The construction of a supramolecular polymeric rotaxane from bipyridine-ruthenium and cyclodextrin†

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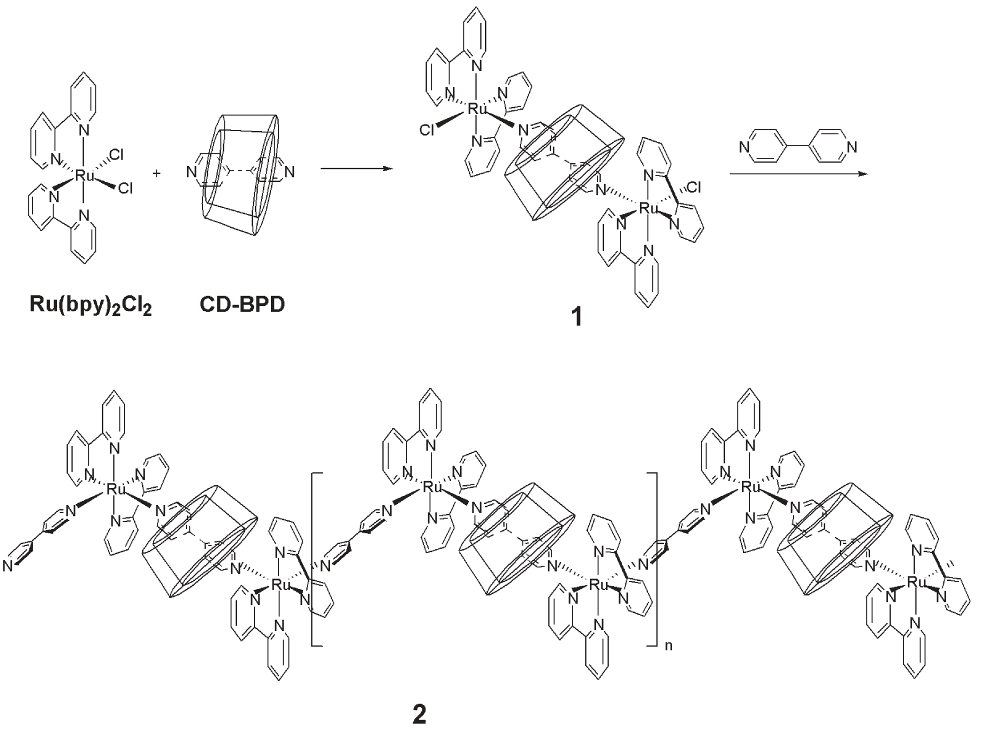
A luminescent supramolecular link is constructed by a very simple method using bipyridine-ruthenium and cyclodextrin, which displays not only a quasi-linear structure, but also a satisfactory fluorescence emission in both solution and the solid state.

Nanoscale supramolecular assemblies constructed by synthetic receptors, especially cyclodextrins, have become a recent challenge in chemistry and material science because of their potential to serve as molecular devices, molecular machines and functional materials *etc.*[1,2] Indeed, the inherent ability of cyclodextrins to selectively and effectively bind with molecular substrates enables them to be assembled into polyrotaxanes and molecular tubes using organic molecules or polymer chains as templates.[3–7] Also, superior to simple bipyridine-metal complexes, octahedron-like polypyridine-ruthenium complexes have attracted considerable attention due to their interesting photochemical, electrochemical and magnetic properties.[8–14] Recently, we have reported a polymeric rotaxane constructed from an inclusion complex of β-cyclodextrin and 4,4′-bipyridine (CD-BPD) by coordination with nickel(II) ions, in which the 4,4′-bipyridine unit was shown to penetrate through the cyclodextrin cavity in order to coordinate with the metal ions.[15] This method could be used as a new way to prepare the molecular missing link, which means a link that can be assembled and disassembled easily, based on cyclodextrins.

In the present paper, we report the construction of a new cyclodextrin-containing polyrotaxane possessing luminescent $Ru(bpy)_2$ centers (bpy = 2,2′-bipyridine), which is characterized by ^1H NMR, circular dichroism, FT-IR, UV-vis, elemental analysis and static light scattering. It is noted that the use of cyclodextrins in the construction process is vital as, even after many attempts, the $Ru(bpy)_2$-based assembly does not form in the absence of cyclodextrins. Further characterization by scanning tunneling microscopy (STM) and transmission electron microscopy (TEM) reveals that the resultant assembly exists as a zig-zag chain with an approximate length of 250 nm. As expected, the assembly emits a significant fluorescence both in aqueous solution and in the solid state. As a result, this work provides a simple and



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† Electronic supplementary information (ESI) available: preparation of complex **1** and assembly **2**; UV-vis, circular dichroism and fluorescence spectra of $Ru(bpy)_2Cl_2$, CD-BPD, complex **1** and assembly **2**; TEM and STM images of assembly **2**. See http://www.rsc.org/suppdata/cc/b4/b415930f/

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convenient method to prepare cyclodextrin-supporting functional materials.

Reaction of the inclusion complex CD-BPD[15] with $Ru(bpy)_2Cl_2$[16] in aqueous solution produces the precursor **1** as a precipitate. However, in the absence of cyclodextrins, the reaction of $Ru(bpy)_2Cl_2$ with 4,4′-bipyridine produces several products, which are too soluble to precipitate in water or ethanol and difficult to purify by silica gel chromatography or on a Sephadex column. In addition to elemental analysis and FT-IR, UV-vis and ^1H NMR spectroscopy provide useful evidence to support the formation of **1**. The UV-vis spectrum of $Ru(bpy)_2Cl_2$ shows a characteristic absorption around 456 nm which is assigned to the metal–ligand charge-transfer (MLCT) transition of the $Ru(bpy)_2$ unit. After reaction with CD-BPD, this transition red-shifts to 460 nm, which indicates that the CD-BPD unit is coordinated to the $Ru(bpy)_2$ moiety. Further evidence is found in the comparable study of the ^1H NMR spectra of $Ru(bpy)_2Cl_2$, CD-BPD and complex **1**. Fig. 1b shows the ^1H NMR spectrum of complex **1**, which exhibits NMR signals corresponding to both CD-BPD and $Ru(bpy)_2Cl_2$ protons. Then, as seen in Fig. 1, a change in the chemical shift of all the aromatic protons in CD-BPD after reaction with $Ru(bpy)_2Cl_2$ relative to a free molecule is observed: the *meta* protons (H-b) shift downfield (27 Hz) and *ortho* protons (H-a) shift upfield (12 Hz). In the control experiment, the physical mixture of $Ru(bpy)_2Cl_2$ with CD-BPD (molar ratio 2 : 1) gives a ^1H NMR spectrum that corresponds simply to a superposition of the spectra of individual $Ru(bpy)_2Cl_2$ and CD-BPD components. In addition, circular dichroism spectra show that CD-BPD gives a relative strong positive and a weak negative Cotton effect peak. However, after reaction with $Ru(bpy)_2Cl_2$, the resultant complex **1** displays a circular dichroism spectrum that is distinctly different from that of the parent CD-BPD, showing a negative and three positive Cotton effect peaks. In the control experiment, $Ru(bpy)_2Cl_2$ only shows negligible circular dichroism signals as compared with those of CD-BPD and complex **1**. Both these phenomena indicate that a complex has formed between $Ru(bpy)_2$ and CD-BPD.

After obtaining the desired precursor **1**, the building block is used to construct the supramolecular assembly **2** through the linkage of 4,4′-bipyridine (BPD) molecules. The stoichiometric 1 : 1 **1**/BPD coordination in **2** is confirmed by the results of elemental analysis and Job's experiment. Moreover, the Ru-bipyridine MLCT transition of **2** displays an obvious bathochromic shift (13 nm) as compared with that of **1**, which may indicate that the incorporation of 4,4′-bipyridine with precursor **1** results in a more stable supramolecular species. After addition of 4,4′-bipyridine to complex **1**, the NMR integrations corresponding to 4,4′-bipyridine protons become stronger (Fig. 1c), which also implies the association of 4,4′-bipyridine linker with complex **1**. Interestingly, with the introduction of the linking 4,4′-bipyridine unit, assembly **2** gives a series of opposite (two negative and one positive) Cotton effect peaks to those (two positive and one negative peaks) of complex **1** in the wavelength range from 243 to 320 nm. These opposite circular dichroism signals, along with UV-vis and NMR results, provide evidence for the formation of assembly **2**. Additionally, static light scattering experiments were performed (in 0.1 M NaCl aq. solution) and a weight-average molecular weight for **2** of 1.6×10^5 g/mol was obtained.

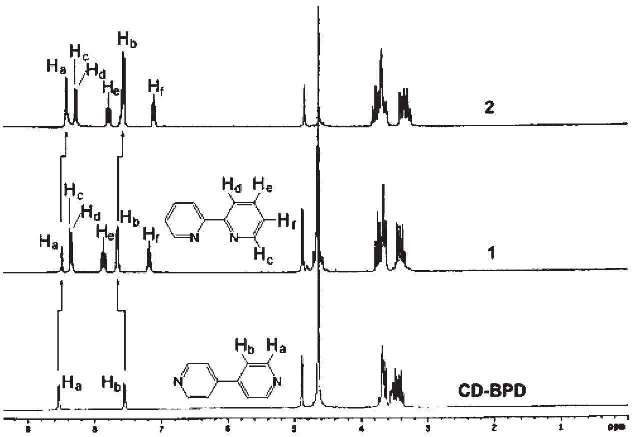

Fig. 1 From bottom to top: ^1H NMR spectra of (a) CD-BPD, (b) complex **1** and (c) assembly **2** in D_2O.

TEM and STM experiments were performed according to reported methods (Fig. 2).[6,15] The TEM image obtained at a concentration of (1.0×10^{-3} M) gives an insight into the size and shape of the polyad assembly constructed by bipyridine, ruthenium, and β-cyclodextrin. The image shows a quasi-linear arrangement of **2** with an approximate length of 250 nm and an average width of *ca.* 10 nm. Therefore, we deduce that the individual assemblies of **2** may aggregate to form fibres at relatively high concentrations. The STM image recorded at a low concentration (1.0×10^{-5} M) provides a nice profile of the individual assembly **2**, which also shows a quasi-linear shape on a graphite substrate with an average width of 2 nm and an average height of 0.9 nm. This conformation is reasonable from the viewpoint of the coordination geometry of ruthenium(II). It is demonstrated that ruthenium(II) in $Ru(bpy)_2Cl_2$ adopts an octahedron conformation, where two Ru–Cl bonds are located in the same plane and the Cl–Ru(II)–Cl angle is approximately 90°. When coordinated with ligands, one or two chlorine atoms in $Ru(bpy)_2Cl_2$ will be replaced *in situ.*[17] According to this coordination geometry, two adjacent 4,4′-bipyridine units in assembly **2** should be coplanar and located perpendicular to each other. On the basis of this information, we performed Corey–Pauling–Kultun (CPK) molecular model studies to explore the possible conformation of assembly **2**, and the results showed that **2** may adopt a zig-zag conformation.

Benefiting from the fascinating photophysical property of bipyridine-ruthenium(II) units, the assembly **2** displays a

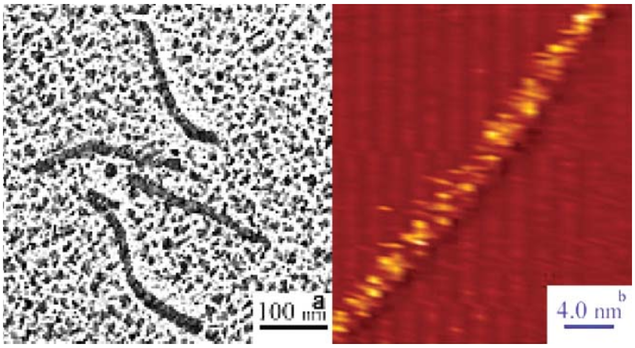

Fig. 2 (a) TEM (1.0×10^{-3} M) and (b) STM (1.0×10^{-5} M) images of assembly **2**.

satisfactory luminescent behavior in both aqueous solution and the solid states. When excited at 456, 460 or 473 nm (MLCT absorption of Ru(bpy)$_2$Cl$_2$, **1** or **2** respectively), assembly **2** usually displays higher fluorescence quantum yields than Ru(bpy)$_2$Cl$_2$ or **1** in aqueous solution. The obtained quantum yields[18] (with the excited wavelength shown in parentheses) are 6.70% (456 nm), 6.68% (460 nm), 6.33% (473 nm) for Ru(bpy)$_2$Cl$_2$, 7.82% (456 nm), 7.68% (460 nm), 7.28% (473 nm) for **1**, and 8.76% (456 nm), 8.30% (460 nm), 7.63% (473 nm) for **2**, respectively. The enhanced fluorescence behavior may be attributed to the cyclodextrin effectively shielding the bipyridine-ruthenium(II) fluorophore from the deactivating water attack. Additionally, the relatively rigid structure of **2** could also contribute to the improved luminescence. It is significant that the assembly **2** can also emit strong fluorescence in the solid state. More interestingly, **2** displays not only a relative strong fluorescence emission around 574 nm, like that of Ru(bpy)$_2$Cl$_2$, but also a new emission around 701 nm with a satisfactory intensity (see ESI). These luminescent properties of the polyrotaxane assembly **2** will enhance its potential application in functional photophysical and/or photochemical materials.

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