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Molecular Orbital (LUMO). The red shift in the absorption and Occupied Molecular Orbital (HOMO) and Lowest Unoccupied are predominantly governed by the energy gap between the Highest into larger supramolecular assemblies for vectorial energy transfer.

ligands are achiral and stereopure and can be easily incorporated bidentate ligands are synthetically less appealing due to absence of < 1 ns, ~ 0.095) complexes exhibit more advantageous photophysical near-infrared Ru(II)-chromophores and -emitters are especially fibre-optic communication and biomedical imaging, deep-red to near-infra-red Ru(III)-chromophores and -emitters are especially useful. While [Ru(bpy)2]2+-type (bpy = 2,2'-bipyridine, τPL ~ 1 μs, ΦPL ~ 0.095) complexes exhibit more advantageous photophysical properties than the [Ru(tpy)2]2+-type (tpy = 2,2':6',2'-terpyridine, τPL < 1 ns, ΦPL = 10^-6) complexes (C1 in Chart 1), the complexes of bidentate ligands are synthetically less appealing due to absence of stereospecificity. 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.

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). The LUMO based on the π*-orbital of the tpy-A ligand stabilised whereas the tpy-D ligand destabilises the HOMO-metal-centered τ(tpy) 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. (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. (iii) Tridnate ligands with reduced steric strain and increasing field strength compared to those

Two novel mer-Ru(II) heteroleptic complexes containing strongly 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 λPL ~ 835 nm with associated excited-state lifetimes (τPL) of ~ 10 ns. The enhanced photophysical properties of these complexes compared to those of [Ru(tpy)2]2+ (tpy = 2,2':6',2'-terpyridine; λabs < 575 nm, λPL ~ 629 nm and τPL ~ 0.25 ns) are due to the larger MLCT-ML 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. In general, the interest in these compounds stems from their potential application as light harvesters in dye-sensitised solar cells, water-splitting catalysis, and electroluminescent dyes in organic light-emitting devices. In view of many civilian and military aspects, particularly in fibre-optic communication and biomedical imaging, deep-red to near-infrared Ru(III)-chromophores and -emitters are especially useful. While [Ru(bpy)2]2+-type (bpy = 2,2'-bipyridine, τPL ~ 1 μs, ΦPL ~ 0.095) complexes exhibit more advantageous photophysical properties than the [Ru(tpy)2]2+-type (tpy = 2,2':6',2'-terpyridine, τPL < 1 ns, ΦPL = 10^-6) complexes (C1 in Chart 1), the complexes of bidentate ligands are synthetically less appealing due to absence of stereospecificity. 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.

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of a tpy ligand, that help increase the excited state lifetime and red-shift the triplet MLCT emission maxima (C4 in Chart 1).
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 (CS and C6 in Chart 1).\textsuperscript{7b,13-15} 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 1MLCFT fashion and emit by Vis/NIR emission at r.t. with relatively long excited-state lifetime.\textsuperscript{1,14}

Recently Hanan and co-workers used the ligands 2,6-bis(3,4,7,8-tetrahydro-2H-pyrimido[1,2-a]pyrimidine (dpgy or L1) and 2,6-bis(3,4,7,8-tetrahydro-2H-pyrimido[1,2-a]pyrimidine)-1(6H)-yl)pyrazine (dpgz 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(dpgy/dpgz)Cl\textsubscript{3}])\textsuperscript{15} compared to those of [Ru(tpy)\textsubscript{2}]\textsuperscript{2+} and [Re(tpy)CO\textsubscript{3}][L\textsubscript{2}]\textsuperscript{2+} (where L = MeCN, pyridine, PPh\textsubscript{3}, PF\textsubscript{6})\textsuperscript{1,14}. The dpgy ligand was employed with [Ru(tpy)Cl\textsubscript{2}]\textsuperscript{2+} precursor to form helteroletic [Ru(tpy)(dpgy)]\textsuperscript{2+} complex. In these cases, the 4'-position of the tpy ligands either contained electron donating R-biphenyl 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 dpgy and dpgz ligands that are also coordinated with electron withdrawing -CO\textsubscript{2}H functionalised tpy ligand. The idea of using a -CO\textsubscript{2}H functionalised tpy ligand was to use the -CO\textsubscript{2}H group as an anchor to the mesoporous TiO\textsubscript{2} in a dye-sensitised solar cell, which will be published in due course. The optoelectronic properties of these complexes containing a donating dpgy/dpgz 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)\textsuperscript{1,13,14} -{(2,2',6',2'-terpyridin)-4'-y}benzoic acid (CO\textsubscript{2}H-Hph-tpy)\textsuperscript{15} and [Ru(CO\textsubscript{2}H-Hph-tpy)Cl\textsubscript{3}]\textsuperscript{16} were synthesized using literature procedures. The stoichiometric reaction of L1 and L2 with Ru(CO\textsubscript{2}H-Hph-tpy)Cl\textsubscript{3} in refluxing n-butanol, in presence of few drops of 4-ethylmorpholine, provided complexes 1, [Ru(CO\textsubscript{2}H-Hph-tpy)(L1)][(PF\textsubscript{6})\textsubscript{3}] and 2, [Ru(CO\textsubscript{2}H-Hph-tpy)(L2)][(PF\textsubscript{6})\textsubscript{3}] in good yields (51-59%, Scheme 1).

![Scheme 1](image)

Scheme 1. Synthesis of complexes 1 and 2. (a) Ru(CO\textsubscript{2}H-Hph-tpy)Cl\textsubscript{3} (1 equiv.) in n-butanol at reflux for 20 h in presence of 4-ethylmorpholine, followed by the addition of aqu. NH\textsubscript{4}PF\textsubscript{6}, and column chromatography purification.

The appearance of multiple peaks over 0-4 ppm region in \textsuperscript{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 ES1).\textsuperscript{13,14}

Single crystals of 1, suitable for X-ray structure diffraction, were obtained by slow vapour diffusion of diethyl ether 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, ES1). The Ru-N bond distance (1.939(2) Å) to the central pyridine ring of CO\textsubscript{2}H-Hph-tpy is the shortest among all Ru-N bonds and the Ru-N bond distances closely resemble those observed in [Ru(Ph-tpy)\textsubscript{2}][PF\textsubscript{6}]\textsubscript{2}.\textsuperscript{17} The bite angle subtended by the two trans N-atoms of L1 and the Ru-atom (N7-Ru1-N10 = 172.40(10)\textdegree) is noticeably increased from that exhibited by the CO\textsubscript{2}H-Hph-tpy ligand (N1-Ru1-N3 = 159.07(10)\textdegree), which indicates a more perfect octahedral geometry around Ru(II) in complex 1, compared to that in [Ru(Ph-tpy)\textsubscript{2}][PF\textsubscript{6}]\textsubscript{2}. The average C\textsubscript{pp}pp-N\textsubscript{pp}pp-N\textsubscript{pp}pp dihedral angle of 51.2\textdegree 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 mono-electronic by DPV when compared to Fc/Fc\textsuperscript{+}. At positive potentials, complexes 1 and 2 show quasi-reversible Ru(II)/III-HOMO-based oxidations at 0.52 V and 0.59 V, respectively, as suggested by DFT calculations (Figures 2 and Table S3 in ES1). Owing to the strong π-donation from the hpp moieties to the metal based orbitals, these E\textsubscript{1/2} values are ~ 800 mV less positive than that observed for the Ru(III/II) couple in [Ru(tpy)\textsubscript{2}]\textsuperscript{2+} (E\textsubscript{1/2} vs. SCE = 1.31 V),\textsuperscript{18} and fall closely to the oxidation potential observed for the cyclometalated complex [Ru(tpy)(1,3-di(2-pyridyl)benzene)]\textsuperscript{2+} (E\textsubscript{1/2} vs. SCE = 0.51 V).\textsuperscript{19} The stronger electron withdrawing effect of a pyrazine moiety (σ = 0.25; σ = Hammett parameter)\textsuperscript{20} in L2 compared to the same of a pyridine moiety (σ = 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\textsubscript{HOMO} = -9.89 eV) and 2 (E\textsubscript{HOMO} = -10.09 eV) compared to that of [Ru(tpy)\textsubscript{2}]\textsuperscript{2+} (E\textsubscript{HOMO} = -11.17 eV) are in good agreement with the lower anodic potentials measured for 1 and 2 (Figures 2 and Tables S4, S5 in ES1) in comparison to [Ru(tpy)\textsubscript{2}]\textsuperscript{2+}.
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 1, the second peak was found to be irreversible for 2 (Figure S11, ESI). As suggested by DFT calculations of 1 and 2, the LUMO predominantly resides on COHPh-tpy ligand, thereby the first reduction peak is believed to be based on the COHPh-tpy ligand. The more electron-rich metal center in 1 and 2, compared to that in [Ru(tpy)]2+ (E_{red} vs SCE = -1.23 V), increases back-donation to the COHPh-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+ (E_{LUMO} = -7.58 eV), respectively (Table S3 in ESI).

The UV-vis absorption spectra of 1 and 2 in dry acetonitrile solutions display varying contributions of ligand-centered (LC) π→π* transitions in the UV region (λ_{max} ≤ 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 (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 1MLCT Ru(dπ)→π*(tpy) transition of L1, while the transition at 396 nm for 2 is a HOMO-2→LUMO+2 and is primarily consisted of 1MLCT Ru(dπ)→π*(tpy) transition of L2 with minor 1MLCT contribution from Ru(dπ)→COHPh-tpy(π*) (Tables S7, S8 in ESI). It may be noted that such a band near 345 nm is usually observed for [RuN4(diimine)]2+ chromophores.21 For both the complexes the lower energy transitions at 530-620 nm is dominated by transitions among frontier MOs, such as HOMO→LUMO, HOMO-1 or 2→LUMO, HOMO→LUMO+1 and these transitions are attributed to the 1MLCT and singlet ligand-to-ligand charge transfer (LLCT) transitions, predominantly dominated by 1MLCT while the contribution from 1LLCT transition is minor. The most noticeable feature in the visible region is that the lowest energy 1MLCT maxima of 1 and 2 are red-shifted by ~ 150 nm with respect to that of [Ru(tpy)]2+ (λ_{max} = 474 nm).18b,c Ligands L1 and L2 are expected to interact with the tpy[dRu] 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 dπ→π* 1MLCT 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_{em}) 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 (MLCT) from Ru(dπ) 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 1MLCT emission from a bis(tridentate) RuN6 complex.20,21,22 As expected the emission wavelength is red-shifted upon introduction of L1/L2 in place of a tpyridine ligand in [Ru(tpy)]2+ (λ_{em} = 629 nm) and [Ru(Ph-tpy)]2+ (λ_{em} = 670 nm). Complexes 1 and 2 exhibit ~ 40 times longer τ_{em} values compared to that of [Ru(tpy)]2+ (τ_{em} = 0.25 ns).23 This fact is due to a larger bite angle (N-Ru-N ~ 173° in 1 and 2, N-Ru-N ~ 158° in [Ru(bpp)(tpy)]2+) and stronger α-donation compared to those of a tpy moiety that help to destabilise the 3MC state of 1 and 2 and consequently diminishing the process of thermal non-radiative deactivation via 3MC state. It has been shown that substitution of a 2,6-bis(8′-quinolinyl)pyridine (bpp) ligand with a tpy ligand, that exhibits lower bite angle upon coordination than bpp, diminishes the lifetime of the [Ru(bpp)(tpy)]2+ complex to only 7.4 ns compared to 3 μs in [Ru(bpp)(tpy)]2+.23 Although substituted by Ph-tpy, the strong α-donation and larger bite angle of L1/L2 upon coordination, comparable to that of bpp (177.6°), render the 3MC states higher in energy and thus increasing the lifetime by ~ 40 times.

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]).

Figure 3. Absorption and normalized emission spectra of 1 and 2 in dry, deaerated MeCN solutions at r.t.
Notes and references

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Novel heteroleptic Ru(II)-polypyridyl complexes were synthesised that exhibit panchromatic absorption up to 750 nm and $^4$MLCT NIR emission at $\lambda_{\text{em}} > 830$ nm.

Reversible electrochemistry, Panchromatic absorption, NIR emission