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## Blue-green emissive cationic iridium(III) complexes using partially saturated strongly-donating guanidyl-pyridine/-pyrazine ancillary ligands†

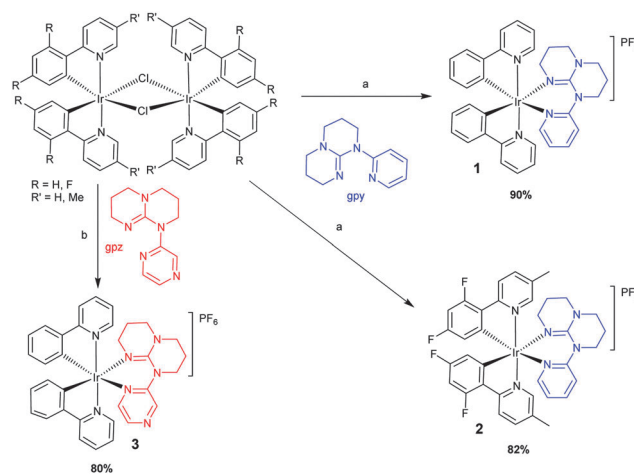
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A new class of cationic iridium(III) complexes of the form  $[(C^{\wedge}N)_2Ir-(N^{\wedge}N)][PF_6]$  is reported, where  $C^{\wedge}N$  = cyclometalating 2-phenylpyridinato, ppy, or 2-(2,4-difluorophenyl)-5'-methylpyridinato, dFMepy, and  $N^{\wedge}N$  = 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  $[(ppy)_2Ir(bpy)][PF_6]$ , **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,<sup>1</sup> solar energy harvesters,<sup>2</sup> in sensing or bioimaging<sup>3</sup> and photosensitizers for hydrogen production from water.<sup>4</sup> Generally, the photophysical properties of these complexes can be finely tuned through concomitant modification of the cyclometalating and ancillary ligands. In particular, replacing the 2,2'-bipyridine (bpy) in the archetypal  $[(ppy)_2Ir(bpy)][PF_6]$ , **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,<sup>5a</sup> imidazole,<sup>5b</sup> 1,2,3-triazole,<sup>5c</sup> tetrazole<sup>5d</sup> and pyrazole<sup>5e</sup>-based ancillary ligands have all been investigated.<sup>5f</sup> 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.<sup>6</sup> The incorporation of strongly donating H-hpp (where H-hpp = 1,3,4,6,7,8-hexahydro-2*H*-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.<sup>7</sup> These ligands conferred large red-shifts of between 120–270 nm of the lowest triplet energy metal-to-ligand charge-transfer, <sup>3</sup>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).<sup>6</sup> Herein, we present the first three examples of cationic iridium(III) 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*).

The gpy and gpz ligands were synthesized in high yields (95% and 82%) according to the literature.<sup>6a</sup> These ligands were



**Scheme 1** Syntheses of **1–3** (a) i. 2.1 equiv. gpy in DCM/MeOH (1:1), 50 °C, 19 h; ii.  $NH_4PF_6$  (aq). (b) i. 2.1 equiv. gpz in DCM/MeOH (1:1), 50 °C, 19 h; ii.  $NH_4PF_6$  (aq).

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used to cleave  $[(ppy)_2Ir(\mu-Cl)]_2$  and  $[(dFMeppy)_2Ir(\mu-Cl)]_2$  ( $dFMeppy = 2-(2,4\text{-difluorophenyl})\text{-5-methylpyridinato}$ ) and complexes **1–3** were obtained in high yield (80–90%) following an anion metathesis with aq.  $NH_4PF_6$  (Scheme 1). They were fully characterized by  $^1H$ ,  $^{13}C$ ,  $^{19}F$ -NMR spectroscopy, melting point and HR-MS analyses (Fig. S1–S11 in ESI $^\dagger$ ). Resonances in the  $^1H$  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.<sup>8</sup> The splitting of the methylene protons suggest that they are diastereotopic as also observed for analogous Ru complexes.<sup>6b–e</sup>

Crystals of **3** suitable for X-ray structural determination were grown by slow evaporation from a mixture of DCM and diisopropylether (1:1, v/v) (Fig. 1). Selected crystallographic parameters are tabulated in Table S1 (ESI $^\dagger$ ). Selected bond distances and angles are in Table S2 (ESI $^\dagger$ ). The Ir(III)-ion is coordinatively saturated and in a distorted octahedral geometry. The C $^\wedge$ N carbon atoms are found to be mutually *cis* disposed, similar to the solid-state structure of **C1** (CCDC 745138).<sup>9</sup> The average Ir–C<sub>ppy</sub> (2.005(10) Å) and Ir–N<sub>ppy</sub> (2.054(8) Å) bond lengths are similar to those in **C1** [Ir–C<sub>ppy</sub> (2.013(3) Å); Ir–N<sub>ppy</sub> (2.045(3) Å)]. The N<sub>N $\wedge$ N</sub>–Ir–N<sub>N $\wedge$ N</sub> 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**.

The UV-visible absorption spectra of **1–3** are shown in Fig. S12 (ESI $^\dagger$ ) and calculated molar absorptivities are reported in Table S3 (ESI $^\dagger$ ). The absorption profiles are similar to other heteroleptic cationic iridium(III) complexes reported in the literature.<sup>10</sup> TD-DFT studies assign the bands below 300 nm as predominantly ligand-centred spin allowed  $\pi\text{-}\pi^*$  transitions from both ligands with minor contributions from  $^1MLCT$  and  $^1LLCT$  ( $^1MLCT = \text{singlet metal-to-ligand charge transfer}$  and  $^1LLCT = \text{singlet ligand-to-ligand charge transfer}$ ).<sup>11</sup> The absorption bands in the 300–450 nm region are mainly mixed spin-allowed CT transitions (for relative contributions see Tables S5–S7, ESI $^\dagger$ ) 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

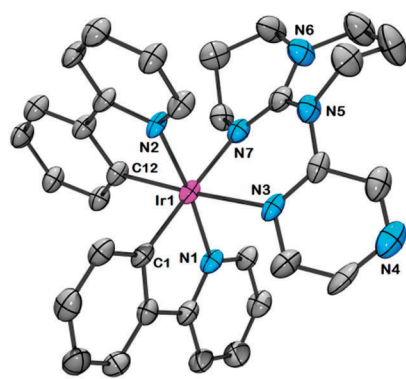


Fig. 1 ORTEP view of complex **3**. Hydrogen atoms, an anion and a solvated dichloromethane molecule have been omitted for clarity. Ellipsoids correspond to a 50% probability level.

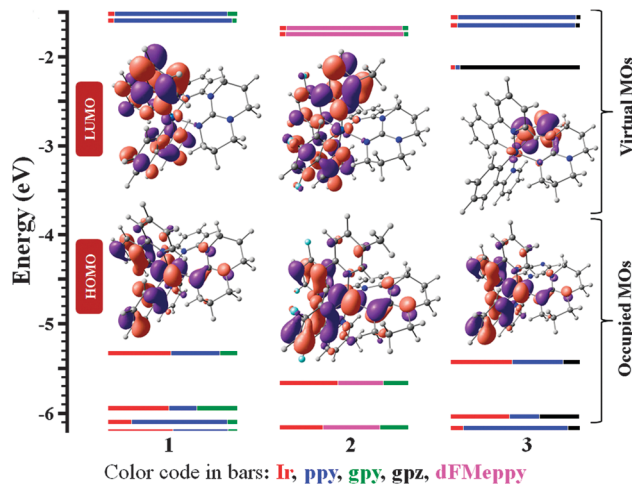


Fig. 2 Calculated frontier MO energies of **1–3**, obtained from TD-DFT [(rb3lyp/LanL2DZ(f) for Ir(III)) and (6-31g\*\* for C,H,N,(F))] with CPCM(CH<sub>3</sub>CN) and 0.5 eV threshold of degeneracy. Kohn–Sham MOs of **1**, **2** and **3** are also shown (contours isovalue: 0.03).

$[Ru(bpy)_3]^{+2}$ .<sup>6a</sup> The red-shift in the absorption spectra of **1–3** is due to a destabilization of the metal/C $^\wedge$ 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 Fig. S15, ESI $^\dagger$ ). The decreasing optical gap (inset figure of Fig. S12, ESI $^\dagger$ ) from **2** to **1** to **3** aligns with the computed HOMO–LUMO (LUMO = lowest unoccupied molecular orbital) energy gap ( $\Delta E$  of **2** = 3.91 eV;  $\Delta E$  of **1** = 3.72 eV;  $\Delta E$  of **3** = 3.31 eV) (Fig. 2 and Table S3, ESI $^\dagger$ ).

The electrochemical behaviour of **1–3** was monitored by cyclic voltammetry (CV) and the CV traces in deaerated MeCN containing 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte and using Fc/Fc<sup>+</sup> as an internal standard at 298 K are shown in Fig. S13 and S14 (ESI $^\dagger$ ). The detailed CV data vs. SCE (Fc/Fc<sup>+</sup> = 0.38 V in MeCN)<sup>12</sup> are summarized in Table S4 (ESI $^\dagger$ ) 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 of **1–3** falls between 0.99 to 1.21 V (Fig. S14, ESI $^\dagger$ ) and is assigned to the Ir<sup>III/IV</sup> redox couple with contributions from the C $^\wedge$ N ligands.<sup>5f</sup> These oxidation potentials are cathodically shifted to a significant extent compared to other heteroleptic iridium(III) cationic complexes bearing similar C $^\wedge$ N ligands, (**C1**:  $E_{ox}^{1/2} = 1.27$  V vs. SCE;  $[(dFMeppy)_2Ir(bpy)]PF_6$ , **C2**:  $E_{ox}^{1/2} = 1.55$  V vs. SCE). Indeed, DFT calculations show that the HOMOs of **1–3** are constituted almost equally with iridium and the C $^\wedge$ 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** ( $E_{ox}^{1/2} = 1.21$  V) is more positive compared to that of **1** ( $E_{ox}^{1/2} = 0.99$  V) due to the electron withdrawing fluorine atoms on the C $^\wedge$ N ligands, which increase the stability of HOMOs. The  $E_{ox}^{1/2}$  of **3** is slightly more positive (1.04 V) compared to that of **1**, although both contain the same cyclometallating ppy ligand. This is due to



Table 1 Optoelectronic properties of **1–3** in degassed MeCN<sup>a</sup>

$\lambda_{\text{em}}/\text{nm}$	$\Phi_{\text{PL}}/\%$	$\tau_{\text{e}}/\mu\text{s}$	$k_{\text{r}}/10^5 \text{ s}^{-1}$	$k_{\text{nr}}/10^5 \text{ s}^{-1}$	$E_{1/2}^{\text{ox}}/\text{V}$ ( $\Delta E_{\text{p}}$ , mV)	$E_{1/2}^{\text{red}}/\text{V}$ ( $\Delta E_{\text{p}}$ , mV)
<b>1</b> 503	60	2.1	2.9	1.9	0.99 (88)	-2.13
<b>2</b> 470, 498	62	2.6	2.3	1.4	1.21 (72)	-2.12
<b>3</b> 640	0.2	0.02	1.0	499	1.04 (92)	-1.60 (95)

<sup>a</sup>  $\Phi_{\text{PL}}$  was measured at 298 K using quinine sulfate ( $\Phi_{\text{PL}} = 54\%$ , in 0.5 N  $\text{H}_2\text{SO}_4$ ) as in ref. 16.  $k_{\text{r}} = \Phi/\tau$  and  $k_{\text{nr}} = (1 - \Phi)/\tau$ . CV values are in V vs. SCE.<sup>9</sup>  $\Delta E_{\text{p}} = |E_{\text{pa}} - E_{\text{pc}}|$ , where  $E_{\text{pa}}$  = anodic peak potential and  $E_{\text{pc}}$  = cathodic peak potential;  $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$  and result from one-electron processes. A non-aqueous  $\text{Ag}/\text{Ag}^+$  electrode (silver wire in a solution of 0.1 M  $\text{AgNO}_3$  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.

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 (Fig. S13 and Table S4, ESI<sup>†</sup>). 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**:  $E_{\text{red}}^{1/2} = -1.38$  V; **C2**:  $E_{\text{red}}^{1/2} = -1.34$  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 ( $\text{N}^{\wedge}\text{N}$ ). For instance, the first reduction waves of  $[(\text{ppy})_2\text{Ir}(\text{btl})]\text{PF}_6^{13\text{a}}$  and  $[(\text{ppy})_2\text{Ir}(4\text{-pytl})]\text{PF}_6^{13\text{b}}$  were found, respectively, at -1.99 and -2.25 V vs. SCE (btl = 1,1'-benzyl-4,4'-bi-1H-1,2,3-triazolyl and 4-pytl = 4-methyl-3-(pyridin-2-yl)-1,2,4-triazole). In the case of complexes  $[(\text{dFppy})_2\text{Ir}(3\text{-pytl})]^{14\text{a}}$  and  $[(\text{Fphtl})_2\text{Ir}(3\text{-pytlph})]\text{PF}_6^{14\text{b}}$  (where 3-pytl = 2-(1,2,3-triazol-5-yl)pyridine, Fphtl = 1-benzyl-4-(4-fluorophenyl)-1H-1,2,3-triazole and 3-pytlph = 2-(1-phenyl-1,2,3-triazol-4-yl)pyridine, respectively) the reduction waves were observed at -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 have the same gpy ancillary ligand. On the other hand, the first reduction wave of **3** is at -1.60 V with gpz as the ancillary ligand. The  $\sigma$ -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  $\text{C}^{\wedge}\text{N}$  ligands whereas in **3** it is localized on the pyrazine (Tables S8–S10 and Fig. S15, ESI<sup>†</sup>). In **1** and **2**, the absorption band for the HOMO–LUMO is predominantly ppy  $\pi$ - $\pi^*$  in nature while for **3** it is mixed CT, *i.e.*, the LUMO is different in both cases.

The steady-state emission spectra of **1–3** were recorded in degassed MeCN at 298 K and are shown in Fig. 3. The photophysical data are summarized in Table 1. The emission spectra for **1** and **3** are broad and featureless, indicative of mixed <sup>3</sup>CT emission while the spectrum of **2** is structured, pointing to significant <sup>3</sup>LC-based emission. TD-DFT calculations (Fig. S16–S18, ESI<sup>†</sup>)

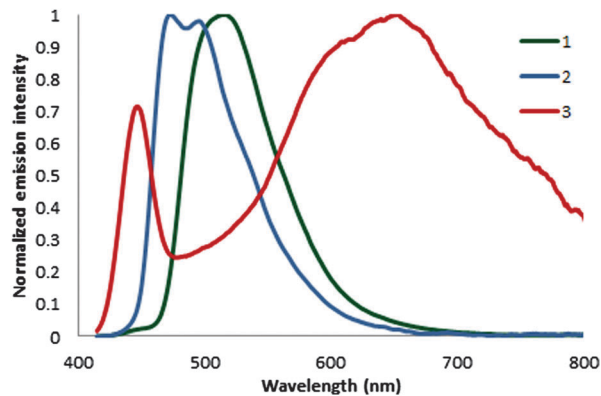


Fig. 3 Normalized emission spectra of **1–3** ( $\lambda_{\text{exc}} = 395$  nm) recorded in degassed MeCN at 298 K. The first band at 450 nm for compound **3** correspond to a Raman band of MeCN.

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  $\text{C}^{\wedge}\text{N}$  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 of **3** is at 640 nm, which is significantly red-shifted as compared to those of **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 as compared to those of **C1** ( $\lambda_{\text{max}} = 602$  nm) and **C2** ( $\lambda_{\text{max}} = 527$  nm).<sup>15</sup> This effect is again due to the strong  $\sigma$ -donating nature of the 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.

The photoluminescence quantum yields,  $\Phi_{\text{PL}}$ , in degassed MeCN for **1** and **2** are ca. 61%. Complex **3**, by contrast is very poorly emissive ( $\Phi_{\text{PL}} = 0.2\%$ ) due to a two-order increase in the non-radiative decay rate constant,  $k_{\text{nr}}$ . 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  $\mu\text{s}$ , respectively, and are significantly longer than that of **C1** ( $\tau_{\text{e}} = 0.275 \mu\text{s}$ )<sup>15</sup> while the  $\tau_{\text{e}}$  of **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.<sup>6</sup>

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.

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