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Short communication

Synthesis of ru(bpy)$_3$-viologen and its complex included by *p*-sulfonatocalix[4]arene in a U-type binding manner

Shuaifan Wu, Gang Wang, Lei Zou, Qiaochun Wang, Xiang Ma*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, PR China

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ABSTRACT

A novel Ru(bpy)$_3$–viologen guest **RPV** and a reference compound **PV** are well designed and synthesized. Ru(bpy)$_3$ based guest compound **RPV** prefers to form a novel U-type complex **RPV**$\subset$**SC4** with *p*-sulfonatocalix[4]arene (**SC4**) host. Binding manner of the complex has been fully studied by ^{1}H NMR, ESI-MS and 2D NOE NMR spectra. The 1:1 Binding ratio is confirmed by UV–Vis measurement and the association constant is determined by ^{1}H NMR titration. In this host–guest system, both Ru(bpy)$_3$ and viologen group show strong interactions with the host **SC4**. Due to the unique U-type structure of **RPV**$\subset$**SC4**, the competitive interactions between Ru(bpy)$_3$ and viologen group were investigated as well.

1. Introduction

Supramolecular assemblies [1,2], usually driven by noncovalent interactions [3,4] (hydrogen binding, hydrophilic/hydrophobic, ionic interactions, π–π stacking), are showing an increasing usage in the areas of nano-structured functional materials, memory devices and biological applications [5–7]. Key points of functional applications of these devices are the structure, for instance, linear supramolecular polymers can be used as the framework for constructing molecular wires [8–10]; molecular containers as well as molecular capsules can be achieved by self-assembled cage-like complexes [11,12]; U-shaped complexes are of special meanings in constructing molecular switches [13].

Water soluble calixarenes, especially *p*-sulfonatocalix[4]arenes, have received considerable interests due to their extensive properties [14], such as separated hydrophilic (rim) and hydrophobic (cavity) areas, inclusion ability to metal ions or other organic guest compounds, different types of the interactions between host and guest compounds [15–19]. Numerous interesting supramolecular assemblies have been constructed with *p*-sulfonatocalix[4]arenes, for instance, linear supramolecular polymers [10], self-assembled cage-like complexes [11], molecule capsule based on ionic interactions etc. [12]. *p*-Sulfonatocalix[4]arenes usually form linear inclusion complex with the terminal portion of methyl-viologen-dication-containing linear guests via electrostatic interaction [10]. Other unusual and novel inclusion complex mode based on *p*-sulfonatocalix[4]arenes, such as U-type self-assembly with linear guests, have seldom been reported. Herein, we constructed a novel *p*-sulfonatocalix[4]arene inclusion complex in a U-type manner employing Ru(bpy)3–viologen as guest, which has a special supramolecular assembly conformation and can be used potentially to mimic some folding biological systems.

Ruthenium bipyridine derivatives [20–23], simple but well-known dyes, are of particular importance in constructing molecular level devices (e.g. switches [24], wires [8,9] and logic gates [25]). Their unique photochemical and electrochemical behaviors especially the outer–sphere association abilities with DNA, cyclic anions and water-soluble calixarenes have been extensively investigated in the past 30 years [26–29].

The binding manner of a very simple methyl viologen dication (**MV**) and **SC4** in both solution and solid state have been fully investigated in previous works [30]. It has been reported and proved that **SC4** and viologen can form a stable inclusion complex with high association constant in the manner of having only one methyl group being included into the upper rim of **SC4** rather than including the whole viologen unit inside, owing to the limited dimensional cavity space of **SC4** [31]. Herein, when a ruthenium–2,2′-bipyridine–viologen (**RPV**) guest employed to bind

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* Corresponding author. Tel./fax: +86 21 6425 2758.
E-mail address: maxiang@ecust.edu.cn (X. Ma).

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with *p*-sulfonatocalix[4]arenes (**SC4**), a novel U-type complex is immediately formed. Two guest compounds have been synthesized (all the key structures have been confirmed by ^1H NMR, ^{13}C NMR and MS data), one (**RPV**) is the target compound containing $Ru(bpy)_3$ group; the other one (**PV**) without $Ru(bpy)_3$ is prepared as the reference compound.

2. Experimental

2.1. General information

^1H NMR and ^{13}C NMR spectra were measured on a Brüker AV-400 spectrometer (the ^{13}C NMR spectra of compound **3** and compound **4** were measured on a Varian Mercuryplus 300 MHz spectrometer), 2D NOESY NMR spectra were recorded on a Brüker AV-500 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on an HP5989 mass spectrometer. Absorption spectra were done on a Varian Cary 500 UV/Vis spectrophotometer (1-cm quartz cell used). Luminescence emission spectra were recorded on a Varian Cary Eclipse Luminescence Spectrophotometer (1-cm quartz cell used). Melting points were determined by using an X-6 micro-melting point apparatus. Tris(2,2′-bipyridyl)dichlororuthenium(II) hexahydrate, 2,2′-bipyridine, 3-hydroxy-6-(2-pyridyl)pyridine, *p*-sulfonatocalix[4]arene (**SC4**), N-methyl-4,4′-bipyridine iodide, 1,5-dibromopentane, ammonium hexafluorophosphate, cis-Ru(bpy)$_2$Cl$_2$•2H$_2$O, 1,1′-dimethyl-4,4′-bipyridine-1,1′-diium iodide, silver hexafluorophosphate, tetrabutylaminochlorate and the inorganic reagents were commercially available and used as received. All the solvents were dried by 4Å molecular sieve and distilled before used.

2.2. Synthesis

2.2.1. 5-(4-bromobutoxy)-2,2′-bipyridine 1

A suspension of 0.50 g (2.9 mmol) 2,2′-bipyridin-5-ol and 0.80 g (5.8 mmol) K_2CO_3 in 30 ml acetone was stirred for 30 min at 50 °C, then 1.9 g (8.7 mmol) 1,4-dibromobutane was added and refluxed for another 4 h. After the mixture was cooled to room temperature, precipitate was removed by filtration, the filtrate was concentrated under reduced pressure, 50 ml hexane was added and the product was collected by filtration to afford compound **1** 0.65 g (72.8%). Mp 68.9–70.3 °C. ^1H NMR ($CDCl_3$), δ ppm = 8.64 (d, J = 4.8 Hz, 1H), 8.36–8.29 (m, 3H), 7.78 (dd, J = 2.0, 8.0 Hz, 1H), 7.30 (dd, J = 2.8, 8.8 Hz, 1H), 7.27–7.23 (m, 1H), 4.11 (t, J = 5.6 Hz, 2H), 3.51 (t, J = 6.4 Hz, 2H), 2.15–2.07(m, 2H), 2.05–1.97(m, 2H). ^{13}C NMR ($CDCl_3$), δ ppm = 156.035, 155.387, 149.055, 137.245, 136.836, 122.925, 121.700, 121.525, 120.401, 67.389, 33.235, 29.298, 27.824. HRMS (ESI, *m*/*z*): calcd for $C_{14}H_{16}N_2OBr$, 307.0446, found 307.0443.

2.2.2. Synthesis of compound 3

A mixture of 0.40 g (1.3 mmol) compound **1** and 0.82 g (2.6 mmol) compound **2** in acetonitrile was refluxed for 4 days. Then the mixture was cooled to room temperature, precipitate was collected by filtration and washed with 2 ml acetonitrile, after the counter anion exchanged with NH_4PF_6 to get compound **3** (0.3589 g, 40%). Mp 228–229 °C. ^1H NMR (DMSO-d$_6$), δ ppm = 9.41 (d, J = 7.2 Hz, 2H), 9.27 (d, J = 6.8 Hz, 2H), 8.78 (d, J = 6.8 Hz, 2H), 8.73 (d, J = 7.2 Hz, 2H), 8.63 (d, J = 4 Hz, 1H), 8.38 (d, J = 3.2 Hz, 1H), 8.34 (d, J = 8.8 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.90 (dd, J = 1.6, 7.6 Hz, 1H), 7.52 (dd, J = 3.2, 9.2 Hz, 1H), 7.41–7.36 (m, 1H), 4.78 (t, J = 7.6 Hz, 2H), 4.43 (s, 3H), 4.19 (t, J = 6.0 Hz, 2H), 2.24–2.15 (m, 2H), 1.89–1.80 (m, 2H). ^{13}C NMR (DMSO-d$_6$), δ ppm = 156.809, 156.711, 149.799, 149.229, 148.785, 148.568, 147.288, 146.507, 137.971, 137.890, 127.210, 126.892, 124.021, 122.414, 121.909, 120.269, 67.985, 61.262, 48.684, 28.258, 25.788. HRMS (ESI, *m*/*z*): $[M-PF_6^-]^+$ calcd for $C_{25}H_{26}F_6N_4OP$, 543.1737, found 543.1732.

2.2.3. Synthesis of compound 4

A solution of cis-Ru(bpy)Cl$_2$•2H$_2$O 0.2283 g (0.438 mmol) and $AgPF_6$ 0.2218 g (0.877 mmol) in 10 ml acetone was stirred at room temperature for 10 h. The precipitate was filtered and washed with 5 ml acetone. 0.302 g (0.438 mmol) compound **3** was added to the filtrate. The reaction flask was wrapped with aluminum foil and refluxed under Ar atmosphere for 12 h. After it was cooled to room temperature, the solvent was removed under reduced pressure. Crude product was purified by column chromatography, using silica gel and a mixture of CH_3CN/H_2O/sat. KNO_3 8/1/1 as elute. The red band was collected, and the counter anion was exchanged with NH_4PF_6 to get compound **4**•4PF$_6$ (0.223 g, 36.5%). A solution of 0.12 g (0.086 mmol) compound **4**•4PF$_6$ and 0.144 g (0.517 mmol) tetrabutylaminochlorate in 5 ml dry acetone was stirred at room temperature to produce a precipitate which was collected by filtration and washed with acetone to provide compound **4**•4Cl (0.075 g, 91%). Mp>250 °C. ^1H NMR (DMSO-d$_6$), δ ppm = 9.55 (d, J = 5.6 Hz, 2H), 9.36 (d, J = 6.4 Hz, 2H), 8.95–8.82 (m, 9H), 8.78 (d, J = 8.0 Hz, 1H), 8.22–8.09 (m, 5H), 7.89 (dd, J = 2.4, 9.2 Hz, 1H), 7.83 (d, J = 5.6 Hz, 1H), 7.78 (d, J = 5.6 Hz, 1H), 7.74–7.67 (m, 2H), 7.64 (d, J = 5.2 Hz, 1H), 7.59–7.51 (m, 4H), 7.45 (t, J = 6.4 Hz, 1H), 7.17 (d, J = 2.8 Hz, 1H), 4.79 (t, J = 7.6 Hz, 2H), 4.47 (s, 3H), 4.16–4.03 (m, 2H), 2.11–2.00 (m, 2H), 1.76–1.67 (m, 2H). ^{13}C NMR (D_2O), δ ppm = 157.771, 157.336, 157.248, 157.199, 157.116, 152.041, 151.796, 151.734, 151.397, 149.511, 149.154, 148.729, 147.373, 146.626, 139.726, 136.624, 136.564, 136.514, 126.624, 126.566, 127.401, 127.256, 126.796, 126.364, 125.470, 125.289, 125.240, 125.182, 124.070, 123.015, 122.992, 68.923, 60.634, 48.621, 28.009, 25.419. HRMS (ESI, *m*/*z*): $[\mathbf{4}\bullet 4PF_6\text{-}2PF_6^-]^{2+}$ calcd for $C_{45}H_{42}F_{12}N_8OP_2Ru$, 551.0899, found 551.0742.

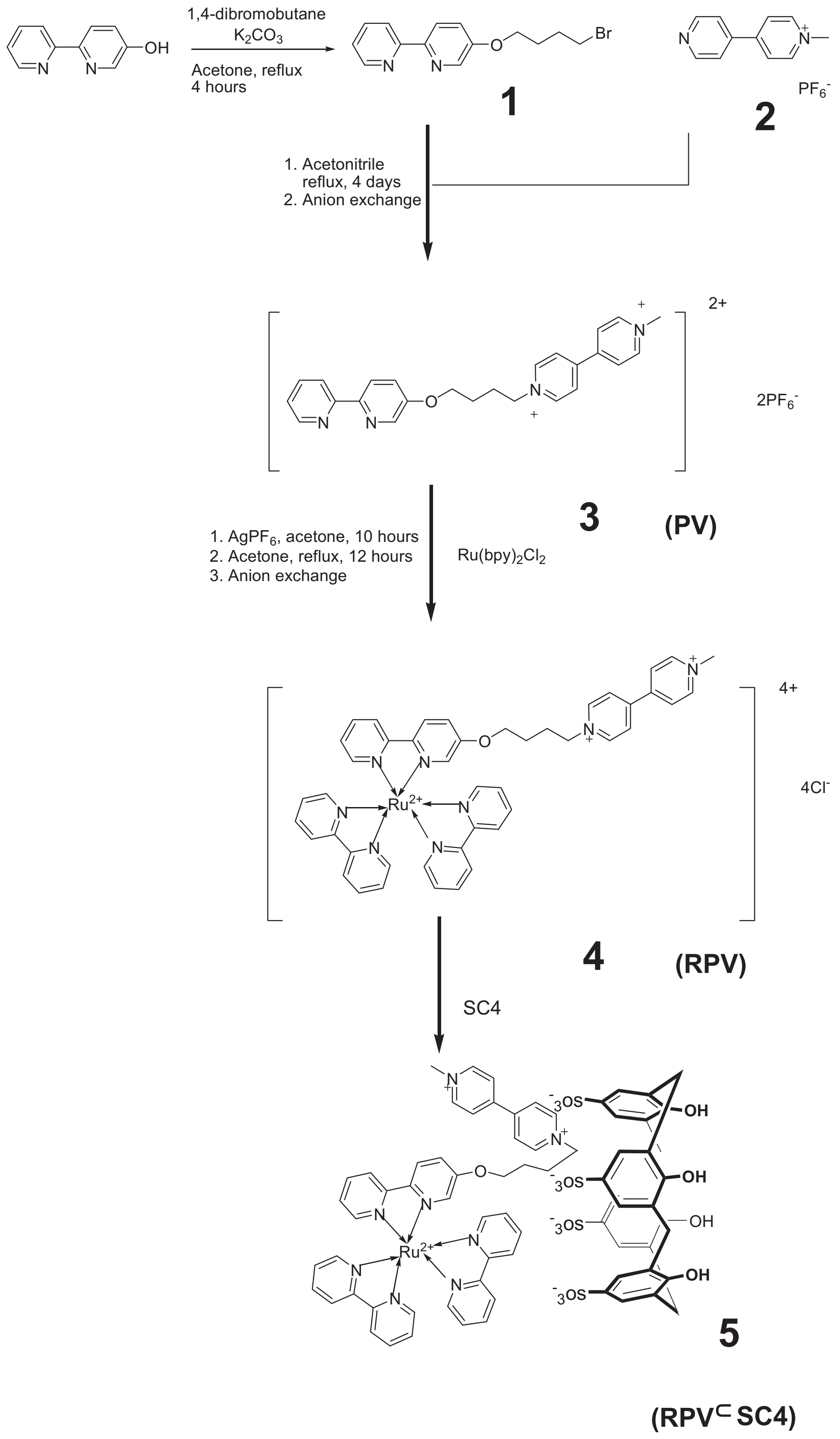
2.2.4. Synthesis of compound 5

The synthetic route to compound **5** is outlined in Scheme 1. 0.050 g (0.052 mmol) of compound **4** was dissolved in H_2O then 0.436 g (0.052 mmol) of **SC4** was added. After sonicated for 1 min, the precipitate was filtrated and dried to afford compound **RPV**⊂**SC4** (0.831 g, 95%). Mp>250 °C. ^1H NMR (DMSO-d$_6$), δ ppm = 8.80 (t, J = 7.6 Hz, 4H), 8.73–8.65 (m, 2H), 8.56 (d, J = 6.0 Hz, 2H), 8.46 (d, J = 5.6 Hz, 2H), 8.32 (d, J = 6.0 Hz, 2H), 8.24 (d, J = 6.0 Hz, 2H), 8.19–8.02 (m, 6H), 7.79 (d, J = 5.2 Hz, 1H), 7.73–7.65 (m, 3H), 7.62 (t, J = 6.4 Hz, 1H), 7.60–7.54 (m, 2H), 7.50 (t, J = 6.8 Hz, 2H), 7.41 (t, J = 6.4 Hz, 1H), 7.25 (s, 8H), 7.09 (d, J = 1.6 Hz, 1H), 4.43–3.60 (m, 11H), 3.60–3.51 (m, 2H), 2.84–2.64 (m, 2H), 0.90–0.72 (m, 2H), 0.72–0.53 (m, 2H). ESI-MS : *m*/*z* 1597.2263 $[RPV + SC4\text{-}2Na-4Cl-H]^-$; *m*/*z* 1551.2256 $[RPV + SC4\text{-}4Na-4Cl-H]^-$.

3. Results and discussion

3.1. Binding manner of SC4 with PV

The counter anion of **PV**•2PF$_6$ is exchanged with tetrabutylaminochlorate to afford **PV**•2Cl, which can be included into the cavity of **SC4** in both DMSO and H_2O. The host–guest complex is firstly analyzed by ^1H NMR (Figs. 1A, B) and 2D NOE NMR (Fig. 2) spectroscopies in DMSO-d$_6$. On addition of one equiv of **SC4** to a DMSO-d$_6$ solution containing **PV** (*ca.* 1.0×10^{-2} M), only the protons of viologen moiety exhibit visible up-field shifts, which gives evidence that the viologen group is included by **SC4** and the 2,2′-bipyridine unit is not affected by **SC4** cavity. Furthermore, the differences in $\Delta\delta$ values ($H_e > H_{\alpha1} > H_{\beta1} > H_{\beta2} > H_{\alpha2}$) indicate that the viologen group of **PV** is immersed into the cavity of **SC4** in its axial orientation. 2D NOESY NMR experiments confirm the inclusion geometry of the host–guest complex (Fig. 2). The NOE cross-peaks between the aromatic protons of **SC4** and the protons



Scheme 1. Synthetic route of **RPV⊂SC4**.

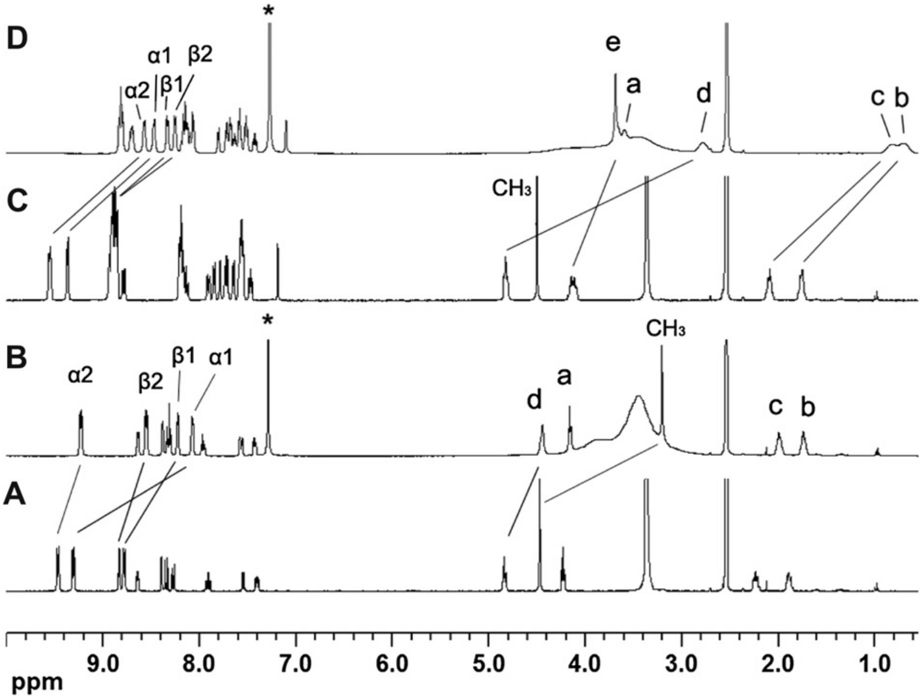


Fig. 1. ^{1}H NMR spectra (400 MHz in DMSO-d_6 at 298 K) of (A) **PV**; (B) 1:1 adduct of **PV** and **SC4**; (C) **RPV**; (D) self-assembly complex **RPV**⊂**SC4**. " * " represents the signal of aromatic protons of **SC4**.

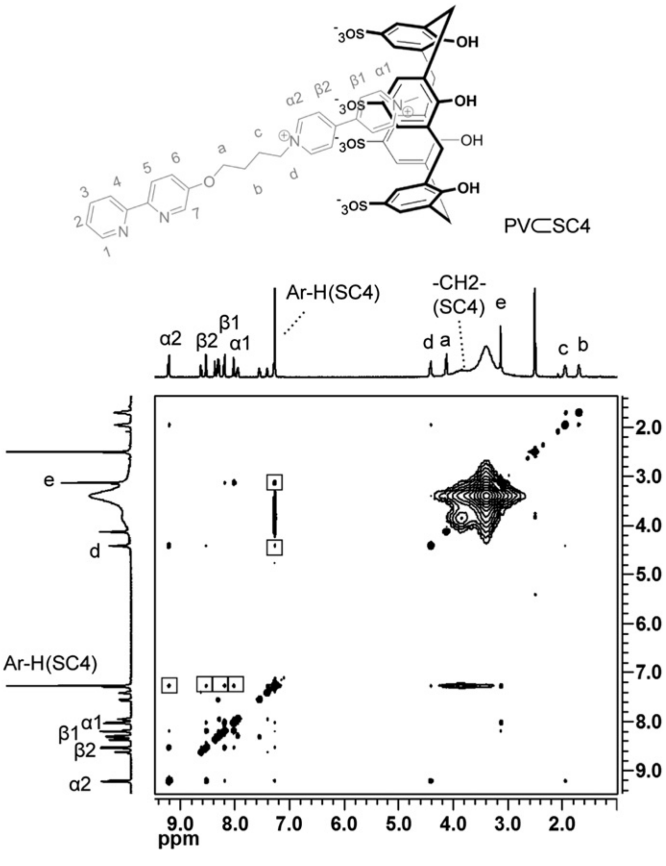
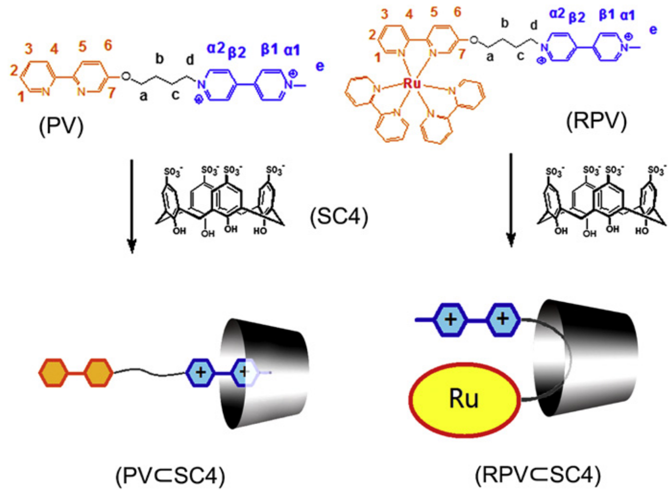


Fig. 2. 2D NOE ^{1}H NMR spectrum of **PV**⊂**SC4** in DMSO-d_6 recorded at 298 K.

of **PV** (H_e, $H_{\alpha 1}$, $H_{\beta 1}$, $H_{\beta 2}$, $H_{\alpha 2}$ and H_d) suggest that viologen moiety is located inside the **SC4** cavity. Neither the NOE correlations between 2,2′-bipyridine protons and the aromatic protons of **SC4** nor the NOE correlations between viologen moiety and the methylene protons of **SC4** are observed. Therefore, according to the data mentioned above, the binding manner of **SC4** with **PV** in DMSO-d_6 is determined. As shown in Scheme 2, only the end part of viologen group of **PV** is included into the **SC4** cavity, but does not penetrate through the cavity, just like an arrow hitting the target.

3.2. Binding manner of SC4 with RPV

Based on such a steady host–guest system, a new compound **RPV** (2,2′-bipyridine ruthenium coordinately linked with **PV**) is



Scheme 2. The deduced binding manners of **PV** with **SC4** and U-type complex formed between **RPV** and **SC4** in H_2O. The anions are omitted here for clarity.

synthesized to study the competitive interactions brought by metal ions. According to early reports, tris-chelates of transition metal ions are able to form outer-sphere associations with water-soluble calixarenes, this kind of self-assembly behaviors are confirmed both in solution and in solid state (X-ray data). Surprisingly, after addition of one equiv of **SC4** to an aqueous solution of **RPV** (*ca.* 1.0×10^{-2} M), red precipitates are formed immediately (no precipitates are formed after mixing **SC4** and **PV** in H_2O). The collection products are fully characterized by high resolution mass spectrometry and NMR spectroscopy. The ESI-MS spectra in both negative mode (Fig. S1) and positive mode (Fig. S2) confirm the formation of a 1:1 adduct. ^{1}H NMR spectroscopy further gives the evidence that a 1:1 inclusion complex **RPV**⊂**SC4** was formed (Fig. 1C, D).

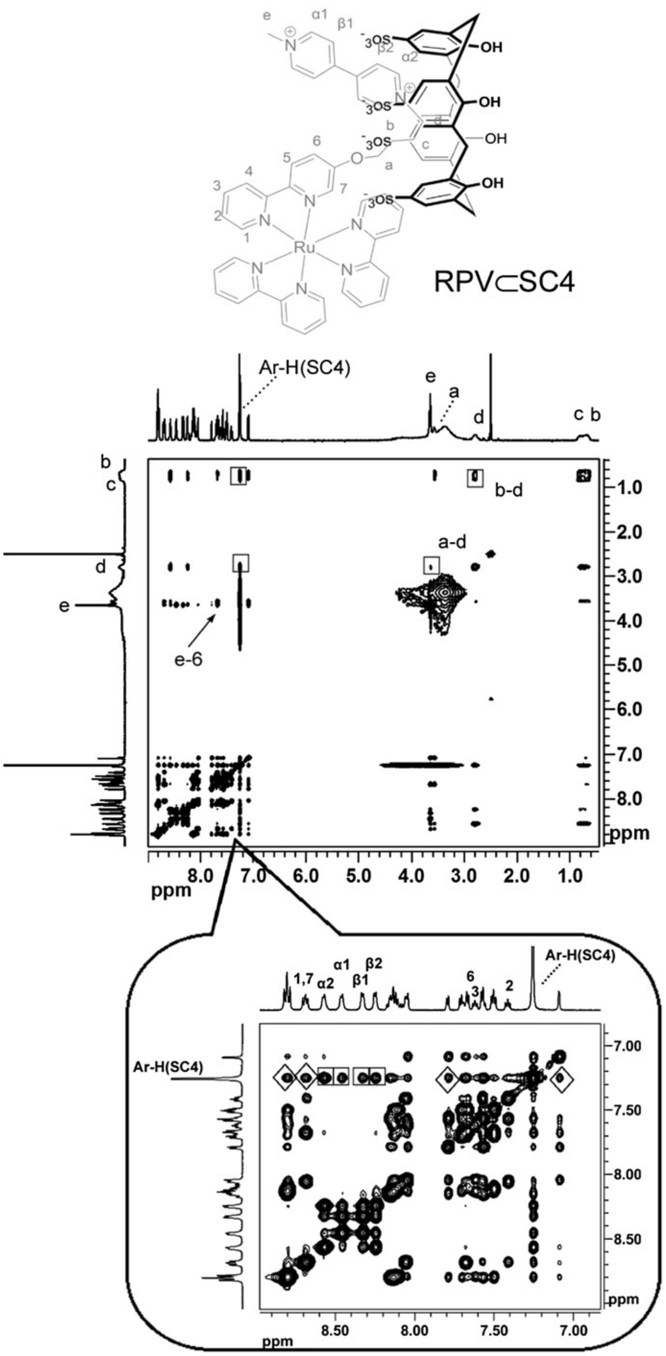


Fig. 3. 2D NOE ^{1}H NMR spectrum of **RPV**⊂**SC4** in DMSO-d_6 recorded at 298 K (poor solubility in other deuterated solvents).

As shown in Fig. 1D, both the alkyl chain protons and the aromatic ones of viologen motif of the self–assembly complex **RPV**⊂**SC4** have an extensive up-field shifts comparing with the dumbbell **RPV** (Fig. 1C). However, the shifts of the proton signals of the alkyl bridge (H_a, H_b, H_c and H_d) are much larger than those aromatic ones ($H_{\alpha1}$, $H_{\beta1}$, $H_{\beta2}$ and $H_{\alpha2}$) of the viologen fragment. These results suggest that both the alkyl chain and the viologen moiety are influenced by the **SC4** cavity. Moreover, the alkyl bridge is located in a deeper position of the **SC4** cavity. The protons of three 2,2′-biprydine groups exhibit slightly up-field shifts, which indicates that the Ru(bpy)$_3$ is close to the upper rim of **SC4** and only partially included into the cavity. Also, 2D NOESY NMR experiments were performed to investigate the binding manner of **SC4** with **RPV**. As shown in Fig. 3, the spectra exhibit a series of cross-peaks representing the correlations between **SC4** with both viologen and Ru(bpy)$_3$; The NOEs between the alkyl chain protons (H_b, H_c and H_d) and aromatic ones of **SC4** are found; There is also another obvious NOE correlation between the methyl protons H_e of viologen and the aromatic proton H_6 of Ru(bpy)$_3$ unit at the other end of **RPV**, indicating that two groups are very close to each other; Furthermore, NOE correlations between the head protons of the alkyl chain and the tail ones are found (H_a–H_d, H_b–H_d), which means the alkyl bridge is bent to a U-type shape. It is noteworthy that aromatic protons of **SC4** show NOE correlations with almost all protons of Ru(bpy)$_3$ owing to the overlapping of some signals, but as reported previously, the **SC4** cavity is too small for deep inclusion of the Ru(bpy)$_3$ group or viologen unit [31].

The self-assembly experiments are also performed in DMSO-d_6 solution to avoid the precipitates formation in aqueous solution, which gives the same results. And the 1:1 binding ratio is further confirmed by UV titration (Fig. 4). The binding constants are determined as $K = 1.7 \times 10^3$ M^{-1} by NMR titration (Fig. 5, more details see supplementary material) [32]. Therefore, the data mentioned above evidently indicates that **SC4** and **RPV** form a 1:1 U-type binding complex in both aqueous solution and DMSO solution, where the Ru(bpy)$_3$ and one positive charge of viologen bind closely with the upper rim of **SC4**, and the alkyl chain between them is included into the cavity of **SC4** (see Scheme 2).

3.3. Competitive interactions between Ru(bpy)$_3$ and viologen

A series of experiments are carried out to investigate the competitive interactions between Ru(bpy)$_3$ group and viologen unit. The binding manner of a very simple methyl viologen dication

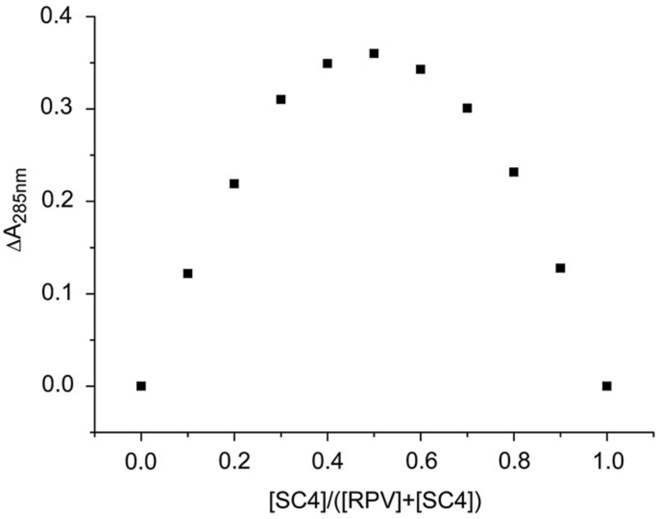


Fig. 4. Job plot of **SC4/RPV** complex in DMSO at 298 K. C(**SC4**)+C(**RPV**) = 2.7×10^{-5} M.

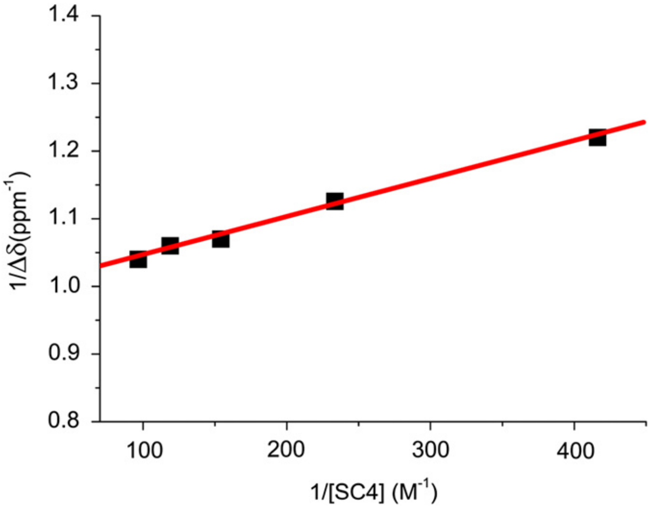


Fig. 5. Benesi-Hildebrand treatment of the ^{1}H NMR titration (400 MHz in DMSO-d$_6$ at 298 K) data to get the association constant between **RPV** and **SC4**. The concentration of **RPV** is kept at 2.10 mM, upon addition of excess **SC4** (2.40–10.33 mM), the chemical shifts of the methyl protons are documented. All the data are obtained at the absolute steady state, the value of association constant is determined as $K = 1.7 \times 10^3$ M^{-1}.

(**MV**) and **SC4** in both solution and solid state have been fully investigated in previous works [30].

After addition of one equiv of Ru(bpy)$_3$Cl$_2$•6H$_2$O to a DMSO-d$_6$ solution of **MV**⊂**SC4**, both the down-field shifts of the protons of methyl viologen (**MV**) and the slightly up-field shifts of the protons of Ru(bpy)$_3$ are observed (Fig. S3), which means **MV** is expelled to a shallow position of the **SC4** cavity by Ru(bpy)$_3$ but is still under the influence of the cavity. It does not show any changes in ^{1}H NMR spectra when mixing equal equivalent of Ru(bpy)$_3$Cl$_2$•6H$_2$O and **MV** to the DMSO-d$_6$ solution. Once **SC4** is added, the same spectra changes can be detected, which confirms the formation of a ternary assembly complex.

2D NOE NMR experiments further give the evidences that both Ru(bpy)$_3$Cl$_2$•6H$_2$O and **MV** are cooperatively interact with **SC4**. Without the addition of **SC4**, no NOE correlations between Ru(bpy)$_3$ and **MV** can be observed. In the ternary complex, 2D NOE NMR spectrum exhibits a series of cross-peaks representing the correlations between Ru(bpy)$_3$, **MV** and **SC4**. But different from **RPV**⊂**SC4**, the NOEs between Ru(bpy)$_3$ and **MV** are not found (Fig. S4), this can attribute to the absence of alky bridge which links Ru(bpy)$_3$ and **MV** tightly.

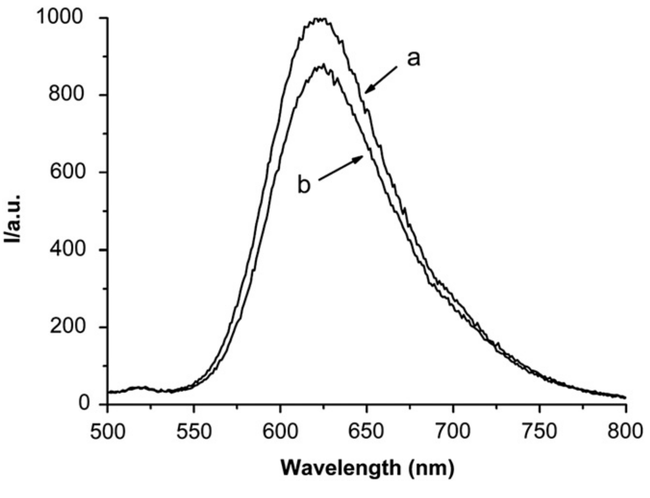


Fig. 6. Luminescence emission spectra of (a) **RPV** (1.00×10^{-5} M); (b) addition of 1 equiv of **SC4**. ($\lambda_{ex} = 450$ nm, $\lambda_{max} = 625$ nm, DMSO, 298 K).

These results evidently demonstrate that in the self-assembly system of **RPV**⊂**SC4**, both Ru(bpy)$_3$ unit and viologen motif show strong interactions (including electrostatic interactions, hydrophobic interactions, and charge transfer interactions [33]) with **SC4**, meanwhile, Ru(bpy)$_3$ group shows competitive interactions with viologen unit.

3.4. Luminescence properties

Addition of **SC4** to a DMSO solution of **RPV** results in the luminescence quenching of **RPV**. After addition of one equiv of **SC4**, an obvious decrease can be detected in the luminescence intensity at $\lambda_{max} = 625$ nm (Fig. 6), a total 13% luminescence intensity decrease could be observed, which is consistent with the previous works [27,33].

4. Conclusion

In summary, a novel Ru(bpy)$_3$–viologen guest **RPV** was prepared and a 1:1 U-type complex **RPV**⊂**SC4** based on **SC4** and Ru(bpy)$_3$-viologen guest **RPV** was constructed. The U-type self-assembly complex has been fully characterized by ^{1}H NMR, 2D ^{1}H NOE NMR and mass spectrometry. In this host–guest system, the competitive interactions between Ru(bpy)$_3$ and viologen part are confirmed. This work provides a new binding manner of host–guest systems based on ruthenium, viologen and ***p***-sulfonatocalix[4]arene, which can be used to design new supramolecular structures potentially valuable for artificial supramolecular folding assembly to mimic biological systems.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.dyepig.2012.04.020.

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