Accepted Manuscript

Synthesis, structural characterisation and luminescent anion sensing studies of a Ru(II)polypyridyl complex featuring an aryl urea derivatised 2,2'-bpy auxiliary ligand

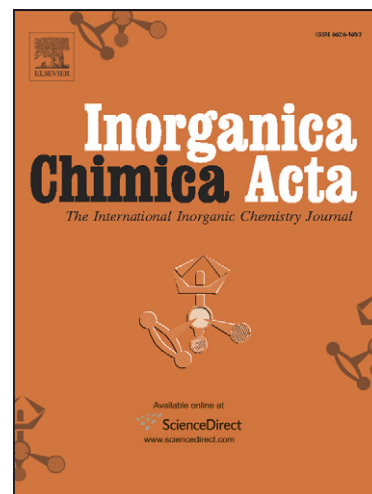Jonathan A. Kitchen, Elaine M. Boyle, Thorfinnur Gunnlaugsson

Please cite this article as: J.A. Kitchen, E.M. Boyle, T. Gunnlaugsson, Synthesis, structural characterisation and luminescent anion sensing studies of a Ru(II)polypyridyl complex featuring an aryl urea derivatised 2,2'-bpy auxiliary ligand, *Inorganica Chimica Acta* (2011), doi: 10.1016/j.ica.2011.10.026

Synthesis, structural characterisation and luminescent anion sensing studies of a Ru(II)polypyridyl complex featuring an aryl urea derivatised 2,2'-bpy auxiliary ligand

Jonathan A. Kitchen,[*] Elaine M. Boyle and Thorfinnur Gunnlaugsson[*]

School of Chemistry, Centre for Synthesis and Chemical Biology, Trinity College Dublin, Dublin 2, Ireland. Fax: +353 1671 2826; Tel: + 353 1 896 3459; E-mails: jkitchen@tcd.ie and gunnlaut@tcd.ie

The inclusion of a urea functionality into the coordination sphere of a Ru(II)-polypyridyl complex (**Ru·L$_1$**) resulted in a system that can function as an effective long wavelength emissive fluorescent anion sensor. The MLCT emission of **Ru·L$_1$** is sensitive to the binding of acetate, phosphate and pyrophosphate but *not* fluoride in organic solvent. In addition, **Ru·L$_1$** can distinguish between phosphate and pyrophosphate with an emission increase upon binding of $H_2PO_4^-$ ("***turn on***" sensor) and an emission decrease upon binding of $HP_2O_7^{3-}$ ("***turn off***" sensor), which occurs via hydrogen bonding to the urea receptor moiety as demonstrated by carrying out NMR titrations as well as by employing $[Ru(II)bipy_3](PF_6^-)_2$ as a model compound that lacks the anion receptor moiety.

Keywords: Ru(II), polypyridyl, anion sensing, luminescence, urea receptors, hydrogen bonding

1. Introduction

The luminescent sensing of anions has become an active area of research in the last decade.[1-5] Such sensing usually requires the use of a receptor motif that can bind anions; often through hydrogen bonding, or through electrostatic binding to cationic or Lewis Acid centres, such as ammonium moieties and metal ions. For the latter, the ion-pairing can give rise to strong binding, which can be employed in competitive media.[6,7] In particular, the use of luminescent metal ion complexes, where the anion binding/recognition occurs directly at the meal ion; and hence, is a consequence of competitive binding or exchange of anions for solvent molecules within the first coordination sphere of the metal ion, has been shown to be a powerful means of forming luminescent sensors.[8,9] Such binding usually results in significant perturbation of the various photophysical properties of the metal ion complexes; giving rise to changes in wavelengths, lifetimes or quantum yields, all of which can be monitored to quantify the anion binding affinity.[10,11] Alternatively, the anion recognition/sensing can take place at a designed receptor moiety that is part of the auxiliary ligands used in the formation of such metal ion complexes.[12-15] This is a more versatile means of achieving both better selectivity and sensitivity for the anion recognition.[16-19] Herein, we explore the use of combined electrostatic binding and hydrogen bonding for the recognition and sensing of anions; an area of research we have recently started investigating through the use of transition metal ion complexes in competitive solvents.[14,20,21] We show that by appending a urea moiety to part of a bi-pyridine ligand, via a phenyl spacer, and using such ligands in the formation of Ru(II) polypyridyl complexes, anion sensing can be achieved through both hydrogen bonding as well as through electrostatic interactions.[22] Moreover, we demonstrate that depending on the nature of the anion, *i.e.* charge, structure and size, the metal to ligand charge transfer (MLCT) emission from such complexes, can be either '*switched on*' or '*switched off*', upon binding to anions. We also demonstrate that phosphate anions can be selectively detected over other anions, such as halides, using such Ru(II) polypyridyl complexes through monitoring of changes in both the ground and the excited states as a consequence of anion binding and/or exchange. The example featured in this communication, the Ru(II) complex **Ru·L$_1$**, is a prime example of our design, where the emission, which occurs at a long wavelength, is

highly sensitive to the nature of the anions, and we demonstrate, that in the case of **Ru·L₁**, the primary recognition mode affecting the MLCT emission is hydrogen bonding and not deprotonation,[23] as the emission arising from **Ru·L₁** is not sensitive to anions such as F⁻, while being highly sensitive to both phosphate, and pyrophosphate.

2. Experimental

2.1. General Information

All reactions were carried out in 2-5 mL or 10-20 mL Biotage Microwave Vials in a Biotage Initiator Eight EXP microwave reactor. Elemental analyses were carried out at the Microanalytical Laboratory, School of Chemistry and Chemical Biology, University College Dublin. Infrared spectra were recorded on a Perkin-Elmer-Spectrum-One FT-IR spectrometer equipped with a Universal-ATR sampling accessory; solid samples were recorded directly as neat samples; in cm⁻¹. NMR data were recorded on a Bruker-DPX-400-Avance spectrometer (400.13 (^{1}H) and 100.6 MHz (^{13}C)) or a Bruker-AV-600 spectrometer (600.13 (^{1}H) and 150.2 MHz (^{13}C)), in commercially available deuterated solvents; δ in ppm relative to SiMe₄ (= 0 ppm) referenced relative to the internal solvent signals, J in Hz; data were processed with Bruker Win-NMR 5.0 and Topspin 2.1 softwares. Absorption spectra were measured in 1-cm quartz cuvettes with a Varian-Cary-50 spectrophotometer. Baseline correction was applied for all spectra. Emission spectra were measured with a Varian-Cary-Eclipse luminescence spectrometer. X-ray data were collected on a Rigaku Saturn 724 CCD Diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data sets were collected using Crystalclear-SM 1.4.0 software. Data integration, reduction and correction for absorption and polarization effects were all performed using Crystalclear-SM 1.4.0 software. Space group determinations were obtained using Crystal structure ver. 3.8. The structures were solved by direct methods (SHELXS-97) and refined against all F^2 data (SHELXL-97).[24] All H-atoms, except for O-H and N-H protons, were positioned geometrically and refined using a riding model with d(CH) = 0.95 Å, Uiso = 1.2Ueq (C). OH and NH protons were found from the difference map and fixed to the attached atoms with U_H = 1.2U_X.

2.2. Reagents

All chemicals were purchased from commercial sources and used as received. 4-[2,2']Bipyridyl-4-phenylamine were prepared using published procedures.[25] Solvents were HPLC grade and were used without further purification.

2.3. Synthesis of *1-(4-[2,2']Bipyridyl-4-phenyl)-3-(3-nitrophenyl)-urea* (**L₁**): 3-Nitro-phenyl-isocyanate (66 mg, 0.40 mmol) was added to a solution of 4-[2,2']bipyridyl-4-phenylamine (100 mg, 0.404 mmol) in CH₃CN (15 mL) and heated at 100°C under microwave irradiation for 40 minutes. The resulting pale precipitate was filtered and dried *in vacuo* to yield an off white powder (98 mg, 59 %). Anal. calcd. for C₂₃H₁₇N₅O₃ (411.13 gmol⁻¹): C 67.15, H 4.16, N 17.07. Found: C 67.05, H 4.22, N 16.85 %. NMR δ_H (600 MHz, DMSO-*d₆*): 9.32 (1H, s, N⁴*H*), 9.16 (1H, s, N³*H*), 8.75-8.72 (2H, m, C¹_H & C¹⁰*H*), 8.67 (1H, s, C⁷*H*), 8.60 (1H, s, C¹⁹*H*), 8.44 (1H, d, C⁴*H*), 7.98 (1H, t, C³*H*), 7.86 (3H, d, C¹²*H* & C¹⁶*H* & C²³*H*), 7.77 (1H, d, C⁹*H*), 7.74 (1H, d, C²¹*H*), 7.69 (2H, d, C¹³*H* & C¹⁵*H*), 7.59 (1H, t, C²²*H*), 7.50 (1H, dd ,C²*H*). NMR δ_C (150 MHz, DMSO-*d₆*): 155.9 (C⁶), 155.2 (C⁵), 152.3 (C¹⁷), 149.9 (C¹⁰), 149.3 (C¹), 148.1 (*C*²⁰), 147.7 (C⁸), 140.9 (*C*¹⁸), 140.7 (*C*¹⁴), 137.4 (C³), 130.7 (C¹¹), 130.1 (*C*²²), 127.4 (C¹² & C¹⁶), 124.5, 124.3 (C²), 120.9 (C⁹), 120.6 (C⁴), 118.9 (C¹³ & C¹⁵), 116.9 (C⁷), 116.5 (*C*²¹), 112.2 (*C*¹⁹). IR (neat) 3060, 1723, 1590, 1550, 1521, 1461, 1417, 1390, 1342, 1317, 1240, 1184,

2

1167, 1097, 1074, 998, 820, 789, 739, 726, 678 cm^{-1}. HRMS (ESI) 412.1411 ([M+H]$^+$, $C_{23}H_{18}N_5O_3$ requires 412.1410).

2.4. Synthesis of [Ru^{II}(**L$_1$**)(bpy)$_2$](PF$_6$)$_2$ (**Ru·L$_1$**): Ligand **L$_1$** (85 mg, 0.2 mmol) was suspended in 4 mL of ethanol/water (1:1) in a 2-5 mL Biotage Microwave Vial. To this suspension was added solid *cis*-bis-(2,2'-bipyridine) ruthenium chloride (98 mg, 0.2 mmol) and the resulting dark mixture heated at 120°C under microwave irradiation for 45 minutes. The resulting clear deep-red solution was added to an aqueous solution of excess ammonium hexafluorophosphate resulting in a bright orange precipitate. This was purified by column chromatography on silica eluting with 40:4:1 CH$_3$CN:H$_2$O:NaNO$_{3(sat. aq.)}$ to yield a red solid (45 mg, 20%). Anal. calcd, for $C_{43}H_{33}N_9O_3F_{12}P_2Ru$ (1115.103 gmol^{-1}): C 46.17, H 2.98, N 11.30. Found: C 45.81, H 2.98, N 11.40 %. NMR δ$_H$ (400 MHz, CD$_3$CN) 8.75 (1H, d), 8.71 (1H, d), 8.60 (1H, t), 8.54 (4H, dd), 8.11-8.07 (4H, m), 8.01 (1H, s, N*H*), 7.94 (1H, s, N*H*), 7.89 (3H, m), 7.85 (1H, d), 7.79-7.71 (8H, m), 7.65 (1H, dd), 7.57 (1H, t), 7.45-7.42 (6H, m). IR (neat) 3094, 1711, 1594, 1520, 1466, 1426, 1347, 1320, 1239, 1190, 824, 761, 730, 658 cm^{-1}. HRMS (MALDI) 970.1414 ([M-PF$_6$]$^+$, $C_{43}H_{33}N_9O_3RuPF_6$ requires 970.1404).

3. Results and Discussion

3.1. Synthesis and characterisation of **L$_1$** and Ru(II) complex **Ru·L$_1$**

Ligand **L$_1$** was prepared by the reaction of 4-[2,2']bipyridyl-4-phenylamine with 3-nitro-phenyl-isocyanate in CH$_3$CN at 100°C under microwave irradiation to give an off-white precipitate in 59% yield (Figure 1a). Both ^{1}H NMR (600 MHz, DMSO-d_6) spectra and microanalytical data were consistent with the expected structure. The expected m/z peaks and isotopic distribution patterns were also observed in the mass spectra of **L$_1$** (found, 412.1411; calc. for [**L$_1$**+H]$^+$, 412.1410 m/z).

The molecular structure of **L$_1$** was furthermore, established by X-ray crystallography. Poor quality pale yellow irregular plates of **L$_1$·H$_2$O** were grown from the slow evaporation of ethanol and the low temperature (108 K) X-ray structure determined.† The ligand **L$_1$** crystallises as a mono-hydrate (**L$_1$·H$_2$O**) in the monoclinic space group *C*2/*c* with one molecule in the asymmetric unit (Figure 2a). The molecule is relatively flat with mean plane angles <29° and the 2,2'-bpy nitrogen atoms (N(1) and N(2)) are orientated in a *trans* like configuration. Packing interactions in **L$_1$·H$_2$O**, shown in Figure 2b, involve the urea nitrogen atoms acting as H-bond donors to the interstitial water molecule
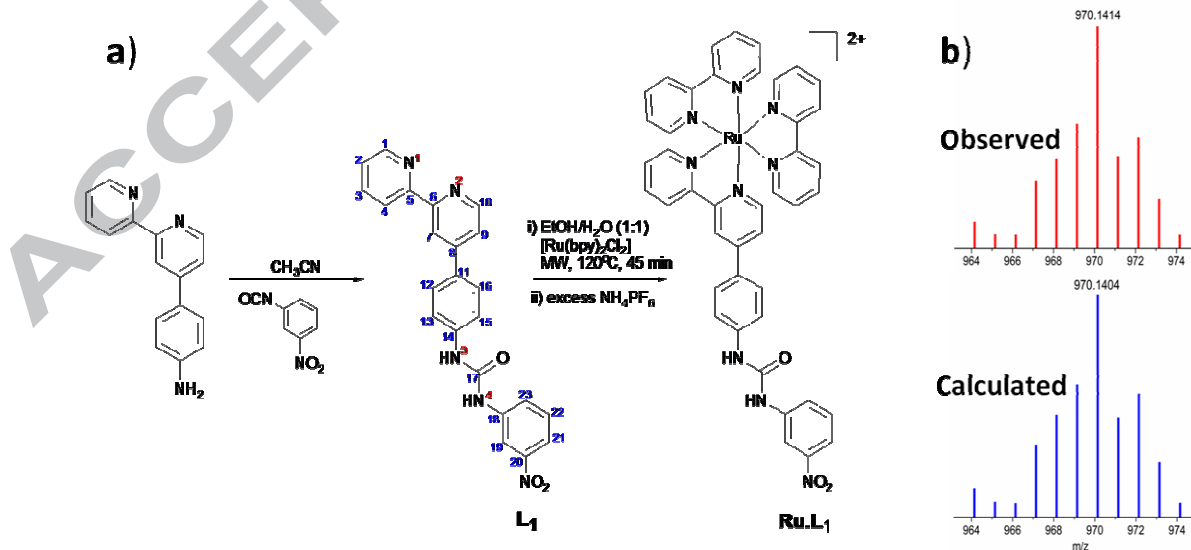

Figure 1: (a) Schematic representation of synthesis of **L$_1$** and **Ru.L$_1$**. (b) observed (red) and calculated (blue) mass spectra of [Ru(bpy)$_2$(**L$_1$**)(PF$_6$)]$^+$.

3

[N(3)···O(100) = 2.896(5) Å, <(N(3)-H(3X)···O(2)) = 160° and N(4)···O(100) = 2.943(5) Å, <(N(4)-H(4X)···O(2)) = 156°]. In addition, the water molecule is hydrogen bonded to pyridyl nitrogen atoms on two symmetry generated adjacent molecules [O(100)···N(1)' = 2.866(5) Å, <(O(100)-H(10X)···N(1)') = 168° and O(100)···N(2)' = 2.843(5) Å, <(O(100)-H(10Y)···N(2)') = 176°].
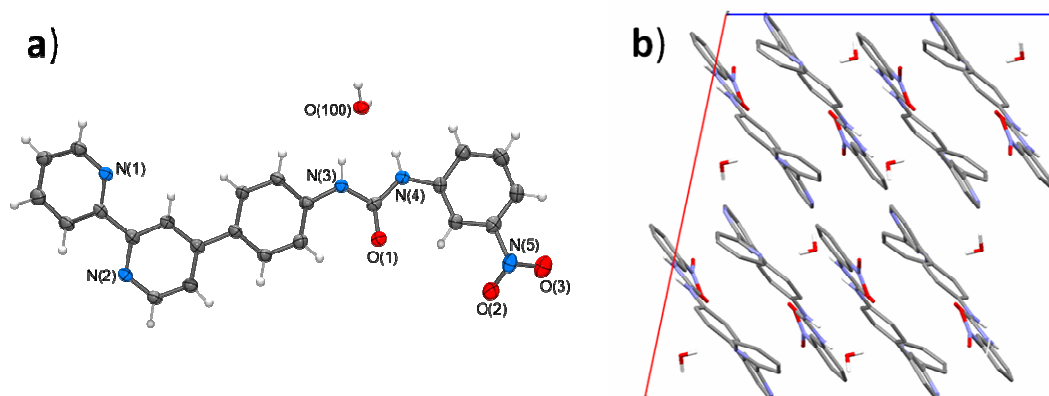

Figure 2: (a) Perspective view of the crystal structure of **$L_1 \cdot H_2O$**. (b) View of packing in **$L_1 \cdot H_2O$** viewed down the crystallographic *c*-axis.

The complexation of **L_1** and *cis*-bis-(2,2'-bipyridine) ruthenium chloride was carried out in a solvent mixture of ethanol and water (1:1) under microwave irradiation at 120°C for 45 minutes. The resulting clear red/orange solution was added to an aqueous solution of excess ammonium hexafluorophosphate yielding a bright orange precipitate. This was purified further by flash column chromatography on silica (eluting with 40:4:1 CH_3CN:H_2O:$NaNO_{3(sat. aq.)}$) to give **$Ru \cdot L_1$** in 20% yield. Microanalytical data was consistent with that expected for **$Ru \cdot L_1$**, while the IR spectra showed the characteristic shifts associated with complexation. Moreover, the ^{1}H-NMR (400 MHz, CD_3CN) data for **$Ru \cdot L_1$** indicated successful formation of the desired complex; the formation of which was further confirmed by ESI, which showed the expected peak and isotopic distribution pattern for the formation of **$Ru \cdot L_1$** (found, 970.1414; calc. for $[Ru \cdot L_1 - PF_6]^+$, 970.1404 m/z), see Figure 1b.

The molecular structure of **$Ru \cdot L_1$** was also established by X-ray diffraction experiments. Small, poor quality, red rod shaped crystals were grown from the vapour diffusion of diethyl ether into an acetonitrile solution of **$Ru \cdot L_1$** and the low temperature structure (108 K) determined. Unfortunately the data was not of sufficient quality to allow for a full refinement. Nevertheless, it did allow for the connectivity of **$Ru \cdot L_1$** to be established (See TOC).

3.2. Photophysical properties of **$Ru \cdot L_1$** and anion complexation studies

The photophysical properties of both the ligand, **L_1**, and the Ru(II) polypyridyl complex, **$Ru \cdot L_1$**, were investigated. The UV/vis spectrum of **L_1** was similar to those obtained for other urea based compounds, with a broad peak at λ_{max} = 288 nm in CH_3CN. The UV-Visible absorption spectra of **$Ru \cdot L_1$** in CH_3CN gave rise to a broad MLCT band centred at 450 nm and three bands at shorter wavelengths of 334 nm, 286 nm and 245 nm, respectively (Figure. 3a). The fluorescence emission spectra of **$Ru \cdot L_1$** showed a broad emission band at 615 nm upon excitation into the MLCT absorption band a 450 nm, and the fluorescence excitation spectra of **$Ru \cdot L_1$** (λ_{em} = 615 nm) structurally matched that of the absorption spectra (Figure 3).
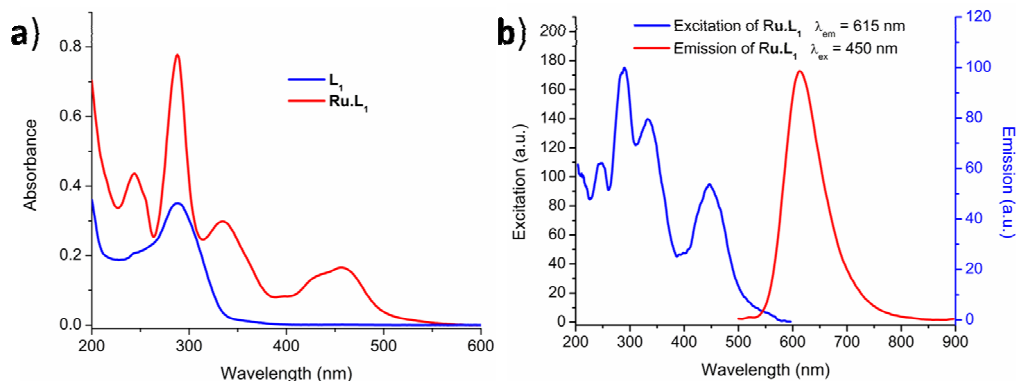
4

Figure 3: (a) The absorption spectra of **L₁** (—) and **Ru·L₁** (—) in CH₃CN (ca. 1×10^{-5} M). (b) The emission spectrum (—, λ_{ex} = 450 nm) and resulting excitation spectrum (—, λ_{em} = 615 nm) of **Ru·L₁**.

The effect of the anion interacting with **Ru·L₁** was next investigated in CH₃CN. These preliminary results are summarised in Figure 4, and showed that in general, the addition of an excess of some anions (including $H_2PO_4^-$, $HP_2O_7^{3-}$, OAc^-, SO_4^{2-} and F^-) as their tetrabutyl ammonium (TBA) salts to **Ru·L₁** resulted in dramatic changes to the absorption and emission spectra; in particular the addition of $HP_2O_7^{3-}$ was quite significant, giving rise to a large degree of quenching of the emission spectrum. Having established that anions give rise to modulation of the photophysical properties of **Ru·L₁** we carried out detailed anion titrations, observing the changes to both the absorption spectra and the fluorescence emission spectra of **Ru·L₁** upon the addition of $H_2PO_4^-$, $HP_2O_7^{3-}$, OAc^-, SO_4^{2-} and F^- as their TBA salts in this solvent.
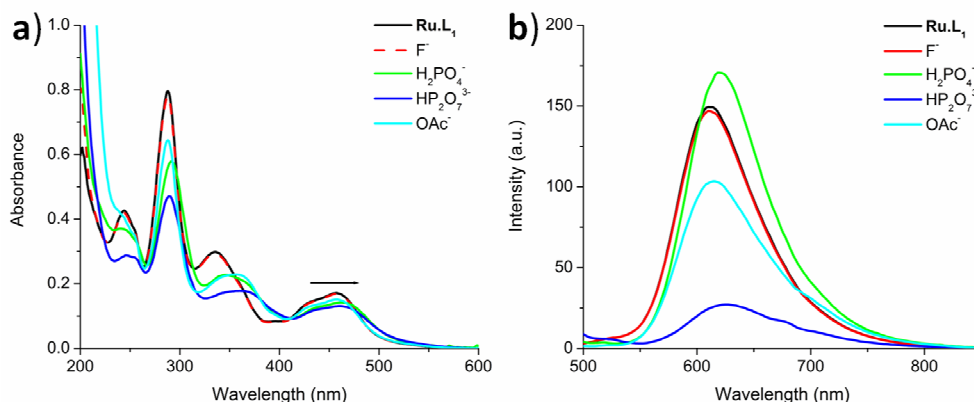

Figure 4: (a) The changes in the absorption spectra of **Ru·L₁** in CH₃CN in the absence and presence of F^-, $H_2PO_4^-$, $HP_2O_7^{3-}$ and OAc^-. (b) the corresponding changes in the emission spectra upon excitation at 450 nm.

The changes observed in the absorption spectra upon titration with OAc^- are shown in Figure 5a and show a slight decrease in all absorption bands and a significant red-shift for the 334 nm transition. Only a slight decrease in the MLCT band was observed with no noticeable shift in λ_{max}. We were able to analyse these results by fitting the changes in the absorption spectra using the non-linear regression analysis program SPECFIT, to 1:1, 1:2 and 1:3 (host:guest) stoichiometries, which demonstrated high affinity of **Ru·L₁** for OAc^-, with a binding constant of $\log K_{1:1}$ = 7.72 ($\pm$ 0.26) for the 1:1 binding; while we also observed some higher order stoichiometries, with $\log K_{1:2}$ = 6.06 ($\pm$ 0.63) and $\log K_{1:3}$ = 2.16 ($\pm$ 0.78), being determined for the 1:2 and 1:3 (sensor:anion) binding, respectively . The high 1:1 binding clearly demonstrates the role of the Lewis Acid centre in **Ru·L₁**, which makes the urea moiety

5

a much better hydrogen bonding donor. The binding of OAc⁻ gave moderate changes to the emission spectra of **Ru·L₁**, as shown in Figure 5b and fitting the observed changes gave similar binding constants to that of the absorbance data with log $K_{1:1}$ = 6.86 (± 0.19), log $K_{1:2}$ = 4.41 (± 0.51) and log $K_{1:3}$ = 2.65 (± 0.99). The origin of this binding we attribute to the interaction of the anion with the urea moiety, which takes place through hydrogen bonding. Indeed, analysis of the binding event, by constructing a speciation distribution diagram demonstrated that within the addition of one equivalent of the anion, ca. 90% of the sensor is complexed to the anion, Figure 5b, inset. However, in competition to this binding, is the 1:2 stochiometry, which can either be due to a weaker interaction with the urea moiety, or more likely, through electrostatic interactions with the metal complex itself. This latter phenomenon, is more likely, as at higher anion concentrations, the 3:1 stochiometry becomes the dominant one; a species most likely to be that of electrostatic interactions and charge balancing.
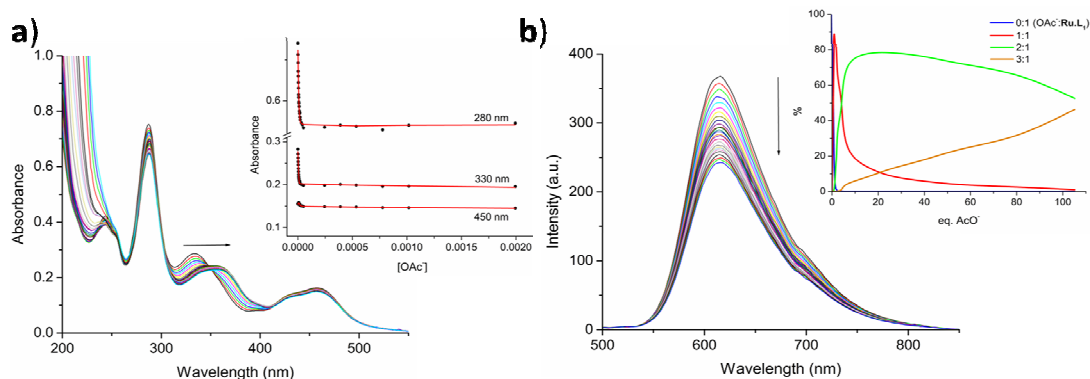

Figure 5: The changes observed in the absorption (a) and emission (b) spectra of **Ru·L₁** in CH₃CN upon titration with TBA OAc⁻. Inset a): experimental binding isotherms for the absorption titration and their corresponding fit by means of SPECFIT (–); b) the speciation distribution derived from the fitting of the changes in the emission spectra.

Figure 6: The changes observed in the absorption (a) and emission (b) spectra of **Ru·L₁** in CH₃CN upon titration with TBA H₂PO₄⁻. Inset a): experimental binding isotherms for the absorption titration and their corresponding fit by means of SPECFIT (–); b) the speciation distribution derived from the fitting of the changes in the emission spectra.
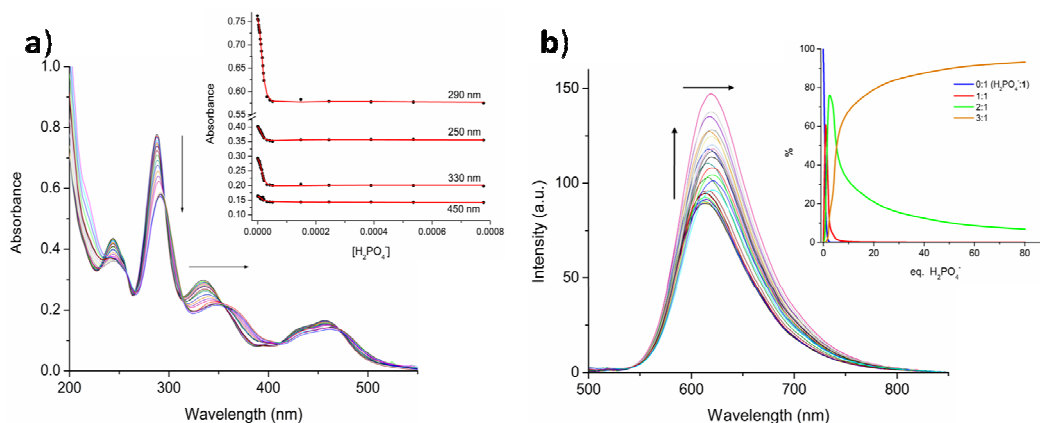
Larger changes in the absorption spectra of **Ru·L₁** were observed upon titration with $H_2PO_4^-$; where all the transitions were red-shifted to a greater extent than seen for OAc⁻ (Figure 6a). Once more, fitting of the changes observed was carried out using non-linear regression analysis, and in this case,

6

they were again best fit to 1:1, 1:2 and 1:3 binding stoichiometries, with log $K_{1:1}$ = 6.55 (± 0.20), log $K_{1:2}$ = 5.48 (± 0.37) and log $K_{1:3}$ = 4.18 (± 0.41), being determined. Once more, the initial 1:1 binding gave rise to the formation of higher anion:complex species (See Figure 6b, inset). In this case the 1:1 binding constant was slightly lower than that of OAc-, and the hydrogen bonding complex was formed in a slightly lower yield. Interestingly, the emission spectra were quite different to the titration of OAc-. Rather than a slight quenching on addition up to ~1 equivalent of anion, as was observed in the case of OAc-, there was an increase in the emission intensity, accompanied by a red-shift. However, upon addition of an excess of $H_2PO_4^-$ the emission intensity began to decrease. However, it never fell below the initial intensity of **Ru·L₁** (as shown in Figure 6b). Fitting of the changes observed in the fluorescence titration using non-linear regression analysis gave a similar binding profile of 1:1, 1:2 and 1:3 binding stoichiometries, with comparable binding constants where log $K_{1:1}$ = 6.85 (± 0.12), log $K_{1:2}$ = 5.85 (± 0.24) and log $K_{1:3}$ = 4.14 (± 0.35). These results again showed that both the absorption and the emission spectra could be monitored to observe the anion sensing of **Ru·L₁**.

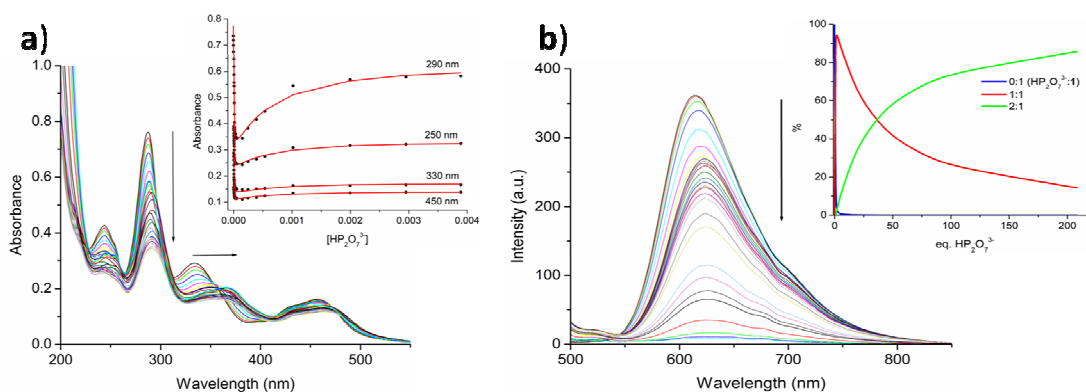Figure 7: The changes observed in the absorption (a) and emission (b) spectra of **Ru·L₁** in CH_3CN upon titration with TBA $HP_2O_7^{3-}$. Inset a): experimental binding isotherms for the absorption titration and their corresponding fit by means of SPECFIT (–); b) the speciation distribution derived from the fitting of the changes in the emission spectra.

However, the most significant changes in the absorption spectra of **Ru·L₁** were observed upon titration with $HP_2O_7^{3-}$ (Figure 7a). Whilst the same red-shift was observed as seen above; there was a much more dramatic decrease in the intensity of all transitions upon addition of excess $HP_2O_7^{3-}$. In this instance, the fitting of the changes in absorption were best represented by 1:1, which was formed in high yield (as seen as an inset in Figure 7b, inset) and 1:2 binding stoichiometries alone; with no
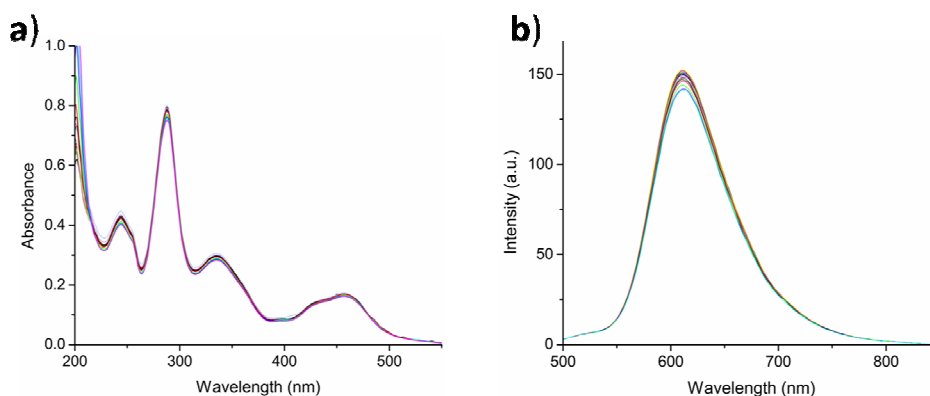

Figure 8: The changes observed in the absorption (a) and emission (b) spectra of **Ru·L₁** in CH_3CN upon titration with F-.

1:3 stoichiometry being determined, and a log $K_{1:1}$ = 5.63 (± 0.09) and log $K_{1:2}$ = 3.12 (± 0.18). Large changes were also observed in the emission spectrum upon addition of $HP_2O_7^{3-}$. However, significant quenching of the emission band was also observed along with a red-shifting of the emission maximum. After addition of a large excess (>100 equiv.) of $HP_2O_7^{3-}$ there was almost complete quenching (>90 %) of the emission band (Figure 7b). Fitting of the fluorescence data gave the same speciation as observed for the absorption data fit with 1:1 and 1:2 binding stoichiometries. The binding constants for $HP_2O_7^{3-}$ were determined as log $K_{1:1}$ = 6.52 (± 0.19) and log $K_{1:2}$ = 3.48 (± 0.39), where the binding constant for the 1:1 stoichiometry was slightly higher than that observed for the absorption data. To further explore the nature of the anion binding interactions seen above for **Ru·L₁**, we also investigated the changes in the luminescence of $[Ru(II)bipy_3](PF_6^-)_2$ upon addition of these same anions in CH_3CN, as this system would function as a model compound, lacking the urea anion receptor. These titrations showed that in the case of OAc^- and F^- no significant changes occurred in either the absorption or the emission spectra upon addition of 400 equivalents of these anions. In the case of $H_2PO_4^-$, $HP_2O_7^{3-}$, and SO_4^{2-} no spectral changes occurred either; but after the addition of 28 equivalents of $H_2PO_4^-$, 5 equivalents of $HP_2O_7^{3-}$, and 3 equivalents of SO_4^{2-} a precipitation occurred, which would suggest some anion exchange interactions with $[Ru(II)bipy_3](PF_6^-)_2$. These results clearly support our findings above that the modulation in the Ru(II) centered MLCT emission are primarily due to the binding of these anions to the urea moiety in **Ru.L₁**.

We also carried out titrations of **Ru.L₁** using SO_4^{2-} and F^-, unfortunately SO_4^{2-} caused precipitation (in a similar manner to that seen for $[Ru(II)bipy_3](PF_6^-)_2$) of the **Ru·L₁**, in the early stages of the titration and we were unable to obtain any binding constants. Titration of **Ru·L₁** with F^- gave very surprising results; no change in either the absorption nor the emission spectra even upon addition of up to 400 equivalents of anion (Figure 8), mirroring that seen for $[Ru(II)bipy_3](PF_6^-)_2$, despite the fact that this anion can function as a base and deprotonate the urea receptor in CH_3CN. This result is quite strange, and in contrast to many other anion sensors developed in which F^- often results in dramatic changes to the absorbance or emission spectra through deprotonation of N-H receptors and subsequent modulation in the various photophysical properties of the sensors.

3.3. ¹H NMR titrations of **Ru.L₁**

Further studies are currently underway in our laboratory on **Ru·L₁** and related structures, including in-depth ¹H-NMR anion titrations in order to help deduce the nature of the anion recognition events occurring. In particular we are focusing on elucidating the nature of the 1:2 and 1:3 stoichiometries that were required to obtain good fits for the absorption/fluorescence titrations. Preliminary ¹H-NMR titrations (400 MHz) carried out on **Ru·L₁** using $H_2PO_4^-$, $HP_2O_7^{3-}$, and F^- in DMSO-d_6 have shown that in the case of $H_2PO_4^-$ and $HP_2O_7^{3-}$, the N-H resonances assigned to the urea protons were all in fast exchange, and became broadened and shifted down-field upon binding to $H_2PO_4^-$ and $HP_2O_7^{3-}$. For the former, such changes occurred between 0.1→1 equivalents, after which a precipitation occurred. These results again, show the direct interaction of the urea protons with the anion and confirm that the changes seen above in the absorption and the emission spectra are indeed due to anion binding event through hydrogen bonding. In contrast, in the case of $HP_2O_7^{3-}$, such precipitation occurred earlier in the titration, after the addition of ca. 0.5 equivalents, while in the case of F^- the resonances became broadened, and impossible to follow after ca. 0.3 equivalents. These changes were also accompanied by the formation of a triplet at ca. 16 ppm which is indicative of the formation of bifluoride (HF_2^-).[26,27] While such deprotonation was not evident in the absorption or the luminescence studies above, however this could be due to lower concentrations of both the sensor and the anions in CH_3CN. We are currently investigating this in greater detail using various NMR analyses, as well as solid state crystallographic analysis, which will shed some light on this

8

phenomenon, and be be crucial to both designing anion selective sensors and elucidating complex binding phenomenon - where both hydrogen bonding, deprotonation and electrostatic binding interactions dictate the overall anion sensing action.

4. Conclusions

In summary, we have shown that the incorporation of a urea moiety into a Ru(II)-polypyridyl complex (**Ru·L₁**) results in a system that can function as an effective long wavelength emissive fluorescent anion sensor for several anions in organic solutions, where the binding sensitivity is very high. Preliminary ^{1}H NMR titrations have also demonstrated that these interactions are predominantly due to hydrogen bonding between the urea receptor and the anions. We also demonstrate that by simple design, the use of hydrogen bonding motifs and electrostatic binding can give rise to good selectivity for such structures. In particular, we have demonstrated that **Ru·L₁** is able to differentiate between phosphate and pyrophosphate in CH_3CN as it acts as an emission "*turn on*" sensor for $H_2PO_4^-$ and an emission "*turn-off*" sensor for $HP_2O_7^{3-}$. In contrast, using $[Ru(II)bipy_3](PF_6^-)_2$ did not in general lead to such spectroscopic changes. Interestingly there was no change on addition of F^- to **Ru·L₁**, and only subtle changes on the addition of OAc^- and SO_4^{2-}. We are currently investigating the use of other, similar, Ru(II)-polypyridyl complexes for use as luminescent anion sensors and DNA binding agents by altering the number of receptors, and the nature of the anion binding groups.

5. Supplementary Information

†**Crystal data: L₁·H₂O**, $C_{23}H_{19}N_5O_4$, M = 429.43, monoclinic, a = 19.544(4), b = 13.535(3), c = 16.471(3) Å, β = 101.92(3)°, V = 4263.3(15) Å^3, T = 108(2) K, space group $C2/c$, Z = 8, 20263 reflections measured, 3544 unique (Rint = 0.0960). Final $wR2$ = 0.3050 (all data) and R1 = 0.1148 (I>2σ). CCDC 838999 contains the supplementary crystallographic data for ligand **L₁·H₂O**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

References

[1] Duke, R. M.; Veale, E. B.; Pfeffer, F. M.: Kruger, P. E.: Gunnlaugsson, T. *Chem Soc. Rev*. **2010**, 39, 3936.

[2] (a) Gunnlaugsson, T.; Glynn, M.; Tocci (née Hussey), G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev*. **2006**, *250*, 3094. (b) dos Santos, C. M.G.; Harte, A. J.; Quinn, S.; Gunnlaugsson, T. *Coord. Chem. Rev*. **2008**, *252*, 2512; (c) Leonard, J. P.; Nolan, C. B.; Stomeo, F.; Gunnlaugsson, T. *Top. Curr. Chem.* **2007**, *281*, 1.

[3] (a) Gale, P. A., *Chem Soc. Rev*. **2010**, 39, 3746. (b) Li, A.-F.; Wang, J.-H.; Wang, F.; Jiang, Y.-B. *Chem Soc. Rev*. **2010**, 39, 3729. (c) Amendola, V.; Fabbrizzi, L.; Mosca, L. *Chem Soc. Rev*. **2010**, 39, 3889.

9

[4] Padros P. Quesada, R. *Supramol. Chem*, **2008**, *20*, 201. (b) Gale, P. A., Garcia-Garrido, S. E.; Garric, J. *Chem. Soc. Rev.,* **2008**, *37*, 151. (c) Gale P. A.; Quesada, R. *Coord. Chem. Rev*. **2006**, *250*, 3219. (d) Gunnlaugsson, T.; Ali H.D.P.; Glynn, M.; Kruger, P.E.; Hussey G. M. Pfeffer F. M.; dos Santos, C. M. G.; Tierney, J.; *J. Fluoresc.* **2005**, *15,* 287.

[5] (a) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev*, **2003**, *103*, 4419. (b) Suksai, C.; Tuntulani, T. *Chem. Soc. Rev*., **2003**, *32*, 192. (c) Callan, J. F.; de Silva, A.P.; Magri, D.C. *Tetrahedron,* **2005**, *36*, 8551; (d) de Silva, A.P.; Gunaratne, H.Q.N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher J. T.; Rice, T. E. *Chem. Rev*. **1997**, *97*, 1515.

[6] Fabbrizzi, L.; Licchelli, M.; Rabaioli, G.; Taglietti, A. F. *Coord. Chem. Rev.* **2000**, 205, 85.

[7] (a) Leonard, J. P.; Nolan, C. B. Stomeo F.; Gunnlaugsson, T. *Top. Curr. Chem.*, **2007**, 281, 1; (b) Gunnlaugsson T.; Stomeo, F. *Org. Biomol. Chem.*, **2007**, 5, 1999; (c) Pope, S. J. A. *Polyhedron,* **2007**, 26, 4818; (d) Pandya, S.; Yu, J.; Parker, D. *Dalton Trans*. **2006**, 2757.

[8] (a) Massue, J.; Quinn, S. J.; Gunnlaugsson, T. *J. Am. Chem. Soc.* **2008,** *130*, 6900; (d) Bonnet, C. S.; Massue, J.; Quinn, S. J.; Gunnlaugsson, T. *Org. Biomol. Chem.* **2009,** *7*, 3074 (c) Plush, S.E; Gunnlaugsson, T. *Dalton Trans*., **2008**, 3801. (d) Plush, S.E; Gunnlaugsson, T. *Org. Lett.,* **2007**, 9, 1919. (e) Tsukube, H.; Shinoda, S.; *Chem. Rev*., **2002**, 102, 2389; (f) Parker, D. *Chem. Soc. Rev*., **2004**, 33 156. (g) Gunnlaugsson, T.; Harte, A. J.; Leonard, J. P.; Nieuwenhuyzen, M. *Chem. Commun.* **2002**, 2134.

[9] (a) Beer, P. D.; Timoshenko, V. Maestri, M.; Passaniti P.; Balzani, V. *Chem. Commun*., **1999**, 1755; (b) Beer; P.D. *Chem. Commun*., **1996**, 689.

[10] (a) Leonard, J. P.; dos Santos, C. M. G.; Plush, S. E.; McCabe, T., Gunnlaugsson, T. *Chem. Commun*., **2007**, 129. (b) Gunnlaugsson, T.; Harte, A. J.; Leonard, J. P.; Nieuwenhuyzen, M. *Supramol. Chem.* 2003, 15, 505.

[11] Amendola, V.; Boiocchi, M.; Colasson, B.; Fabbrizzi, L. *Inorg. Chem.* **2006**, 45, 6138.

[12] (a) Saha, D.; Das, S.; Bhaumik, C.;, Dutta, S.; Baitalik, S. *Inorg. Chem*., **2010**, *49*, 2334. (b) Berni, E.; Gosse, I.; Badocco, D.; Pastore, P.; Sojic, N.; Pinet, S. *Chem. Eur. J.* **2009**, *15*, 5145.

[13] Turner, D. R.; Spencer, E. C.; Howard, J. A. K.; Tocher, D. A.; Steed, J. W. *Chem. Commun.* **2004**, 1352.

[14] Elmes, R. B. P.; Gunnlaugsson, T. *Tetrahedron Lett.*, **2010**, *51*, 4082.

[15] Goodman, M. S.; Weiss, J.; Hamilton, A. D. *Tetrahedron Lett.* **1994**, 35, 8943. (b) Norsten, T. B.; Chichak, K.; Branda, N. R. *Chem. Commun.* **2001**, 1794.

[16] Fan, S-H.; Li, Q.; Wang K-Z. *Inorg. Chem. Acta*, **2009**, 362. 5155; dos Santos C. M. G Gunnlaugsson, T. *Supramol. Chem*., **2009**, *21*, 173.

[17] (a) Goswami. S.; Chakrabarty. R. *Tetrahedron Lett*. **2009**, 44, 5994; (b) Zapata, F.; Caballero, A.; Espinosa, A.; Tárraga, A.; Molina, P. *Org. Chem,* **2008**, *73*, 4034; (c) Fisher, M. G.; Gale, P. A.; Light, M. E.; Loeb, S. J. *Chem. Commun*., **2008**, 5695; (d)

[18] (a) Perez. J.; Riera, L. *Chem. Soc. Rev.,* **2008**, *37*, 2658; (b) Ghosh. A.; Ganguly. B.; Das, A. *Inorg. Chem*. **2007**, *46*, 9912; (c) Pelleteret, D.; Fletcher, N. C.; Doherty, A. P. *Inorg. Chem*., **2007**,

46, 4386; (d) Ros-Lis, J. V.; Martinez-Manez, R.; Soto, J.; McDonagh, C.; Guckian, A. *Eur. J. Inorg. Chem.*, **2006**, 2647.

[19] (a) Bayly, S. R.; Beer, P. D. *Struct. Bond.* **2008**, *129*, 45; (b) Pratt, M. D.; Beer, P. D.; *Tetrahedron*, **2004**, *49*, 11227.

[20] Ryan, G. J.; Quinn, S.; Gunnlaugsson, T. *Inorg. Chem.*, **2008**, *47*, 401.

[21] (a) Nonat, A. M.; Quinn, S. J.; Gunnlaugsson, T. *Inorg. Chem.* **2009,** *48*, 4646. (b) Senechal-David, K.; Pope, S. J. A.; Quinn, S.; Faulkner S.; Gunnlaugsson, T. *Inorg. Chem.*, **2006**, *45*, 10040.

[22] We first explored this combined recognition possibility using lanthanide ion complexes: (a) dos Santos, C. M. G.; Gunnlaugsson T. *Dalton Trans.,* **2009**, 4712. (b) dos Santos, C. M. G.; Fernandez, P. B.; Plush, S. E.; Leonard J. P.; Gunnlaugsson, T. *Chem. Commun.*, **2007**, 3389.

[23] Cametti, M.; Rissanen, K. *Chem. Commun.*, **2009**, 2809.

[24] Sheldrick, G. M. *Acta Crystallogr., Sect. A*, **2008**, *A64*, 112

[25] Johansson, O.; Borgstrom, M.; Lomoth, R.; Palmblad, M.; Bergquist, J.; Hammarstrom, L.; Sun, L.; Akermark, B. *Inorg. Chem.* **2003**, *42*, 2908.

[26] (a) Duke, R. M.; O'Brien, J. E.; McCabe T.; Gunnlaugsson, T. *Org. Biomol. Chem.*, **2008**, *6*, 4089. (d) dos Santos, C. M. G.; McCabe, T.; Watson, G. W.; Kruger, P. E.; Gunnlaugsson, T. *J. Org. Chem.*, **2008**, *73*, 9235. (c) Duke, R. M.; Gunnlaugsson, T. *Tetrahedron Lett.* **2007**, *48*, 8043. (d) Gunnlaugsson, T.; Kruger, P. E.; Jensen, P.; Pfeffer, F. M.; Hussey, G. M. *Tetrahedron Lett.*, **2003**, *44*, 8909.

[27] (a) Gale, P. A.; Hiscock, J. R.; Moore, S. J.; Caltagirone, C.; Hursthouse, M. B.; Leight, M. E. *Chem., Asian J.*, **2010**, *5*, 555. (b) Cametti, M.; Rissanen, K. *Chem. Commun.*, **2009**, 2809. (c) Boiocchi, M.; Del Boca, L.; Gomez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monzani. E. *J. Am. Chem., Soc.*, **2004**, *50*, 16507.

11

- We include a urea functionality into a Ru(II)-polypyridyl complex (**Ru·L₁**).
- We examine changes in photophysical properties of **Ru·L₁** on addition of anions.
- Luminescence of **Ru·L₁** is modulated by acetate, phosphate and pyrophosphate.
- **Ru·L₁** can distinguish between phosphate and pyrophosphate.

Modulation in MLCT emission

I_F

Ru.L$_1$

+ H$_2$PO$_4^-$

+ F$^-$

+ HP$_2$O$_7^{3-}$

Wavelength (nm)
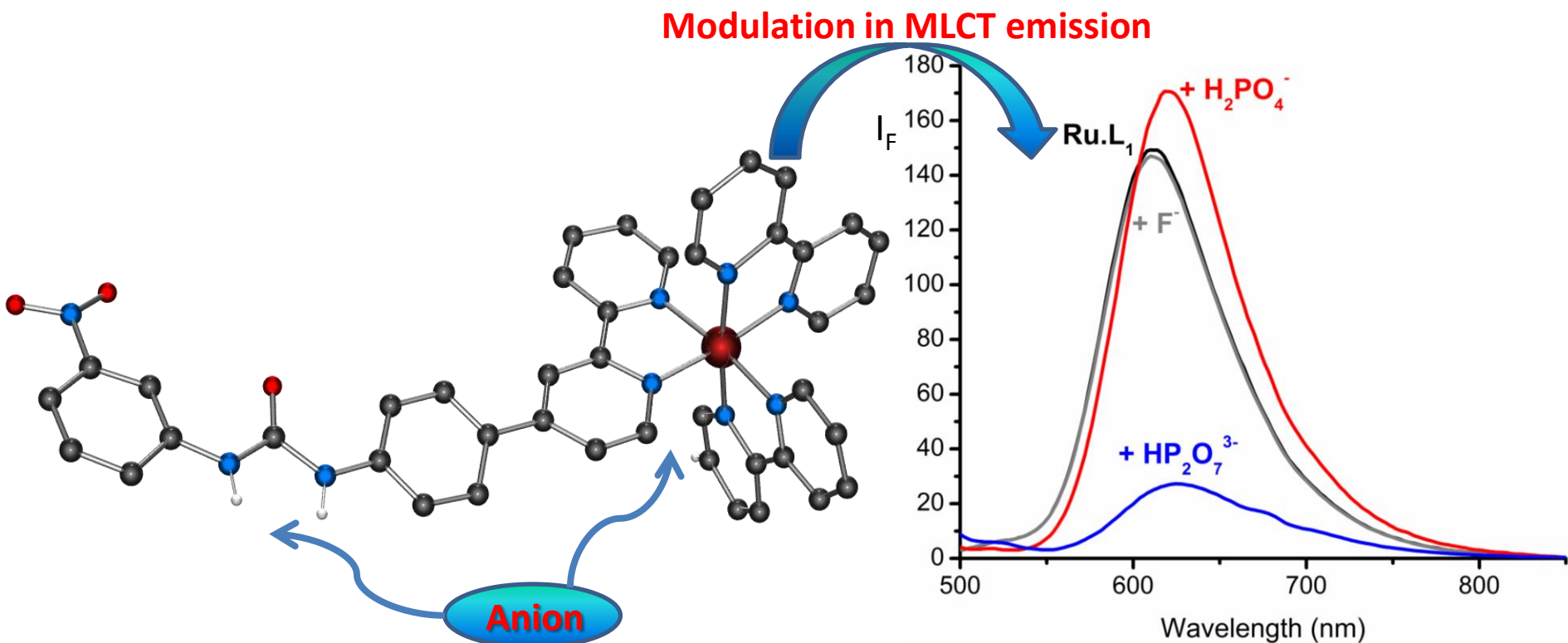
Anion

The synthesis, solid state structure and photophysical analysis of a new type of Ru(II) polypyridyl based MLCT emissive sensor for anions is presented. The anion sensing in CH$_3$CN is shown to be both selective for phosphate and pyrophosphate, both of which are recognized with high affinity.