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Facile syntheses of tridentate ligands for room-temperature luminescence in ruthenium complexes

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Received (in Columbia MO, USA) 20th March 2002, Accepted 8th May 2002
First published as an Advance Article on the web 23rd May 2002

A new family of easily prepared and functionalised terpyridine-like ligands exhibit room-temperature luminescence as their Ru(II) complexes.

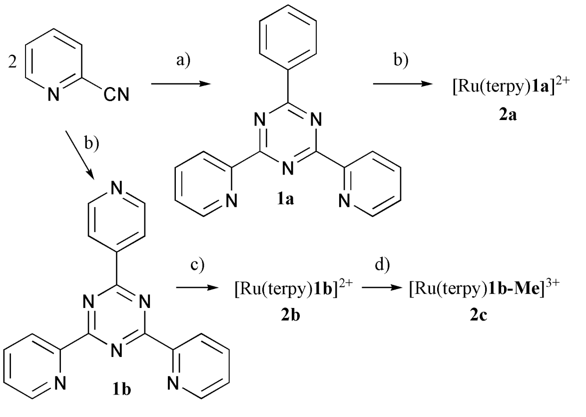
Over the past 25 years ruthenium polypyridyl complexes have attracted considerable attention due to their useful photophysical properties.[1] The prototypical Ru(bpy)$_3^{2+}$ motif (bpy = 2,2′-bipyridine) has a long room-temperature (r.t.) excited-state lifetime, which is critical for applications in practical devices.[2] However, the Ru(bpy)$_3^{2+}$ motif is stereogenic, which means that higher nuclearity complexes are a complicated mixture of isomers.[3] The achiral Ru(tpy)$_2^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) motif gives unique products in polymetallic complexes when substituted in the 4′-position,[4] thus simplifying synthesis; however, it is essentially non-luminescent at r.t.[5] Recent efforts to increase the r.t. luminescence lifetimes of Ru(II) complexes of tridentate ligands have met with success,[6] but usually required multi-step syntheses or expensive starting materials. Herein we report on the synthesis of triazine-based tridentate ligands that exhibit improved r.t. excited-state lifetimes in their Ru(II) complexes. Their inexpensive starting materials and the facile formation of their quaternized metal complexes makes them ideal candidates for incorporation in larger supramolecular devices.[7]

Although the synthesis and complexation of *s*-triazine ligands is well-described (*e.g.*, tris-2-pyrimidyltriazine[8] and tris-2-pyridyltriazine[9]), almost no attention has been given to the synthesis of asymmetric tridentate ligands containing a central triazine such as **1a** and **1b**.[10]

The ligands were synthesised by two routes (Scheme 1).† Ligand **1a** was produced by the reaction of lithium *N*,*N*-dimethylbenzamidinate with two equivalents of 2-cyanopyridine in ether (Scheme 1(a)). The microcrystalline precipitate was isolated by filtration in 90% yield. Ligand **1b** was produced in a melt reaction of 4-cyanopyridine and 2-cyanopyridine with NaH as catalyst. The main by-products, *s*-(2-pyridyl)triazine and 2,4-di(4′-pyridyl)-6-(2‴-pyridyl)triazine, were easily separated by complexation with Ni(II)[11] and recrystallisation from EtOH to afford **1b** in 24% yield (Scheme 1(b)). Both reactions could be scaled up to produce multi-gram quantities of ligands **1a** and **1b**. The ruthenium complexes **2a** and **2b** were prepared in 71% and 56% yield, respectively, by allowing **1a** and **1b** to react in ethylene glycol with Ru(tpy)Cl$_3$ at reflux (Scheme 1(c)). Allowing **2b** to react with MeI in acetonitrile at r.t. gave the N-methylated product [Ru(tpy)(**1b**-Me)]$^{3+}$ in near quantitative yield (Scheme 1(d)). This contrasts sharply with the lack of reactivity in other Ru complexes with pendant 4-pyridyl substituents.[12]

The X-ray crystal structure of heteroleptic ruthenium complex **2a** (Fig. 1) contains mutually orthogonal ligands of tpy and **1a**.‡ The pseudo-octahedral geometry around the metal ion is similar to that of Ru(tpy)$_2^{2+}$.[13] The Ru–N bond length (central triazine N) is 1.9648(16) Å compared to 1.9824(16) Å for the central pyridine N in the tpy moiety. The phenyl ring in ligand **1a** is twisted by 1.2° compared to the central triazine ring. This dihedral angle is lower than that found in any ruthenium 4′-phenyl-2,2′:6′,2″tpy complex.[14] In the case of **2a**, there are no unfavourable H···H interactions *ortho* to the interannular bond and the triazine N lone pairs are available for H-bonding to C–H groups on the phenyl substituent of **1a**. This also has consequences in the electrochemistry and photochemistry of complexes **2a** and **2b** (*vide infra*).

The electrochemistry of metal complexes **2a** and **2b** is similar to that of Ru(tpy)$_2^{2+}$ with a single one-electron oxidation, predominately metal-based in nature, and a series of three ligand-based reductions for **1a** and **1b** (Fig. 2). The oxidation potential is shifted to more positive potentials by 0.1 V compared to Ru(tpy)$_2^{2+}$ (+1.3 V) due to the greater stabilisation of the metal-based orbitals by the triazine ring of ligands **1** compared to the pyridine ring of tpy. The difference in the oxidation potential between **2a** (+1.40 V) and **2b** (+1.45 V) implies a relatively long-range interaction between the 4-pyridyl N position of the ligand and the metal ion. This is further exemplified by the increase in oxidation potential upon methylation of **2b** to produce **2c** (+1.51 V). The ligand-based reduction potentials for **2a** (−0.78 V) and **2b** (−0.70 V) are also



Scheme 1 The synthesis of ligands **1a** and **1b** and their ruthenium terpyridine complexes **2a** and **2b**: (a) Lithium *N*, *N*-dimethylbenzamidinate, diethyl ether, r.t., 30 min; (b) 4-cyanopyridine, NaH, 180 °C, 30 min; (c) Ru(tpy)Cl$_3$, ethylene glycol, reflux, 10 min; (d) MeI, r.t., 24 h (**1b**-Me is ligand **1b** methylated in the 4-pyridyl position).

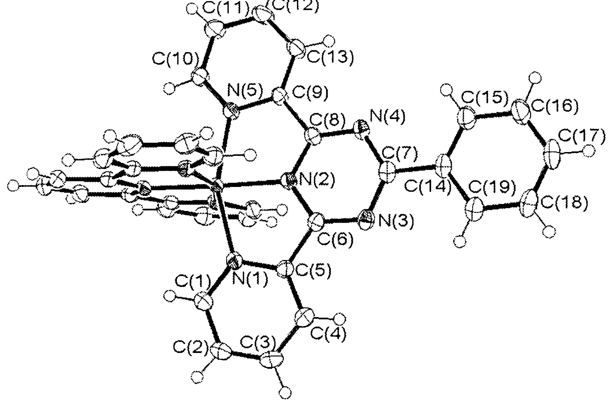


Fig. 1 ORTEP plot of ruthenium complex **2a**. The acetonitrile of solvation, PF$_6$ anions and tpy labelling have been omitted for clarity.

DOI: 10.1039/b202758e

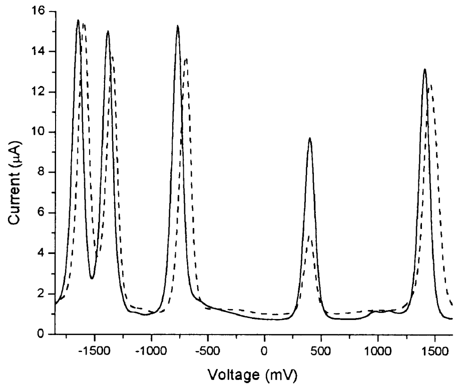


Fig. 2 Squarewave voltammograms of complexes **2a** (solid line) and **2b** (dashed line) in acetonitrile with 0.1 M TBAPF$_6$ and ferrocene/ferrocinium as internal reference (0.395 V *vs.* SHE).

significantly less negative than in Ru(tpy)$_2^{2+}$ (-1.24 V) due to the electron deficient nature of triazine ring.

The photophysical properties of the complexes are also similar to those of Ru(tpy)$_2^{2+}$. The electronic absorption spectra (Fig. 3) show the same general profile, with ligand based absorptions predominating in the UV region (**2a**: $\lambda_{\max}$ = 281 nm, ε = 50600 M^{-1} cm^{-1}; **2b**: $\lambda_{\max}$ = 273 nm, ε = 55300 M^{-1} cm^{-1}; **2c**: $\lambda_{\max}$ = 281 nm, ε = 45900 M^{-1} cm^{-1}) and MLCT absorptions in the visible region (**2a**: $\lambda_{\max}$ = 472 nm, ε = 17800 M^{-1} cm^{-1}; **2b**: $\lambda_{\max}$ = 476 nm, ε = 17600 M^{-1} cm^{-1}; **2c**: $\lambda_{\max}$ = 497 nm, ε = 14900 M^{-1} cm^{-1}). The energy of these absorptions is red-shifted with respect to the parent complex due to the decrease in energy of the acceptor orbital. The absorption is also affected by substitution at the triazine 4-position with a slight shift from 472 nm in **2a** to 476 nm in **2b**. Note that there is no significant difference in the $\Delta E_{\text{ox-red}}$ of the two complexes, as seen in the similar energies of the MLCT transitions, despite the difference in potentials.[15]

The most significant differences are in the luminescence properties of **2a** and **2b**, which show strong room-temperature luminescence in acetonitrile, approximately 2.5 and 3 times greater than [Ru(tpy)(4′-*p*-tolyl-2,2′:6′,2″-tpy)]$^{2+}$, one of the most widely used room-temperature luminescent complexes of a tpy-like ligand.[4b] The nitrogen containing complex **2b** exhibits a lower energy emission (714 nm) as compared to **2a** (700 nm). Thus, the change from C to N at the 4′-pyridyl position has a greater effect in the excited state than in the ground state, which implies that there is increased electron density at this position in the excited state. Methylated complex **2c** does not emit up to 800 nm, the limit of our equipment. This may indicate either an emission lower than 800 nm, or a non-radiative mechanism for excited-state deactivation.

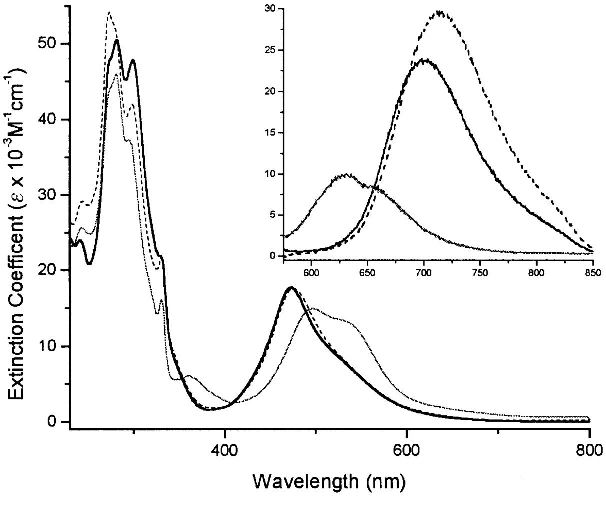


Fig. 3 UV-visible data for **2a** (solid line), **2b** (dashed line), and **2c** (gray line). Inset: emission data (corrected for absorption): **2a** (solid line), **2b** (dashed line), and [Ru(tpy)(ttp)]$^{2+}$ (gray line). Spectra were recorded at r.t. in argon purged acetonitrile (ttp = 4′-*p*-tolyl-2,2′:6′,2″-tpy).

In summary, we have described the facile syntheses of a new family of terpyridine-like ligands, the ruthenium complexes of which exhibit room-temperature luminescence in solution. These ligands offer the synthetic adaptability of terpyridine and the longer-lived excited-state lifetimes of bipyridine complexes. As such they represent excellent candidates for use as probes in photophysical studies of larger polymetallic systems. Work is continuing into this area along with the investigation of a wider range of substituents on the triazine ring.

We thank the NSERC of Canada, the Province of Ontario and the Research Corporation for financial support.

Notes and references

† **1a**: To a mixture of LiNMe$_2$ (200 mg) in diethyl ether (50 mL) was added benzonitrile (400 mg). After stirring for 30 min, 2-cyanopyridine was added (800 mg). Over 2 h a microcrystalline solid formed which was collected by filtration. Yield = 1.12 g (93%). **1b**: A mixture of 4-cyanopyridine (5 g), 2-cyanopyridine (5 g) and NaH (200 mg) was heated to 180 °C for 30 min. On cooling the solid was dissolved in hot toluene (500 mL) and filtered. While still hot, the toluene was extracted with an aqueous Ni solution (3 g of NiCl$_2$·6H$_2$O in 200 mL of water). On cooling, KCN (5 g) was added and a fine precipitate formed. The crude product was collected by filtration and recrystallised from ethanol. Yield = 2.4 g (24%).

‡ *Crystal data* for C$_{34}$H$_{23}$F$_{12}$N$_9$P$_2$Ru·0.5CH$_3$CN were collected on a Bruker APEX at 150 K using Mo-Kα radiation (λ = 0.71073 Å). Relections measured: 47295; unique data: 11037, M = 976.68, monoclinic, space group $P2_1/c$, a = 9.2165(4), b = 32.6459(14), c = 12.5834(5) Å, β = 92.037(1), U = 3783.7(3) Å^3, Z = 4, μ(Mo-Kα) = 0.601 mm^{-1}, R_1 [$I > 2\sigma(I)$] = 0.0376, wR_2 (all unique data) = 0.0573. CCDC reference number 181953. See http://www.rsc.org/suppdata/cc/b2/b202758e/ for crystallographic data in CIF or other electronic format.

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