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A novel conjugated [2]rotaxane with an Ru-containing axle constructed from a carboxy-functionalized bis-terpyridyl ruthenium complex and β-cyclodextrin: Synthesis, characterization, and properties

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ABSTRACT

A novel Ru-containing conjugated [2]rotaxane, which utilizes a carboxy-functionalized bis-terpyridyl ruthenium complex as an end group, has been prepared by Suzuki coupling in the presence of β-cyclodextrin (β-CD). The structure has been characterized by NMR spectroscopy and ESI mass spectrometry. Its photophysical properties have shown that insulation by the cyclodextrin reduces the fluorescence intensity compared to that of the free dumbbell.

1. Introduction

Recently, some interlocked molecules, such as rotaxanes and catenanes, have attracted growing attention by virtue of their unique structures and potential applications in molecular devices [1]. Rotaxanes have been prepared by threading an axle into a ring, then blocking the ends using bulky groups [2,3]. Various organic functional groups have been introduced as end groups, while transition metals with ligands have also been employed as component molecules [4] and in kinetically stabilized rotaxanes [5]. However, few of the hitherto reported rotaxanes with metal-containing axles have contained conjugated axles. Bis-terpyridyl metal complexes possess interesting photophysical properties [6] and play important roles in building conjugated functional supramolecular devices [7]. Considering bis-terpyridyl metal complexes as precursors, coupling reactions can be envisaged as providing a possible strategy for the construction of conjugated rotaxanes with metal-containing axles. In this paper, we describe the synthesis and characterization of a novel Ru-containing conjugated [2]rotaxane, which utilizes a carboxy-functionalized bis-terpyridyl ruthenium complex as the stopper and β-cyclodextrin (β-CD) as the macrocycle.

2. Results and discussion

2.1. Synthesis and characterization

Suzuki coupling in aqueous solution may be used to efficiently synthesize conjugated rotaxanes, a protocol developed by Anderson and co-workers [8]. The [2]rotaxane **9** ⊂ β-CD was readily obtained by Suzuki coupling of diboronic acid **8** and carboxy-functionalized bis-terpyridyl ruthenium complex **7** in the presence of β-cyclodextrin and palladium(II) acetate in aqueous potassium carbonate solution under nitrogen at 50 °C (Scheme 1) [8,9]. **9** ⊂ β-CD was isolated in 35% yield by preparative thin-layer chromatography (eluent: methanol/butanol/ammonia, 5:5:2). The free dumbbell **9** was also synthesized by using the same conditions as those for the synthesis of **9** ⊂ β-CD but in the absence of β-cyclodextrin.

Both **9** ⊂ β-CD and the dumbbell **9** are poorly soluble in the usual solvents (CH_3CN, DMF, CH_3OH and DMSO) for bis-terpyridyl ruthenium complexes, such that their maximum concentrations are insufficient for NMR spectroscopy. However, these compounds dissolve well in CH_3OH or DMSO containing a little acid. The poor solubility of these compounds may result from loss of the elements of HPF_6, and the addition of acid will inhibit this process [10].

The structure of the present rotaxane was confirmed by NMR spectroscopy and ESI mass spectrometry. In the mass spectrum of **9** ⊂ β-CD ammonium salt, the molecular ion corresponds to the tetraanion formed by the loss of four ammonium cations (Fig. S4). NMR spectra of **9** ⊂ β-CD and dumbbell **9** were obtained

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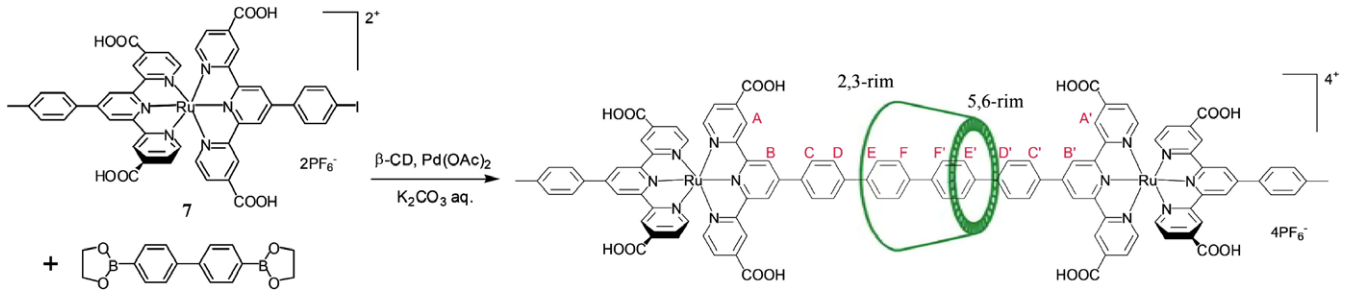

Scheme 1. Synthesis of **9** ⊂ β-CD.

from samples dissolved in d_6-DMSO containing a small quantity of *d*-TFA. As shown in Fig. 1a, the aromatic protons of dumbbell **9** gave rise to simple peaks, indicating the formation of a symmetric structure. However, the aromatic protons of **9** ⊂ β-CD showed splitting and peak shifts owing to the asymmetric structure included in the β-CD cavity (Fig. 1b). For example, the signals of the aromatic protons B and C in dumbbell **9** are seen as single peaks, but the signals of the corresponding aromatic protons in **9** ⊂ β-CD split into two separate resonances due to B/B′ and C/C′. The signals of protons D/D′, E/E′, and F/F′ of the axle in **9** ⊂ β-CD are shifted to higher field with respect to those of free dumbbell **9**.

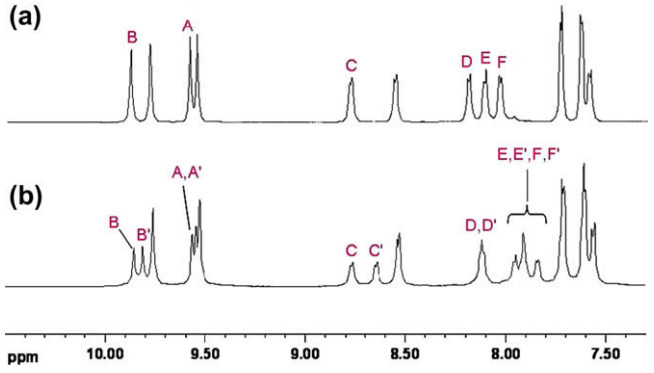

Fig. 1. ^{1}H NMR (600 MHz) spectra (in d_6-DMSO with a trace of *d*-TFA, 25 °C): (a) dumbbell **9**; (b) **9** ⊂ β-CD.

Significant differences in the resonance frequencies of the free and interlocked β-CD are also evident when comparing the corresponding ^{1}H NMR spectra (Fig. 2). The signals of protons H3/H5/H6/H6′ and H2/H4 of interlocked β-CD (Fig. 2a) are resolved into discrete peaks compared with those of free β-CD (Fig. 2b) [11]. This can be attributed to the aromatic ring current of the threaded guest. The above results confirm the formation of a [2]rotaxane with interlocked β-CD.

A 2D NOESY experiment provided further evidence for the formation of **9** ⊂ β-CD (Fig. 3). NOEs between the two components

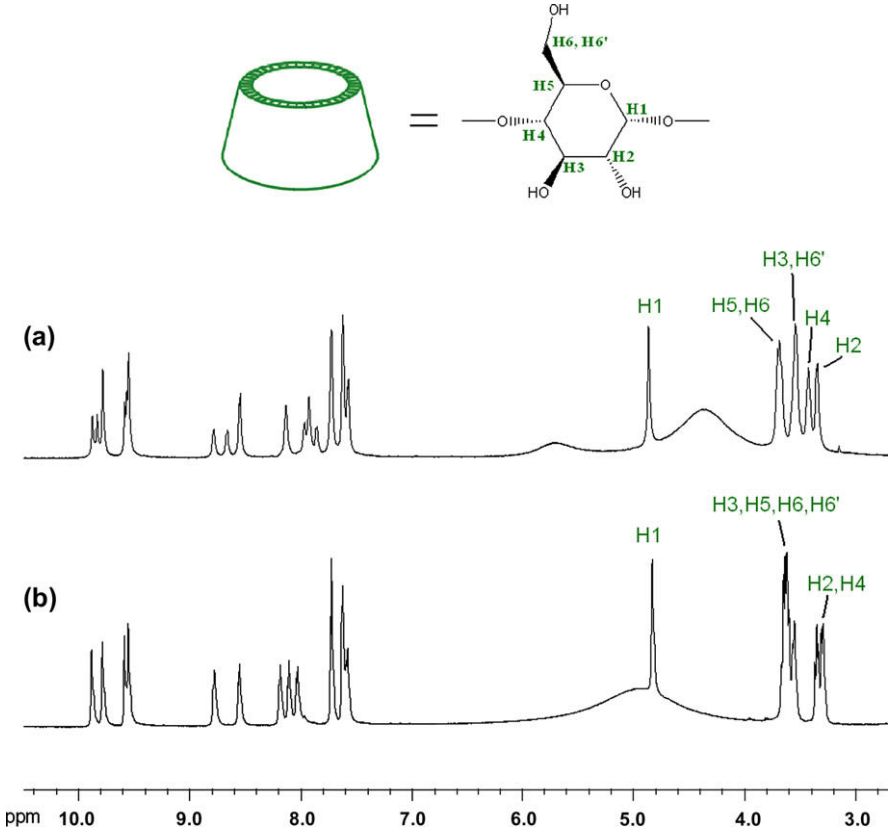

Fig. 2. ^{1}H NMR (600 MHz) spectra (in d_6-DMSO with a trace of *d*-TFA, 25 °C): (a) **9** ⊂ β-CD; (b) dumbbell **9** and an equimolar amount of free β-CD.

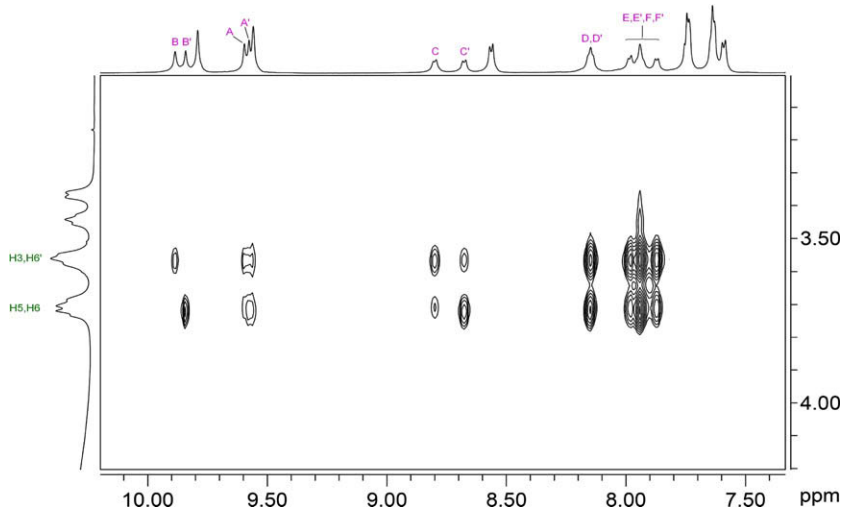

Fig. 3. ^{1}H NOESY NMR (600 MHz) spectrum of **9** ⊂ β-CD (in d_6-DMSO with a trace of *d*-TFA, 25 °C).

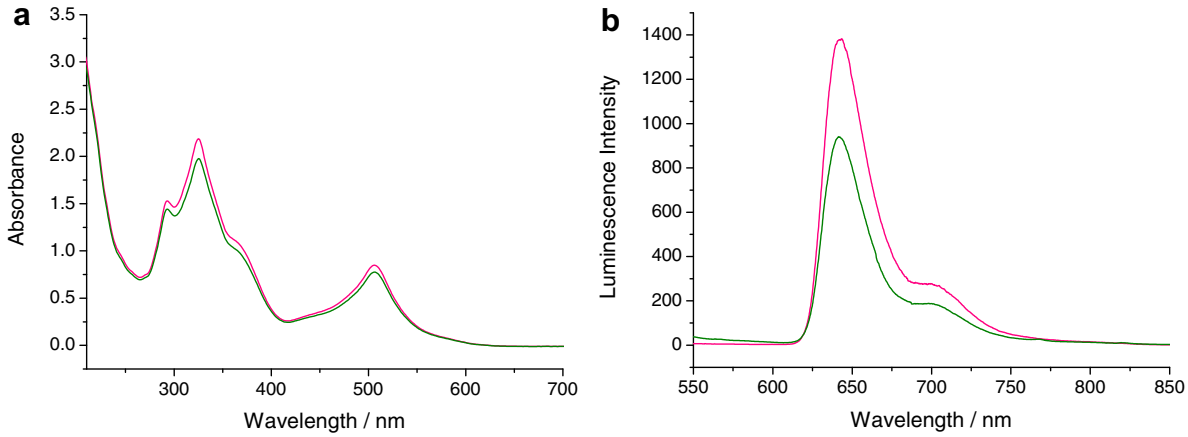

Fig. 4. (a) Absorption spectra of dumbbell **9** (pink line) and **9** ⊂ β-CD (green line), each at 10 μm in methanol solution; (b) fluorescence spectra of dumbbell **9** (pink line) and **9** ⊂ β-CD (green line) at 77 K, at 10 μM in ethanol/methanol (4:1, v/v) glass (λ_{ex} = 510 nm). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

showed that the cyclodextrin was mainly located on the central axle. As shown in Fig. 3, protons H3 of the wider 2,3-rim and H5 of the narrower 5,6-rim of the β-cyclodextrin in **9** ⊂ β-CD show NOEs to the axle protons B, C, D, E, F, F′, E′, D′, C′, and B′. Protons H6 and H6′ of the β-cyclodextrin show NOEs to proton A′ of the bis-terpyridyl ruthenium component.

2.2. Physical properties

The UV/Visible absorption and fluorescence spectra of **9** ⊂ β-CD have been compared with those of free dumbbell **9** (Fig. 4). Both **9** ⊂ β-CD and the dumbbell **9** display intense absorption bands in the visible region due to metal-to-ligand charge-transfer (^{1}MLCT) transitions, as well as broad intense bands in the UV region attributable to ligand-centered (^{1}LC) transitions (Fig. 4a) [12]. The two complexes display very weak fluorescence at room temperature because of the short fluorescence lifetimes. In a frozen glass at 77 K, however, intense fluorescence spectra can be obtained [13]. When **9** ⊂ β-CD and the dumbbell are excited at 510 nm, **9** ⊂ β-CD emits with λ_{max} = 641.6 nm while dumbbell **9** emits with λ_{max} = 643.4 nm, but the former band is of somewhat lower intensity than the latter (Fig. 4b). This result is in agreement with that obtained by Anderson [14] for a symmetrical heptamethine chromophore threaded through α-cyclodextrin.

The redox behaviors of **9** ⊂ β-CD and dumbbell **9** (1 mm in CH_3CN) have been investigated by cyclic voltammetry and square-wave voltammetry techniques with 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte. TFA (50 mM in CH_3CN) was added to increase the solubility. **9** ⊂ β-CD and dumbbell **9** exhibit quasi-reversible oxidation waves at 1.126 and 1.128 V, respectively, which can be ascribed to a one-step two-electron process, corresponding to $Ru_2^{II,II}/Ru_2^{III,III}$ oxidation. There is no electronic communication between the two metal centers in either **9** ⊂ β-CD or dumbbell **9** because of the long distance between them.

The thermal stability of **9** ⊂ β-CD has been examined by heating at 80 °C in d_6-DMSO for three days. ^{1}H NMR spectra recorded before and after the heating did not show any noticeable differences, indicating that unthreading did not take place. Even after one day at 100 °C in d_6-DMSO, no sign of unthreading was detected.

3. Conclusion

In summary, we have reported an effective synthesis of a novel conjugated [2]rotaxane with an Ru-containing axle that utilizes carboxy-functionalized bis-terpyridyl ruthenium complexes as end groups. The photophysical properties of the [2]rotaxane have shown that insulation by the cyclodextrin reduces the fluorescence

intensity compared to that of the free dumbbell. This synthetic strategy offers a potential method for the construction of homodyad (same metal ions) and heterodyad (different metal ions) metal-containing conjugated rotaxanes bearing bis-terpyridyl metal (Fe, Ru, Os, Ir, etc.) complexes as end groups.

4. Experimental

4.1. General

Unless otherwise noted, all starting materials were purchased from commercial sources and were used without further purification. Preparative thin-layer chromatography (TLC) was performed using glass plates precoated with GF 254. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Mercury Plus-400 and Unityinova-600 with ^{13}C{1H} cryoprobe. NOESY was performed on VARIAN UNITYINOVA-600. Electron impact ionization (EI) mass spectra were carried on Trace MS 2000, respectively electrospray ionization (ESI) mass spectra were carried on Finnigan LCQ. Elementary analysis was obtained on Vario EL III. UV–Vis spectra were performed on Hitachi U-3310. Fluorescence data were recorded on Hitachi Model F-4500. The syntheses of intermediates **2**, **5** and **8** have been reported [15]. The synthetical procedures of compounds **1**, **3**, **4**, **6** and **7** were shown in Supplementary material.

4.2. Synthesis of rotaxane (9 ⊂ β-CD)

Degassed water was added to a mixture of **7** (138 mg, 0.1 mmol), **8** (14.7 mg, 0.05 mmol), potassium carbonate (140 mg, 1 mmol), and β-cyclodextrin (900 mg, 0.8 mmol) under nitrogen. The solution was then heated to 50 °C overnight. Then palladium(II) acetate (1 mg, 4.5 μmol) was added, the mixture was stirred for 24 h. The mixture was then allowed to cool, diluted with deionized water (10 mL), and filtered through paper. A 60% aq. HPF_6 (2 mL) was added and the resulting suspension was centrifuged. The supernatant was removed and the solid was washed twice with water (40 mL). The solid was dissolving in minimum ammonia, then separated by preparative thin-layer chromatography (eluent: 5:5:2 methanol/butanol/ammonia). The product band was eluted with methanol/ammonia 5:1. The obtained eluent was reduced to 10 mL, then acidated with excess 60% aq. HPF_6. The collected precipitate was washed with water and dried under vacuum to give the pure rotaxane **9** ⊂ β-CD as a red powder. **9** ⊂ β-CD was dissolved in minimum ammonia, then evaporated under vacuum. The obtained ammonium salt was used for mass spectra. ^{1}H NMR (600 MHz, d_6-DMSO) δ 9.87 (s, 2H), 9.83 (s, 2H), 9.78 (s, 4H), 9.56 (m, 8H), 8.78 (d, J = 6.6 Hz, 2H), 8.63 (d, J = 7.8 Hz, 2H), 8.55 (d, J = 7.8 Hz, 4H), 8.13 (s, 4H), 7.95 (m, 6H), 7.86 (d, J = 7.2 Hz, 2H), 7.72 (d, J = 5.4 Hz, 8H), 7.62 (s, 8H), 7.57 (d, J = 7.8 Hz, 4H), 4.86 (s, 7H), 3.69 (m, 14H), 3.55 (s, 14H), 3.43 (d, J = 7.8 Hz, 7H), 3.35 (d, J = 8.4 Hz, 7H), 2.54 (s, 6H). ESI-MS m/z calcd for $C_{148}H_{148}N_{16}O_{51}Ru_2$ 3169.8; found, $[M-4NH_4]^{4-}$ 775.0.

4.3. Synthesis of dumbbell (**9**)

Complex **9** was synthesized following the same routes, but without the addition of β-cyclodextrin. It was purified by dissolved in minimum ammonia, then separated by chromatography (silica gel, eluent: 10:10:1 methanol/butanol/ammonia) to give the pure dumbbell **9** as a deep red powder. Dumbbell **9** was dissolved in minimum ammonia, then evaporated under vacuum. The obtained ammonium salt was used for mass spectra. (600 MHz, d_6-DMSO) δ 9.89 (s, 4H), 9.79 (s, 4H), 9.59 (s, 4H), 9.56 (s, 4H), 8.79 (d, J = 6.6 Hz, 4H), 8.57 (d, J = 7.2 Hz, 4H), 8.20 (d, J = 7.2 Hz, 4H), 8.12 (d, J = 7.8 Hz, 4H), 8.04 (d, J = 7.2 Hz, 4H), 7.74 (d, J = 4.8 Hz, 8H), 7.64 (d, J = 5.4 Hz, 8H), 7.59 (d, J = 6.6 Hz, 4H), 2.54 (s, 6H). ESI-MS m/z calcd for $C_{106}H_{78}N_{16}O_{16}Ru_2$ 2034.4; found, $[M-4NH_4]^{4-}$ 489.7.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.047.

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