared from 4-methoxybenzaldehyde and 1-(pyridin-2-yl)ethanone according to the reported literature.[13] Then, compound **4** reacted with 4-chloromethyldibenzo-24-crown-8 under basic condition to afford terpyridine modified dibenzo-24-crown-8 (**1**) in 72% yield. Fullerene-containing ammonium salt (**2**) was synthesized by Hirsch−Bingel reaction of benzyl malonate and C_{60}, followed by protonation and counterion exchange.[14]
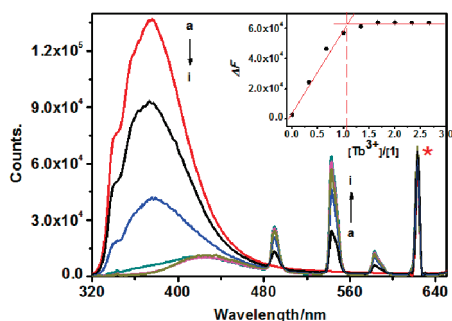
Figure 1. Emission spectra of **1** (1.0×10^{-5} M) upon addition of $Tb(NO_3)_3 \cdot 6H_2O$ ($0-2.66 \times 10^{-5}$ M, from a to i) in $CH_3CN/CHCl_3$ (1:1, v/v) solution ($\lambda_{ex} = 319$ nm). Inset: fluorescence changes of **1** at 544 nm. The asterisk corresponds to $2\lambda_{ex}$ signal.
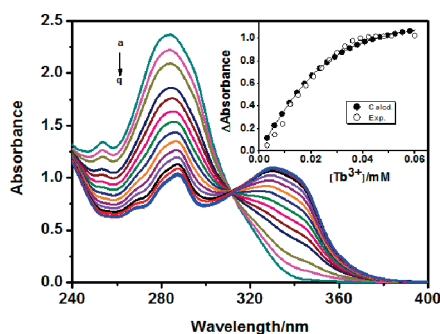

Figure 2. Absorbance spectral changes of **1** (5.0×10^{-5} M) upon addition of $Tb(NO_3)_3 \cdot 6H_2O$ ($0-6.0 \times 10^{-5}$ M, from a to q) in $CH_3CN/CHCl_3$ (1:1, v/v) solution. Inset: nonlinear least-squares analysis of the differential intensity to calculate K_s.

The quantitative investigation of the coordination complex of **1** with Tb^{3+} was examined by means of the fluorescence spectroscopy titration. As seen in Figure 1, the fluorescence intensity of **1** at 375 nm assigned to the terpyridine moiety was dramatically decreased upon addition of $Tb(NO_3)_3 \cdot 6H_2O$ to a solution of **1** in $CH_3CN/CHCl_3$, accompanied with the obvious bathochromic shift to 475 nm. In contrast, the emission of Tb^{3+} at 491 nm ($^5D_4 \rightarrow {}^7F_6$), 544 nm ($^5D_4 \rightarrow {}^7F_5$), 586 nm ($^5D_4 \rightarrow {}^7F_4$), and 622 nm ($^5D_4 \rightarrow {}^7F_3$, overlapped the $2\lambda_{ex}$ signal)[15] was gradually increased with a quantum yield of 0.050. According to these observations, we can deduce that the strong fluorescence emission of $[\mathbf{1} \cdot Tb]^{3+}$ complex may attribute to an energy transfer (ET) process, that is, the energy was transferred from the excited state of terpyridine moiety to Tb^{3+}. Moreover, the coordination stoichiometry between **1** and Tb^{3+} was explored by the molar ratio method using fluorescence spectrometry. The curve of ΔF (complex-induced changes of fluorescence intensity) versus $[Tb^{3+}]/[\mathbf{1}]$ molar ratio showed an inflection point at a molar ratio of 1, implying a 1:1 $\mathbf{1}/Tb^{3+}$ coordination (Figure1, inset), which was further confirmed by the Job's experiment as described below.

We further performed ^1H NMR titration to examine the binding abilities between **1** and **2**, showing that Ha and Ha' shifted downfield 0.46 ppm, whereas Hb shifted upfield 0.19 ppm, respectively (Figure S4, Supporting Information). Detailed discussion on the formation of $[\mathbf{1} \cdot Tb]^{3+}$ complex were obtained from absorption spectroscopy experiment. As discerned in Figure 2, with the stepwise addition of $Tb(NO_3)_3 \cdot 6H_2O$ to a
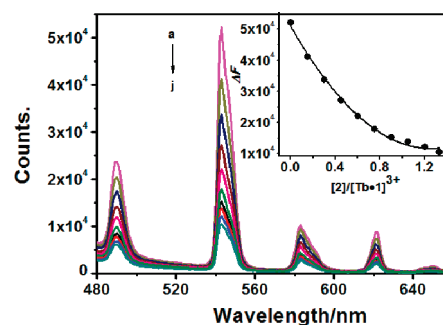

Figure 3. Emission spectra of $[\mathbf{1} \cdot Tb]^{3+}$ complex (1.0×10^{-5} M) upon addition of **2** ($0-1.33 \times 10^{-5}$ M, from a to j) in $CH_3CN/CHCl_3$ (1:1, v/v) solution ($\lambda_{ex} = 340$ nm). Inset: fluorescence changes of $[\mathbf{1} \cdot Tb]^{3+}$ at 544 nm upon the addition of **2**.

solution of **1**, the absorption peak of **1** at 285 nm was gradually declined while the absorption peak at 345 nm was enhanced in proportion, accompanied by an isosbestic point at 319 nm. These phenomena described above jointly indicated the conversion of free ligand **1** to the $[\mathbf{1} \cdot Tb]^{3+}$ complex. Job's plot was also performed to confirm the coordination stoichiometry between **1** and Tb^{3+}, which showed a maximum peak at a molar fraction of 0.5, corresponding to a 1:1 $\mathbf{1}/Tb^{3+}$ stoichiometry (Figure S5, Supporting Information). After validating the 1:1 binding stoichiometry, the complex formation constant (K_s) between **1** and Tb^{3+} was calculated to be $(1.8 \pm 0.7) \times 10^5$ M^{-1} by analyzing the sequential changes in absorption intensity (ΔA) of **1** at varying concentrations of Tb^{3+} using a nonlinear least-squares curve-fitting method (Figure 2, inset), indicating the high affinity of terpyridine and lanthanide ions.

As an intriguing class of molecules with unique physical and chemical properties, fullerene and its analogues are known to have excellent photosensitizing activities, especially under visible and near-infrared lights.[16] Many efforts have been devoted to the preparation of various donor−acceptor systems by coordination of fullerene derivatives bearing one pyridine or polypyridine[17] unit with transition metals.[18] When 1.3 equiv of compound **2** bearing the C_{60} moiety was added to the solution of $[\mathbf{1} \cdot Tb]^{3+}$, approximately 90% of the fluorescence intensity of metal−ligand complex was quenched at 544 nm with a quantum yield of 0.005 (Figure 3). These results were well consistent with our previous observations.[11] Considering the fullerenes are good electron acceptors,[18,19] these results indicated that there should be an intramolecular PET process in [2]pseudorotaxane $[Tb \cdot \mathbf{1} \cdot \mathbf{2}]^{3+}$ from the excited singlet state of $[\mathbf{1} \cdot Tb]^{3+}$ complex to C_{60} moiety in solution. To confirm the assumption of PET mechanism in the formation of [2]pseudorotaxane, some control experiments were carried out. Instead of **2** with dibenzylammonium hexafluorophosphate which did not contain C_{60} as an electron acceptor, the luminescence of the metal−ligand complex $[\mathbf{1} \cdot Tb]^{3+}$ was almost unchanged, which provided further evidence for the PET process in self-assembled dyads $[Tb \cdot \mathbf{1} \cdot \mathbf{2}]^{3+}$ (Figure S6, Supporting Information). As shown in Figure S7, when even 100 equiv of K^+ was added in the solution of **1**, the absorption intensity was slightly changed, indicating that the interactions between terpyridine moiety and K^+ were negligible.

In addition, cyclic voltammetry experiments were performed in order to investigate the PET process quantitatively.[18] The peaks at -0.70, -1.22, and -1.74 V were assigned to reduction potentials of **2**, and the peak at 1.20 V was assigned to oxidation
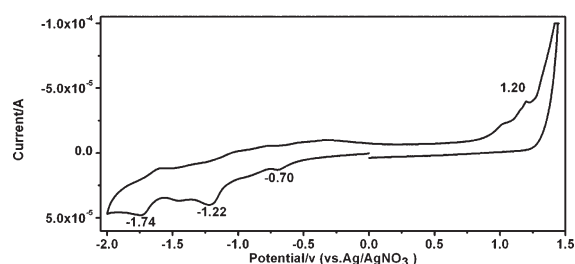
Figure 4. Cyclic voltammogram of [2]pseudorotaxane $[Tb \cdot 1 \cdot 2]^{3+}$ in CH_2Cl_2 containing 0.1 M $(t\text{-}C_4H_9)_4NClO_4$ as the supporting electrolyte at 100 mVs^{-1} ($[Tb \cdot 1 \cdot 2]^{3+} = 5 \times 10^{-4}$ M, vs Ag/AgNO$_3$).
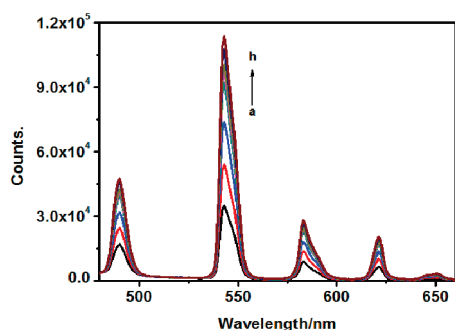
Figure 5. Emission spectra of the $[Tb \cdot 1 \cdot 2]^{3+}$ complex (1×10^{-5} M) upon addition of K$^+$ ($0-1.3 \times 10^{-5}$ M, from a to h) in CH$_3$CN/CHCl$_3$ (1:1, v:v) solution ($\lambda_{ex} = 340$ nm).

potential of $[1 \cdot Tb]^{3+}$, respectively (Figure 4, as well as Figures S8 and 9, Supporting Information). Furthermore, the Rehm–Weller equation (eq 1) was introduced to evaluate the Gibbs free energy (ΔG_{PET}) of an electron-transfer reaction, where $E_{0,0}$ is the excited singlet energies of $[1 \cdot Tb]^{3+}$ (2.28 eV), E_{ox} and E_{red} values are the oxidation potential of $[1 \cdot Tb]^{3+}$ (1.20 V) and the reduction potential of **2** (-0.70 V), respectively, ε is the dielectric constant of the solvent ($\varepsilon_{CH2Cl2} = 9.1$), and d is the center distance between C$_{60}$ and terpyridine that could be estimated as 7.50 Å from the optimized molecule modulation of $[Tb \cdot 1 \cdot 2]^{3+}$ (Figure S10, Supporting Information). Therefore, ΔG_{PET} was calculated to be -0.59 eV. Although there may be errors in calculating of free-energy changes, due to the irreversible electrochemical data in the present system,[20] the ΔG_{PET} value was negative enough to drive the PET reaction in a thermodynamically favorable way.

$$\Delta G_{PET} = E_{ox} - E_{red} - \Delta E_{0,0} - \frac{14.4}{\varepsilon d} \qquad (1)$$

Taking advantages of the different binding abilities, it is well-documented that the assembling/disassembling processes of [2]pseudorotaxane based on DB24C8 and secondary dialkylammonium salts can be reversibly governed by adding K$^+$ and 18C6 in series, which is proved to be a simple and accessible strategy for constructing supramolecular switch systems.[7,8,11] When KPF$_6$ was added to the solution of [2]pseudorotaxane, the lanthanide emission of $[1 \cdot Tb]^{3+}$ complex was observed, suggesting that the dialkylammonium ion was expelled from the cavity of DB24C8 by K$^+$. Subsequently, the intramolecular PET process from $[1 \cdot Tb]^{3+}$ to fullerene was suppressed and the ET process was restored (Figure 5). In addition, [2]pseudorotaxane could be regenerated along with the reproduction of the luminescence
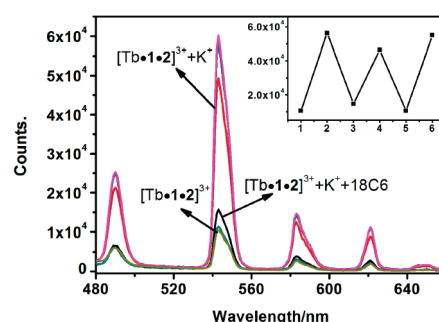

Figure 6. Emission spectral changes observed for $[Tb \cdot 1 \cdot 2]^{3+}$, $[Tb \cdot 1 \cdot 2]^{3+}$ in the presence of K$^+$, and $[Tb \cdot 1 \cdot 2]^{3+}$ in the presence of K$^+$ and 18C6, respectively. Inset: the emission changes of $[Tb \cdot 1]^{3+}$ (1×10^{-5} M) in the presence of **2** (1, 1.1×10^{-5} M) and added KPF$_6$ (2, 1.2×10^{-5} M; 4, 2.6×10^{-5} M; 6, 4.0×10^{-5} M) and 18C6 (3, 1.2×10^{-5} M; 5, 2.6×10^{-5} M) in CH$_3$CN/CHCl$_3$ (1:1, v:v) solution at 544 nm ($\lambda_{ex} = 340$ nm).

Scheme 2. Schematic Representation of the Presumed Coordination Mode for the $[Tb \cdot 1 \cdot 2]^{3+}$ Complex and Their PET–ET Process
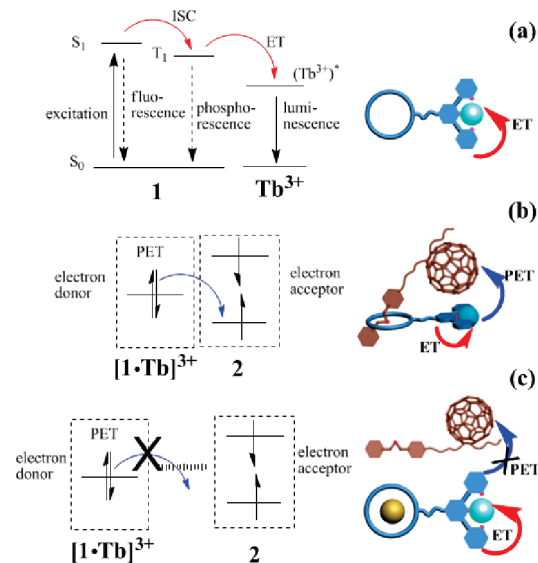
quenching when adding the pristine 18C6 to the solution. The reversibility can be recycled in several times (Figure 6). Thus, a reversibly connected donor–acceptor conjugate of metal–ligand complex and fullerene derivative based on a [2]pseudorotaxane between DB24C8 and secondary dibenzylammonium ions was successfully constructed and the electronic communications between donor and acceptor sites could be efficiently adjusted via an ion-controlled binding and release strategy.

The possible mechanism for the switch may be explained as follows. Before complexation with fullerene-containing ammonium salt **2**, the terpyridine moiety as a sensitizer or an antenna can absorb the excitation light with a larger absorption coefficient and then transfer its energy to the lanthanide ion through intersystem crossing, by which Tb^{3+} enters its emission states (Scheme 2a). When the highly emissive lanthanide complex $[Tb \cdot 1]^{3+}$ was coordinated with acceptor **2**, the energy transfer (ET) process was synchronously suppressed to a certain extent,

leading to an intramolecular PET process from $[Tb \cdot 1]^{3+}$ to **2** as acceptors (Scheme 2b). Instead, when $[Tb \cdot 1 \cdot 2]^{3+}$ complex was disassembled by K^+, the effect of randomly diffusional collision was a predominant factor between donors and acceptors, resulting in the recovery of the lanthanide luminescent emission (Scheme 2c). Since the donors and acceptors must be in close proximity to achieve the effective PET, it can be seen that the noncovalent interactions play a crucial role in the intramolecular electron transfer process that draw the donor and acceptor chromophores much closer.

In conclusion, a DB24C8 derivative bearing one terpyridine unit (**1**) was synthesized, and its coordination to Tb^{3+} displayed a satisfactory luminescent emission as a result of ET from ligand to lanthanide ions. Furthermore, [2]pseudorotaxane $[Tb \cdot 1 \cdot 2]^{3+}$ was constructed by fullerene-containing ammonium salt (**2**) and $[1 \cdot Tb]^{3+}$, giving an intramolecular PET process with the highly efficient quenching of the singlet excited state of $[1 \cdot Tb]^{3+}$. It is significant that the PET process could be reversibly controlled by the binding and release of the cationic guests. Consequently, these obtained results may provide a novel perspective for the design of the molecular machines based on relatively complex interlocking systems with controlled photophysical behaviors.

EXPERIMENTAL SECTION

Preparation of 4′-[4-(4-Hydroxymethyldibenzo-24-crown-8)phenyl]-2,2′:6′,2″-terpyridine (1). Compound **4** (65 mg, 0.2 mmol) was dissolved in dry DMF (20 mL), and to this solution were added 4-chloromethyldibenzo-24-crown-8 (100 mg, 0.2 mmol) and K_2CO_3 (55.2 mg, 0.4 mmol). The resulting mixture was kept under reflux in an inert atmosphere for 24 h. The reaction mixture was evaporated to dryness, the residue was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were dried with Na_2SO_4, filtered under vacuum, and evaporated to dryness. The crude product was purified by flash column chromatography (SiO_2) eluting with EtOAc to afford **1** as a white solid (113 mg, 72%): ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.84 (m, 8H), 3.90−3.95 (m, 8H), 4.12−4.20 (m, 8H), 5.03 (s, 2H), 6.83−6.92 (m, 5H), 6.99 (d, 2H), 7.09 (d, 2H), 7.35 (t, 2H), 7.84−7.92 (m. 4H), 8.64−8.75 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 69.5, 69.9, 71.3, 113.7, 114.0, 114.2, 115.3, 118.3, 120.8, 121.4, 123.8, 128.5, 129.8, 131.0, 136.7, 149.1, 149.7, 155.8, 156.4, 159.8; ESI-MS m/z 808.32 $[M + Na]^+$. Anal. Cald for $C_{46}H_{47}N_3O_9$: C, 70.30; H, 6.03; N, 5.35. Found: C, 69.88; H, 5.94; N, 5.14.

ASSOCIATED CONTENT

ⓢ Supporting Information. Characterizations of **1**, ^1H NMR titration of **1** and **2**, Job's plots of $1/Tb^{3+}$ system, electrochemical data of $[Tb \cdot 1]^{3+}$ and **2**, the optimized molecule modulation of [2]pseudorotaxane $[Tb \cdot 1 \cdot 2]^{3+}$, and the control experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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