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PAPER
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Yellowish and blue luminescent graphene oxide quantum dots
prepared via a microwave-assisted hydrothermal route using
H2O2 and KMnO4 as oxidizing agents
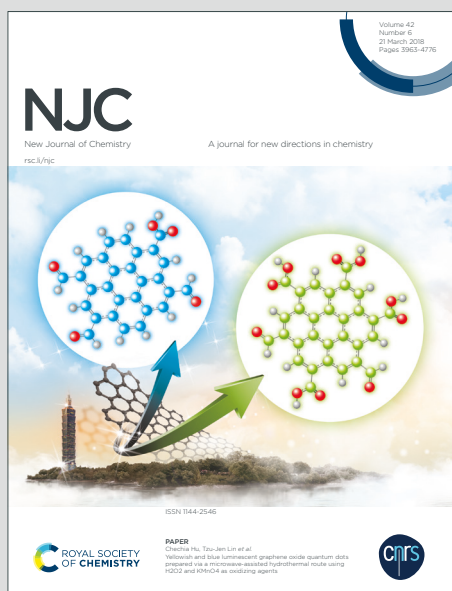
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Panchromatic Ru(II)-polypyridyl complexes as NIR emitters

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**Two novel *mer*-Ru(II) heteroleptic complexes containing stongly donating tridentate ligands (dgpy and dgpz) were synthesised and optoelectronically characterised. These complexes exhibited quasi-reversible ligand- and metal-based redox events and panchromatic absorption with the lowest energy absorption maxima trailing up to 750 nm. These panchromatic dyes were found to be NIR emissive at $\lambda_{PL} \sim 835$ nm with associated excited-state lifetimes (τ_{PL}) of ~ 10 ns. The enhanced photophysical properties of these complexes compared to those of $[Ru(tpy)_2]^{2+}$ (tpy = 2,2':6',2"-terpyridine; $\lambda_{abs} < 575$ nm, $\lambda_{PL} \sim 629$ nm and $\tau_{PL} \sim 0.25$ ns) are due to the larger ^3MLCT-^3MC energy-gap as a combined effect of larger bite angle and strong σ-donation offered by the dgpy and dgpz ligands.**

Facile ligand modifications around a Ru(II) ion in Ru(II)-polypyridyl complexes afford these complexes to exhibit remarkable electrochemical and photophysical properties.[1] In general, the interest in these compounds stems from their potential application as light harvesters in dye-sensitised solar cells,[2] water-splitting catalysis,[3] and electroluminescent dyes in organic light-emitting devices.[4] In view of many civilian and military aspects, particularly in fibre-optic communication[5] and biomedical imaging,[6] deep-red to near-infrared Ru(II)-chromophores and -emitters are especially useful. While $[Ru(bpy)_3]^{2+}$-type (bpy = 2,2'-bipyridine, $\tau_{PL} \sim 1$ μs, $\Phi_{PL} \sim 0.095$) complexes exhibit more advantageous photophysical properties than the $[Ru(tpy)_2]^{2+}$-type (tpy = 2,2':6',2"-terpyridine, $\tau_{PL} < 1$ ns, $\Phi_{PL} \sim 1 \times 10^{-6}$) complexes (**C1** in **Chart 1**), the complexes of bidentate ligands are synthetically less appealing due to absence of stereospecificity.[7] On the other hand, Ru(II) complexes of tridentate ligands are achiral and stereopure and can be easily incorporated into larger supramolecular assemblies for vectorial energy transfer.[8]

The optoelectronic properties of Ru(II)-polypyridyl complexes are predominantly governed by the energy gap between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO). The red shift in the absorption and emission spectra resulting from a narrowing of this energy gap is a key in the design of NIR emitters. On this note, various ligands are often judiciously designed to alter the HOMO-LUMO energy gap and in turn the optoelectronic properties of the complexes of interest. Many strategies have been used to red-shift the emission spectra and prolong the excited-state lifetimes of complexes with tridentate ligands, e.g., (i) incorporation of electron-donating (D)/-accepting (A) functionalities on to the backbone of a tpy ligand (complex **C2** in **Chart 1**).[9] The LUMO based on the π*-orbital of the tpy-A ligand stabilised whereas the tpy-D ligand destabilises the HOMO-metal-centered π(t_{2g}) orbital. In other words, both substituents concur to lower the HOMO-LUMO energy gap and the excited-state energy compared to those in parent unsubstituted homoleptic analogue.[9] (ii) The carbonyl functionality in the fpbpyk chelate of complex **C3** (**Chart 1**), in part, elongates the π conjugation and hence decreases the energy of the metal-to-ligand charge transfer (MLCT) band. Thus, complex **C3** containing the fpbpyk chelate showed the MLCT absorption and emission spectra being further red-shifted from that of the non-ketone homolptic analogue.[10] (iii) Tridentate ligands with reduced steric strain and increasing field strength compared to those
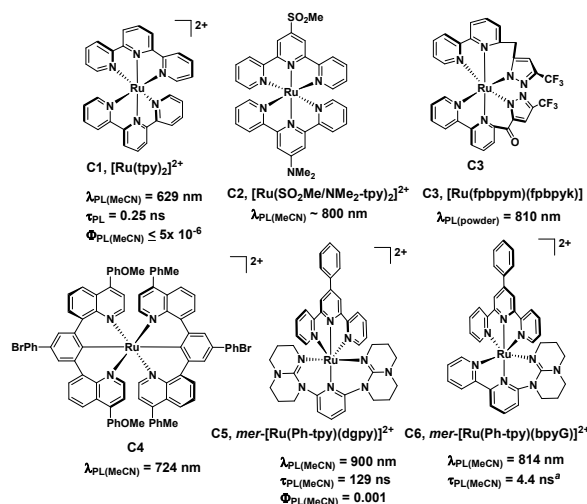
Chart 1. Benchmark (**C1-C6**) Ru(II)-polypyridyl complexes with their relevant photophysical properties.

of a tpy ligand, that help increase the excited state lifetime[11] and red-shift the triplet MLCT emission maxima (**C4** in **Chart 1**).[11a,12] (iv)

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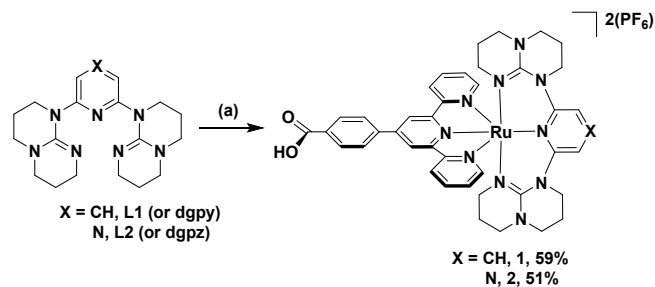Email: akp5@st-andrews.ac.uk

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Tridentate ligands with strongly donating moiety such as 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine (**H-hpp**) that is capable of forming six-membered chelate upon coordination to a metal-ion (**C5** and **C6** in **Chart 1**).[7b,13a-c] (V) Introduction of multidentate bridging ligands, e.g., 2,3,5,6-tetrakis-(2-pyridyl)pyrazine, 2,3-bis(2-pyridyl)pyrazine or 2,3-di(2-pyridyl)-5,6-diphenylpyrazine to afford bimetallic Ru(II)-Ru(II) or Ru(II)-Pt(II) complexes and others, such that, they absorb visible light strongly (in ^{1}MLCT fashion) and emit by Vis/NIR emission at r.t. with relatively long excited-state lifetime.[13d]

Recently Hanan and co-workers used the ligands 2,6-bis(3,4,7,8-tetrahydro-2H-pyrimido[1,2-a]pyrimidin-1(6H)-yl)pyridine (dgpy or **L1**) and 2,6-bis(3,4,7,8-tetrahydro-2H-pyrimido[1,2-a]pyrimidin-1(6H)-yl)pyrazine (dgpz or **L2**) that comprise two strongly donating hpp moieties. These ligands were coordinated with Ru(II), Re(I) or Co(III) ions and the luminescence properties of these complexes were shown to be dramatically enhanced (or induced for [Co(dgpy/dgpz)$_2$]$^{3+}$) compared to those of [Ru(tpy)$_2$]$^{2+}$ and [Re(tpy)(CO)$_2$(L)]$^+$ (where L = MeCN, pyridine, PEt$_3$, PPh$_3$).[13,14] The dgpy ligand was employed with [Ru(tpy)Cl$_3$] precursor to form heteroleptic [Ru(tpy)(dgpy)]$^{2+}$ complex. In these cases, the 4′-position of the tpy ligands either contained electron donating *t*Bu-phenyl group or electronically decent bromo-phenyl group for further functionalization. The optoelectronic properties of these complexes were investigated whereas the properties of analogous complexes containing electron withdrawing functionalised tpy still remain of interest. Herein, we report the structure-property relationship study of two novel heteroleptic Ru(II) complexes of both dgpy and dgpz ligands that are also coordinated with electron withdrawing -CO$_2$H functionalised tpy ligand. The idea of using a -CO$_2$H functionalised tpy ligand was to use the -CO$_2$H group as an anchor to the mesoporous TiO$_2$ in a dye-sensitised solar cell, which will be published in due course. The optoelectronic properties of these complexes containing a donating dgpy/dgpz ligand and accepting tpy ligand are investigated and compared with those of the structurally analogous literature reported complexes.

The *N*-heterocyclic ligands **L1** and **L2** (**Scheme 1**),[13,14] 4-([2,2′:6′,2″-terpyridin]-4′-yl)benzoic acid (CO$_2$HPh-tpy)[15] and [Ru(CO$_2$HPh-tpy)Cl$_3$][16] were synthesized using literature procedures. The stoichiometric reaction of **L1** and **L2** with Ru(CO$_2$HPh-tpy)Cl$_3$ in refluxing *n*-butanol, in presence of few drops of 4-ethylmorpholine, provided complexes **1**, [Ru(CO$_2$HPh-tpy)(**L1**)][(PF$_6$)$_2$] and **2**, [Ru(CO$_2$HPh-tpy)(**L2**)][(PF$_6$)$_2$] in good yields (51-59%, **Scheme 1**).

Scheme 1. Syntheses of complexes **1** and **2**. (a) Ru(CO$_2$HPh-tpy)Cl$_3$ (1 equiv.) in *n*-butanol at reflux for 20 h in presence of 4-ethylmorpholine, followed by the addition of aqu. NH$_4$PF$_6$ and column chromatography purification.

The appearance of multiple peaks over 0-4 ppm region in ^{1}H NMR spectra of **1** and **2** suggests that upon coordination to the metal center, the exchange between the equatorial and axial protons in the saturated backbone of **L1** and **L2** are slow compared to the NMR time

scale, as observed in analogous Ru(II) complexes (**Figures S1** and **S3** in ESI).[13,14]

Single crystals of **1**, suitable for X-ray structure diffraction, were obtained by slow vapour diffusion of diethylether into concentrated acetone-acetonitrile (1:1, v/v) solution of **1**. Selected crystallographic parameters are tabulated in **Tables S1** and **S2** (ESI). The Ru(II) centre has the expected distorted octahedral geometry with meridionally coordinated tridentate ligands (**Figure S9**, ESI). The Ru-N bond distance (1.939(2) Å) to the central pyridine ring of CO$_2$HPh-tpy is the shortest among all Ru-N bonds and the Ru-N bond distances closely resemble those observed in [Ru(Ph-tpy)$_2$][PF$_6$]$_2$.[17] The bite angle subtended by the two trans N-atoms of **L1** and the Ru-atom (N7-Ru1-N10 = 172.40(10)°) is noticeably increased from that exhibited by the CO$_2$HPh-tpy ligand (N1-Ru1-N3 = 159.07(10)°), which indicates a more perfect octahedral geometry around Ru(II) in complex **1**, compared to that in [Ru(Ph-tpy)$_2$][PF$_6$]$_2$. The average C$_{alkene,hpp}$-N$_{hpp}$-C$_{py}$-N$_{py}$ dihedral angle of 51.2° indicates a broken π-conjugation between the pyridyl and the **hpp** units.

The electrochemical behaviors of complexes **1** and **2** were examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) and redox values are reported *vs.* SCE (**Figure 1**). The redox processes were found to be monoelectronic by DPV when compared to Fc$^+$/Fc. At positive potentials, complexes **1** and **2** show quasi-reversible Ru(III/II)-HOMO-based oxidations at 0.52 V and 0.59 V, respectively, as suggested by DFT calculations (**Figure 2** and **Table S3** in ESI). Owing to the strong σ-donation from the hpp moieties to the metal based orbitals, these E$_{1/2}^{Ox}$ values are ~ 800 mV less positive than that observed for the Ru(III/II) couple in [Ru(tpy)$_2$]$^{2+}$ (E$_{Ox1}$ *vs.* SCE = 1.31 V),[18] and fall closely to the oxidation potential observed for the cyclometalated complex [Ru(tpy)(1,3-di(2-pyridyl)benzene)]$^+$ (E$_{Ox1}$ *vs.* SCE = 0.51 V).[19] The stronger electron withdrawing effect of a pyrazine moiety (σ$_I$ = 0.25; σ$_I$ = Hammett parameter)[20] in **L2** compared to the same of a pyridine moiety (σ$_I$ = 0.18) in **L1** is noticeable in 70 mV anodic shift of first oxidation potential of **2** compared to that of **1**. The higher energy calculated for the HOMO of **1** (E$_{HOMO}$ = -9.89 eV) and **2** (E$_{HOMO}$ = -10.09 eV) compared to that of [Ru(tpy)$_2$]$^{2+}$ (E$_{HOMO}$ = -11.17 eV) are in good agreement with the lower anodic potentials measured for **1** and **2** (**Figure 2** and **Tables S4**, **S5** in ESI) in comparison to [Ru(tpy)$_2$]$^{2+}$.
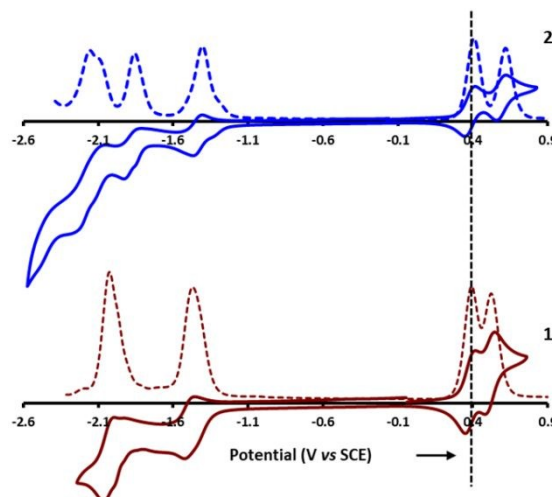
Figure 1: Cyclic voltammograms of **1** (maroon) and **2** (blue) in bold lines in dry, degassed CH$_3$CN. Differential pulse voltammograms of **1** (maroon) and **2** (blue) are presented in dotted lines. Vertical line at 0.38 mV represents the Fc$^+$/Fc couple in both the voltammograms.

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At negative potentials, both complexes display three quasi-reversible to irreversible reduction peaks in the range of -1.44 V to -2.73 V (**Figure 1**). While the third reduction peak was found to be quasi-reversible for **2**, the same was found to be irreversible for **1** (**Figure S11**, ESI). As suggested by DFT calculations of **1** and **2**, the LUMO predominantly resides on CO_2HPh-tpy ligand, thereby the first reduction peak is believed to be based on the CO_2HPh-tpy ligand. The more electron-rich metal center in **1** and **2**, compared to that in $[Ru(tpy)_2]^{2+}$ (E_{red1} *vs.* SCE = -1.23 V), increases back-donation to the CO_2HPh-tpy ligand and accordingly cathodically shifts the ligand-based reduction, albeit to a lesser extent than that observed for the oxidation couple.[19a] The destabilization of the LUMO of **1** (E_{LUMO} = -6.98 eV) explains the shift of 50 mV and 260 mV to more negative values measured for the first reduction potential of **1** compared to those of **2** (E_{LUMO} = -7.13 eV) and $[Ru(tpy)_2]^{2+}$ (E_{LUMO} = -7.58 eV), respectively (**Table S3** in ESI).
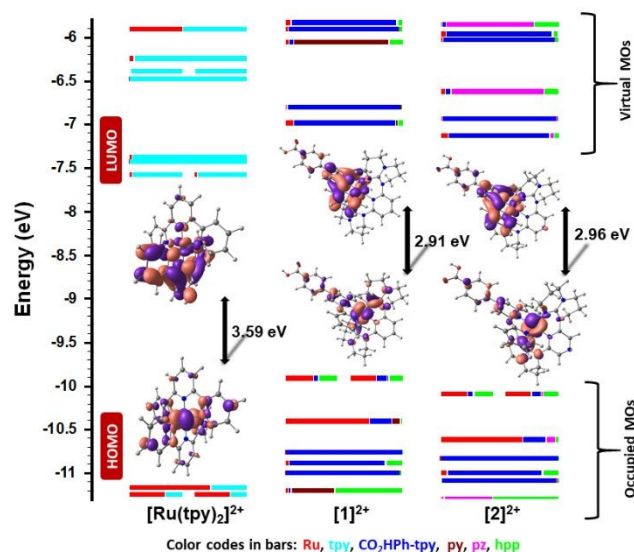

Figure 2. Calculated Kohn-Sham energy level diagram and electron density distribution images of the HOMO, LUMO of $[1]^{2+}$ and $[2]^{2+}$ using DFT calculations (b3lyp/SBKJC-VDZ[Ru], 6-31G**[C,H,N,O]).

The UV-vis absorption spectra of **1** and **2** in dry acetonitrile solutions display varying contributions of ligand-centered (LC) $\pi\rightarrow\pi^*$ transitions in the UV region ($\lambda_{abs} \leq 290$ nm) as suggested by TD-DFT calculations of **1** and **2** (**Figures S12-S14**, **Tables S6-S8** in ESI). Singlet metal-to-ligand charge transfer (^{1}MLCT) bands come into play in the region 315-325 nm in conjunction with LC transitions. For **1**, the absorption band at ~ 390 nm is predominantly a HOMO-1→LUMO+2 transition and predominantly composed of ^{1}MLCT Ru($d\pi$)→Py(π^*) transition of **L1**, while the transition at 396 nm for **2** is a HOMO-2→LUMO+2 and is primarily consisted of ^{1}MLCT Ru($d\pi$)→Pz(π^*) transition of **L2** with minor ^{1}MLCT contribution from Ru($d\pi$)→CO_2HPh-tpy(π^*) (**Tables S7**, **S8** in ESI). It may be noted that such a band near 345 nm is usually observed for $[RuN_4(diimine)]^{2+}$ chromophores.[21] For both the complexes the lower energy transitions at 530-620 nm is dominated by transitions among frontier M.O.s, such as HOMO→LUMO, HOMO-(1 or 2)→LUMO, HOMO→LUMO+1 and these transitions are attributed to the ^{1}MLCT and singlet ligand-to-ligand charge transfer (^{1}LLCT) transitions, predominantly dominated by ^{1}MLCT while the contribution from ^{1}LLCT transition is minor. The most noticeable feature in the visible region is that the lowest energy ^{1}MLCT maxima of **1** and **2** are red-

shifted by ~ 150 nm with respect to that of $[Ru(tpy)_2]^{2+}$ (λ_{abs} = 474 nm).[13b,c] Ligands **L1** and **L2** are expected to interact with the $t_2[d(Ru)]$ orbitals of Ru(II) more strongly than tpy. This interaction reduces the energy-gap between the metal-based HOMO and tpy-based LUMO and hence the observed red-shift in $d\pi\rightarrow\pi^*$ ^{1}MLCT transition.[21]

The emission spectra of complexes **1** and **2** were measured in deaerated acetonitrile solution at 298 K upon excitation at 550 nm. The emission maxima for complexes **1** and **2** appear at 839 and 834 nm, respectively (**Figure 3** and **Table S9** in ESI), with associated excited-state lifetimes (τ_{PL}) of 9.03 ns for **1** and 11.06 ns for **2**. The nature of the emissions in both the complexes is ascribed as triplet metal-to-ligand charge transfer (^{3}MLCT) from Ru($d\pi$) to tpy(π^*) by unrestricted DFT calculations as the spin density in both the complexes is distributed predominantly over the Ru(II) ion and the tpy moiety (**Figure S16**, ESI). The DFT calculated emission energies of **1** and **2** are found at 932 and 886 nm with relative errors of 11% and 6.2% in calculations, respectively. To the best of our knowledge these complexes are among the rare examples of such a low energy ^{3}MLCT emission from a bis(tridentate) $Ru^{II}N_6$ complex.[7b,13b-c,22] As expected the emission wavelength is red-shifted upon introduction of **L1/L2** in place of a terpyridine ligand in $[Ru(tpy)_2]^{2+}$ (λ_{em} = 629 nm) and $[Ru(Ph$-tpy$)_2]^{2+}$ (λ_{em} = 670 nm). Complexes **1** and **2** exhibit ~ 40 times longer τ_{PL} values compared to that of $[Ru(tpy)_2]^{2+}$ (τ_{PL} = 0.25 ns).[23] This fact is due to larger bite angle (N-Ru-N ~ 173° in **1** and **2**, N-Ru-N ~ 158° in $[Ru(tpy)_2]^{2+}$) and stronger σ-donation compared to those of a tpy moiety that help to destabilise the ^{3}MC state of **1** and **2** and consequently diminishing the process of thermal non-radiative deactivation *via* ^{3}MC state. It has been shown that substitution of a 2,6-bis(8'-quinolinyl)pyridine (**bqp**) ligand with a tpy ligand, that exhibits lower bite angle upon coordination than **bqp**, diminishes the lifetime of the $[Ru(bqp)(tpy)]^{2+}$ complex to only 7.4 ns compared to 3 µs in $[Ru(bqp)_2]^{2+}$.[11b] Although substituted by Ph-tpy, the strong σ-donation and larger bite angle of **L1/L2** upon coordination, comparable to that of **bqp** (177.6(7)°), render the ^{3}MC states higher in energy and thus increasing the lifetime by ~ 40 times
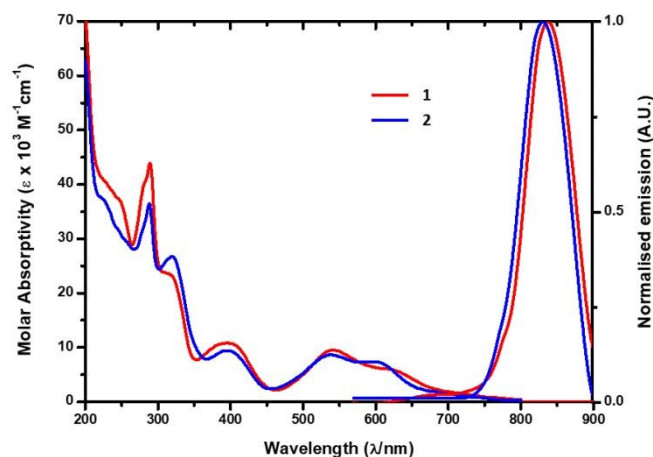
Figure 3. Absorption and normalized emission spectra of **1** and **2** in dry, deaerated MeCN solutions at r.t.

in **1** or **2** compared to that of $[Ru(tpy)_2]^{2+}$. The stark difference in the excited-state lifetime values between $[Ru(Ph$-tpy$)(dgpy)]^{2+}$ and complexes **1** or **2** is possibly due to the introduction of the electron withdrawing $-CO_2H$ group that helps to stabilize the ^{3}MLCT state, such that the decay via radiative pathway is more pronounced in the later complex. This fact is also supported by an increase in the photoluminescent quantum yield of **1** and **2** (Φ_{PL} = 0.005-0.006 in deareated MeCN) in comparison to that of $[Ru(Ph$-tpy$)(dgpy)]^{2+}$ (Φ_{PL}

= 0.001 in deareated MeCN) and higher rate of radiative decay constants of **1** and **2** (k_r = 5.53-5.44 x 10^5 s^{-1}) with respect to that of [Ru(Ph-tpy)(dgpy)]$^{2+}$ (k_r = 0.77 x 10^4 s^{-1}) (**Table S9**, ESI).

The small values of full-width at half-maxima (fwhm) of the emission spectra of **1** and **2** as 1060 and 1080 cm^{-1}, respectively, indicate a small structural change at the excited-state compared to that in the ground state (S_0). This fact suggests a strong ovelap of the vibrational levels of S_0 and the triplet state (T_1), such that the energy-gap law comes into play. As a consequence, the excited electron quickly comes back to a higher vibrational level of the ground state by strong phosphorescence and subsequently non-radiatively stabilises to the lowest vibrational level of the ground state.

Conclusions

In conclusion, two novel heteroleptic Ru(II) complexes comprising electron accepting CO_2HPh-tpy and electron donating **L1** or **L2** ligands were synthesised and characterised by a set of analytical techniques including single crystal XRD. Due to flexibility of the saturated aliphatic backbone the N_{hpp}-Ru-N_{hpp} is noticeably larger (172.40(10)^o) than that offered by the CO_2HPh-tpy ligand (159.07(10)^o). Due to strong σ-donation by the ligands **L1** or **L2**, the Ru(III/II) oxidation potential was found to be ~ 800 mV cathodically shifted compared to that found in [Ru(tpy)$_2$]$^{2+}$. This fact suggests that although ligands **L1** and **L2** are neutral in nature, their electron donating power is comparable to that of a cyclometallating N^C^N or carbene type ligand.[19] As a consequence, complexes **1** and **2** exhibited very red-shifted ^{1}MLCT absorption (> 120 nm) and ^{3}MLCT emission (> 200 nm) profiles compared to those of [Ru(tpy)$_2$]$^{2+}$. The excited-state lifetimes and photoluminescence quantum yields of **1** and **2** were found to be ~ 40 and 5000 times higher compared to those of [Ru(tpy)$_2$]$^{2+}$ at r.t. To the best of our knowledge, these complexes are amongst the rare examples of NIR-emissive mononuclear Ru(II)-N_6 complexes. Compared to analogous Ru(II) complexes where an electron acceptor is not present (e.g., **C5** in **Chart 1**), complexes **1** and **2** exhibited blue-shifted emission and higher photoluminescence quantum yields, a fact that is in agreement with energy-gap law. Thus, with enticing electrochemical properties, panchromatic absorption and NIR emission these complexes may serve as potential photosensitisers in DSSCs and luminescent probes in cancer biology.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

Notes and references

1   M. D. Kärkäs, O. Verho, E. V. Johnston, B. Åkermark, *Chem. Rev.*, 2014, **114**, 11863.
2   (a) B. O'Regan and M. Gräetzel, *Nature*, 1991, **353**, 737.(b) Y. Cao, Y. Bai, Q. Yu, Y. Cheng, S. Liu, D. Shi, F. Gao, P. Wang, *J. Phys. Chem. C*, 2009, **113**, 6290.
3   R. Eisenberg, *Science*, 2009, **324**, 44.
4   H. J. Bolink, L. Cappelli, E. Coronado, M. Gräetzel and M. K. Nazeeruddin, *J. Am. Chem. Soc.*, 2006, **128**, 46.
5   W. Lin, Y. Zheng, J. Zhang, X. Wan, *Macromolecules*, 2011, **44**, 5146.
6   Z. Guo, S. Park, J. Yoon, I. Shin, *Chem. Soc. Rev.*, 2014, **43**, 16.
7   (a) A. K. Pal, G. S. Hanan, *Chem. Soc. Rev.*, 2014, **43**, 6184; (b) B. Laramée-Milette, G. S. Hanan, *Dalton Trans.*, 2016, **45**, 12507; (c) F. R. Keene, *Coord. Chem. Rev.*, 1997, **166**, 121.
8   (a) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810; (b) F. Barigelletti and L. Flamigni, *Chem. Soc. Rev.*, 2000, **29**, 1; (c) S. Sharma, F. Lombeck, L. Eriksson, O. Johansson, *Chem. Eur. J.* 2010, **16**, 7078.
9   M. Maestri, N. Armaroli, V. Balzani, E. C. Constable and A. M. W. Cargill Thompson, *Inorg. Chem.*, 1995, **34**, 2759.
10 J.-L. Chen, Y. Chi and K. Chen, *Inorg. Chem.*, 2010, **49**, 823.
11 (a) T. Schlotthauer, B. Suchland, H. Görls, G. A. Parada, L. Hammarström, U. S. Schubert and M. Jäger, *Inorg. Chem.*, 2016, **55**, 5405; (b) M. Abrahamsson, M. Jäger, R. J. Kumar, T. Oesterman, P. Persson, H.-C. Becker, O. Johansson and L. Hammarström, *J. Am. Chem. Soc.*, 2008, **130**, 15533.
12 J.-L. Chen, Y. Chi, K. Chen, Y.-M. Cheng, M.-W. Chung, Y.-C. Yu, G.-H. Lee, P.-T. Chou, C.-F. Shu, *Inorg. Chem.*, 2010, **49**, 823.
13 (a) A. K. Pal, S. Nag, J. M. Ferreira, V. Brochery, G. L. Ganga, A. Santoro, S. Serroni, S. Campagna, G. S. Hanan, *Inorg. Chem.*, 2014, **53**, 1679; (b) A. K. Pal, N. Zaccheroni, S. Campagna, G. S. Hanan, *Chem. Commun.*, 2014, **50**, 6846; (c) A. K. Pal, S. Serroni, N. Zaccheroni, S. Campagna, G. S. Hanan, *Chem. Sci.*, 2014, **5**, 4800; (d) S.-H. Wu, S. E. Burkhardt, J. Yao, Y.-W. Zhong, H. D. Abruña, *Inorg. Chem.*, 2011, **50**, 3959.
14 (a) A. K. Pal, G. S. Hanan, *Dalton Trans.*, 2014, **43**, 11811; (b) A. K. Pal, P. D. Dauphin, G. S. Hanan, *Chem. Commun.*, 2014, **50**, 3303; (c) A. K. Pal, G. S. Hanan, *Dalton Trans.*, 2014, **43**, 6567; (d) A. K. Pal, C. Li, G. S. Hanan, E. Zysman-Colman, *Angew. Chem. Int. Ed.*, 2018, **130**, 8159; h) A. K. Pal, P. K. Mandali, D. K. Chand, G. S. Hanan, *Synlett*, 2015, **26**, 1408.
15 J. Wang, G. S. Hanan, *Synlett*, 2005, **8**, 1251.
16 M.-P. Santoni, A. K. Pal, G. S. Hanan, A. Proust, B. Hasenknopf, *Inorg. Chem. Commun.*, 2011, **14**, 399.
17 E. C. Constable, C. E. Housecroft, E. A. Medlycott, M. Neuburger, F. Reinders, S. Reymann, S. Schaffner, *Inorg. Chem. Commun.*, 2008, **11**, 805.
18 A. Harriman, A. Mayeux, A. D. Nicola, R. Ziessel, *Phys. Chem. Chem. Phys.*, 2002, **4**, 2229.
19 (a) S. H. Wadman, M. Lutz, D. M. Tooke, A. L. Spek, F. Hartl, R. W. A. Havenith, G. P. M. van Klink, G. van Koten, *Inorg. Chem.*, 2009, **48**, 1887; (b) P. G. Bomben, K. C. D. Robson, P. A. Sedach, C. P. Berlinguette, *Inorg. Chem.*, 2009, **48**, 9631. (c) W.-W. Yang, Y.-W. Zhong, S. Yoshikawa, J.-Y. Shao, S. Masaoka, K. Sakai, J. Yao, M.-a. Haga, *Inorg. Chem.*, 2012, **51**, 890.
20 C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
21 N. Aydin, C, W. Schlaepfer, *Polyhedron*, 2001, **20**, 37.
22 See complexes **6**(PF$_6$)$_2$ and **7**(PF$_6$)$_2$ in B.-B. Cui, J.-Y. Shao, Y.-W. Zhong, *Organometallics*, 2014, **33**, 4220.
23 M. Beley, J. P. Collin, J. P. Sauvage, H. Sugihara, F. Heisel and A. Miehé, *J. Chem. Soc., Dalton Trans.*, **1991**, 3157.

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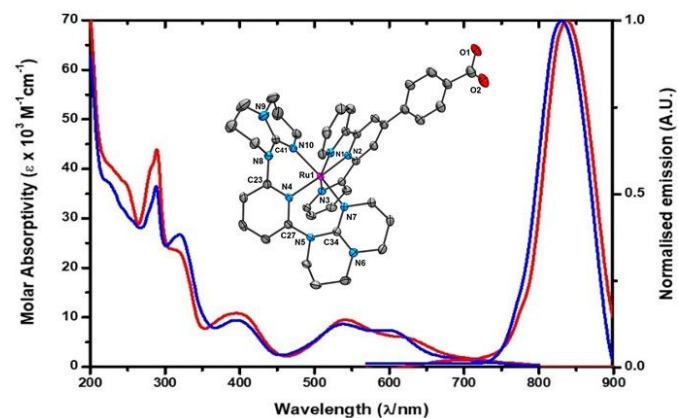
Reversible electrochemistry, Panchromatic absorption, NIR emission

Novel heteroleptic Ru(II)-polypyridyl complexes were synthesised that exhibit panchromatic absorption up to 750 nm and ^{3}MLCT NIR emission at λ_{em} > 830 nm.