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PAPER

Selective anion sensing by a ruthenium(II)–bipyridyl-functionalized tripodal tris(urea) receptor†

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A tripodal tris(urea) ligand with 2,2′-bipyridyl (bpy) substituents (**L**) has been designed and synthesized, which coordinates with three equivalents of $Ru(bpy)_2Cl_2{\cdot}2H_2O$, followed by treatment with NH_4PF_6, to afford the anion receptor $[(bpy)_6Ru_3L](PF_6)_6$ (**1**). The anion-binding behavior of the ligand **L** and the Ru^{II}–bpy functionalized receptor **1** toward different anions was investigated by ^1H NMR (for **L** and **1**), fluorescence, and UV-vis spectroscopy (for **1**). Both compounds showed selective recognition of SO_4^{2-} or $H_2PO_4^-$ ions in the 1 : 1 binding mode in the NMR studies. The Ru^{II} complex **1** displayed the metal-to-ligand charge transfer emission at 600 nm, which was quenched on addition of the sulfate and dihydrogen phosphate ions. Quantitative fluorescence titration experiments were carried out and the stability constants (log *K*) of the complex **1** with SO_4^{2-} and $H_2PO_4^-$ ions were obtained to be 4.73 and 4.69 M^{-1} (1 : 1 binding mode), respectively.

Introduction

The design of new chemosensors for anionic species has received considerable attention because of the fundamental roles anions play in a wide range of environmental, chemical and biological processes.[1] For the synthesis of anion sensors,[2–6] the urea and thiourea groups are excellent candidates owing to their ability to form strong hydrogen bonds with the anionic guests. Since Reinhoudt and coworkers[7] introduced the tris(2-aminoethyl)amine moiety into the framework of anion hosts containing amide groups, which could selectively bind the $H_2PO_4^-$ anion, a number of tripodal tris(urea) receptors with well-organized C_3-clefts have been designed to encapsulate the sulfate or phosphate ion.[8] These two anions are troublesome species that can interfere with the waste treatment processes and cause environmental problems, and their extraction is challenging due to their high solvation energies.[9] To this end, the tripodal receptors provide a promising approach for the separation of sulfate and phosphate ions.

Fluorescent chemosensors appear to be particularly attractive due to their advantages such as simplicity, high sensitivity, low background noise, and low detection limit.[1c,10] Generally, the fluorophores may be organic compounds or metal-based fluorescent subunits. In the latter case, the $Ru(bpy)_3^{2+}$ moiety has been widely used in the development of fluorogenic anion sensors because Ru^{II} complexes have a relatively long wavelength MLCT emission band and proved to be very useful in the investigation of anion binding.[10b,11] Beer and coworkers have designed a variety of Ru(II)–bipyridyl containing sensors with hydrogen bond donors (*e.g.* amide) and studied their anion binding properties.[1d,12]

We have focused our studies on the anion binding with a series of urea-based receptors.[13] A pyridyl-substituted tripodal tris-urea (L^{py}) has been synthesized, which can selectively encapsulate the sulfate ion in a capsule formed by two receptor molecules.[13a,b] Recently, we modified the receptor L^{py} by replacing the pyridyl terminals by the redox-active ferrocenyl groups as an electrochemical reporting unit (L^{Fc}),[13c–e] and by the quinolinyl groups (L^{Qn}) for the fluorescent signaling purpose.[13f] In the current work, we attached the 2,2′-bipyridyl groups to the terminals of the tripodal tris(urea) backbone and synthesized the ligand **L** (Scheme 1), which coordinates to the $Ru(bpy)_2^{2+}$ fragments to afford the anion receptor $[(bpy)_6Ru_3L](PF_6)_6$ (**1**). Both **L** and **1** exhibit good selectivity for the tetrahedral anions SO_4^{2-} and $H_2PO_4^-$.

Results and discussion

The tripodal ligand **L** was synthesized from 5-isocyanato-2,2′-bipyridine[14] and tris(2-aminoethyl)amine under nitrogen (Scheme 1). Single crystals have been obtained by slow evaporation of its methanol solution. The preliminary structure showed a 1D chain linked by intermolecular urea···urea hydrogen bonds involving all the three urea arms.[13a,e] Unfortunately, the crystals

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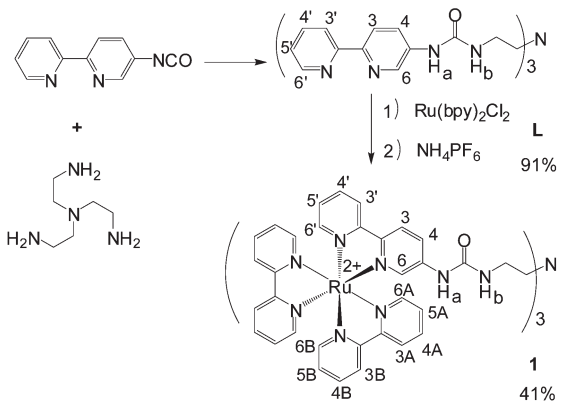
†Electronic supplementary information (ESI) available: ^1H NMR and fluorescence studies of the anion binding properties of **L** and **1**. See DOI: 10.1039/c2dt12488b



Scheme 1 Synthesis of the ligand **L** and receptor **1**.

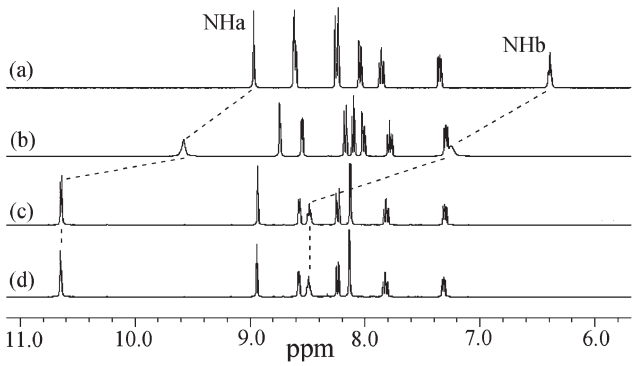


Fig. 1 Changes of the NMR signals of the urea NH groups in **L** with addition of SO_4^{2-} in DMSO-d_6: (a) **L**; (b) **L** + 0.5 equiv. SO_4^{2-}; (c) **L** + 1 equiv. SO_4^{2-}; (d) **L** + 2 equiv. SO_4^{2-} (as Bu_4N^+ salt).

diffracted poorly and did not allow satisfactory structural refinement, and many attempts to grow better crystals have been unsuccessful. The Ru–bpy functionalized receptor $[(bpy)_6Ru_3L](PF_6)_6$ (**1**) was synthesized as a red powder by the reaction of **L** with $Ru(bpy)_2Cl_2{\cdot}2H_2O$[15] in ethanol. The ligand **L** and complex **1** were characterized by NMR, IR spectroscopy, mass spectrometry, and elemental analysis. ESI-MS spectrum of **1** displayed peaks at *m*/*z* 756.2 for $[M - HPF_6 - 3PF_6^-]^{3+}$ and *m*/*z* 1278.6 for $[M - 2PF_6^-]^{2+}$, which agree with the calculated values of 756.1 and 1279.6, respectively. The anion binding properties of **L** and **1** were investigated by ^{1}H NMR, fluorescence, and UV-vis methods.

Anion binding behavior of L and 1

^{1}H NMR titrations. ^{1}H NMR studies of the ligand **L** with different anions were carried out in DMSO-d_6. The urea NH groups displayed large downfield shifts when 1 equiv. of SO_4^{2-} ($\Delta\delta$: Ha, 1.69; Hb, 2.10 ppm) or $H_2PO_4^-$ ($\Delta\delta$: Ha, 1.18; Hb, 1.07 ppm) ions (as Bu_4N^+ salt) were added. No further changes appeared with more SO_4^{2-} or $H_2PO_4^-$ ions, thus indicating a 1 : 1 binding mode (Fig. 1 and 2). The OAc^- ion induced considerable downfield shifts, which is common for urea-based receptors due to the high basicity and complementary Y shape of OAc^- with the urea group.[13f,16] Other anions (HSO_4^-, Cl^-, Br^-, I^-, NO_3^-, and ClO_4^-; as Bu_4N^+ salt) resulted in only slight or no changes (Fig. S1, ESI†). The SO_4^{2-} and $H_2PO_4^-$ binding

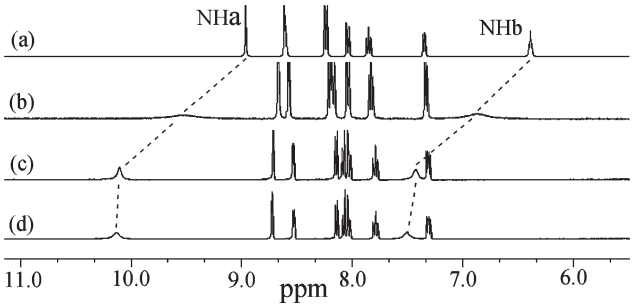


Fig. 2 Changes of the NMR signals of the urea NH groups in **L** with addition of $H_2PO_4^-$ in DMSO-d_6: (a) **L**; (b) **L** + 0.5 equiv. $H_2PO_4^-$; (c) **L** + 1 equiv. $H_2PO_4^-$; (d) **L** + 2 equiv. $H_2PO_4^-$ (as Bu_4N^+ salt).

constants were obtained by fitting the ^{1}H NMR titration data by the EQNMR program,[17] which are larger than 10^4 M^{-1} (Fig. S2 and S3, ESI†).

When the photoluminescent $Ru(bpy)_2^{2+}$ groups were introduced to the ligand **L**, the tris-(Ru–bpy)$_3$ substituted receptor **1** was obtained. The interactions of receptor **1** with anions were also examined by ^{1}H NMR titrations conducted in DMSO-d_6 solutions. In the case of the SO_4^{2-} ion, slow exchange processes were observed during the titration of one equivalent of SO_4^{2-} ions (as the Bu_4N^+ salt).[13d,18] A new set of ^{1}H NMR signals appeared besides those of the receptor, which can be attributed to the anion complex formed at the expense of the free receptor **1**. The intensity of the new signals increased gradually with the addition of SO_4^{2-} ions, while the signals of receptor **1** decreased and disappeared completely after one equiv. of the SO_4^{2-} ions were added. There were no further changes when more anions were added.

Notably, the NHa signal in the newly appeared anion complex split into two peaks with a 2 : 1 integration ratio when sulfate ions were added, which may be caused by the asymmetric environment of one $Ru(bpy)_3^{2+}$ terminal from the other two arms in the tripodal anion complex **1**.[19] Moreover, downfield shifts of the urea NH protons ($\Delta\delta_{NHa}$ = 1.03 and $\Delta\delta_{NHb}$ = 0.74 ppm) compared to **1** were observed (Fig. 3a) due to the formation of hydrogen bonds. During the process of adding $H_2PO_4^-$ to receptor **1** in DMSO-d_6, however, a fast exchange phenomenon was observed. Gradual downfield shifts of the urea NH protons occurred with the addition of $H_2PO_4^-$ ions, and the NH peaks were significantly broadened (Fig. 3b). The 1 : 1 binding mode with both anions was confirmed by the results of Job's plots (Fig. S4, ESI†). Addition of Cl^- anions resulted in slight downfield shifts of the urea NH protons (Fig. S5, ESI†), and titration of chloride ions gave a binding constant of log K = 2.86 M^{-1} (error: 10.1%) calculated by the EQNMR program (Fig. S6, ESI†). Other anions (Br^-, I^-, NO_3^-, and ClO_4^-; as Bu_4N^+ salt) caused no changes of the spectrum, while the AcO^- induced comparable changes as in the case of the ligand **L** (Fig. S5, ESI†).

Fluorescence studies on the anion-binding properties of the Ru^{II} complex 1

The binding properties of the receptor $[(bpy)_6Ru_3L](PF_6)_6$ (**1**) to various anions were studied by fluorescence titration experiments

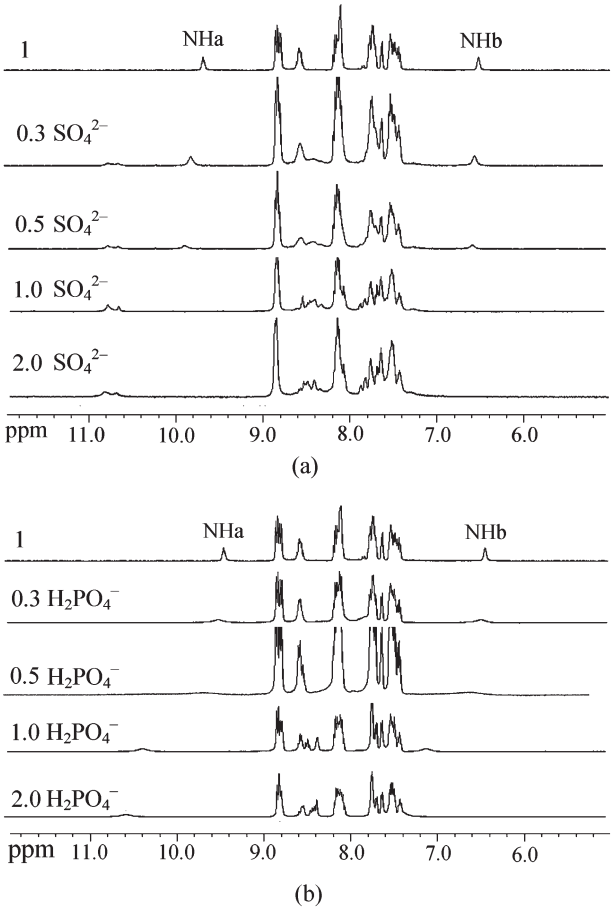


Fig. 3 ^{1}H NMR (DMSO-d_6, 400 MHz) spectra of receptor **1** upon titration of SO_4^{2-} (a) and $H_2PO_4^-$ (b) ions (as Bu_4N^+ salt).

in CH_3CN at room temperature. Upon excitation at 447 nm, complex **1** showed the characteristic metal-to-ligand charge transfer (MLCT) emission band of Ru–bipyridyl complexes at 600 nm. On addition of 1 equiv. of SO_4^{2-} or $H_2PO_4^-$ anions, a decrease of the emission intensity with a slight red shift (about 5 nm) was observed, while other anions (such as HSO_4^-, Cl^-, Br^-, I^-, NO_3^- and ClO_4^-) induced slight or no significant changes of the emission intensity (Fig. 4). The results indicate that complex **1** has a strong binding affinity for SO_4^{2-} and $H_2PO_4^-$ ions due to the excellent complementarity of these anions to the tripodal binding sites. This fluorescence quenching of the tripodal metallo-receptor **1** by anions is in contrast to the intensity enhancement observed in Ru^{II} bipyridyl amide systems with chloride and dihydrogen phosphate anions, which was assigned as a consequence of the bound anion rigidifying the receptor and inhibiting vibrational and rotational relaxation modes of nonradiative decay.[12a] In our system, change of the rigidity of the receptor upon anion binding might not be significant since each $Ru(bpy)_3^{2+}$ moiety is modified by only one urea arm. However, the urea binding sites are attached directly to the bpy groups, and the decrease of emission intensity could be tentatively explained by the binding interactions of the anions, especially SO_4^{2-} or $H_2PO_4^-$ ions, to the urea units affecting the excited states of bpy ligands and disfavoring the MLCT process of the $Ru(bpy)_3^{2+}$ complex.

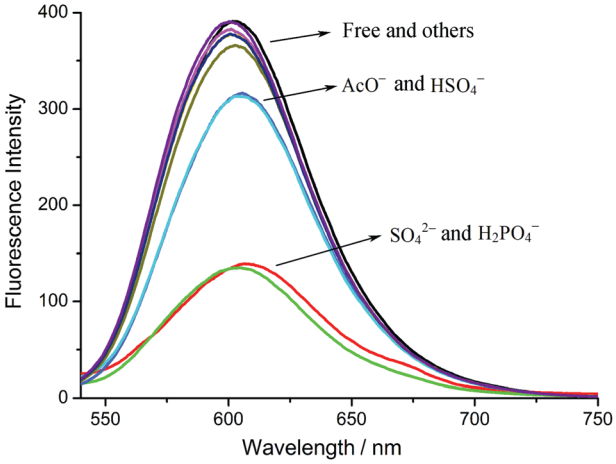


Fig. 4 Fluorescence emission spectra of the receptor $[(bpy)_6Ru_3L](PF_6)_6$ (**1**) (5×10^{-6} M in CH_3CN) upon addition of 10 equiv. of different anions (Cl^-, Br^-, I^-, AcO^-, NO_3^-, SO_4^{2-}, $H_2PO_4^-$, HSO_4^-, ClO_4^-; as Bu_4N^+ salts). Excitation at 447 nm.

Quantitative investigations of the binding affinity of complex **1** with SO_4^{2-} and $H_2PO_4^-$ anions have been carried out in CH_3CN by fluorescence titrations (Fig. 5). The emission intensity of **1** decreased gradually with increasing SO_4^{2-} or $H_2PO_4^-$ concentration. The linear relationship obtained in the Benesi–Hildebrand plot suggested the formation of the 1 : 1 anion binding complex.[20a,21] The binding constants (log K) were calculated from the variation in the fluorescence intensity at 600 nm by plotting $1/(I_0 - I)$ against $[\text{anion}]^{-1}$, which were 4.73 (R = 0.995) and 4.69 (R = 0.994) M^{-1} for SO_4^{2-} and $H_2PO_4^-$ (1 : 1 binding mode), respectively. These results are consistent with the previous reports of similar tripodal receptors that show good recognition for the tetrahedral sulfate and phosphate ions.[8d,g]

The binding affinities of the receptor **1** toward various anions in the presence of water have been evaluated by the fluorescence method. In a CH_3CN–5% H_2O solution, complex **1** showed selective recognition of the SO_4^{2-} or $H_2PO_4^-$ ion (Fig. S7, ESI†), which is similar to the phenomenon in CH_3CN. However, with more water in the mixed solvents, the binding affinity dropped dramatically. Notably, the HSO_4^- anion also showed a strong response in this system, which may be due to the bisulfate converting to sulfate under the water-containing experimental conditions.[8g] The anion selectivity of **1** was also assessed by competitive experiments performed in CH_3CN–5% H_2O solution. In the presence of other anions, the emission spectra showed similar features to those with the SO_4^{2-} and $H_2PO_4^-$ ions, revealing a good selectivity for these two anions (Fig. S8, ESI†).

UV-vis studies on the anion-binding properties of the Ru^{II} complex 1

In the UV-vis spectrum in CH_3CN (1×10^{-5} M), complex **1** showed an intense broad absorption band at 450 nm as well as a peak at about 288 nm. The absorption bands found in the region below 400 nm can be ascribed to ligand-centered (^{1}LC) transitions, while the lower-energy peak is assigned as spin-allowed

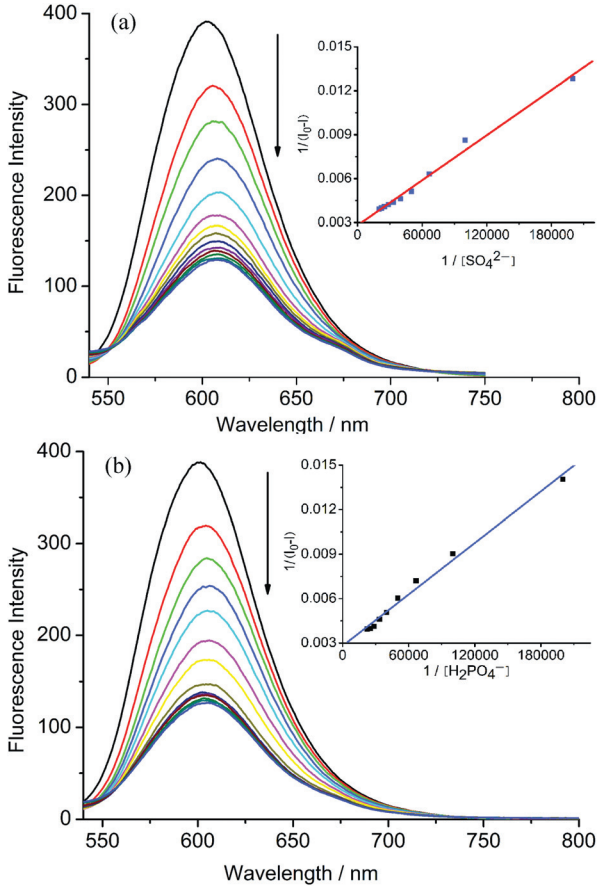


Fig. 5 (a) Fluorescence titration of receptor **1** (5×10^{-6} M in CH_3CN) with SO_4^{2-} (up to 15×10^{-5} M). Inset: plot of $1/(I_0 - I)$ *versus* $1/[SO_4^{2-}]$ giving a satisfactory straight line; (b) Fluorescence titration of the receptor **1** (5×10^{-6} M in CH_3CN) with $H_2PO_4^-$ (up to 15×10^{-5} M). Inset: plot of $1/(I_0 - I)$ *versus* $1/[H_2PO_4^-]$ giving a satisfactory straight line.

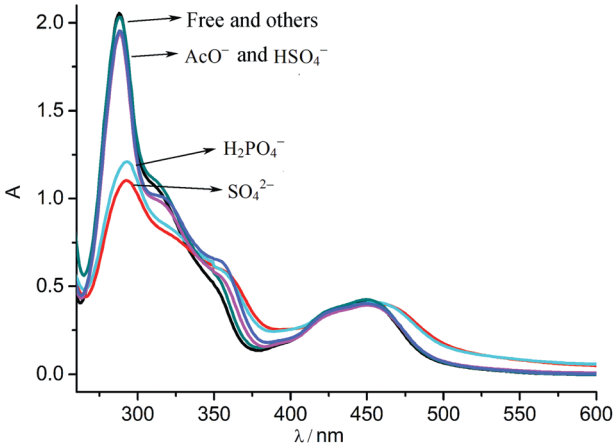


Fig. 6 Absorption spectra of the receptor $[(bpy)_6Ru_3L](PF_6)_6$ (**1**) (1×10^{-5} M in CH_3CN) upon addition of 10 equiv. of representative anions (Cl^-, Br^-, I^-, AcO^-, NO_3^-, $H_2PO_4^-$, HSO_4^-, ClO_4^- as Bu_4N^+ salts).

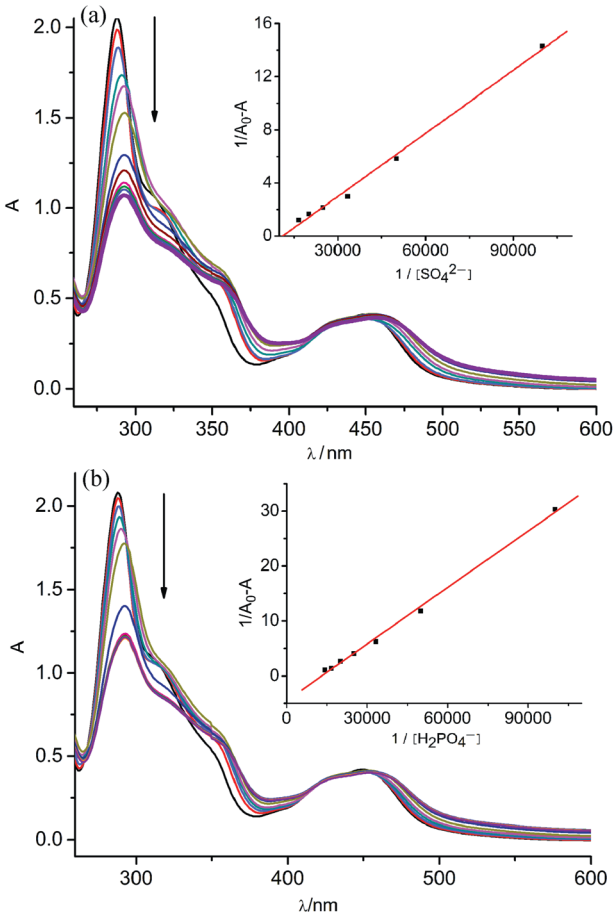


Fig. 7 (a) UV-vis titration of receptor **1** (1×10^{-5} M in CH_3CN) with SO_4^{2-} (up to 2×10^{-4} M). Inset: plot of $1/(A_0 - A)$ *versus* $1/[SO_4^{2-}]$ giving a satisfactory straight line; (b) UV-vis titration of **1** (1×10^{-5} M in CH_3CN) with $H_2PO_4^-$ (up to 2×10^{-4} M). Inset: plot of $1/(A_0 - A)$ *versus* $1/[H_2PO_4^-]$ giving a satisfactory straight line.

metal-to-ligand charge transfer (^{1}MLCT) corresponding to the overlap of Ru(dπ) → bpy(π*) and Ru(dπ) → L(π*).[22] Upon titration of SO_4^{2-} and $H_2PO_4^-$ ions (as Bu_4N^+ salt), the absorption at 450 nm increased gradually with a bathochromic shift (*ca*. 8.0 nm) and the band at 288 nm decreased gradually with a slight bathochromic shift (*ca*. 5.0 nm) (Fig. 6). Addition of other anions such as AcO^-, HSO_4^-, ClO_4^-, NO_3^-, Cl^-, Br^- and I^- resulted in small or no noticeable changes, which is in agreement with the results of NMR and fluorescence titrations. Quantitative investigations of the binding of **1** with SO_4^{2-} and $H_2PO_4^-$ anions have also been carried out in CH_3CN (Fig. 7), which confirmed the 1 : 1 binding mode. The binding constants [log K = 4.05 (R = 0.997) and 4.12 (R = 0.998) M^{-1}] were obtained from the variation in the absorption peak intensity at 288 nm by plotting the ratio of $1/(A_0 - A)$ against $[anion]^{-1}$, which compare well with the results of fluorescence titration.

Conclusion

We have synthesized a novel tripodal tris(2,2′-bipyridylurea) ligand (**L**) and the corresponding Ru–bpy functionalized fluorescent anion sensor $[(bpy)_6Ru_3L](PF_6)_6$ (**1**). ^{1}H NMR, fluorescence, and UV-vis studies demonstrated that the Ru^{II} complex **1** exhibits good selectivity for SO_4^{2-} and $H_2PO_4^-$ anions. The

sensor **1** showed the characteristic metal-to-ligand charge transfer emission band at 600 nm of the Ru–bpy complexes, while addition of the sulfate and phosphate anions resulted in the quenching of the emission intensity with slight bathochromic shifts. The stability constants were obtained by fluorescent and UV-vis titrations.

Experimental section

General

All chemicals and solvents were commercially available and were used without further purification. The ligand **L** was synthesized by the reaction of 2,2′-bipyridyl acyl azide and tris-(2-aminoethyl)amine. The 2,2′-bipyridyl acyl azide was obtained from 5-carboxy-2,2′-bipyridine, which was prepared according to the literature procedure.[14a] The ruthenium(II) complex **1** was obtained by reaction of the ligand **L** with $Ru(bipy)_2Cl_2{\cdot}2H_2O$.[15] ^1H and ^{13}C NMR spectra were recorded on a Mercury plus-400 spectrometer with calibration against the solvent signal (DMSO-d_6 2.50 ppm for ^1H NMR) or TMS. IR spectra were obtained using a Nicolet AVATAR 360 FT-IR spectrometer as KBr pallets. Elemental analyses were done on a VarioEL instrument from Elementaranalysensysteme GmbH. Melting points were detected on an X-4 Digital Vision MP Instrument. Emission spectra were recorded on a Hitachi F7000 fluorescence spectrophotometer equipped with a PX-2 pulsed xenon lamp with an excitation and emission slit width of 2.5 nm. UV-vis titration was carried out with a TU-1810 UV-vis spectrophotometer.

Synthesis

***N*-[2-[Bis[2-[*N*′-(3-2,2′-bipyridyl)ureido]ethyl]-amino]ethyl]-*N*′-(3-2,2′-bipyridyl)urea (L).** 2,2′-Bipyridyl acyl azide (1.20 g, 5.33 mmol) in freshly dried toluene (120 mL) was refluxed under a nitrogen atmosphere for 1 h to give a pale yellow solution. Tris(2-aminoethyl)amine (0.19 g, 1.28 mmol) was added and the mixture was refluxed for 30 min and then cooled to r.t. A white powder was collected and washed with toluene, diethyl ether and dried *in vacuo* (0.86 g, 91%). M.p.: 194–195 °C. ^1H NMR (DMSO-d_6, ppm): 8.98 (s, 3H, Ha), 8.62 (d, 3H, J = 2.8 Hz, H6), 8.60 (d, 3H, J = 4.8 Hz, H6′), 8.25 (s, 3H, H3), 8.23 (s, 3H, H3′), 8.04 (dd, 3H, J_1 = 8.8 Hz, J_2 = 2.4 Hz, H4), 7.85 (m, 3H, H4′), 7.35 (m, 3H, H5′), 6.39 (t, 3H, J = 5.6 Hz, Hb), 3.25 (d, 6H, J = 6.0 Hz, urea-CH_2), 2.65 (t, 6H, J = 6.4 Hz, urea-CH_2–CH_2). See Scheme 1 for the numbering of the protons. ^{13}C NMR (DMSO-d_6, ppm): 155.3 (bpy-C5), 155.1 (bpy-C2′), 149.0 (C═O), 147.9 (bpy-C6′), 138.7 (bpy-C2), 137.6 (bpy-C4′), 137.0 (bpy-C6), 124.9 (bpy-C3), 123.1 (bpy-C5′), 120.5 (bpy-C4), 119.5 (bpy-C3′), 53.7 (urea-CH_2–), 37.6 (urea-CH_2–CH_2–). ESI-MS: m/z 738.4 $[M + H]^+$, 760.3 $[M + Na]^+$. FT-IR (KBr pellet, cm^{-1}): 3322 (N–H), 3102, 1648 (C═O), 1573, 1541, 1460, 1374, 1259, 853, 795, 744, 651, 622. Anal. calcd for $C_{39}H_{39}N_{13}O_3$ (737.33): C, 63.49; H, 5.33; N, 24.68; Found: C, 63.20; H, 5.04; N, 24.81%.

$[(bpy)_6Ru_3L](PF_6)_6$ (1). $Ru(bipy)_2Cl_2{\cdot}2H_2O$ (76 mg, 0.15 mmol) and **L** (30 mg, 0.041 mmol) were refluxed in ethanol (10 mL) under argon for 24 h. The volume was reduced to half under vacuum and a saturated NH_4PF_6 solution was added to the solution until no further precipitate was observed. The yellow solid was filtered off and washed with water. Yield: 48 mg (41%). M.p.: 263 °C. ^1H NMR (DMSO-d_6, 400 MHz): 9.79 (s, 3H, Ha), 8.83 (dd, J = 8.4 Hz, 12H, H3A, H3B), 8.58 (m, 6H, H3,H3′), 8.14 (m, 18H, H4A, H4B, H4, H4′), 7.74 (m, 15H, H6A, H6B, H6), 7.64 (d, J = 5.6 Hz, 3H, H6′), 7.50 (m, 15H, H5A, H5B, H5′), 6.56 (s, 3H, Hb), 3.00 (s, 6H, urea–CH_2), 2.38 (s, 6H, urea–CH_2–CH_2). ESI-MS: m/z 1278.6 $[M - 2PF_6]^{2+}$, 756.2 $[M - HPF_6 - 3PF_6]^{3+}$. IR (KBr pellet, cm^{-1}): 3396, 3083, 2925, 1696 (C═O), 1541, 1465, 1221, 840, 761, 556. Anal. calcd for $[(bpy)_6Ru_3L](PF_6)_6$ ($C_{99}H_{87}F_{36}N_{25}O_3P_6Ru_3$): C 41.75, H 3.08, N 12.30; Found: C 41.44, H 2.81, N 12.12%.

Acknowledgements

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