Luminescence anion sensing via modulation of MLCT emission from a naphthalimide–Ru(II)–polypyridyl complex

Robert B. P. Elmes, Thorfinnur Gunnlaugsson *

School of Chemistry, Centre for Synthesis and Chemical Biology, Trinity College Dublin, Dublin 2, Ireland

ARTICLE INFO

ABSTRACT

The selective sensing of fluoride (F⁻; an important breakdown product of some chemical warfare agents such as sarin) was achieved by observing quenching in the metal to ligand charge transfer (MLCT) emission of the 1,8-naphthalimide–ruthenium conjugate **Ru–Nap-NH₂**, which occurs at long wavelengths in CH_3CN, using steady state fluorescence spectroscopy. The F⁻ recognition was also visible to the naked eye, with a clear colour change from yellow to red. The sensing mechanism is most likely initially via hydrogen bonding, between the anion and the amine, which, at higher concentrations, gives rise to deprotonation of the acidic 4-amino-1,8-naphthalimide moiety. However, counter ion effects may also be contributing to the overall emission changes. Other anions such as acetate, phosphate and chloride also give rise to quenching in the fluorescence emission with only minor changes in the UV–vis absorption spectra of **Ru–Nap-NH₂**. Moreover, phosphate also gave rise to shifts in the λ_{max} in the emission spectra.

The recognition and sensing of anions have become an important area of supramolecular chemistry.[1–3] Many anions play an important role in both physiology and in the environment, and several examples of both colorimetric and fluorescence sensors have been developed.[4–6] To date, most anion sensors have been based on the use of both hydrogen bonding-based receptors,[7,8] and positively charged systems, such as (poly)ammonium,[9] guanidinium[10] or Lewis acids,[11] where the anion binding/recognition can occur either through hydrogen bonding or electrostatic interactions.[12] While the sensing of biologically relevant anions should ideally be achieved using water soluble agents/sensors,[13] it is most commonly carried out in organic media.[14] In solvents such as DMSO, CHCl₃ and CH_3CN, other recognition processes can also take place, such as deprotonation, a phenomenon investigated in detail by Gale and co-workers,[15] Tian and co-workers[16] and Fabbrizzi and co-workers,[17] as well as our own research group.[18] Using the 4-amino-1,8-naphthalimide structure, which possesses long wavelength absorption (λ_{max} Abs ≈ 440 nm), and emission spectra (λ_{max} Em ≈ 520 nm), due to the presence of an internal charge transfer (ICT), we have shown that basic anions such as fluoride (F⁻) can cause deprotonation of the 4-amino moiety giving rise to a quenching of the naphthalimide emission.[18] We have also used the 4-amino-1,8-naphthalimide chromophore for the sensing of cations and in the imaging of bone structures,[19] and in the development of novel DNA-binding agents.[20] An example of the latter is the Ru(II)–polypyridyl complex **Ru–Nap-NH₂** shown in Scheme 1,

which binds strongly to DNA in competitive media, with concomitant changes in both the ground and the excited state properties of both the naphthalimide and the Ru(II) metal to ligand charge transfer (MLCT) transitions.[20b] Herein, we show that this structure
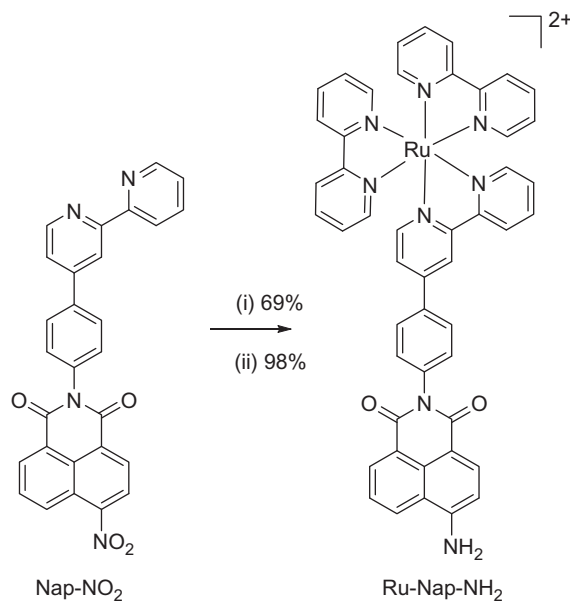
Scheme 1. Synthesis of the Ru(II)-based sensor **Ru–Nap-NH₂** from the precursor **Nap-NH₂**. Reagents: (i) Ru(bpy)₂Cl₂, DMF/H₂O, Ar, Δ; (ii) Pd/C, MeOH.

* Corresponding author. Tel.: +353 1 896 3459; fax: +353 1 671 2826.
E-mail address: gunnlaut@tcd.ie (T. Gunnlaugsson).
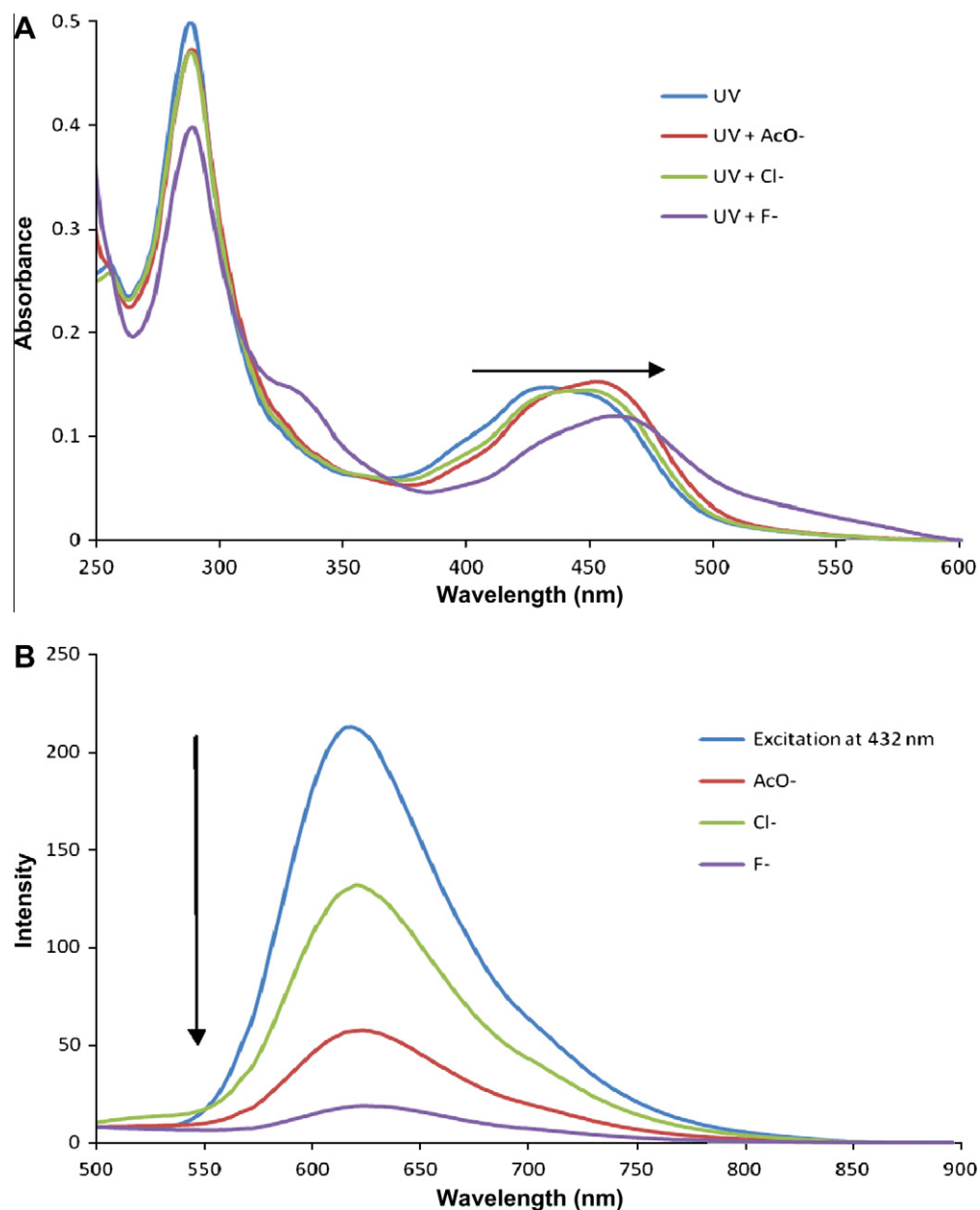
Figure 1. (A) The changes in the absorption spectra of **Ru–Nap-NH$_2$** in CH$_3$CN in the absence (—) and the presence of AcO$^-$, Cl$^-$ and F$^-$ as their TBA salts. (B) The corresponding changes in the emission spectra upon excitation at 432 nm.

can also function as an anion sensor, showing a strong bias for fluoride (F$^-$)[21] over other anions such as acetate (AcO$^-$) and other halides, in CH$_3$CN solution. The advantage of this system over that previously developed by us[18] is that the anion recognition at the naphthalimide site interferes with the energy transfer mechanism from the naphthalimide moiety to the Ru(II) MLCT excited state, causing the long wavelength red Ru-centred emission to be effectively fully quenched.

The use of transition metal ion-based polypyridyl complexes in anion sensing has been demonstrated by Beer and co-workers[22] as well as by Sessler and co-workers[23] who have used phen–Co(II) complexes and hydrogen bonding dipyrrolylquinoxaline systems, while Tian and co-workers[16] have employed zinc porphyrin naphthalimide triads. More recently Baitalik and co-workers[24] used Ru(II) complexes of 4,5-bis(benzimidazol-2-yl)imidazole ligands in anion sensing, while Sojic and Pinet[25] developed a guanidinium 3,3′-functionalised bipyridyl Ru(II) complex for anion sensing. The

synthesis of the **Ru–Nap-NH$_2$** complex was previously reported by us,[19] involving the formation of **Ru–Nap-NO$_2$** from **Nap-NO$_2$** in a two-step synthesis, as summarised in Scheme 1.

In CH$_3$CN solution, Figure 1A, the absorption spectrum of **Ru–Nap-NH$_2$** gave rise to a broad band centred at 432 nm, assigned to the naphthalimide unit and the MLCT transitions (ε = 11,694 cm^{-1} M^{-1}), and a narrower band at shorter wavelengths assigned to intraligand and naphthalimide π–π transitions (ε = 39,365 cm^{-1} M^{-1}). Upon addition of an excess of various anions, little or no changes were observed in the absorption spectrum, the most significant being seen upon addition of F$^-$ (as tetra-n-butylammonium (TBA) salt), where the long wavelength band was red shifted, and the appearance of a shoulder, centred at ca. 340 nm, was observed, which was assigned to the naphthalimide π–π transition (Fig. 1A). The transitions were also clearly visible in the excitation spectrum. These changes are somewhat smaller than previously seen for such 1,8-naphthalimide-based sensors that possess acidic protons, for

example, the 4-amino moiety that can be deprotonated.[18] In contrast to these results, significant changes were observed in the emission spectrum of **Ru–Nap-NH₂** in the presence of various anions, Figure 1B. Excitation at 432 nm (which should address both the naphthalimide and the MLCT absorption bands) gave rise to the formation of a long wavelength emitting and broad emission band entered at 615 nm, assigned to the MLCT emission alone, and a shoulder at ca. 505 nm which we assigned to the naphthalimide emission. As excitation at 432 nm addresses both excited states, the lack of any naphthalimide emission suggests that an efficient energy transfer mechanism exists from the naphthalimide singlet excited state (Nap S^1) to the MLCT*. Upon addition of the aforementioned anions, considerable changes were seen in the MLCT emission, Figure 1B,

being most pronounced for F⁻, where the emission was quenched by ca. 91%, while AcO⁻ and Cl⁻ gave rise to 73% and 39% emission quenching, respectively. Furthermore, no noticeable shifts were observed in the λ_{max} upon addition of these anions. In contrast, ions such as Br⁻ and I⁻ did not give rise to any changes in the absorption spectrum of **Ru–Nap-NH₂**, and the fluorescence emission was only marginally quenched (less than 5%); excluding anion recognition by heavy atom effect quenching.[26] We also carried out these spectroscopic titrations in DMSO and on all occasions, the same behaviour was observed as seen in CH₃CN mentioned above.

Having established that these anions gave rise to significant modulation in the MLCT-based emission spectrum of **Ru–Nap-NH₂**, we carried out detailed anion titrations, observing the
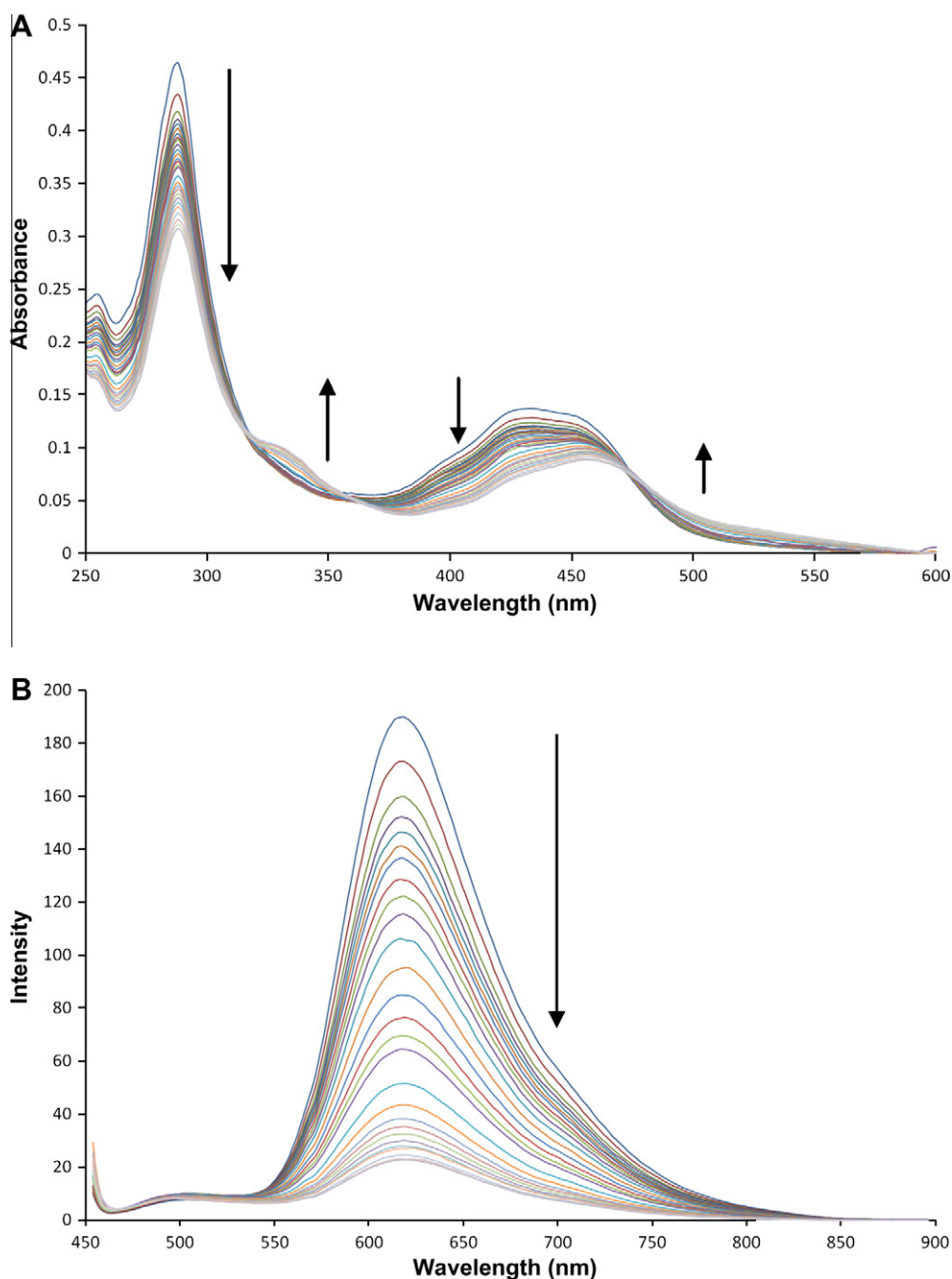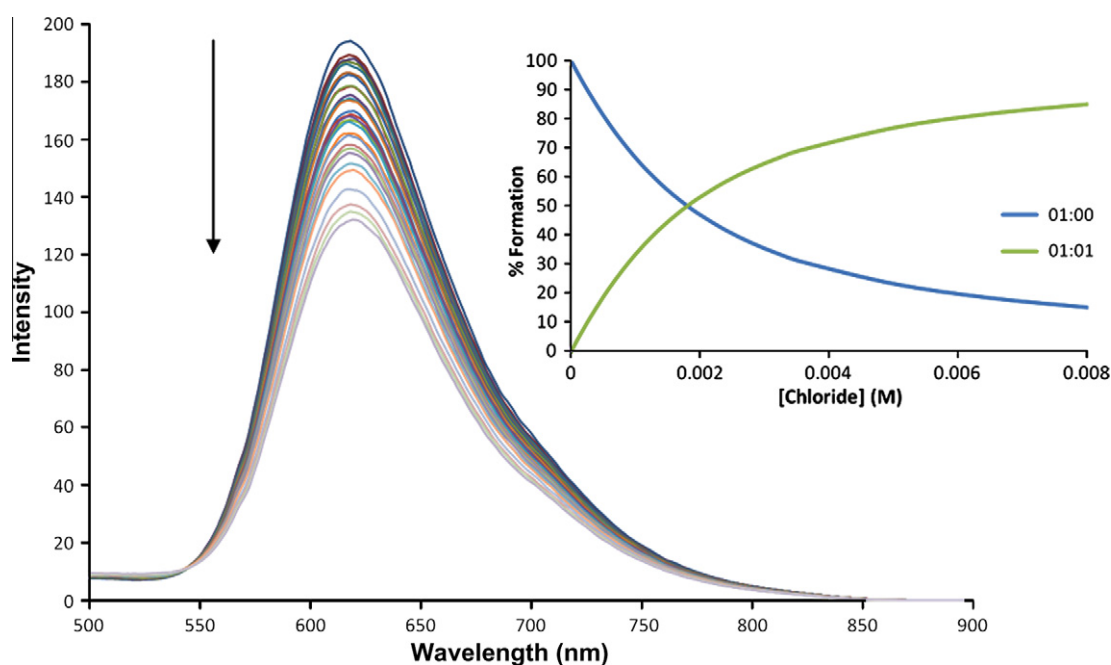

Figure 2. (A) The changes in the absorption spectrum of **Ru–Nap-NH₂** in CH₃CN upon titration with TBAF [F⁻] = 0→8.5 × 10⁻³. (B) The corresponding changes in the emission spectrum upon excitation at 432 nm.

changes in both the ground and the excited state properties of **Ru–Nap-NH₂**. The changes observed in the absorption spectrum upon titration with F⁻ in CH₃CN are shown in Figure 2A and clearly demonstrate that the MLCT band was red-shifted upon interaction with F⁻, and that the high energy transitions were also affected. The changes in the absorption spectra were also found to be reversible upon addition of competitive hydrogen bonding solvents such as EtOH and water. We were able to analyse these results by fitting the absorption changes using the non-linear regression analysis programme SPECFIT, to both 1:1 and 1:2 (host:guest) binding stoichiometries. For F⁻, this gave $\log K_{1:1} = 4.24$ (±0.01) and $\log K_{1:2} = 2.6$ (±0.13). Similarly, F⁻ greatly affected the emission spectrum, which was quenched, as demonstrated in Figure 2B. Again, the changes were best fitted to two-step binding interactions, which gave $\log K_{1:1} = 4.20$ (±0.25) and $\log K_{1:2} = 3.7$ (±0.37). While the former correlates well with the value determined from the changes in the absorption spectrum, the 1:2 binding interaction is significantly higher. The changes in the emission spectrum were reversible upon addition of water, where the emission was 'switched back on'. At higher concentrations of the sensor $(1.1 \times 10^{-3}$ M) the recognition of F⁻ was also clearly visible to the naked eye as demonstrated in the graphical abstract, whereby the solution changed from yellow to red. These changes were also reversible upon addition of water.

Similarly, the titration of **Ru–Nap-NH₂** with AcO⁻ and Cl⁻ also gave rise to changes in its absorption spectrum. However, these were, as demonstrated in Figure 1, much less pronounced than that seen for F⁻ (Fig. 2A), and we were unable to accurately determine the binding affinity from fitting these changes using non-linear regression analysis. Nevertheless, the concomitant changes in the emission spectrum were significant enough to allow for such an analysis. The overall changes observed in the emission spectrum of **Ru–Nap-NH₂** upon titration with Cl⁻ are shown in Figure 3. Also shown in Figure 3, as an inset, is the speciation distribution diagram obtained after fitting the changes in the emission spectrum, which were best fitted to 1:1 stoichiometry; giving $\log K_{1:1} = 2.90$ (±0.056). Similarly, AcO⁻ gave rise to significant changes in the emission spectrum of **Ru–Nap-NH₂**, which were best fitted to both

1:1 and 1:2 binding interactions, giving $\log K_{1:1} = 4.25$ (±0.065) and $\log K_{1:2} = 3.11$ (±0.081). As stated above, and demonstrated in Figure 1B, no measureable shifts were observed in the λ_{max} of the MLCT emission for these titrations. We also carried out titrations using $H_2PO_4^-$ and HSO_4^-. While HSO_4^- did not give rise to any significant changes in either the absorption or the emission spectrum, $H_2PO_4^-$ gave rise to ca. 50% quenching in the MLCT emission. Both the MLCT and the π–π transitions in the absorption spectrum being red-shifted (Fig. 4A), the λ_{max} of the MLCT emission was significantly affected, being red-shifted by ca. 20 nm over the course of the titration. The changes in the absorption and the emission spectra are shown for the $H_2PO_4^-$ titration in Figure 4A and B, respectively, and demonstrate differing anion behaviour to that seen above in Figure 2. The changes in the emission spectrum in Figure 4B were best fitted using 1:1 binding stoichiometry, giving $\log K_{1:1} = 4.52$ (±0.084), the speciation distribution diagram being shown in Figure 4B as an inset. To evaluate the specificity for $H_2PO_4^-$ over other anions, the absorption and the emission spectra of **Ru–Nap-NH₂** were recorded in the presence of excess $H_2PO_4^-$. Upon addition of excess F⁻, further quenching in the MLCT emission was observed. However, the emission was not blue-shifted back to the λ_{max} seen in Figure 2B. Despite this, the MLCT transition in the absorption spectrum (which mirrored that observed in Fig. 4A prior to the addition of F⁻) was blue-shifted and the shoulder, centred at ca. 340 nm in Figure 2, disappeared. While it is difficult to draw any firm conclusion from this experiment, it does show that possibly more than one anion recognition mechanism is contributing to the changes seen above.

With a view to shedding some light on the sensing mechanism for the above-mentioned anions, we also investigated the spectral changes in the ¹H NMR (400 MHz), in both DMSO-d_6 and CD₃CN, of **Ru–Nap-NH₂** with AcO⁻, Cl⁻ and F⁻. In DMSO-d_6, all of these anions gave rise to significant changes in the ¹H NMR spectrum, where several resonances were shifted upfield upon addition of AcO⁻ and Cl⁻. This would indicate that these anions are interacting with the sensors via possible hydrogen bonding between the anion and the 4-amino moiety of the naphthalimide fluorophore. Similarly, F⁻ was also shown to give rise to large changes in the ¹H

Figure 3. The changes observed in the emission spectrum of **Ru-Nap-NH₂** in CH₃CN upon titration with TBACl: [Cl⁻] = 0→8.5 × 10⁻³ M. Inset: The speciation distribution diagram derived from the fitting of the changes in the emission spectrum.
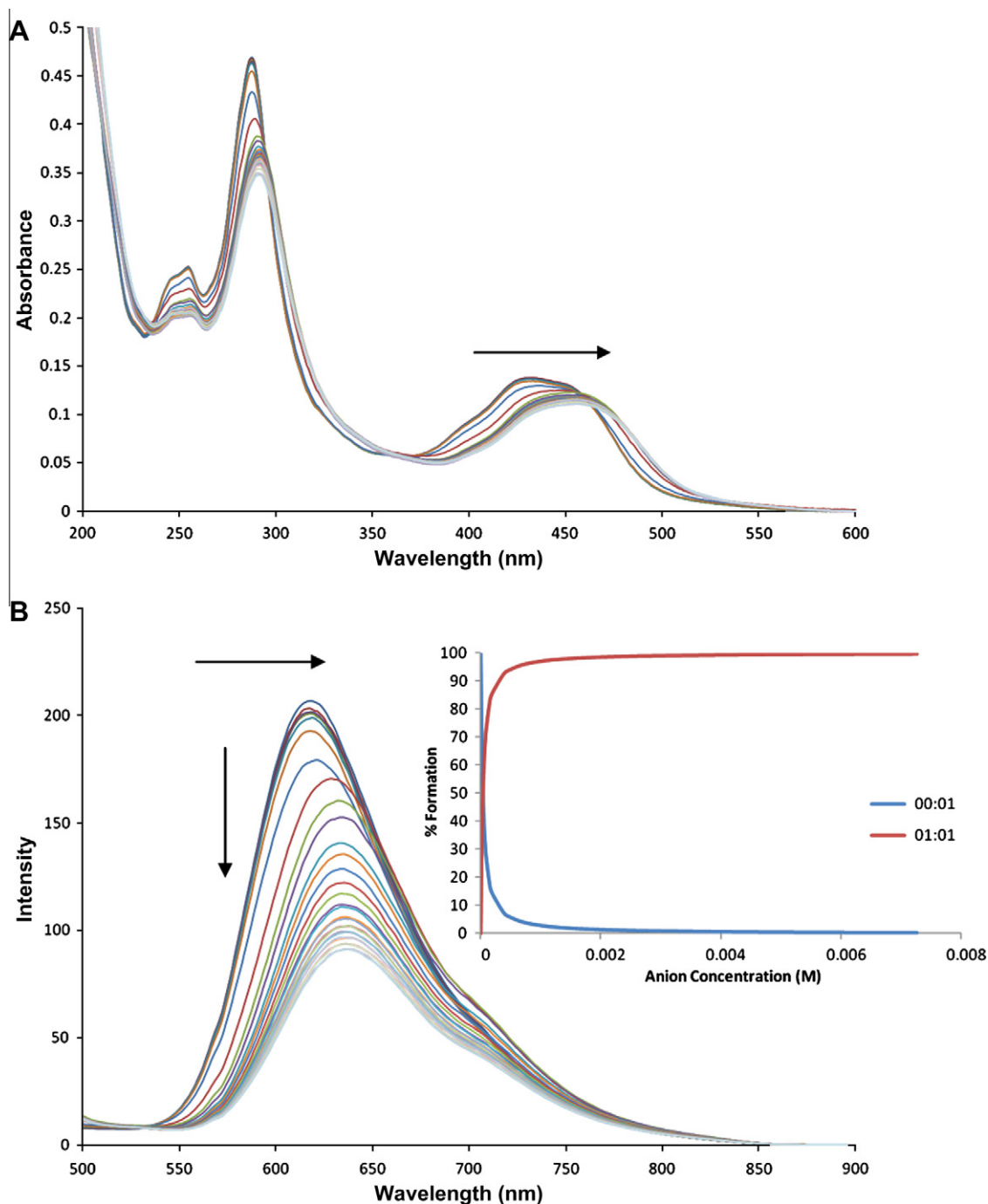
Figure 4. (A) The changes in the absorption spectrum of **Ru–Nap-NH₂** in CH₃CN upon titration with TBAH₂PO₄ solution: $[H_2PO_4^-] = 0 \rightarrow 6.7 \times 10^{-3}$ M. (B) The corresponding changes in the emission spectrum upon excitation at 432 nm. *Inset*: The speciation distribution diagram derived from the fitting of the changes in the emission spectrum.

NMR, possibly due to deprotonation of the amine. Furthermore, in the case of F⁻, the formation of a triplet at ca. 16 ppm was also observed at higher equivalents, which is usually taken as an indication for the formation of HF₂⁻.[18]

When these ¹H NMR experiments were repeated in CD₃CN, the addition of these anions gave rise to precipitation, which is most likely due to anion exchange with the PF₆⁻ counterions, rendering Ru–**Nap-NH₂** insoluble at such a high concentration (mM versus µM for absorption/fluorescence titrations).

On all accounts, this causes significant quenching of the MLCT-based emission. Hence, it is possible that the formation of the MLCT excited state, achieved by population of the naphthalimide

moiety (functioning as an antenna), as well as direct excitation of the MLCT band, is significantly diminished after this 'binding' event. However, Cl⁻ would not normally be expected to be able to deprotonate the 4-amino-napthalimide moiety,[18] but the presence of the Ru(II) centre could contribute to an enhanced acidity of these protons.[27] We are currently analysing this in greater detail as well as investigating the use of other Ru(II) polypyridyl-based complexes for use in luminescence anion sensing.

In summary, we have shown that the naphthalimide-based Ru(II)–polypyridyl complex **Ru–Nap-NH₂** can function as a highly effective and long wavelength emissive fluorescent anion sensor for several anions in organic solution, where F⁻ gives rise to the

largest changes in both the absorption (which were visible to the naked eye) and the emission spectra, the latter being almost fully quenched.

References and notes

1. Gunnlaugsson, T.; Glynn, M.; Tocci (née Hussey), G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094.
2. Sessler, J. L.; Gale, P. A.; Cho, W. S. *Anion Receptor Chemistry*; Royal Society of Chemistry: Cambridge, UK, 2006; 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.
3. Caltagirone, C.; Gale, P. A. *Chem. Soc. Rev.* **2009**, *38*, 520; Gale, P. A. *Acc. Chem. Res.* **2006**, *39*, 465; Gale, P. A.; Quesada, R. *Coord. Chem. Rev.* **2006**, *250*, 3219; Steed, J. W. *Chem. Commun.* **2006**, 2637; Beer, P. D.; Sambrook, M. R.; Curiel, D. *Chem. Commun.* **2006**, 2105; Evans, L. S.; Gale, P. A.; Light, M. E.; Quesada, R. *New J. Chem.* **2006**, *30*, 1019; Wu, F. Y.; Li, Z.; Guo, L.; Wang, X.; Lin, M. H.; Zhao, Y. F.; Jiang, Y. B. *Org. Biomol. Chem.* **2006**, *4*, 624; Ghosh, K.; Adhikari, S. *Tetrahedron Lett.* **2006**, *47*, 8165; dos Santos, C. M. G.; McCabe, T.; Watson, G. W.; Kruger, P. E.; Gunnlaugsson, T. *J. Org. Chem.* **2008**, *73*, 9235; Ali, H. D. P.; Quinn, S. J.; McCabe, T.; Kruger, P. E.; Gunnlaugsson, T. *New J. Chem.* **2009**, *33*, 793; dos Santos, C. M. G.; McCabe, T.; Gunnlaugsson, T. *Tetrahedron Lett.* **2007**, *48*, 3135; Lin, C.-I.; Selvi, S.; Fang, J.-M.; Chou, P.-T.; Lai, C.-H.; Cheng, Y.-M. *J. Org. Chem.* **2007**, *72*, 3537; Ghosh, K.; Sen, T.; Fröhlich, R. *Tetrahedron Lett.* **2007**, *48*, 2935.
4. Pfeffer, F. M.; Gunnlaugsson, T.; Jensen, P.; Kruger, P. E. *Org. Lett.* **2005**, *7*, 5375; Evans, L. S.; Gale, P. A.; Light, M. E.; Quesada, R. *Chem. Commun.* **2006**, 965; Jun, E. J.; Swamy, K. M. K.; Bang, H.; Kim, S. J.; Yoon, J. Y. *Tetrahedron Lett.* **2006**, *47*, 3103.
5. Lee, J. W.; Park, S. Y.; Cho, B.-K.; Kim, J. S. *Tetrahedron Lett.* **2007**, *48*, 2541; Nicolini, J.; Testoni, F. M.; Schuhmacher, S. M.; Machado, V. G. *Tetrahedron Lett.* **2007**, *48*, 3467; Xu, Z.; Kim, S.; Lee, K.-H.; Yoon, J. *Tetrahedron Lett.* **2007**, *48*, 3797; Luxami, V.; Kumar, S. *Tetrahedron Lett.* **2007**, *48*, 3083; Devaraj, S.; Saravanakumar, D.; Kandaswamy, M. *Tetrahedron Lett.* **2007**, *48*, 3077.
6. dos Santos, C. M. G.; Gunnlaugsson, T. *Tetrahedron Lett.* **2007**, *48*, 3135; dos Santos, C. M. G.; Gunnlaugsson, T. *Dalton Trans.* **2009**, 4712.
7. Duke, R. M.; O'Brien, J. E.; McCabe, T.; Gunnlaugsson, T. *Org. Biomol. Chem.* **2008**, *6*, 4089; Quinlan, E.; Matthews, S. E.; Gunnlaugsson, T. *Tetrahedron Lett.* **2006**, *47*, 9333; Pfeffer, F. M.; Buschgens, A. M.; Barnett, N. W.; Gunnlaugsson, T.; Kruger, P. E. *Tetrahedron Lett.* **2005**, *46*, 6579; Gunnlaugsson, T.; Davis, A. P.; Glynn, M. *Chem. Commun.* **2001**, 2556.
8. Lowe, A. J.; Dyson, G. A.; Pfeffer, F. M. *Org. Biomol. Chem.* **2007**, *5*, 1343; Pfeffer, F. M.; Lim, K. F.; Sedgwick, K. J. *Org. Biomol. Chem.* **2007**, *5*, 1795; Pfeffer, F. M.; Kruger, P. E.; Gunnlaugsson, T. J. *Org. Biomol. Chem.* **2007**, *5*, 1894; Pfeffer, F. M.; Seter, M.; Lewcenko, N.; Barnett, N. W. *Tetrahedron Lett.* **2006**, *47*, 5251.
9. García-España, E.; Díaz, P.; Llinares, J. M.; Bianchi, A. *Coord. Chem. Rev.* **2006**, *250*, 2952.
10. Schmuck, C. *Coord. Chem. Rev.* **2006**, *250*, 3053.
11. 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; Goswami, S.; Chakrabarty, R. *Tetrahedron Lett.* **2009**, *44*, 5994; Zapata, F.; Caballero, A.; Espinosa, A.; Tárraga, A.; Molina, P. *Org. Chem.* **2008**, *73*, 4034; Fisher, M. G.; Gale, P. A.; Light, M. E.; Loeb, S. J. *Chem. Commun.* **2008**, 5695; Perez, J.; Riera, L. *Chem. Soc. Rev.* **2008**, *37*, 2658; Ghosh, A.; Ganguly, B.; Das, A. *Inorg. Chem.* **2007**, *46*, 9912; Pelleteret, D.; Fletcher, N. C.; Doherty, A. P. *Inorg. Chem.* **2007**, *46*, 4386; Ros-Lis, J. V.; Martinez-Manez, R.; Soto, J.; McDonagh, C.; Guckian, A. *Eur. J. Inorg. Chem.* **2006**, 2647.
12. Yang, R.; Liu, W.-X.; Shen, H.; Huang, H.-H.; Jiang, Y.-B. *J. Phys. Chem. B* **2008**, *112*, 5105; Ali, H. D. P.; Kruger, P. E.; Gunnlaugsson, T. *New J. Chem.* **2008**, *32*, 1153.
13. Gunnlaugsson, T.; Kruger, P. E.; Jensen, P.; Tierney, J.; Ali, H. D. P.; Hussey, G. M. *J. Org. Chem.* **2005**, *70*, 10875.
14. Examples include: Lin, C.; Simov, V.; Drueckhammer, D. G. *J. Org. Chem.* **2007**, *72*, 1742; Davis, A. P.; O'Brien, J. E.; Glynn, M. *Org. Biomol. Chem.* **2005**, *3*, 48; Gunnlaugsson, T.; Davis, A. P.; Hussey, G. M.; Tierney, J.; Glynn, M. *Org. Biomol. Chem.* **2004**, *2*, 1856; Gunnlaugsson, T.; Davis, A. P.; O'Brien, J. E.; Glynn, M. *Org. Lett.* **2002**, *4*, 2449.
15. Camiolo, S.; Gale, P.; Hursthouse, M. B.; Light, M. E. *Org. Biomol. Chem.* **2003**, *1*, 741.
16. Li, Y.; Cao, L. F.; Tian, H. *J. Org. Chem.* **2006**, *71*, 8279; Xu, Z.-W.; Tang, J.; Tian, H. *Chin. Chem. Lett.* **2008**, *19*, 1353; Liu, B.; Tian, H. *J. Mater. Chem.* **2005**, *15*, 2681; Liu, B.; Tian, H. *Chem. Lett.* **2005**, *34*, 686.
17. Amendola, V.; Esteban-Gomez, D.; Fabbrizzi, L.; Liechelli, M. *Acc. Chem. Res.* **2006**, *44*, 8690; Esteban-Gomez, D.; Fabbrizzi, L.; Liechelli, M. *J. Org. Chem.* **2005**, *70*, 5717; Bonizzoni, M.; Fabbrizzi, L.; Taglietti, A.; Tiengo, E. *Eur. J. Org. Chem.* **2006**, 3567.
18. Veale, E. B.; Tocci, G. M.; Pfeffer, F. M.; Kruger, P. E.; Gunnlaugsson, T. *Org. Biomol. Chem.* **2009**, *7*, 3447; Veale, E. B.; Gunnlaugsson, T. *J. Org. Chem.* **2008**, *73*, 8073; Duke, R. M.; Gunnlaugsson, T. *Tetrahedron Lett.* **2007**, *48*, 8043; Gunnlaugsson, T.; Kruger, P. E.; Lee, T. C.; Parkesh, R.; Pfeffer, F. M.; Hussey, G. M. *Tetrahedron Lett.* **2003**, *44*, 6575; Gunnlaugsson, T.; Kruger, P. E.; Jensen, P.; Pfeffer, F. M.; Hussey, G. M. *Tetrahedron Lett.* **2003**, *44*, 8909.
19. Parkesh, R.; Lee, T. C.; Gunnlaugsson, T. *Tetrahedron Lett.* **2009**, *50*, 4114; Gunnlaugsson, T.; Lee, T. C.; Parkesh, R. *Org. Biomol. Chem.* **2007**, *5*, 310; Gunnlaugsson, T.; Lee, T. C.; Parkesh, R. *Org. Biomol. Chem.* **2003**, *1*, 3265.
20. (a) Veale, E. B.; Frimannsson, D. O.; Lawler, M.; Gunnlaugsson, T. *Org. Lett.* **2009**, *11*, 4040; (b) Ryan, G. J.; Quinn, S.; Gunnlaugsson, T. *Inorg. Chem.* **2008**, *47*, 401.
21. Cametti, M.; Rissanen, K. *Chem. Commun.* **2009**, 2809.
22. Bayly, S. R.; Beer, P. D. *Struct. Bond.* **2008**, *129*, 45; Pratt, M. D.; Beer, P. D. *Tetrahedron* **2004**, *49*, 11227.
23. Plitt, P.; Gross, D. E.; Lynch, V. M.; Sessler, J. L. *Chem. Eur. J.* **2007**, *13*, 1374; Mizuno, T.; Wei, W. H.; Eller, L. R.; Sessler, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 1134.
24. Saha, D.; Das, S.; Bhaumik, C.; Dutta, S.; Baitalik, S. *Inorg. Chem.* **2010**, *49*, 2334.
25. Berni, E.; Gosse, I.; Badocco, D.; Pastore, P.; Sojic, N.; Pinet, S. *Chem. Eur. J.* **2009**, *15*, 5145.
26. Gunnlaugsson, T.; Bichell, B.; Nolan, C. *Tetrahedron* **2004**, *60*, 5799.
27. The effect seen in Figure 3 could also be due to contribution from counter ion exchange, a phenomenon that has not been extensively explored for use in such anion sensing.