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Journal Name

COMMUNICATION

Blue-Green Emissive Cationic Iridium(III) Complexes Using Partially Saturated Strongly-Donating Guanidyl-pyridine/pyrazine Ancillary Ligands

Kamrul Hasan,[a] Amlan K. Pal,[a] Thomas Auvray,[a] Eli Zysman-Colman*[b] and Garry S. Hanan*[a]

A new class of cationic iridium(III) complexes of the form [(C^N)₂Ir(N^N)][PF₆] is reported, where C^N = cyclometallating 2-phenylpyridinato, ppy, or 2-(2,4-difluorophenyl)-5′-methylpyridinato, dFMeppy, and N^N = guanidyl-pyridine, gpy, or pyrazine, gpz, as the ancillary ligand. A large blue-shift in the emission coupled with a 7-to-9 fold enhancement in photoluminescence quantum yield and microsecond emission lifetimes were observed for the complexes containing the partially saturated gpy ligand as compared to the benchmark complex [(ppy)₂Ir(bpy)][PF₆], C1, where bpy is 2,2′-bipyridine.

Cationic iridium(III) complexes are the subject of tremendous recent interest due to their use as photophysically active materials in a wide assortment of applications, e.g., lighting devices,[1] solar energy harvesters,[2] in sensing or bioimaging[3] and photosensitizers for hydrogen production from water.[4] Generally, the photophysical properties of these complexes can be finely tuned through concomitant modification of the cyclometallating and ancillary ligands. In particular, replacing the 2,2′-bipyridine (bpy) in the archetypal [(ppy)₂Ir(bpy)][PF₆], **C1**, with other bidentate heterocyclic ligands has proven to be very effective in modulating the emission energy (ppy = 2-phenylpyridinato). For instance, complexes bearing phenanthroline-,[5a] imidazole-,[5b] 1,2,3-triazole-,[5c] tetrazole-[5d] and pyrazole[5e]-based ancillary ligands have all been investigated.[5f] To the best of our knowledge partially saturated, strongly-donating neutral *N,N′*-bidentate heterocycles have not been explored as ancillary ligands with iridium(III) complexes. Very recently multi-dentate guanidyl-based ligands and their ruthenium complexes have been studied by the Hanan group.[6] The incorporation of strongly donating H-hpp (where H-hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine or commonly known as guanidine in this work) moieties into *N*-heterocycles by means of C-N bond-forming reactions gave rise to electron-rich bidentate or tridentate chelates.[7] These ligands conferred large red-shifts of between 120-270 nm on the lowest triplet energy metal-to-ligand charge-transfer, [3]MLCT, emission band of their Ru(II)-complexes as compared to [Ru(bpy)₃]²⁺ and [Ru(tpy)₂]²⁺ (tpy = 2,2′:6′,2′′-terpyridine).[6] Herein, we present the first three examples of cationic iridium complexes that incorporate neutral bidentate 2-guanidylpyridine, gpy, and 2-guanidylpyrazine, gpz as the ancillary

ligand (Scheme **1**) and contrast their photophysical properties to those of **C1**. The observed optoelectronic properties align with the density functional theory (DFT) and time-dependant DFT (TD-DFT) studies (*vide infra*).
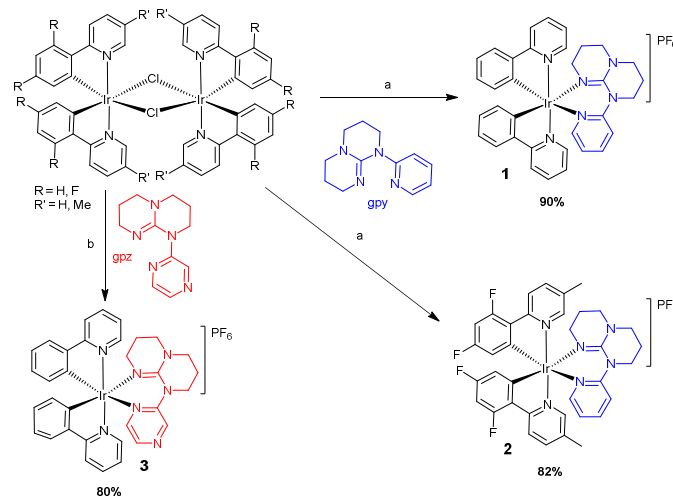
Scheme 1. Syntheses of **1-3** (a) i. 2.1 equiv. gpy in DCM/MeOH (1:1), 50 °C, 19 h; ii. NH₄PF₆ (aq). (b) i. 2.1 equiv. gpz in DCM/MeOH (1:1), 50 °C,19 h; ii. NH₄PF₆ (aq).

The gpy and gpz ligands were synthesized in high yields (95% and 82%) according to the literature.[6a] These ligands were used to cleave [(ppy)₂Ir(μ-Cl)]₂ and [(dFMeppy)₂Ir(μ-Cl)]₂ (dFMeppy = 2-(2,4-difluorophenyl)-5-methylpyridinato) and complexes **1-3** were obtained in high yield (80-90%) following an anion metathesis with aq. NH₄PF₆ (Scheme **1**). They were fully characterized by ^{1}H-, ^{13}C-, ^{19}F-NMR spectroscopy, melting point and HR-MS analyses (Figures **S1-S11** in ESI). Resonances in the ^{1}H NMR spectra of **1-3** corresponding to the saturated aliphatic backbone of the ancillary ligand were observed between 1 to 4 ppm as found in other complexes with saturated ligands.[8] The splitting of the methylene protons suggest that they are diastereotopic as also observed for analogous Ru complexes.[6b-e]

Crystals of **3** suitable for X-ray structural determination were grown by slow evaporation from a mixture of DCM and di*iso*propylether (1:1, v/v), Figure **1**. Selected crystallographic parameters are tabulated in Table **S1**. Selected bond distances and angles are in Table **S2**. The Ir(III)-ion is coordinatively saturated and in a distorted octahedral geometry. The C^N carbon atoms are found to be mutually *cis* disposed, similar to the solid-state structure of **C1** (ccdc 745138).[9] The average Ir-C_{ppy} (2.005(10) Å) and Ir-N_{ppy} (2.054(8) Å) bond lengths are similar to those in **C1** [(Ir-C_{ppy} (2.013(3) Å); Ir-N_{ppy} (2.045(3) Å)]. The $N_{N^\wedge N}$-Ir-$N_{N^\wedge N}$ bite angle (83.8(3)°) of the gpz is wider than when bpy is the ancillary ligand in **C1**, 76.2(1)° due to formation of a six-membered chelate ring present in **3**.
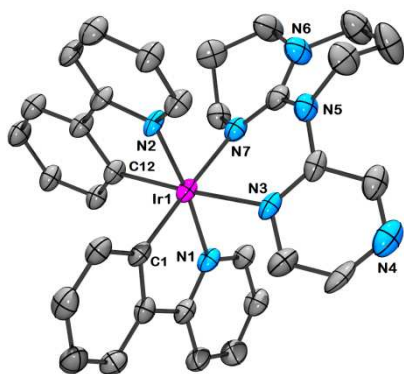

Figure 1. ORTEP view of complex **3**. Hydrogen atoms, an anion and a solvated dichloromethane molecule have been omitted for clarity. Ellipsoids correspond to a 50% probability level

The UV-visible absorption spectra of **1-3** are shown in Figure **S12** and calculated molar absorptivities are reported in Table **S3**. The absorption profiles are similar to other heteroleptic cationic iridium(III) complexes reported in the literature.[10] TD-DFT studies assign the bands below 300 nm as predominantly ligand-centred spin allowed π–π* transitions from both ligands with minor contributions from [1]MLCT and [1]LLCT ([1]MLCT = singlet metal-to-ligand charge transfer and [1]LLCT = singlet ligand-to-ligand charge transfer.[11], The absorption bands in the 300-450 nm region are mainly mixed spin-allowed CT transitions (for relative contributions see Tables **S5-S7**) with non-negligible contribution from ligand-centred transitions. The lowest energy absorption bands in **1-3** are slightly red-shifted by 23-41 nm compared to **C1** (420 nm) in an analogous manner to the trend observed with [(bpy)₂Ru(gpy/gpz)]$^{+2}$ *vs.* reference [Ru(bpy)₃]$^{+2}$.[6a] The red-shift in the absorption spectra of **1-3** is due to a destabilization of the metal/C^N-localized HOMO as a result of increased electron density on the iridium conferred by the electron-donating gpy ligand (HOMO = Highest Occupied Molecular Orbital, Tables **S8-S10** and Figure **S15**). The decreasing optical gap (inset figure of Figure **S12**) from **2** to **1** to **3** aligns with the computed HOMO-LUMO (LUMO = Lowest Unoccupied Molecular Orbital) energy gap (ΔE of **2** = 3.91 eV; ΔE of **1** = 3.72 eV; ΔE of **3** = 3.31 eV) (Table **S3**).
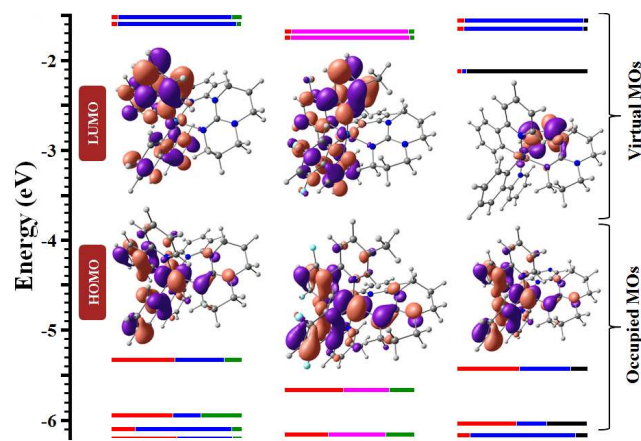
Color code in bars: **Ir**, **ppy**, **gpy**, **gpz**, **dFMeppy**

Figure 2. Calculated frontier MO energies of **1-3**, obtained from TD-DFT [(rb3lyp/LanL2DZ(f) for Ir(III)) and (6-31g** for C,H,N,(F))] with CPCM(CH₃CN) and 0.5 eV threshold of degeneracy. Kohn-Sham MOs of **1**, **2** and **3** are also shown.

The electrochemical behaviour of **1-3** was monitored by cyclic voltammetry (CV) and the CV traces in deaerated MeCN containing 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte and using Fc/Fc$^+$ as an internal standard at 298 K are shown in Figures **S13** and **S14**. The detailed CV data *vs.* SCE (Fc/Fc$^+$ = 0.38 V in MeCN)[12] are summarized in Table **S4** while only first redox potentials are listed in Table **1**. In the anodic scan, all of the complexes showed three successive oxidation waves, the first quasi-reversible and the other two irreversible. The first oxidation wave in **1-3** falls between 0.99 to 1.21 V (Figure **S14**) and is assigned to the $Ir^{III/IV}$ redox couple with contributions from the C^N ligands.[5f] These oxidation potentials are cathodically shifted to a significant extent compared to other heteroleptic iridium(III) cationic complexes bearing similar C^N ligands, (**C1**: $E^{1/2}_{ox}$ = 1.27 V in SCE ; [(dFMeppy)₂Ir(bpy)][PF₆], **C2**: $E^{1/2}_{ox}$ = 1.55 V in SCE). Indeed, DFT calculations show that the HOMOs of **1-3** are constituted almost equally with iridium and the C^N ligands with a progressive increase in the calculated energy of the HOMO of **2** (E_{HOMO} = -5.66 eV) to **3** (E_{HOMO} = -5.43 eV) to **1** (E_{HOMO} = -5.32 eV), which is in excellent agreement with experiment. The first oxidation potential of **2** ($E^{1/2}$ox = 1.21 V) is more positive compared to **1** ($E^{1/2}$ox = 0.99 V) due to the electron withdrawing fluorine atoms on the C^N ligands, which increase the stability of HOMOs. The $E^{1/2}$ox of **3** is slightly more positive (1.04 V) compared to **1**, although both contain the same cyclometallating ppy ligand. This is due to modulating influence of the less electron-donating gpz ligand. Overall, the trends observed in the electrochemistry are entirely consistent with those in the electronic spectroscopy.

Upon scanning to negative potential, **1** and **2** show three successive one-electron irreversible reduction-waves whereas complex **3** shows a first quasi-reversible one-electron reduction followed by two irreversible one-electron reduction events (Figure **S13** and Table **S4**). The first of the reduction waves falls between -2.12 to -1.60 V, which are more cathodically shifted compared to benchmark complexes **C1** and **C2** (**C1**: $E^{1/2}_{red}$ = -1.38 V; **C2**: $E^{1/2}_{red}$ = -1.34 V). The more negative reduction potentials in **1-3** are the result of the strongly electron-donating guanidyl moiety. Similar effects were previously observed for more electron rich ancillary ligands (N^N). For instance, the first reduction waves of [(ppy)₂Ir(btl)]PF₆[13a] and [(ppy)₂Ir(4-pytl)]PF₆[13b] were found, respectively, at -1.99 and -2.25 V *vs.* SCE (btl = 1,1'-benzyl- 4,4'-bi-1*H*-1,2,3-triazolyl and 4-pytl = 4-methyl-3-(pyridin-2-yl)-1,2,4-

triazole). In the case of complexes $[(dFppy)_2Ir(3-pytl)]$[14a] and $[(Fphtl)_2Ir(3-pytlph)]PF_6$[14b] (where 3-pytl = 2-(1,2,3-triazol-5-yl)pyridine, Fphtl = 1-benzyl-4-(4-fluorophenyl)-1*H*-1,2,3-triazole and 3-pytlph = 2-(1-phenyl-1,2,3-triazol-4-yl)pyridine, respectively) the reduction waves were observed -2.39 and -1.76 V *vs.* SCE. In our case, the first reduction waves of **1** and **2** are almost identical at -2.13 and -2.12 V, respectively, as indeed both complexes having the same gpy ancillary ligand. On the other hand, the first reduction wave of **3** is -1.60 V with the gpz ancillary ligand. The σ-donating effect is mitigated in **3** due to the presence of the extra inductively electron-withdrawing nitrogen atom in the pyrazine, resulting in a dramatic anodic shift of *ca.* 500 mV of the first reduction potential compared to those of **1** and **2**. The CVs and the DFT calculations demonstrate that the LUMOs of **1** and **2** reside mainly on the C^N ligands whereas in **3** it is localized on the pyrazine (Tables **S8-S10** and Figure **S15**).

The steady-state emission spectra of **1-3** were recorded in degassed MeCN at 298 K and are shown in Figure **3**. The photophysical data are summarized in Table **1**. The emission spectra for **1** and **3** are broad and featureless, indicative of mixed ^{3}CT emission while the spectrum of **2** is structured, pointing to significant ^{3}LC-based emission. TD-DFT calculations (Figure **S16-S18**) corroborate these assignments. The CT emission in **1** is the result of mixed LLCT and MLCT that is mostly LLCT in nature and involves the pyridine moieties of the C^N ligands while the CT emission of **3** is also mixed with almost equal LLCT and MLCT contributions that involve the pyrazine of the gpz ligand. The emission maximum for **3** is at 640 nm, which is significantly red-shifted as compared to **1** and **2**. With the presence of the dFMeppy ligand, the emission maximum in **2** is expectedly blue-shifted to 470 nm. Consistent with the absorption and electrochemical data, the emission maxima for **1** and **2** are hypsochromically shifted compared to **C1** (λ_{max} = 602 nm) and **C2** (λ_{max} = 527 nm).[15] This effect is again due to the strong σ-donating effect of guanidyl moiety that destabilizes both the HOMO and LUMO, the latter to a greater extent resulting in a larger HOMO-LUMO gap. In the case of **3**, the LUMO now resides on the guanidine-based ligand, which is significantly lower in energy due to the electron-deficient pyrazine moiety. In **1** and **2**, the absorption band for the HOMO-LUMO is predominantly ppy π-π* in nature while for **3** it is mixed CT, i.e., the LUMO is different in both cases.
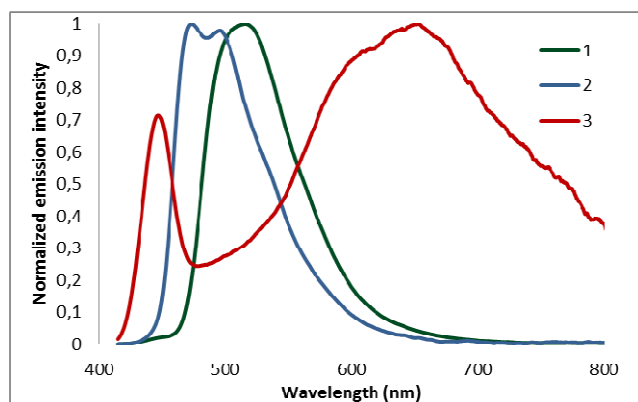

Figure 3. Normalized emission spectra of **1-3** (λ_{exc} = 395 nm) recorded in degassed MeCN at 298 K. The first band at 450nm for compound 3 correspond to a Raman band from the MeCN.

The photoluminescence quantum yields, Φ_{PL}, in degassed MeCN for **1** and **2** are *ca.* 61%. Complex **3**, by contrast is very poorly emissive (Φ_{PL} = 0.2%) due to a two-order increase in the non-radiative decay rate constant, k_{nr}. The inference is that implicating the pyrazine-

based ancillary ligand in the triplet state results in quenched emission. Emission lifetimes for **1** and **2** are 2.1 and 2.6 μs, respectively and are significantly longer than that observed with **C1** (τ_ε = 0.275 μs)[15] while the τ_ε in **3** is only 20 ns. The conformational flexibility present in the saturated backbone of the guanidyl cycle coupled with a triplet state involving the pyrazine moiety, may be responsible for the short observed lifetime in **3**. Indeed, very efficient vibrational deactivation was previously noted for Ru(II) complexes of guanidine-based ligands.[6]

Table 1. Optoelectronic properties of **1-3** in degassed MeCN[a]

	λ_{em} /nm	Φ_{PL} /%	τ_e /μs	k_r /10^5 s^{-1}	k_{nr} /10^5 s^{-1}	$E^1_{1/2}{}^{ox}$ /V (ΔEp, mV)	$E^1_{1/2}{}^{red}$ /V (ΔEp, mV)
1	503	60	2.1	2.9	1.9	0.99 (88)	-2.13
2	470, 498	62	2.6	2.3	1.4	1.21 (72)	-2.12
3	640	0.2	0.02	1.0	499	1.04 (92)	-1.60 (95)

[a] Φ_{PL} measured at 298 K using quinine sulfate (Φ_{PL} = 54%, in 0.5 N H_2SO_4) as the reference.[16] $k_r = \Phi/\tau$ and $k_{nr} = (1 - \Phi)/\tau$. CV values are in V *vs.* SCE.[9] $\Delta E_p = |E_{pa} - E_{pc}|$, where E_{pa} = anodic peak potential and E_{pc} = cathodic peak potential; $E_{1/2} = (E_{pa} + E_{pc})/2$ and result from one-electron processes. A non-aqueous Ag/Ag$^+$ electrode (silver wire in a solution of 0.1 M AgNO$_3$ in MeCN) was used as the pseudoreference electrode; a glassy-carbon electrode was used for the working electrode and a Pt electrode was used as the counter electrode.

In summary, a new class of blue-green emissive iridium(III) cationic complexes with partially saturated guanidyl-containing ancillary ligands is reported. The strong electron-donating character of the guanidyl cycle confers a very large blue shift in the emission compared to benchmark complex **C1** while maintaining high photoluminescence quantum yields and microsecond emission lifetimes. Incorporation of a pyrazine unit in **3** results in near complete quenching of the luminescence with a concomitant red-shift of its emission wavelength. The overall structural, electrochemical and photophysical properties of **1** and **2** are encouraging and current efforts are underway to investigate these complexes as emissive materials in solid-state lighting applications.

Notes and references

[a]Département de Chimie, Université de Montréal, 2900 Edouard-Montpetit, Montréal, Québec H3T-1J4, Canada. E-mail:

garry.hanan@umontreal.ca; Fax: +1-514 343-2468; Tel: +1-514 343-7056

*b*Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife, UK, KY16 9ST, Fax: +44-1334 463808; Tel: +44-1334 463826; E-mail: eli.zysman-colman@st-andrews.ac.uk;

URL: http://www.zysman-colman.com

1 (a) R. D. Costa, E. Ortí, H. J. Bolink, F. Monti, G. Accorsi, and N. Armaroli, *Angew. Chem. Int. Ed.,* 2012, **51**, 8178. (b) T. Hu, L. He, L. Duan and Y. Qiu, *J. Mater. Chem.*, 2012, **22**, 4206. (c) G. E. Schneider, A. Pertegás, E. C. Constable, C. E. Housecroft, N. Hostettler, C. D. Morris, J. A. Zampese, H. J. Bolink, J. M. Junquera-Hernández, E. Ortí and M. Sessolo, *J. Mater. Chem. C*, 2014, **2**, 7047. (d) A. B. Bünzli, H. J. Bolink, E. C. Constable, C. E. Housecroft, J. M. Junquera-Hernández, N. Neuburger, E. Ortí, A. Pertegás, J. J. Serrano-Pérez, D. Tordera and J. A. Zampese, *Dalton Trans.*, 2014, **43**, 738. (e) K. Hasan, L. Donato, Y. Shen, J. D. Slinker and E. Zysman-Colman, *Dalton Trans.*, 2014, **43**, 13672.

2 (a) K. Hasan and E. Zysman-Colman, *Inorg. Chem.*, 2012, **51**, 12560-12564. (b)Y. Shinpuku, F. Inui, M. Nakai and Y.Nakabayashi, *J. Photochem and Photobiol A, Chem.*, 2011, 222, 203.

3 For recent review and examples see; (a) K. K.-W. Lo and S. P.-Y. Li, *RSC Adv.*, 2014, **4**, 10560. (b) K. K.-W. Lo and K. Y. Zhang, *RSC Adv.*, 2012, **2**, 12069. (c) F. Lu and T. Nabeshima, *Dalton Trans.*, 2014, **43**, 9529. (d) Y. You, *Curr. Opin. Chem. Biol.*, 2013, **17**, 699.(e) Y. You, S. Lee, T. Kim, K. Ohkubo, W.-S. Chae, S. Fukuzumi, G.-J. Jhon, W. Nam and S. J. Lippard, *J. Am. Chem. Soc.*, 2011, **133**, 18328.

4 (a) K. Mori, J. Aoyama, M. Kawashimaa and H. Yamashita, *Dalton Trans.*, 2014, **43**, 10541. (b) D. R. Whang, K. Sakai, and S. Y. Park, *Angew. Chem. Int. Ed.* 2013, **52**, 11612. (c) S. Hansen, M.-M. Pohl, M. Klahn, A. Spannenberg and T.Beweries, *ChemSusChem* 2013, **6**, 92. (d) B. F. Disalle and S. Bernhard, *J. Am. Chem. Soc.* 2011, **133**, 11819. (e) F. Gärtner, D. Cozzula, S. Losse, A. Boddien, G. Anilkumar, H. Junge, T. Schulz, N. Marquet, A. Spannenberg, S. Gladiali and M. Beller, *Chem. Eur. J.* 2011, **17**, 6998. (f) L. L. Tinker and S. Bernhard, *Inorg. Chem.*, 2009, **48**, 10507.

5 (a) K. P. S. Zanoni, B. K. Kariyazaki, A. Ito, M. K. Brennaman, T. J. Meyer and N. Y. Murakami Iha, *Inorg. Chem.*, 2014, **53**, 4089. (b) L. He, J. Qiao, L. Duan, G. Dong, D. Zhang, L. Wang, and Yong Qiu, *Adv. Funct. Mater.*, 2009, **19**, 2950. (c) G. J. Barbante, E. H. Doeven, E. Kerr, T. U. Connell, P. S. Donnelly, J. M. White, T. Lópes, S. Laird, D. J. D. Wilson, P. J. Barnard, C. F. Hogan and P. S. Francis, *Chem. Eur. J.* 2014, **20**, 3322. (d) S. Stagni, S. Colella, A. Palazzi, G. Valenti, S. Zacchini, F. Paolucci,M. Marcaccio, R. Q. Albuquerque, L. De Cola, *Inorg. Chem.* 2008, **47**, 10509. (e) L. He, L. Duan, J. Qiao, D. Zhang, L. Wang and Yong Qiu, *Chem. Commun.*, 2011, **47**, 6467. (f) S. Ladouceur and E. Zysman-Colman, *Eur. J. Inorg. Chem.*, 2013, 2985.

6 (a) A. K. Pal, S. Nag, J. G. Ferreina, V. Brochery, G. L. Ganga, A. Santora, S. Serroni, S. Campagna and G. S. Hanan, *Inorg. Chem.*, 2014, **53**, 1679. (b) A. K. Pal, P. D. Ducharme, G. S. Hanan, *Chem. Commun.*, 2014, 50, 3303. (c) A. K. Pal, G. S. Hanan, *Dalton Trans.*, 2014, **43**, 6567. (d) A. K. Pal, N. Zaccheroni, S. Campagna, G. S. Hanan, *Chem. Commun*, 2014, **50**, 6846. (e) A. K. Pal, S. Serroni, N. Zaccheroni, S. Campagna, G. S. Hanan, *Chem. Sci*, 2014, **5**, 4800. (f) A. K. Pal, G. S. Hanan, *Chem. Soc. Rev.*, 2014, **43**, 6184. (g) S. Nag, J. G. Ferreira, L. Chenneberg, P. D. Ducharme, G. S. Hanan, G. L. Ganga, S. Serroni, S. Campagna, *Inorg. Chem.*, 2011, **50**, 7.

7 (a) S. H. Oakley, M. P. Coles and P. B. Hitchcock, *Inorg. Chem.*, 2004, **43**, 7564. (b) M. P. Coles, *Chem. Commun.*, 2009, 3659. (c) M. S. Khalaf, S. H. Oakley, M. P. Coles and P. B. Hitchcock, *Dalton Trans.*, 2010, **39**, 1635.

8 (a) B. De Groot, G. S. Hanan and S. J. Loeb, *Inorg. Chem.*, 1991, **30**, 4644; (b) G. R. Giesbrecht, G. S. Hanan, J. E. Kickham and S. J. Loeb, *Inorg. Chem.*, 1992, **31**, 3286.

9 R. D. Costa, E. Ortí, H. J. Bolink, S. Graber, S. Schffner, M. Neuburger, C. E. Housecroft and E. C. Constable, *Adv. Funct. Mater.*, 2009, **19**, 3456.

10 S. Ladouceur, D. Fortinand E. Zysman-Colman, *Inorg. Chem.* 2010, **49**, 5625 and references cited therein.

11 For overlay of experimental absorption spectra of the complexes in acetonitrile with their predicted transitions and oscillator strength, see Figures S14-S16).

12 V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta,* 2000, **298**, 97.

13 (a) L. Donato, P. Abel and E. Zysman-Colman, *Dalton Trans.*, 2013, **42**, 8402. (b) J. H. van Diemen, J. G. Haasnoot, R. Hage, E. Müller, J. Reedijk, *Inorg. Chim. Acta,* 1991, **181**, 245.

14 (a) E. Orselli, R. Q. Albuquerque, P. M. Fransen, R. Frohlich, H. M. Janssen and L. De Cola, *J. Mater. Chem.*, 2008, **18**, 4579. (b) J. M. Fernandez-Hernandez, S. Ladouceur, Y. Shen, A. Iordache, X. Wang, L. Donato, S. Gallagher-Duval, M. de Anda Villa, J. D. Slinker, L. De Cola and E. Zysman-Colman, *J. Mater. Chem. C*, 2013, **1**, 7440.

15 S. Ladouceur, D. Fortin and E. Zysman-Colman, *Inorg. Chem.*, 2011, **50**, 11514.

16 W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229.

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