ChemComm

Wavelength Selective Separation of Metal Ions Using Electroactive Ligands

Journal:	*ChemComm*
Manuscript ID	CC-COM-04-2018-003371.R1
Article Type:	Communication

ChemComm

COMMUNICATION

Wavelength Selective Separation of Metal Ions Using Electroactive Ligands

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Sahan R. Salpage, Ronald C. Lanzetta, Yan Zhou, Jamie C. Wang, Thomas E. Albrecht-Schmitt, and Kenneth Hanson*[a]

The separation of metal ions can be challenging because of similarities in charge density, size, and binding affinities. Here, we introduce a new photochemical separations strategy that relies on intrinsically unique photophysical properties of the metal ion complexes and the selective transformation of an electroactive ligand.

Due to both cost and public safety concerns, there is an increase in demand for novel methods for the separation of metal ions in applications ranging from water purification[1] to nuclear waste management.[2] Separations strategies such as transmutation,[3] ion exchange,[4] redox chemistries,[5] and other approaches can be expensive, have limited selectivity, or are ineffective due to the similarity in charge density, size, and binding affinity of the metal ions.[6] Photochemical separation (i.e. using light to facilitate chemical transformations) is an intriguing alternative in that it relies on the intrinsically unique photophysical properties of the metal ions and coordination complexes.[7]

The most common type of photochemical separations is by way of photo-reduction where upon excitation, the metal ion is reduced and then separated via coordination with a suitable precipitating agent.[8] Although the approach works well with some rare earths and several *d*-block elements, it requires high energy irradiation (150-300 nm), expensive light sources, hazardous acids, and can be unreliable with metals that have high reduction potentials or for solutions containing more easily reduced ions/solvents.

Here, we introduce an entirely new photochemical separation strategy that relies on chemical transformations of the coordinating ligand, rather than the metal ion. Briefly, a ligand functionalized with an electroactive moiety is bound to metal ions in solution. Then, upon wavelength selective excitation of one of the coordination complexes, photoinduced electron transfer to/from the redox active group causes an irreversible reaction that chemically transforms the ligand.[9] The differences in solubility, size, reactivity, etc. between the initial and reacted complexes can then be used for separations.

For our initial efforts, terpyridine functionalized with a benzenediazonium group (tpy-Ph-N_2^+) was chosen as the electroactive ligand (Fig. 1). Diazonium groups are well known for their ability to undergo an irreversible reduction reaction and have been applied in synthetic organic chemistry,[10] as well as electro- and photo-grafting.[11] The metal ion of interest, ruthenium(II), was selected because of its well understood photophysical properties, reversible single electron oxidation, and its established coordination chemistry with tpy ligands.[12]

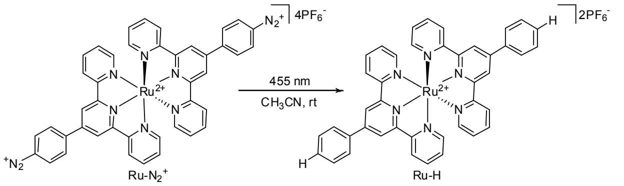

Fig. 1 Structure and photoreaction of Ru(tpy-Ph-N_2^+)$_2$(PF_6)$_4$ (Ru-N_2^+).

The Ru(tpy-Ph-N_2^+)$_2$(PF_6)$_4$ complex (**Ru-N_2^+**) was synthesized following previous published procedures with minor variation (see supporting information). Briefly, the amine substituted ligand (tpy-Ph-NH_2)[13] was reacted with $RuCl_3$ in ethanol to generate Ru(tpy-Ph-NH_2)$_2$(PF_6)$_2$.[14] The complex was then oxidized with $NaNO_2$ and precipitated with KPF_6 yielding[15] **Ru-N_2^+** as indicated by NMR and IR spectroscopy (see Fig. S6-S8). The UV-Vis absorption spectrum of **Ru-N_2^+** (Fig. 2a) has strong π-π* transitions below 350 nm and a lower energy metal-to-ligand charge-transfer (MLCT) transition from 400-600 nm that are characteristic for Ru(tpy)$_2^{2+}$ complexes.[16]

---

[a] Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306, United States. E-mail: hanson@chem.fsu.edu

†Electronic Supplementary Information (ESI) available: Synthesis and characterization of complexes and photoproducts, experimental design, and additional experimental data are reported in SI. See DOI: 10.1039/x0xx00000x

Ru-N$_2$$^+$ in a deaerated solution of MeCN (8 µM) was then irradiated with 455 nm light (100 µW) at 4 ±1°C and the spectral changes were monitored using UV-Vis spectroscopy (Fig. 2a). Experiments were performed at 4 ±1 °C to limit any competitive thermal decomposition of the diazonium functional group (Figure S11).[17] As can be seen in Fig. 2a, upon irradiation of **Ru-N$_2$$^+$** there are changes throughout the entire spectrum with notable shifts in the π-π* and MLCT peak maximum from 290 to 285 nm and 520 to 494 nm, respectively.

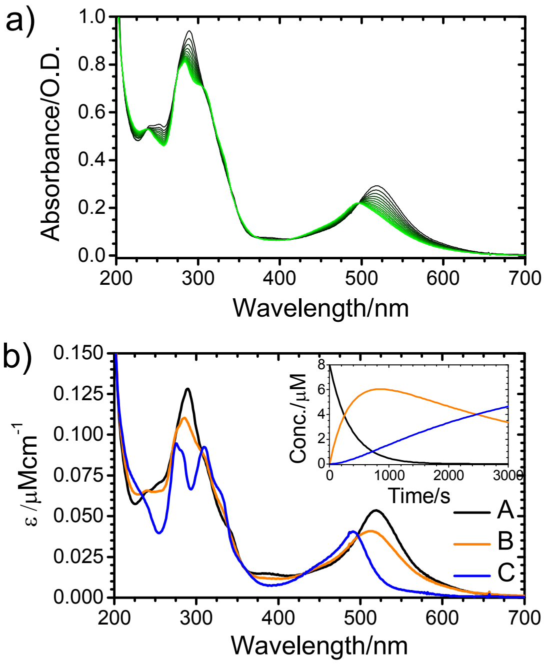

Fig. 2 Changes in the absorption spectra for **Ru-N$_2$$^+$** in MeCN at 4 ±1°C during irradiation with 455 nm light (100 µW). (0 hours (black) to 60 minutes (green) every 5 minutes) b) Absorption spectra and molar extinction coefficients for species A, B, and C from spectral fitting (Inset: Changes in relative concentration of A, B, and C).

The spectral changes could be satisfactorily fit with the SPECFIT/32 global analysis software package using a model with two consecutive first order reactions, A → B → C.[18] The absorption spectra and extinction coefficient for all three species (Fig. 2b) are consistent with Ru(tpy)$_2$$^{2+}$ complexes[19] with the spectra for A and C closely matching **Ru-N$_2$$^+$** and the photoproduct depicted in Fig. 1. The two step process as well as the gradual blue shift in absorption[15] are consistent with the sequential loss of the strongly electron withdrawing diazonium moieties in the order Ru(tpy-Ph-N$_2$$^+$)$_2$ → Ru(tpy-Ph-N$_2$$^+$)(tpy-Ph-H) → Ru(tpy-Ph-H)$_2$. The rate constants for the first step ($k_{A\rightarrow B}$ = 15.37 × 10^{-4} s^{-1}) is more than seven times faster than the second step ($k_{B\rightarrow C}$ = 2.0 × 10^{-4} s^{-1}). While the reaction is fundamentally the same, presumably the slowed kinetics for the second step are at least in part due to filtering effects by the starting material and product which competitively absorb photons and slow the reaction kinetics for B → C.

In an effort to identify the reaction product, 8 µM solution of **Ru-N$_2$$^+$** was irradiated with 455 nm light while monitoring the reaction progress with thin layer chromatography. After 2 hours, the crude mixture was purified using silica gel column chromatography. NMR (Fig. 3) and mass spec analysis of the product are all consistent with the formation of the product, Ru(tpy-Ph-H)$_2$(PF$_6$)$_2$, where the diazonium is replaced by a hydrogen atom as depicted in Fig. 1.

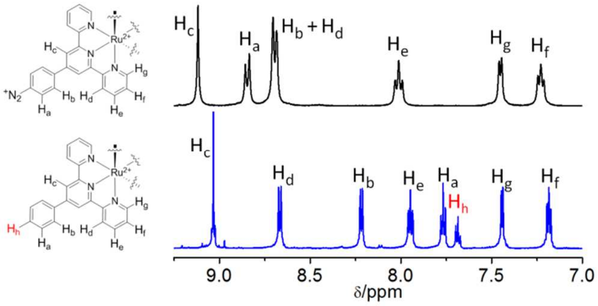

Fig. 3 ^{1}H NMR spectra and peak assignments of Ru-N$_2$$^+$ in deuterated acetonitrile before (top) and after (bottom) irradiation with 455 nm light.

Fig. 3 shows a comparison of ^{1}H NMR of **Ru-N$_2$$^+$** before and after irradiation. The ^{1}H NMR of the isolated photoproduct exhibits significant shifts in the ortho and meta protons of the phenyl group as well as an additional peak at 7.69 ppm that were not present in the starting material. The spectrum of the product is consistent with the formation of Ru(tpy-Ph-H)$_2$(PF$_6$)$_2$ which is not surprising given that diazonium is known to undergo irreversible reduction via single electron transfer,[10a, 20] loss of N$_2$, and concomitant generation of an aryl radical which presumably abstract H from the solvent.[21] It is worth noting that it has previously been shown that the aryl radical can be trapped by a radical scavenger[22] providing an addition tool for tuning the solubility difference between reactants and products.

As a step towards metal ion separations we also generated the iron containing complex, Fe(tpy-Ph-N$_2$$^+$)$_2$(PF$_6$)$_4$ (**Fe-N$_2$$^+$**), following a similar procedure to that described above for ruthenium. Upon exposure to 617 nm light (700 mW), **Fe-N$_2$$^+$** undergoes a similar photochemical reaction with the spectral changes provided in supporting information. The photoreaction for **Fe-N$_2$$^+$** is notably slower than for **Ru-N$_2$$^+$**, even at higher excitation intensities. Despite **Ru-N$_2$$^+$** being excited with higher energy light (l_{ex} = 455 nm) than **Fe-N$_2$$^+$** ($l_{ex}$ = 700 nm) the decrease in reactivity cannot be attributed to the difference in driving force for electron transfer because the excited state oxidation potential ($E_{1/2}$*), calculated using Rehn-Weller formalism, is more negative for Fe(tpy)$_2$$^{2+}$ ($E_{1/2}$* = -1.2 V vs SCE) than for Ru(tpy)$_2$$^{2+}$ ($E_{1/2}$* = -1.1 V vs SCE).[16, 23] Instead the decreased reactivity of **Fe-N$_2$$^+$** is presumably due to the significantly shorter excited state lifetime of Fe(tpy)$_2$$^{2+}$ complexes (τ ≈ 145 fs)[23c] which will result in non-radiative relaxation prior to electron transfer.

Solutions containing a one-to-one mixture of **Ru-N$_2$$^+$** and **Fe-N$_2$$^+$** in deaerated MeCN were irradiated with 455 nm and 700 nm light and the results can be seen in Fig. 4a and 4b, respectively. The starting mixture has low energy absorption peaks at 520 nm and 600 nm from the MLCT transitions of **Ru-N$_2^+$** and **Fe-N$_2^+$**, respectively. Under 455 nm irradiation, with preferential excitation into the ruthenium complex, there are notable spectral shifts to the 520 nm peak but minimal changes at 600 nm. The latter changes coincide with the rate of thermal decomposition of the **Fe-N$_2^+$** complex (Figure S11). Conversely, under 700 nm light, with selective excitation of the Fe complexes MLCT band, the spectral changes are primarily due to a photoreaction of the **Fe-N$_2^+$** complex at 600 nm with the 520 nm peak for the **Ru-N$_2^+$** complex largely unaffected (Fig. 4b).

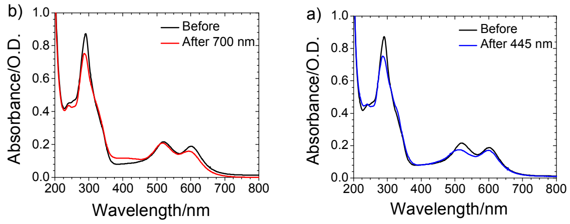

Fig. 4 Changes in the absorption spectra for one-to-one mixture of **Ru-N$_2^+$** and **Fe-N$_2^+$** in MeCN during irradiation with a) 455 nm light (100 μW) 4 ±1°C for 30 minutes and b) 700 nm light (0.5 mJ per pulse at 10 Hz) at 0°C for 4 hours.

As can be seen in Fig. 5, the photoproducts can readily be separated from the starting material using chromatography eluting with a mixture of CH_3CN, water, and sat. KNO_3(aq).[24] The **Fe-N$_2^+$**, **Ru-N$_2^+$**, and mixed solution prior to irradiation (spots A, B, and C, respectively) had limited mobility on silica gel presumably due to their +4 charge. After irradiation of **Fe-N$_2^+$** (spot D) and **Ru-N$_2^+$** (spot G) with 617 or 455 nm, respectively, the less charged photoproducts exhibit much higher mobility and readily eluted on silica gel with an R_f value of 0.6. The similar mobility of the iron and ruthenium photoproducts indicates that the solubility and the separation of these species is primarily dictated by the ligands and not the metal ions.

For the mixed solutions, excitation at 700 nm (spot E) and 455 nm (spot F) results in two distinct colored spots, one remaining on the baseline and one with the same mobility as the photoproduct. UV-Vis spectra of the mobile fraction (Fig. 5b) are in agreement with the photoreacted products of **Fe-N$_2^+$** and **Ru-N$_2^+$**. It is worth noting that a subtle spot at $R_f \approx 0.3$ can be observed in several of the samples. Given the reduced mobility relative to the product, this spot is presumably the partially reacted intermediate (B in Fig. 2b) with only one of the two diazonium moieties cleaved.

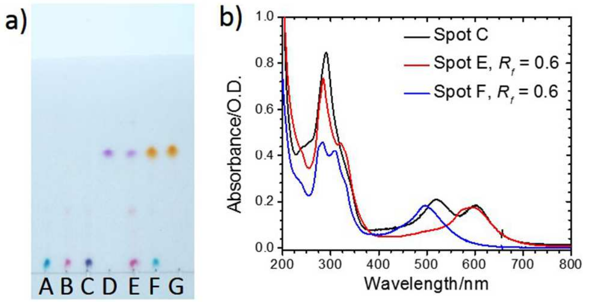

Fig. 5 a) Thin layer chromatography of **Fe-N$_2^+$** (A), **Ru-N$_2^+$** (B), and a 50:50 mixed solution (C) prior to irradiation and **Fe-N$_2^+$** after 617 nm (D), **Ru-N$_2^+$** after 455 nm (G), and a 50:50 mixed solution after 700 nm (E) and 455 nm (F) irradiation. b) UV-Vis absorption spectra of spot C (black) and the mobile fraction (R_f = 0.6) from spots E (red) and F (blue).

This wavelength selective reactivity indicates that this is not a bimolecular process (i.e. there is no *inter*molecular electron transfer) but instead, excitation, electron transfer, and the chemical reaction all occur on a single complex and are rate limited by photon flux. This observation is critical for separations in that any intermolecular electron transfer would negate the selectivity of this method. Reactions of benzenediazonium via *inter*molecular electron transfer are known[20] but as far as we know this is the first example of *intra*molecular photoinduced reaction of a diazonium group.

Conclusions

In conclusion, we have introduced electroactive ligands as a means of photochemically separating metal ions. In this example, a diazonium functionalized terpyridine ligand was coordinated to both Ru^{2+} and Fe^{2+} ions. Upon excitation, the diazonium ligand is irreversibly reduced via single electron transfer resulting in the loss of N_2, and concomitant generation of an aryl radical which then abstracts H from the solvent. For a mixture of metal ions, excitation at 455 nm and 700 nm, results in a wavelength selective photoreaction of the ruthenium and iron complexes, respectively, while the other species remains largely unperturbed. Due to the large difference in charge, the product (2+) can readily be separated from starting material (4+) using thin layer chromatography. As far as we know this is the first example of separating metal ions by way of a wavelength selective photochemical transformation of a ligand. This result opens the door to an entirely new separations strategy that does not rely on the solubility or binding affinity of the metal ion but instead on the intrinsically unique absorption spectrum of the metal complexes and the properties of the reacted ligand. While the separation of Ru^{2+} and Fe^{2+} can be achieved by other means, expanding this strategy to other ions, particularly lanthanides and actinides, could provide a unique method to separate species with nearly identical binding affinities. In fact, given the broad MLCT absorption features of the Ru^{2+} and Fe^{2+} complexes reported here, selective excitation and quantitative separations is in all likelihood not possible. However, the narrow and unique absorption features of lanthanide and actinide complexes makes them ideal candidates for this wavelength selective separations strategy.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported as part of the Center for Actinide Science and Technology (CAST), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under award no. DESC0016568. Mass spectroscopy analysis was performed at Mass Spectrometry Research and Education Center at University of Florida supported by grant NIH S10 OD021758-01A1.

References

[1] a F. Fu, Q. Wang, *Journal of Environ. Manage* 2011, ***92***, 407; b P. A. Turhanen, J. J. Vepsäläinen, S. Peräniemi, *Sci. Rep.* 2015, ***5***, 8992.
[2] E. Macerata, E. Mossini, S. Scaravaggi, M. Mariani, A. Mele, W. Panzeri, N. Boubals, L. Berthon, M.-C. Charbonnel, F. Sansone, A. Arduini, A. Casnati, *J. Am. Chem. Soc.* 2016, ***138***, 7232.
[3] T. A. Todd, *Nuclear Energy and the Environment, Vol. 1046*, Am. Chem. Soci., **2010**, 13.
[4] a S. D. Rassat, J. H. Sukamto, R. J. Orth, M. A. Lilga, R. T. Hallen, *Sep. Purif. Technol.* 1999, ***15***, 207; b C. Sarzanini, *J. Chromatogr. A* 1999, ***850***, 213.
[5] a F. David, A. G. Maslennikov, V. P. Peretrukhin, *J. Radioanal. Nucl. Chem.* 1990, ***143***, 415; b J. Khan, B. P. Tripathi, A. Saxena, V. K. Shahi, *Electrochim. Acta* 2007, ***52***, 6719.
[6] a B. Reuben, *Chem. Ind. (London, U. K.)* **2005**, 27; b K. C. Sole, CRC Press, **2008**, 141.
[7] T. Donohue*, Opt. Eng.* 1979, ***18***, 181.
[8] a E. Borgarello, N. Serpone, G. Emo, R. Harris, E. Pelizzetti, C. Minero, *Inorg. Chem.* 1986, ***25***, 4499; b T. Donohue, *Chem. Phys. Lett.* 1977, ***48***, 119; c T. Donohue, *J. Chem. Phys.* 1977, ***67***, 5402; d B. Van den Bogaert, D. Havaux, K. Binnemans, T. Van Gerven, *Green Chem.* 2015, ***17***, 2180.
[9] Y. Zhang, Q. Zhou, Y. Zheng, K. Li, G. Jiang, Y. Hou, B. Zhang, X. Wang, *Inorg. Chem.* 2016, ***55***, 4296.
[10] a I. Ghosh, L. Marzo, A. Das, R. Shaikh, B. König, *Acc. Chem. Res.* 2016, ***49***, 1566; b C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* 2013, ***113***, 5322.
[11] a M. Bouriga, M. M. Chehimi, C. Combellas, P. Decorse, F. Kanoufi, A. Deronzier, J. Pinson, *Chem. Mater.* 2013, ***25***, 90; b S. Gam-Derouich, S. Mahouche-Chergui, M. Turmine, J.-Y. Piquemal, D. B. Hassen-Chehimi, M. Omastová, M. M. Chehimi, *Surf. Sci.* 2011, ***605***, 1889.
[12] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* 1988, ***84***, 85.
[13] M. Trigo-López, A. Muñoz, S. Ibeas, F. Serna, F. C. García, J. M. García, *Sens. Actuators B: Chemical* 2016, ***226***, 118.
[14] a G. D. Storrier, S. B. Colbran, D. C. Craig, *J. Chem. Soc., Dalton Transactions* 1997, 3011; b W. Y. Ng, X. Gong, W. K. Chan, *Chem. Mater.* 1999, ***11***, 1165.
[15] R. Bangle, R. N. Sampaio, L. Troian-Gautier, G. J. Meyer, *ACS Appl. Mater. Interfaces* 2018, ***10***, 3121.
[16] M. Maestri, N. Armaroli, V. Balzani, E. C. Constable, A. M. W. C. Thompson, *Inorg. Chem.* 1995, ***34***, 2759.
[17] R. A. Abramovitch, W. A. Hymers, J. B. Rajan, R. Wilson, *Tetrahedron Lett.* 1963, ***4***, 1507.
[18] *SPECFIT/32*, Spectrum Software Associates, 197M Boston Post Road West, Marlborough,

MA, 01752 USA, **2004**.
[19] P. Lainé, F. Bedioui, P. Ochsenbein, V. Marvaud, M. Bonin, E. Amouyal, *J. Am. Chem. Soc.* 2002, ***124***, 1364.
[20] D. P. Hari, B. König, *Angew. Chem. Int., Ed.* 2013, ***52***, 4734.
[21] C. Pan, H. Zhang, C. Zhu, *Org. Biomol. Chem.* 2015, ***13***, 361.
[22] P. Schroll, D. P. Hari, B. König, *ChemistryOpen* 2012, *1*, 130.
[23] a R. Dieter, W. Albert, *Isr. J. Chem.* 1970, ***8***, 259; b W. Gawelda, A. Cannizzo, V.-T. Pham, F. van Mourik, C. Bressler, M. Chergui, *J. Am. Chem. Soc.* 2007, ***129***, 8199; c Y. Liu, T. Harlang, S. E. Canton, P. Chabera, K. Suarez-Alcantara, A. Fleckhaus, D. A. Vithanage, E. Goransson, A. Corani, R. Lomoth, V. Sundstrom, K. Warnmark, *Chem. Commun.* 2013, ***49***, 6412.
[24] B. Jousselme, G. Bidan, M. Billon, C. Goyer, Y. Kervella, S. Guillerez, E. A. Hamad, C. Goze-Bac, J.-Y. Mevellec, S. Lefrant, *J. Electroanal. Chem.* 2008, ***621***, 277.