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An efficient ruthenium tris(bipyridine)-based luminescent chemosensor for recognition of Cu(II) and sulfide anion in water†

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A novel efficient luminescent chemosensor based on a 1,4,7,10-tetraazacyclododecane (cyclen)-tethered $Ru(bpy)_3^{2+}$ derivative (Ru–cyclen) has been synthesized and characterized. It displays an ON–OFF-type luminescence change with excellent selectivity towards Cu(II) amongst 16 metal ions in 100% aqueous solution. The binding stoichiometry of Ru–cyclen with Cu^{2+} was established by Job plot analysis and mass spectral evidence. Furthermore, the *in situ* generated Ru–cyclen–Cu ensemble recovered luminescence in the presence of S^{2-}, indicating an 'OFF–ON'-type sensing process. Similar phenomena were not observed with other common anions and biothiols, making it a high selective sulfide probe. Finally, the sensing mechanism is confirmed to be displacement approach by NMR, mass and emission spectrometry.

Introduction

Being a toxic traditional pollutant, the sulfide anion has a huge environmental impact and is generated not only from industrial process but also biological metabolism.[1] Continuous exposure to sulfide ions can damage mucous membranes and cause unconsciousness and respiratory problems.[2,3] Once protonated, HS– or H_2S becomes more toxic. At low concentrations, H_2S can induce dizziness and at higher concentrations it can result in permanent damage of brain tissues, or even suffocation.[2–5] The protonated sulfide has also attracted attention due to its role in various physiological processes. For example, recent studies have identified H_2S as the third most biologically active gas following NO and CO.[6,7] It is involved in the mediation of neurotransmission,[8] inhibition of insulin signaling,[9] reduction in blood pressure,[10] relaxation of vascular smooth muscles, and regulation of inflammation.[11] Therefore, development of quick and sensitive method for sulfide detection in aqueous media and in biological systems is of great importance.

The most commonly used methods for selective sulfide anion detection, include chemiluminescence,[12] inductively coupled plasma atomic emission spectroscopy,[13,14] electrochemical methods,[15] ion chromatography[16] and titration.[17] Fluorogenic methods in conjunction with suitable probes have received great attention because of their simple operation, high sensitivity and selectivity. Until now, few selective sensors for sulfide have been reported[18,19] relative to other widely investigated anions such as F^- and CN^-.[20–22] Among these sensors, two main types are involved in the pathway of sulfide sensing. One is termed a 'reactive sensor' based on irreversible chemical reactions and the other is a 'competitive sensor' based on metal–anion affinity. Most organic reactions are time-consuming and reaction conditions are relatively strict, which limits their application. Encouraged by biologically compatible conditions, reversible selective sulfide sensors based on copper sulfide affinity are attractive to us,[23–26] since CuS is a well-known stable and low solubility compound with a K_{sp} value of 6.3×10^{-36}. A few fluorescence sensors for sulfide have been reported,[21–26] however, multifunctional probes with sufficient selectivity over other biothiols in aqueous media are still rare and there is a need for further investigation.

1,4,7,10-Tetraazacyclododecane (cyclen) is an azamacrocyclic compound which has proved to be a versatile metal chelator with excellent water-solubility.[27,28] Moreover, it has been successfully applied in biology, recognition and imaging fields.[29–32] In this work it is employed as an ionophore. Additionally, ruthenium(II) tris-bipyridine complexes have favorable photochemical and photophysical properties, including good photo-stability, long lifetimes, high quantum yields and long Stokes shifts. These complexes have potential applications as probes, sensors and imaging agents as different cell localizations can be obtained by changing the substituents on the ligands.[33–37] Herein, it behaves as chromophore. Therefore, in this paper, a water-soluble ruthenium tris(bipyridine)-based chemosensor by incorporating the cyclen unit

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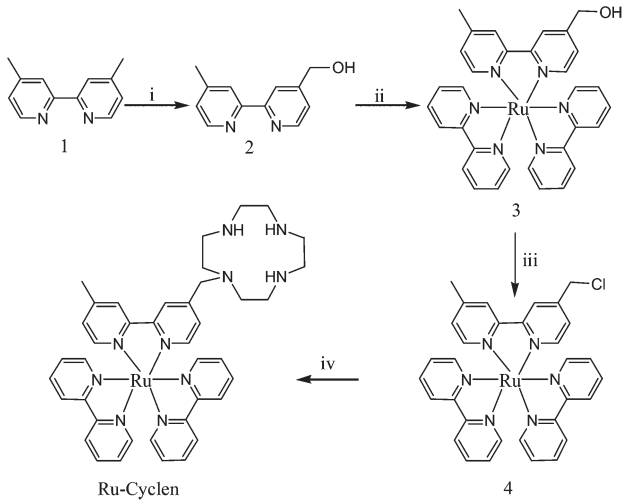


Scheme 1 Synthesis of complex Ru–cyclen (i) (1) SeO_2, dioxane, reflux 24 h; (2) $NaBH_4$, MeOH, rt 1 h; (ii) *cis*-$Ru(bpy)_2Cl_2$, EtOH–H_2O (1 : 1), reflux, 4 h; (iii) $SOCl_2$, reflux, 4 h; (iv) cyclen, Et_3N, CH_3CN, reflux, 4 h.

(Ru–cyclen, Scheme 1) was designed and synthesized. Consequently, Ru–cyclen exhibits 'ON–OFF–ON' mode luminescence change with alternate addition of Cu^{2+} and S^{2-} in 100% aqueous media. Moreover, it has excellent selectivity toward Cu(II) amongst 16 metal ions and the *in situ* generated Ru–cyclen–Cu ensemble is found to be a high sensitive and selective sulfide probe.

Result and discussion

Synthesis and characterisation

The synthesis of Ru–cyclen was carried out *via* a four-step reaction. (Scheme 1) The target complex Ru–cyclen was readily prepared by reaction of an excess of cyclen with chloromethyl substituted ruthenium tris(bipyridine) (**4**), which was obtained by halogenation of the corresponding hydroxylmethyl analogue (**3**) in the presence of $SOCl_2$. Complex **3** was prepared by reaction of *cis*-$Ru(bpy)_2Cl_2$ with the appropriate 4-hydroxymethyl-4′-methyl-2,2′-bipyridine (**2**) in a mixture of ethanol and water under reflux. The key intermediate **2** was synthesized by oxidation of the easily accessible 4,4′-dimethyl-2,2′-bipyridine (**1**) using SeO_2 in dioxane and subsequent reduction with $NaBH_4$ in methanol according to the method of Sun *et al.* All the ruthenium complexes were purified by crystallization and well characterized by ^1H NMR, ^{13}C NMR and TOF-MS (Fig. S11, S14–21, ESI†) complex Ru–cyclen showed an ESI^+-MS molecular ion at *m*/*z* 384.1453, consistent with the formula $C_{40}H_{46}N_{10}Ru$.

Luminescent response of Ru–cyclen to various metal ions

The target complex Ru–cyclen is water soluble, which makes it useful for practical applications. The UV-vis absorption spectrum of Ru–cyclen was measured in 100% aqueous solution at pH = 7.0. As shown in Fig. S1 (ESI†), the absorption spectrum of free Ru–cyclen is extremely similar to that of the parent complex $[Ru(bpy)_3]^{2+}$, consisting of a strong sharp band at 286 nm (π–π* transition of bipyridine), two less intense bands around 244 nm and 450 nm (MLCT transitions). Additionally, almost no significant change in the UV-vis absorption spectra of Ru–cyclen was observed upon addition of various amounts of Cu^{2+} ions (Fig. S1, ESI†). Thus, the Cu^{2+} complexing properties with Ru–cyclen had to be investigated only by emission spectra in the following experiments.

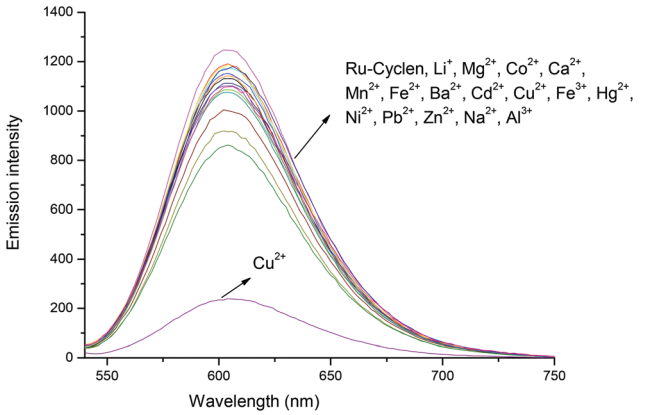


Fig. 1 Luminescence emission spectra of Ru–cyclen (10 μM) upon addition of 10 equiv. of various metal ions (Li^+, Na^+, Mg^{2+}, Al^{3+}, Co^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Ba^{2+}, Cd^{2+}, Fe^{3+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} in 100% aqueous solution.

To evaluate the sensing properties of Ru–cyclen, the emission was studied using various metal ions in 100% water solution at pH = 7.0 upon excitation at 450 nm (Fig. 1 and Fig. S2, ESI†). The free Ru–cyclen exhibited a broad emission peak at a max. of 604 nm. Upon addition of 10 equiv. of Li^+, Na^+, Mg^{2+}, Al^{3+}, Co^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Ba^{2+}, Cd^{2+}, Fe^{3+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, no marked change in the emission profile was noted. However, introduction of 1 equiv. of Cu^{2+} elicited a large decrease in the emission intensity at 604 nm and the quenching efficiency was nearly 80%. Such good selectivity of Ru–cyclen toward Cu^{2+} amongst 16 metal ions may be due to the good thermodynamical stability[38] or particularly large formation constants of the resulting Cu(II)–cyclen complex determined by glass electrode potentiometric titration or spectroscopic titration.[39–41]

To learn more about the responsive nature of Ru–cyclen to Cu^{2+}, the complex was titrated with Cu^{2+} ions in varying concentrations in 100% aqueous solution (Fig. 2). The emission intensity gradually decreased with the addition of increasing concentrations of Cu^{2+} ions and became saturated at about 1 equiv. of Cu^{2+} ions. In good agreement with this finding, the Job plot and ESI-MS (Fig. S3 and S12, ESI†) also show the formation of a 1 : 1 binding mode between Ru–cyclen and Cu^{2+}. Based on the 1 : 1 binding mode, the binding constants (*K*) with Cu^{2+} derived from the luminescence titration was calculated to be 2.36×10^4 with a good correlation coefficient (R^2 = 0.997) using the Bensi–Hidebrand plot (Fig. S4, ESI†).[25,42] The luminescence response of Ru–cyclen toward Cu^{2+} was influenced by pH and the maximal signal was observed in the

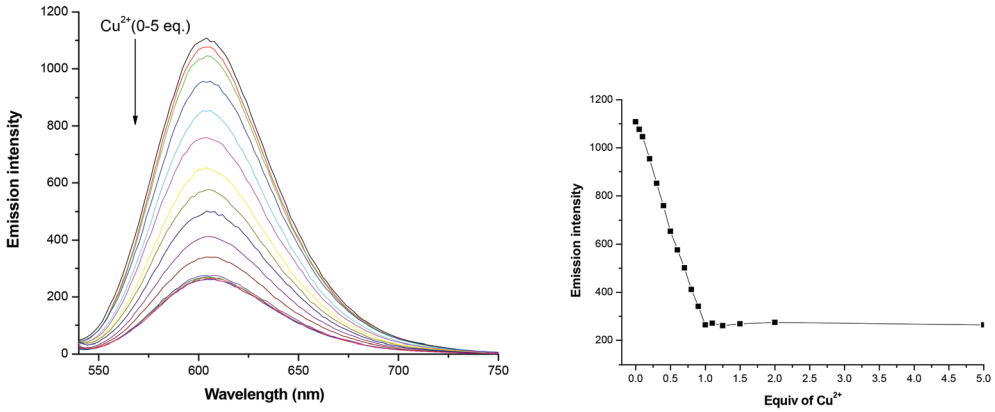


Fig. 2 Changes in the luminescence emission spectrum of Ru–cyclen (10 μM) with increasing concentrations of Cu^{2+} ions (0–5 equiv.) in 100% aqueous solution (left). The emission intensity changes at 604 nm of Ru–cyclen (10 μM) with the amount of Cu^{2+} ions (right).

pH range of 5–11 (Fig. S5, ESI†), indicating that Ru–cyclen can be used to sense Cu^{2+} over a wide pH range. From the Cu^{2+} concentration-dependent luminescence change, the detection limit[43–45] of Ru–cyclen for the determination of Cu^{2+} was calculuated to be 5.4×10^{-6} M (Fig. S6, ESI†). In comparison with the limit of 2×10^{-5} M copper in drinking water determined by EPA (the U.S. Environmental Protection Agency) and with such a high selectivity toward Cu^{2+} rather than other metal ions mentioned above, Ru–cyclen could be used as a highly sensitive and selective luminescent 'ON–OFF' probe for Cu^{2+}.

Luminescence response of the *in situ* generated Ru–cyclen–Cu ensemble to various anions

As described above, when the metal ion of the complex was replaced by an anion, based on the metal-anion affinity, chelating ligands could release the metal and consequently recognize the anions. Accordingly, it is reasonable to hypothesize that in this paper the *in situ* generated Ru–cyclen–Cu ensemble could be a promising 'OFF–ON'-type luminescent sensor for the S^{2-} anion, which could bind with Cu^{2+} to form stable CuS, resulting in the release of Ru–cyclen. To test this idea, the *in situ* generated Ru–cyclen–Cu ensemble was titrated with S^{2-} anions in 100% aqueous media. As shown in Fig. 3, the emission intensity increased with the addition of S^{2-} and the early part of sigmoidal titration with sulfide appears saturated at 15 equivalents of S^{2-}, which may be due to the multiple equilibria between Ru–cyclen, Cu^{2+} and added S^{2-},[46] or maybe the formation of Cu_xS_x rings in solution, which are the building blocks for aqueous CuS molecular clusters, leading to CuS precipitation.[47] From the sulfide concentration-dependent luminescence change, the detection limit[43–45] of the Ru–cyclen–Cu ensemble for the determination of S^{2-} was estimated to be 3.7×10^{-5} M (Fig. S7, ESI†). Furthermore, no obvious luminescence change was observed in response to HEPES buffer solution under the same conditions (Fig. S8, ESI†) however the addition of S^{2-} resulted in a dramatic enhancement of the intensity. Therefore, the *in situ* generated Ru–cyclen–Cu ensemble can also be employed as a S^{2-} sensor under physiological conditions.

To investigate the selectivity of the *in situ* generated Ru–cyclen–Cu ensemble, the response of Ru–cyclen–Cu towards physiologically and environmentally important anions were evaluated (Fig. 4). It was found that 100 equiv. of common anions (*e.g.* F^-, Cl^-, Br^-, I^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$, SO_3^{2-}, $S_2O_3^{2-}$, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, OAC^-, ClO_4^-, NO_3^-) and

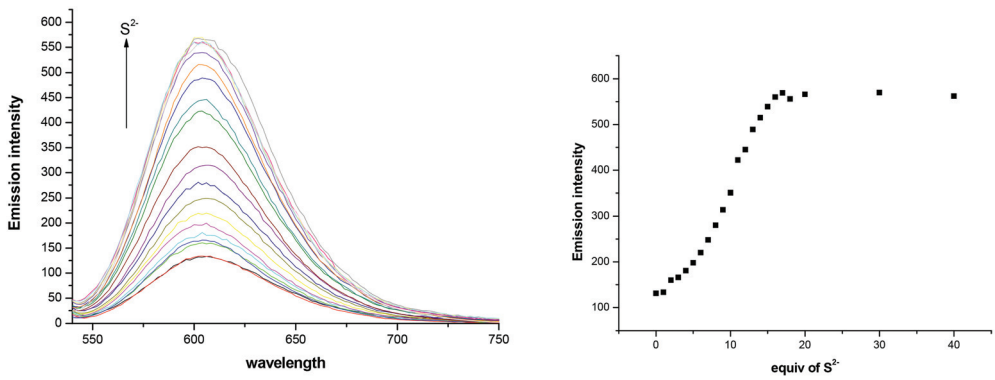


Fig. 3 Changes in the luminescence emission spectrum of Ru–cyclen–Cu system with increasing concentrations of sulfide ions (0–200 μM) in 100% aqueous solution. [Ru–cyclen–Cu] = 5 μM (left). Emission intensity at 604 nm as a function of S^{2-} concentration (right).

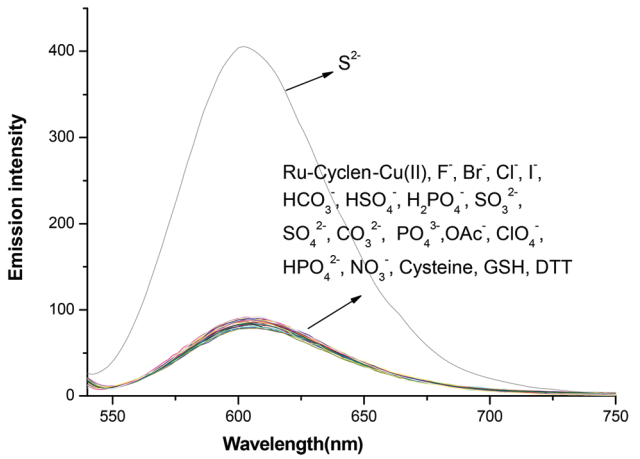


Fig. 4 Emission spectra of Ru–cyclen–Cu (3 μM) ensemble in the presence of various anions and biothiols (20 equiv. for S^{2-}; 100 equiv. for F^-, Cl^-, Br^-, I^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$, SO_3^{2-}, $S_2O_3^{2-}$, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, OAC^-, ClO_4^-, NO_3^-; 1000 equiv. for GSH, DTT, and L-cysteine) in 100% aqueous solution.

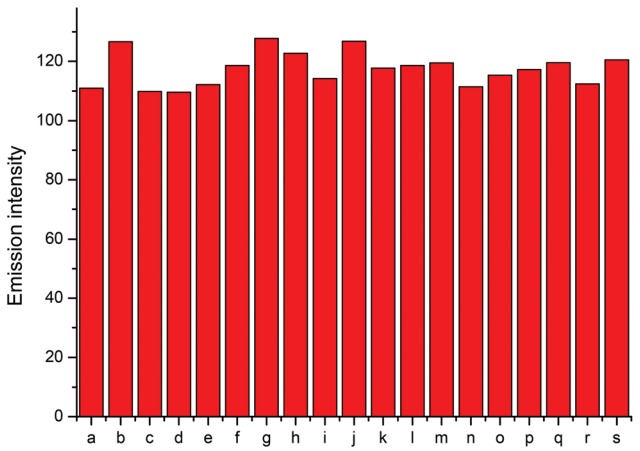


Fig. 5 Emission intensity changes of Ru–cyclen–Cu(II) (1 μM) with sulfide anions (20 μM) in the presence of various of anions or biothiols (100 μM) in water. Key: (a) S^{2-}; (b) S^{2-} + F^-; (c) S^{2-} + Cl^-; (d) S^{2-} + Br^-; (e) S^{2-} + I^-; (f) S^{2-} + CO_3^{2-}; (g) S^{2-} + HCO_3^-; (h) S^{2-} + $H_2PO_4^-$; (i) S^{2-} + SO_3^{2-}; (j) S^{2-} + $S_2O_3^{2-}$; (k) S^{2-} + SO_4^{2-}; (l) S^{2-} + PO_4^{3-}; (m) S^{2-} + OAc^-; (n) S^{2-} + ClO_4^-; (o) S^{2-} + HPO_4^{2-}; (p) NO_3^-; (q) S^{2-} + cysteine; (r) S^{2-} + GSH; (s) S^{2-} + DDT.

1000 equiv. of biological biothiols, including reduced glutathione (GSH), dithiothreitol (DTT) and L-cysteine did not cause any marked luminescence change. In contrast, 20 equiv. of S^{2-} led to a pronounced enhancement of the emission intensity. Thus, the *in situ* generated Ru–cyclen–Cu ensemble can behave as a high selective luminescent 'OFF–ON' sensor for S^{2-}.

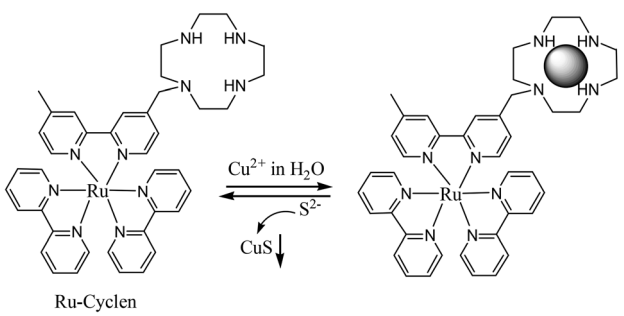
Additionally, to explore whether the Ru–cyclen–Cu ensemble could maintained its sensing response to S^{2-} under the potential competition of other relevant anions, it (1 μM) was treated with sulfide anions (20 μM) in the presence of various anions or biothiols (100 μM) in water. As shown in Fig. 5, all the relevant anions tested have virtually no influence on the fluorescence detection of sulfide anions, suggesting that the Ru–cyclen–Cu ensemble could be useful for selectively sensing sulfide even involving these relevant anions. The luminescence response of the Ru–cyclen–Cu ensemble to S^{2-} is related to pH and the result indicates it can be employed in a wide pH range (pH = 6–11) (Fig. S9, ESI†).

The proposed sensing mechanism

To determine the sensing mechanism, both NMR and mass spectrometry were used to study the sensing process. When addition of 1 equiv. of Cu^{2+} ions to Ru–cyclen in D_2O, the ^1H NMR spectrum was very broad due to the complexation of paramagnetic Cu^{2+} to Ru–cyclen. Whereas, further addition of 20 equiv. of sulfide anions to the Ru–cyclen–Cu ensemble led to a well-resolved spectrum, which is almost identical to that of free Ru–cyclen (Fig. S10, ESI†). Additionally, the ESI-MS spectrum of free Ru–cyclen showed an intense peak at *m*/*z* 384.1453 corresponding to $[Ru\text{–cyclen}]^{2+}$ (Fig. S11, ESI†). After treatment of Ru–cyclen with Cu^{2+} in aqueous media, new peaks at 414.5938 and 433.5816 corresponding to $[Ru\text{–cyclen} + Cu^{2+} - 2H^+]^{2+}$ and $[Ru\text{–cyclen} + Cu^{2+} + Cl^- - H^+]^{2+}$ respectively appeared and the intense peak at *m*/*z* 384.1453 disappeared (Fig. S12, ESI†). However, further addition of sulfide anions resulted in the disappearance of the peaks at *m*/*z* 414.5938 and 433.5816 and the reappearance of the peak at *m*/*z* 384.1369 (Fig. S13, ESI†). Therefore, the studies of NMR, mass spectrometry, and the emission spectrometry indicate that the sensor probably functions by a displacement mechanism (Scheme 2).

Conclusions

In summary, a water-soluble luminescent sensor Ru–cyclen has been synthesized and characterized, for the sequential recognition of Cu(II) and sulfide anions based on the displacement approach . Ru–cyclen exhibits high selectivity and sensitivity for Cu^{2+} in water, which can serve as a luminescent 'ON–OFF' mode sensor. Subsequently, the *in situ* generated Ru–cyclen–Cu ensemble is a good sensor for S^{2-} over other common anions and biothiols in the same media and has the ability to work well over a wide pH range. Thus, it can behave



Scheme 2 The proposed sensing mechanism of Ru–cyclen for Cu^{2+} and S^{2-} in H_2O.

as a potential 'OFF–ON' sensor for S^{2-}. Above all, an 'ON–OFF–ON' mode luminescence recognition system has been constructed and it will be potentially useful in physiological and environmental applications for sulfide anion detection.

Experimental

General

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance II 500 MHz spectrometer in solution (DMSO-d_6, D_2O or $CDCl_3$) with tetramethylsilane as the internal standard. Mass spectra were measured using Bruker microTOF-Q. UV-vis absorption spectra and photoluminescence spectra were obtained on a SHIMADZU UV-2550 spectrophotometer and a HITACHI F-2500 fluorescence spectrometer respectively. All chemicals were purchased from commercial corporations and used without further purification except for methanol, which was distilled from magnesium. *cis*-$[Ru(bpy)_2Cl_2]2H_2O$[48] was prepared according to the literature procedures.

4-Hydroxymethyl-4′-methyl-2,2′-bipyridine (2)

The compound **2** was prepared according to the procedure previously described by Sun *et al.*[49] with a slight modification. To a solution of 4,4′-dimethyl-2,2′-bipyridine (0.3 g, 1.65 mmol) in 1,4-dioxane (20 mL), SeO_2 (0.3 g, 0.27 mmol) was added, then the mixture was heated to reflux for 24 h. The reaction mixture was allowed to cool to room temperature and the black solid was filtered. The solvent was removed under reduced pressure. The resulting pink solid was re-dissolved in chloroform, and the suspension was filtered to remove selenium by-products. After three successive dissolution and filtration treatments, the crude product (0.2 g) was obtained. The resulting solid was suspended in methanol (15 mL) at 0 °C, and sodium borohydride (0.05 g) was added gradually. The mixture was raised to room temperature and stirred for one hour. Saturated Na_2CO_3 solution (1 mL) was added to the mixture and the crude product was extracted with chloroform (3 × 10 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated. 4-Hydroxymethyl-4′-methyl-2,2′-bipyridine (0.15 g, 70%) was obtained after purification by silica gel column chromatography with MeOH–CH_2Cl_2 as eluent (1 : 10). All analytical data were in agreement with those reported by Geren *et al.*[50]

Bis(2,2′-bipyridine)-ruthenium-4′-hydroxylmethyl-4-methyl-2,2′-bipyridine hexafluorophosphate (3)

Bis-2,2′-bipyridyl ruthenium dichloride (55 mg, 0.11 mmol) and 4-hydroxymethyl-4′-methyl-2,2′-bipyridine (**1**) (22 mg, 0.11 mmol) were resolved in the solution of EtOH and H_2O (20 mL, 1 : 1). The mixture was refluxed for 4 h under argon. The solvent was removed by rotary evaporation and the residue was dissolved in 5 mL of water, saturated NH_4PF_6 was added. The resulting precipitate was filtered off, washed with water, and dried in vacuum to give the red-orange solid. The solid was re-dissolved a minimum volume (2 mL) of methanol and the mixture was filtered to remove insoluble products. The solvent was evaporated under reduced pressure and the resulting solid was crystallized with methanol and ether, filtered, and dried in vacuum. The target complex **3** was obtained in a yield of 75% (71 mg). ^1H NMR (d_6-DMSO) δ 2.53 (s, 3H), 4.74 (s, 2H), 7.37 (d, 1H, J = 5.0 Hz), 7.46 (d, 1H, J = 6.5 Hz), 7.51–7.55 (m, 5H), 7.65 (d, 1H, J = 6.0 Hz), 7.74 (t, 4H, J = 6.0 Hz), 8.17 (t, 4H, J = 8.0 Hz), 8.71 (s, 1H), 8.74 (s, 1H), 8.83 (d, 4H, J = 8.5 Hz). ^{13}C NMR (CD_3CN) δ 19.98, 61.23, 120.91, 123.98, 124.39, 124.84, 127.27, 128.13, 137.42, 150.36, 150.51, 150.80, 151.30, 151.44, 153.89, 156.25, 156.56, 156.87. TOF MS ES^+ (m/z) 307.0775 $[M - 2PF_6^-]^{2+}$, calculated. 307.0683.

Bis(2,2′-bipyridine)-ruthenium-4′-chloromethyl-4-methyl-2,2′-bipyridine hexafluorophosphate (4)

Bis(2,2′-bipyridine)-ruthenium-4′-hydroxylmethyl-4-methyl-2,2′-bipyridine hexafluorophosphate (**3**) (45 mg, 0.05 mmol) was reflux in $SOCl_2$ (2 mL) for 4 h under argon. The solvent was removed under reduced pressure and the resulting red-orange solid was crystallized methanol and ether, filtered, and dried in vacuum to afford the final product **4** (45 mg, 98%). ^1H NMR (d_6-DMSO) δ 2.53 (s, 3H), 4.96 (s, 2H), 7.40 (d, 1H, J = 6.0 Hz), 7.52–7.58 (m, 6H), 7.72 (d, 1H, J = 7.0 Hz), 7.75 (t, 4H, J = 6.0 Hz), 8.17 (t, 4H, J = 6.0 Hz), 8.76 (s, 1H), 8.84 (d, 4H, J = 8.0 Hz), 8.90 (d, 1H, J = 1.5 Hz). ^{13}C NMR (CD_3CN) δ 20.51, 43.18, 123.23, 124.08, 125.17, 126.43, 127.36, 128.42, 137.58, 148.31, 150.48, 150.61, 151.40, 151.52, 151.64, 155.89, 156.80, 156.90, 157.36. TOF MS ES^+ (m/z) 316.0646 $[M - 2PF_6^-]^{2+}$, calculated. 316.0571.

Bis(2,2′-bipyridine)-ruthenium-4′-[(1,4,7,10-tetraazacyclododecane)-1-methyl]-4-methyl-2,2′-bipyridine hexafluorophosphate (Ru–cyclen)

Bis(2,2′-bipyridine)-ruthenium-4′-chloromethyl-4-methyl-2,2′-bipyridine hexafluorophosphate (**4**) (36 mg, 0.04 mmol) was dissolved in 2 mL of CH_3CN. 1,4,7,10-Tetraazacyclododecane (52 mg, 0.3 mmol) and Et_3N (30 mg, 0.3 mmol) were added to the solution, and the mixture was refluxed for 4 h under argon. After removal of the solvent by rotary evaporation, the residue was subjected to add 5 mL of water and additional 32 mg of NH_4PF_6 to afford a red-orange solid, which was collected by filtration, washed with water (3 × 10 mL) and dried. The product was crystallized with methanol and ether to give **4** (30 mg, 78%). ^1H NMR (D_2O) δ 2.42 (s, 3H), 2.73–2.95 (br, 16H), 3.88 (s, 2H), 7.13 (d, 1H, J = 5.0 Hz), 7.23–7.27 (m, 5H), 7.53 (d, 1H, J = 6.0 Hz), 7.69–7.73 (m, 5H), 7.92–7.95 (m, 4H), 8.28 (s, 1H), 8.32 (s, 1H), 8.42 (d, 4H, J = 8.0 Hz). ^{13}C NMR (CD_3CN) δ 20.04, 42.81, 44.42, 45.82, 47.62, 58.37, 123.82, 123.92, 123.95, 124.83, 127.24, 128.14, 137.41, 150.16, 150.49, 151.02, 151.20, 151.34, 151.39, 156.00, 156.69, 156.75. TOF MS ES^+ (m/z) 384.1470 $[M - 2PF_6^-]^{2+}$, calculated. 384.1475; 457.1237 $[M - PF_6^- + H^+]^{2+}$, calculated. 457.1283.

Acknowledgements

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