# Synthesis and photophysical properties of naphthyl-, phenanthryl-, and pyrenyl-appended bis(pyridyl)triazine ligands and their Zn(II) and Ru(II) complexes<sup>1</sup>

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Abstract: A family made of four bis(pyridyl)triazine ligands with appended aryl rings, including three fused aromatic rings, have been synthesized, and their corresponding homoleptic Ru(II) and Zn(II) complexes have been prepared and characterized by several means. The free ligands 2,4-di(2-pyridyl)-6-phenyl-1,3,5-triazine (L1); 2,4-di(2-pyridyl)-6-(1naphthyl)-1,3,5-triazine (L2); 2,4-di(2-pyridyl)-6-(9-phenanthryl)-1,3,5-triazine (L3); and 2,4-di(2-pyridyl)-6-(1-pyrenyl)-1,3,5-triazine (L4) were formed in triazine ring-forming reactions from the reactions of the cyano-functionalized aromatic rings with LiNMe<sub>2</sub> followed by the addition of 2 equiv. of 2-cyanopyridine. The metal complexes examined in this study are the homoleptic Ru(II) complexes  $\operatorname{Ru}(\mathbf{L1})_2^{2+}$  (2a),  $\operatorname{Ru}(\mathbf{L2})_2^{2+}$  (2b),  $\operatorname{Ru}(\mathbf{L3})_2^{2+}$  (2c), and  $\operatorname{Ru}(\mathbf{L4})_2^{2+}$  (2d) and Zn(II) complexes  $Zn(L1)_2^{2+}$  (3a),  $Zn(L2)_2^{2+}$  (3b),  $Zn(L3)_2^{2+}$  (3c), and  $Zn(L4)_2^{2+}$  (3d). Also, crystallographic data for the free ligands and Zn(II) and Ru(II) complexes have been obtained in some cases. The redox behaviour and absorption spectra of all the species have been investigated, together with the luminescence properties of the free ligands at room temperature in fluid solution and of the Ru(II) complexes both at room temperature in fluid solution and at 77 K in rigid matrix. The redox data indicate that the free ligands are reduced twice at relatively mild potentials (< -2.30 V vs. SCE), with the first reduction almost independent of the nature of the substituted aryl group. The UV absorption spectra of all the compounds are dominated by intense spin-allowed  $\pi - \pi^*$  transitions mainly centered on the bis(pyridyl)triazine moiety; however, in L2-L4, moderately intense intraligand charge-transfer (ILCT) bands are also present. Such bands are red-shifted in the Zn(II) compounds, while they are obscured in the Ru(II) species by the more intense spin-allowed metal-to-ligand charge-transfer (MLCT) bands. The free ligands exhibit interesting emission properties, ranging from fluorescence from  $\pi - \pi^*$  states to excimeric (in L4) and ILCT (in L2 and L3) emission. In the Ru(II) complexes, strong emission is found at 77 K from triplet MLCT states. For 2c and 2d, the emissive MLCT states are mixed with low-lying triplet ligand-centered states.

Key words: triazine ligands, ruthenium complexes, zinc complexes, ILCT emission.

**Résumé :** On a effectué la synthèse d'une famille formée de quatre ligands bis(pyridyl)triazine portant des noyaux aromatiques, y compris trois noyaux aromatiques dont on a préparé et caractérisé les complexes homoleptiques correspondants du Ru(II) et du Zn(II). Les ligands libres 2,4-di(2-pyridyl)-6-phényl-1,3,5-triazine (L1), 2,4-di(2-pyridyl)-6-(1naphtyl)-1,3,5-triazine (L2), 2,4-di(2-pyridyl)-6-(9-phénanthryl)-1,3,5-triazine (L3) et 2,4-di(2-pyridyl)-6-(1-pyrényl)-1,3,5-triazine (L4) ont été obtenus par des réactions conduisant à des triazines et impliquant l'action du LiNMe<sub>2</sub> sur des cyano portés par noyaux aromatiques fonctionnalisés, suivie par l'addition de deux équivalents de 2-cyanopyridine. Les complexes métalliques examinés dans cette étude sont les complexes homoleptiques du Ru(II), Ru(L1)<sub>2</sub><sup>2+</sup> (2a), Ru(L2)<sub>2</sub><sup>2+</sup> (2b), Ru(L3)<sub>2</sub><sup>2+</sup> (2c) et Ru(L4)<sub>2</sub><sup>2+</sup> (2d) et du Zn(II), Zn(L1)<sub>2</sub><sup>2+</sup> (3a), Zn(L2)<sub>2</sub><sup>2+</sup> (3b), Zn(L3)<sub>2</sub><sup>2+</sup> (3c) et Zn(L4)<sub>2</sub><sup>2+</sup> (3d). Dans certains cas, on a aussi obtenu des données cristallographiques pour les ligands libres et des complexes du Zn(II) et du Ru(II). On a étudié le comportement redox et les spectres d'absorption de toutes les

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espèces, de même que les propriétés de luminescence des ligands libres, à la température ambiante et en solution fluide ainsi que celles des complexes du Ru(II) tant à la température ambiante, en solution fluide, que celles à 77 K, dans une matrice solide. Les données redox indiquent que les ligands libres sont réduits deux fois à des potentiels relativement faibles (< -2,30 V vs SCE) et que la première réduction est pratiquement indépendante de la nature du substituant aryle. La région UV des spectres d'absorption de tous les composés est dominée par d'intenses transitions  $\pi$ - $\pi$ \* permises par les spins et centrés principalement sur la portion bis(pyridyl)triazine; toutefois, dans les ligands L2–L4, on observe aussi la présence de bandes de transfert de charge intraligand (TCIL) d'intensité moyenne. Ces bandes sont déplacées vers le rouge dans les composés du Zn(II) alors que dans les espèces Ru(II) elles sont obscurcies par les bandes de transfert de charge métal à ligand (TCML) permises par les spins et de grande intensité. Les ligands libres possèdent des propriétés d'émission intéressantes allant de la fluorescence des états  $\pi$ - $\pi$ \* aux émissions excimères (dans L4) et aux bandes de transfert de charge intraligand (dans L2 et L3). Dans les complexes du Ru(II), à 77 K, on observe une émission intense de transfert de charge métal à ligand à partir des états triplets. Pour les composés 2c et 2d, les états d'émission TCML sont mixtes avec des états triplets de basse énergie centrés sur le ligand.

*Mots-clés* : ligands de triazine, complexes du ruthénium, complexes du zinc, émission de transfert de charge intraligand (TCIL).

[Traduit par la Rédaction]

# Introduction

Complexes of polypyridine ligands have been the subject of intense research because of their promising photophysical properties and potential applications in areas of lightharvesting devices, luminescent sensors, and photocatalysis. In particular, complexes of d<sup>6</sup> transition-metal ions show promise in these fields because of their relatively long excited-state lifetimes and emission through low-lying MLCT (metal-to-ligand charge-transfer) states (1-5). Over the last two decades, there has been considerable efforts to optimize the photophysical properties of Ru(II) complexes based on 2,2':6',2''-terpyridine (tpy) (2, 6). Indeed, the tridentate motif offers synthetic advantages over bidentate ligands based on 2,2'-bipyridine (bpy), as the latter creates stereocentres in metal complexes with octahedral geometry. Consequently, in larger polynuclear systems, the separation of diastereomers can be problematic despite synthetic advances in the purification of isomers (7, 8). Unfortunately, Ru(II) tpy-type complexes have poor photophysical properties, as the steric strain imposed in N-N-N coordination in tridentate ligand lowers the energy of non-emissive, metal-centred (MC) states, which can be thermally accessed at room temperature. Synthetic strategies have been developed to overcome the deactivation of MLCT excited states, primarily focusing on manipulating the energy of <sup>3</sup>MLCT states relative to <sup>3</sup>MC states. Alternatively, ligand systems have been developed with low energy emissive intraligand charge-transfer (ILCT) states (9). The excited-state energy of the ILCT state in Ru(II) complexes, or complexes of other transition-metal ions, must be significantly lower in energy than the MLCT/MC states to influence the excited-state lifetime (10-14). Alternatively, d<sup>10</sup> Zn(II) metal ions can be employed to study the ILCT emission, as these polypyridine complexes of such metal ions do not exhibit MLCT or MC states at low energies, and their eventual emission can involve ILCT states (13–16). An ILCT transition requires a coordinating motif to acts as an electron acceptor and an appended organic group to act as an electron donor. Tpy is typically an electron acceptor, and a variety of organic groups act as the electron donor. Fused aromatic rings have previously been employed as the organic, electron donating motif, as they offer interesting properties in the excited state through excimer and exciplex formation as well as offering a means of aggregating cations in the solid state through  $\pi$ - $\pi$  interactions (12, 14, 15, 17–19). Herein, we report the synthesis and characterization of a family of triazine ligands with fused aromatic rings appended. The absorption spectra and redox properties of free ligands and of their Zn(II) and Ru(II) complexes are also discussed, together with the luminescence properties of free ligands and Ru(II) complexes.

# **Results and discussion**

#### **Synthesis**

The ligands were synthesized by using a slightly modified version of a previously reported procedure (see Supplementary data for full ligand structures) (20, 21).<sup>3</sup> LiNMe<sub>2</sub> was generated in situ through the slow addition of *n*-BuLi to HNMe<sub>2</sub> in anhyd. diethylether. On addition of the cyano-precursors, an amidinate intermediate formed, which was converted to the appropriate triazine ligand by the addition of 2 equiv. of 2-cyanopyridine. The reaction proceeded slower than previously reported syntheses for non-symmetric triazine ligands and with slightly lower yields. The presence of the adjacent fused aromatic ring may lead to a stabilized amidinate intermediate by intramolecular H-bonding with the C=N<sup>-</sup> motif, which interferes with the cyclization reaction (Scheme 1).

Complexes 2 were synthesized by addition of RuCl<sub>3</sub>·3H<sub>2</sub>O to 2 equiv. of the ligand, with 3 equiv. of AgNO<sub>3</sub> in EtOH. The complexes were purified by column chromatography followed by anion exchange to afford complexes 2b-2d in 56%, 23%, and 11% yields, respectively. The Zn(II) complexes were synthesized by the addition of Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O to a solution of the appropriate ligand in acetonitrile at reflux for 15 min. Precipitation of the product by the addition

<sup>&</sup>lt;sup>3</sup> Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3836. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub\_e.shtml.



Scheme 1. Synthesis of ligands L1-L4 and the complexation of the ligands to form the Ru(II) complexes 2a-2d and Zn(II) complexes 3a-3d.

of diethyl ether afforded the complexes 3a-3d in 68%, 55%, 74%, and 84% yields, respectively. The complexes were characterized in solution by <sup>1</sup>H NMR and in the solid state by elemental analyses.

On complexation to the Ru(II) or Zn(II) metal ions, the pyridyl and pyrenyl signals of ligands are both shifted to lower field owing to the electron-withdrawing effect of the metal ions (Fig. 1). The Zn(II) ion in complex **3d** has a greater electron-withdrawing effect on the pyridyl protons closest to the metal centre ( $H_{5,5''}$  and  $H_{6,6'}$ ) when compared with the Ru(II) complex **2d**. Complex **3d** has limited solubility and reaches saturation point in solution very rapidly as compared with **2d** presumably owing to aggregation caused by the pyrenyl group.

#### Solid-state structures

Crystals suitable for analyses of **L2** were obtained by slow diffusion of hexane into a concentrated solution of **L2** in chloroform. One molecule of water is found in the asymmetric unit with H-bonding to *N*-pyridyl atoms with N–H distances of 2.15 and 2.14 Å. Significant face-to-face  $\pi$ stacking interactions are observed in the extended lattice with each triazine ring overlaying pyridyl rings above and below the plane with centroid-to-centroid distances of 3.6– 3.8 Å (Fig. 2).

Attempts to crystallize **2b** and **3b** as the PF<sub>6</sub> and ClO<sub>4</sub> salts, respectively, were unsuccessful. Red crystals of **2b** were obtained by addition of excess NH<sub>4</sub>BF<sub>4</sub> in methanol to a concentrated solution of **2b** in acetonitrile followed by slow diffusion of isopropyl ether. The complex crystallized in the monoclinic space group P2(1)/n with two cations, four anions, (three PF<sub>6</sub><sup>-</sup> anions and one BF<sub>4</sub><sup>-</sup> anion) and four molecules of acetonitrile. The Zn(II) complexes could be synthesized as the PF<sub>6</sub><sup>-</sup> salts according to a literature procedure (22), and crystals of **3b** were obtained as the PF<sub>6</sub><sup>-</sup> salt by slow diffusion of isopropyl ether into an acetonitrile solution of the complex. Complex **3b** crystallized in the noncentrosymmetric space group P2(1) with two cations, four PF<sub>6</sub> counter-ions and three acetonitrile solvent molecules. In

Fig. 1. <sup>1</sup>H NMR spectra of L4 in CDCl<sub>3</sub> (above), 2d (middle), and 3d (below) in CD<sub>3</sub>CN.  $H_{3,3''}$ ,  $H_{4,4''}$ ,  $H_{5,5''}$ , and  $H_{6,6''}$  refer to the pyridyl protons.



both crystal structures, significant  $\pi$ -stacking interactions were observed in the extended lattice between naphthyl groups and coordinating pyridyl rings with centroid-centroid distances of 3.66 and 3.71 Å for complex **2b** and 3.89 and 3.96 Å in complex **3b** (Fig. 3). The use of non-covalent interactions to aggregate functional assemblies through crystal engineering is appealing as conventional, covalent ap-



Fig. 3. ORTEP representations of  $\pi$ -stacking interactions in the solid-state structures of 2b and 3b. Thermal ellipsoids are set at 30%. Anions and solvent molecules of crystallization were omitted for clarity.



proaches require multistep syntheses (4, 17, 19, 22). Naphthyl-pyridyl,  $\pi$ -stacking interactions were previously observed in naphthyl-appended tpy-based Ru(II) and Fe(II) complexes (19). We previously reported similar interactions in the solid-state structure of complex **2c** in which phenanthryl groups  $\pi$ -stack with pyridyl groups (20). The naphthyl groups twist away from the central triazine rings by 16.6°–36.9° in complex **2b** and 21.5°–29.1° in complex **3b** for the four ligands of the two cations. Intramolecular C–H–N(triazine) H-bonding interactions are still favouring minimal twisting of the naphthyl group relative to the triazine ring and thereby favouring significant mixing of molecular orbitals.

The M–N bond distances in both 2b and 3b are shorter to

the central triazine ring compared with the terminal pyridyl rings as expected owing to the constrained bite angle imposed by tridentate ligands. The Ru–N bond distances, 1.97–1.98 Å to the central triazine ring and 2.09–2.11 Å to the terminal pyridyl rings, are in agreement to those previously reported for related Ru(II) complexes of triazine-based ligands (20, 21). The Zn–N bond distances are slightly longer and similar to those reported for tpy-type ligands (22).

## **Electrochemical properties**

The redox data for the ligands and their complexes are gathered in Table 1. The redox data of ligands L1, L2, and L4 are reported in DMF owing to their poor solubility in acetonitrile. In all of the ligands, an initial reversible

Compound	$E_{1/2}$ (oxidation)		$E_{1/2}$ (reduction)			
L1 <sup>a</sup>			-1.42(84)	-2.25(irr)		
$\mathbf{L2}^{a}$			-1.41(82)	-2.17(irr)		
$L3^b$			-1.42(86)	-2.15(irr)		
$\mathbf{L4}^{a}$	1.54 (irr)		-1.40(75)	-1.84(96)	-2.17(irr)	
$2a^c$	1.51(81)		-0.71(65)	-0.88(69)	-1.51(74)	-1.75(78)
2b	1.52(84)		-0.73(63)	-0.89(68)	-1.52(67)	-1.75(80)
$2c^b$	1.52(85)		-0.72(74)	-0.89(77)	-1.52(79)	-1.75(90)
2d	1.46(irr)	1.66(irr)	-0.75(68)	-0.89(69)	-1.51(88)	-1.74(irr)
3a			-0.79(80)	-0.91(84)	-1.60(86)	-1.77(78)
3b			-0.80(67)	-0.91(77)	-1.59(78)	-1.75(74)
$3c^b$			-0.81(irr)	-0.86(104)	-1.52(103)	-1.73(108)
3d	1.45 (irr)		-0.76(68)	-0.87(76)	-1.52(irr)	

Table 1. Half-wave potentials for ligands L and complexes 2 and 3. Data are in acetonitrile at 200 mV s<sup>-1</sup> vs. SCE, unless otherwise stated.

<sup>a</sup>In DMF.

<sup>b</sup>From ref. 20.

<sup>c</sup>From ref. 21.

triazine-based reduction is observed at -1.40 to -1.42 V vs. SCE. The negligible potential difference among all four ligands indicates that the aryl substituent on the triazine has little influence on this process. A second triazine-based reduction is observed at -2.15 to -2.17 V in L2-L4. This same reduction shifts to a more negative potential in L1 (-2.25 V), indicating the LUMO +1 molecular orbital involves non-negligible mixing of the aromatic and triazine motifs. An additional pyrenyl-based reduction is observed in L4 at -1.84 V. No oxidative processes are observed in L1-L3 within the solvent potential limits. However, the pyrene motif is oxidized at +1.54 V in L4, which is more positive than the tpy-pyrene ligand (+1.49 V) owing to the stabilizing effect of the electron-deficient triazine ring (12). However, overall a lower energy HOMO-LUMO gap is estimated by electrochemistry: 2.94 V for L4 as compared to 3.15 V for tpy-pyrene (12).

The oxidative potentials for the Ru(II)/(III) couple in complexes 2a-2c are in agreement with those previously reported for Ru(II) complexes of triazine ligands (20, 21). However, in complex 2d, the pyrene motif is oxidized prior to the Ru(II) centre at +1.46 V, and the Ru(II)/(III) couple is consequently at a more positive potential and irreversible. In the Zn(II) complex 3d, the pyrene motif is oxidized at +1.45 V. The electron-withdrawing effect of metal coordination results in significant positive shifts in the potentials for the triazine-based reductions for both Ru(II) complexes 2a-2d and Zn(II) complexes 3a-3d. Each triazine ligand has two reductions giving a total of four reductions for complexes 2a-2d and 3a-3c.

#### Absorption spectra

The absorption spectral data for the ligands and their complexes are gathered in Table 2. Figure 4 shows the absorption spectra of some representative compounds. At wavelengths shorter than 350 nm, ligand-based spin-allowed  $\pi$ - $\pi$ \* transitions dominate the spectra. However, less intense bands are also present at longer wavelengths even for the free ligands, particularly for L2–L4. These bands are assigned to aryl-to-bis(pyridyl)triazine charge-transfer transitions (intraligand charge transfer, ILCT). Compound L1

Table 2. Absorption data in acetonitrile.

	$\lambda_{\text{max}} \text{ (nm) } (\epsilon, ((\text{mol/L})^{-1} \text{ cm}^{-1} \times 10^{-3}))$
L1 <sup>a</sup>	243 (25.0); 276 (40.8)
L2	217 (55.8); 243 (27.9); 277 (21.9); 325 sh (9.6)
L3	250 (56.8), 270(35.1), 325 sh (11.4)
L4	240 (27.7); 285 (17.2); 370 (9.6); 400 (7.2)
$2\mathbf{a}^b$	242 (24.4); 284 (73.2); 481 (24.6)
2b	211 (88.4); 274 (50.8); 487 (20.6)
2c	250 (91.9); 271 (83.7); 345 (24.3); 490(30.3)
2d	236 (79.9); 272 (76.5); 380 (20.0); 532(43.8)
3a	249 (25.1); 293 (57.2)
3b	211 (121.8); 254 (49.1); 277 (47.7); 293 sh
	(38.2);388 (18.7)
3c	253 (77.9); 276 sh, 390 (14.9)
3d	238 (89.7); 257 (52.6); 268 (54.9); 281 (44.6);
	297 (46.0); 394 (14.4): 460 (27.9)

<sup>*a*</sup>From ref. 20.

<sup>b</sup>From ref. 21.

does not exhibit a similar low energy absorption band, since the phenyl group is a worse electron-donor group compared with the other fused aromatic rings. On metal complexation, such ILCT bands are expected to shift to lower energy, since the bipyridyltriazine orbitals are stabilized by metal coordination. This is clearly evidenced in the Zn(II) complexes, which exhibit ILCT absorption bands that extend to the visible, in particular for complexes 3b-3d (see Fig. 4, bottom). The ILCT transitions are red-shifted in comparison to Zn(II) tpy complexes with fused aromatic rings (17), as a consequence of the better acceptor properties of the bis(pyridyl)triazine group compared with the terpy. In Ru(II) complexes 2a-2d, the ILCT bands are largely obscured by the spin-allowed metal-to-ligand charge-transfer (MLCT) transitions, which are responsible for the relatively strong absorption bands in the 450-560 nm region (Table 2, Fig. 4, middle). However, the absorption in the 450–560 nm region increases on passing from 2a (not shown in Fig. 4, middle) and 2b to 2c, and even further on going to 2d, which exhibits a maximum at lower energy than the other complexes. This cannot be attributed only to contribution of the ILCT

Fig. 4. Top: absorption spectra of L2, L3, and L4. Middle: absorption spectra of 2b, 2c, and 2d. Bottom: absorption spectra of 3a and 3b. All the spectra are in acetonitrile.



bands in the visible, since the lowest energy bands in **3d**, assigned to the ILCT transition, maximizes at 460 nm, with negligible contribution at wavelengths longer than 500 nm. Most likely, it is the intensity of the spin-allowed MLCT bands, which increases in the series.

The absorption spectra of all the compounds are stable for at least three days and do not exhibit any significant dependence on the concentration, within the range investigated (8 ×  $10^{-6} - 5 \times 10^{-5}$  mol/L).

#### Luminescence properties

The luminescence properties of the free ligands were studied in air-equilibrated acetonitrile solutions at room tempera-

Table 3. Luminescence properties of the free ligands.

	$\lambda_{max}$ (nm)	$\tau$ (ns)
L1	414	1.7
L2	450	2.6
L3	376 sh	20 (67%), 2.3(33%)
	470	2.0
L4	384, 406	22 (85%), 1.7 (15%)
	471	2.2

**Note:** In acetonitrile at 298 K. The percentage of the decay in the biexponential analysis is reported in parentheses. The excitation wavelength is 308 nm.

Fig. 5. Emission spectra of L2, L3, and L4 in acetonitrile.



ture. The luminescence data of the ligands are collected in Table 3, and the emission spectra of L2, L3, and L4 are shown in Fig. 5.

L1 is weakly emissive, with an unstructured emission with a maximum at 414 nm in acetonitrile with an excited-state lifetime of 1.7 ns. The emission is assigned to fluores-cence from the  $\pi$ - $\pi$ \* singlet state, with only a partial phenyl-to-bis(pyridyl)triazine charge-transfer character.

L2 exhibits a broad band with maximum at 450 nm and a lifetime of 2.6 ns. The emission is too low-lying to be  $\pi - \pi^*$ fluorescence from the naphthalene subunit (23, 24), and also too much red-shifted from that of L1 to be  $\pi$ - $\pi$ \* fluorescence mainly involving the bis(pyridyl)triazine. In fact, naphthalene derivatives often exhibit a low-energy emission of excimeric nature. However, naphthalene excimer emission is normally in the range of 400-425 nm (23, 24). On the basis of such comments, we assign the emission of L2 to a (naphthalene-to-bis(pyridyl)triazine) intraligand chargetransfer (ILCT) excited state. Such a state should be very sensitive to the presence of protons, since the acceptor subunit is protonable; indeed, addition of triflic acid leads to disappareance of the 450 nm emission band. As testified by the change in the absorption spectrum of L2 upon triflic acid addition (see Supplementary data, Fig. S1: the ILCT absorption band is significantly red shifted), protonation of the acceptor subunit leads to a stabilization of the ILCT level, which apparently becomes non emissive.<sup>3</sup>

As far as L3 is concerned, an emission band is present with maximum at 470 nm and 2.0 ns lifetime. However, on the blue-edge of the emission band, another emission feature appears, structured (see Fig. 5). When the emission decay is 260

**Fig. 6.** Change of the emission spectrum of **L3** upon protonation. Concentration of **L3** is  $7.1 \times 10^{-6}$  mol/L, and concentration of H<sup>+</sup> is  $1.95 \times 10^{-3}$  mol/L (molar ratio of **L3**:H<sup>+</sup>is 1:3), ( $\lambda_{exc} = 303$  nm, the isosbestic point).



analyzed at 380 nm, a biexponential decay is found (see Table 3), with a long-lived component (20 ns) following a short-lived component (2.3 ns). The short-lived component is assigned to the contribution of the emission with a maximum at 470 nm, and indeed its lifetime agrees with the monoexponential decay recorded at 470 nm (Table 3), whereas the longer-lived component is assigned to the structured emission taking place in the range of 350-400 nm. This latter emission is attributed to fluorescence from the phenanthryl-based  $\pi$ - $\pi$ \* singlet, and the dominant, lowerenergy emission is attributed to the ILCT excited state. To support such an assignment, phenanthrene fluorescence in polar solvents is reported to occur at 347 nm with a lifetime of 60.7 ns (24, 25), values in good agreement with those obtained for our substituted phenanthrene species. As for L2, protonation stabilizes the ILCT level of L3, leading to red shift of the low-energy absorption band and disappearence of the ILCT emission (Figs. S2 and 6).<sup>3</sup>

L4 clearly exhibits a double emission: a structured band, with a maximum at 380 nm, and a broad emission with maximum at about 470 nm (Table 3, Fig. 5). The higher energy emission is assigned to the  $\pi$ - $\pi$ \* singlet state of the pyrenyl subunit, which is reported to occur at about 375 nm in polar solvents (24, 26), and the lowest-energy emission is assigned to the excimer. Indeed, pyrene excimeric emission is reported to occur at the same energy (23). Moreover, the eventual ILCT emission should occur at significantly lower energy than 470 nm, as the ILCT level in L4 is stabilized compared with the same level in L3 (see absorption spectra) (27). A supporting experiment for the assignment of the lowenergy emission of L4 to an excimeric state is also the concentration dependence of the emission spectrum; indeed on increasing concentration (e.g., from 5  $\times$  10<sup>-6</sup> mol/L to 2  $\times$ 10<sup>-5</sup> mol/L), the low-energy emission band significantly increases with respect to the high-energy emission feature. As for what found for L3, the analysis of the emission decay at 480 nm yields a monoexponential behaviour, while analysis of the decay at 380 nm gives a biexponential behaviour, with the shorter-lived component corresponding (within the ex**Fig. 7.** Change of the emission spectrum of **L4** upon protonation. Concentration of **L4** is  $4.9 \times 10^{-6}$  mol/L, and concentration of H<sup>+</sup> is  $1.95 \times 10^{-3}$  mol/L (molar ratio of **L4**:H<sup>+</sup>is 1:3), ( $\lambda_{exc} = 340$  nm).



perimental uncertainties) to the 480 nm emission lifetime (Table 3).

As for L2 and L3, addition of triflic acid leads to disappearance of the lower-energy band, while the higher-energy  $\pi$ - $\pi$ \* (monomeric) emission remains unaffected (Fig. 7; for the changes on absorption spectrum upon acid addition, see Supplementary data).<sup>3</sup> Whereas the emission changes upon acid addition of L4 are experimentally equivalent to those of L3, their interpretation is slightly different, as the origin of the 470 nm broad emission is different in the two compounds. In principle, proton addition is not expected to have a direct effect on excimer formation; in this case, it could change the association constant for excimer formation, since the pyrene "substituent" (i.e., the bis(pyridyl)triazine subunit) is protonable, and the excimer would become positively charged. However, if this would happen, the monomer emission would increase, and this is not found experimentally; therefore, protonation seems to not affect monomer/ excimer ratio. This strongly suggests that the consequence of the protonation is that the ILCT state, potentially a quencher for both monomer and excimer emission, is displaced to lower energy, thereby increasing the driving force for the quenching process(es). This is supported by the effect of protonation on the absorption spectrum of L4 (see Supplementary data).<sup>3</sup> It is suggested that quenching of the excimer emission of L4 upon acid addition can be attributed to deactivation of the excimer to the proton-stabilized ILCT state (non emissive), which in the protonated species is significantly lower-lying than the excimeric state, where it was almost isoenergetic in the non-protonated species, so that the change in driving force is significant (it would pass from a very small value to a significant value). Most likely, the monomer emission is already partially quenched in L4 by the ILCT state and increasing the driving force for this quenching process as a consequence of protonation has only negligible effects on monomer emission. However, this explanation should be considered as tentative, since we cannot perform quantitative calculations based on the effective driving force values, which are unknown.

Unfortunately, the study of the luminescence properties of the Zn(II) complexes **3a–3d** gave non reproducible results,

 Table 4. Luminescence of the Ru(II) complexes.

$\lambda_{\max} \ (nm)^a$	τ (μs)
672	1.4
665	1.5
665	24
690	25
	$\begin{array}{c} \lambda_{\max} \ (nm)^a \\ 672 \\ 665 \\ 665 \\ 690 \end{array}$

**Note:** In EtOH/MeOH 4:1 ( $\nu/\nu$ ) at 77 K. The excitation wavelength is 408 nm. <sup>*a*</sup>Higher-energy feature.

<sup>b</sup>From ref. 21.

most likely since the compounds were poorly stable at the concentrations used for the luminescence experiments (lower than  $8 \times 10^{-6}$  mol/L), a somewhat not unexpected behaviour for Zn(II) polypyridine complexes (15). Luminescence properties of the Zn(II) compounds **3a–3d** are therefore not investigated here.

Ru(II) polypyridine complexes based on tridentate ligands are very weakly emitting at room temperature (Table 4) because of the presence of a low-lying metal-centered (MC) state, which deactivates the potentially luminescent MLCT state (2, 3, 5, 28). This is evidently even more true for Ru(II) complexes of bis(pyridyl)triazine ligands, as this ligand has probably a weaker ligand field strength than tpy, like the absence of room-temperature emission of other homoleptic Ru(II) complexes based on substituted bis(pyridyl)triazine ligands seems to suggest (21). As a matter of fact, 2b, 2c, and 2d are not luminescent at all at room temperature, and **2a** (21) is only weakly luminescent ( $\lambda = 710$  nm,  $\tau = 8$  ns,  $\Phi = 9 \times 10^{-5}$ ). All of the four Ru(II) complexes are emissive at 77 K from their lowest energy MLCT triplet (Table 4, Fig. 8), demonstrating that the MC state is no longer populated in this condition. The emission is partially structured, as expected for a MLCT emission at low temperature (29, 30), and the vibrational progression is typical of C=C and C=N stretching. However, the 77 K emission properties of 2a-2d show interesting differences, the larger one being the longer lifetimes (one order of magnitude longer, see Table 4) exhibited by 2c and 2d compared with 2a and 2b. The reason for such longer lifetimes can have two origins: (i) delocalization of the MLCT state towards the larger phenanthryl and pyrenyl moieties, which can be coplanar with the triazine ring, so that the geometry of the excited state becomes closer to the geometry of the ground state, decreasing Franck-Condon factor for radiationless decay; (ii) mixing of the MLCT state with a closely-lying, longerlived ligand-centered (<sup>3</sup>LC) state. This <sup>3</sup>LC state could be the triplet of the ILCT state, which is expected to be lower in energy for the phenanthryl- and pyrenyl-containing ligands. In fact, hypothesis (i) would suggest that the first reduction potentials of 2c and 2d are less negative than those of the other two ruthenium(II) complexes, but this is not the case (see Table 1). Moreover, delocatization of the MLCT state over the aryl moieties should red shift the emission spectrum of 2c compared with 2a and 2b, and this is not experimentally found. For these reasons, hypothesis (ii) appears to be preferred. At this point, it should be recalled that the presence of closely-lying states have already been reported to be able to influence the dynamics of the lumines-



cent level, even at 77 K and without affecting the energy of the emitting level (31).

## Conclusion

Introducing fused aromatic rings to the triazine-based tridentate ligands offers a means to significantly stabilize the ILCT band compared with their analogous systems based on tpy. As a consequence, room-temperature emission studies of L2-L4 indicate that some of their emissive excited states have significant charge-transfer character. In the case of L4, an excimer emission is also found. On complexation, the ILCT states are red-shifted in the Zn(II) complex, as clearly evidenced by the absorption spectra. Unfortunately, luminescence of the Zn(II) complexes cannot be investigated, since the compounds are poorly stable at the low concentrations needed for luminescence experiments. In Ru(II) complexes, the potentially emissive MLCT excited states are quenched at room temperature by the presence of low-lying metalcentered states, whereas MLCT emission takes place at 77 K in rigid matrix with (for 2c and 2d) some contribution from closely lying LC (most likely, ILCT) triplet states.

## **Experimental section**

# General methods and equipment

NMR spectra were recorded in CD<sub>3</sub>CN at RT on a Bruker AV400 spectrometer at 400 MHz for <sup>1</sup>H NMR and at 100 MHz for <sup>13</sup>C NMR. Chemical shifts are reported in ppm relative to residual solvent protons (1.93 ppm for acetonitrile- $d_3$ ) and the carbon resonance of the solvent. Absorption spectra were measured on a Cary 500i UV-vis NIR spectrophotometer. Luminescence spectra were obtained with a Horiba Jobin-Yvon Fluoromax P spectrofluorimeter equipped with a Hamamatsu R3896 photomultiplier and were corrected for photomultiplier response using a program purchased with the fluorimeter. Emission lifetimes were measured with an Edinburgh OB-900 single-photon counting spectrometer equipped with a Hamamatsu PLP-2 laser diode (pulse width at 408 nm, 59 ps) and with a PicoQuant PDL 800-D pulsed laser diode (pulse width at 308 nm, 50 ps). The emission decay traces (emission lifetimes measured at about the emission maximum wavelengths) were analyzed

by Marquadt algorithm. For each measurement, at least five determinations were carried out.

Electrochemical measurements were carried out in argonpurged acetonitrile at RT with a BAS CV50W multipurpose equipment interfaced to a PC. The working electrode was a Pt electrode. The counter electrode was a Pt wire, and the pseudo-reference electrode was a silver wire. The reference was set using an internal 1 mmol/L ferrocene/ferrocinium sample at 395 mV vs. SCE in acetonitrile and 432 mV in DMF. The concentration of the compounds was about 1 mmol/L. Tetrabutylammonium hexafluorophosphate was used as supporting electrolyte, and its concentration was 0.10 mol/L. Cyclic voltammograms were obtained at scan rates of 50, 100, 200, and 500 mV/s. For irreversible oxidation processes, the cathodic peak was used as E, and the anodic peak was used for irreversible reduction processes. The criteria for reversibility were the separation of approximately 60 mV between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. The number of exchanged electrons was measured with OSWV and by taking advantage of the presence of ferrocene used as the internal reference.

Experimental uncertainties are as follows: absorption maxima,  $\pm 2$  nm; molar absorption coefficient, 10%; emission maxima,  $\pm 5$  nm; excited-state lifetimes, 10%; and redox potentials,  $\pm 10$  mV.

#### **Synthesis**

Compounds L1, L3, 2a, 2c, and 3c were synthesized as previously described (20, 21).

#### General procedure for L2 and L4

*n*-BuLi (1.6 mol/L in hexanes, 1.1 equiv.) was added dropwise to a stirred solution of  $HNMe_2$  (2 mol/L in THF, 1.1 equiv.) in anhyd. Et<sub>2</sub>O under an inert atmosphere. The mixture was stirred for 20 min until a white suspension formed and the cyano-arene (1 equiv.) was added to the mixture. The mixture was stirred for 4 h further followed by addition of 2-cyanopyridine (2 equiv.). The reaction mixture was stirred overnight and worked up by stirring for 30 min in air followed by removal of Et<sub>2</sub>O under reduced pressure. The residue was recrystallized three times from water:ethanol and the solid collected, washed with diethyl ether to yield L2 as a white solid in 35% yield and L4 as a yellow solid in 26% yield.

#### L2

As per the general procedure using *n*-BuLi (1.6 mol/L in hexanes, 5.1 mL, 8.1 mmol), HNMe<sub>2</sub> (2 mol/L in THF, 4.1 mL, 8.1 mmol), 9-cyanophenathrene (1.50 g, 7.39 mmol), and 2-cyanopyridine (1.44 mL, 15.0 mmol) in 150 mL anhyd. ether. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 9.07 (d, 1H, J = 8.6 Hz) H<sub>nap</sub>; 8.99 (dd, 2H, J = 4.3, 0.5 Hz) H<sub>6,6</sub>"; 8.86 (d, 2H, J = 8.0 Hz) H<sub>3,3</sub>"; 8.58 (d, 1H, J = 7.3 Hz) H<sub>nap</sub>; 8.09 (d, 1H, J = 8.2 Hz) H<sub>nap</sub>; 7.99 (m, 3H) H<sub>4,4</sub>", H<sub>nap</sub>; 7.67 (2H, m) 2H<sub>nap</sub>; 7.60 (3H, m) H<sub>5,5</sub>", H<sub>nap</sub>. <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 124.59, 124.80, 125.31, 125.83, 126.21, 127.20, 128.42, 130.83, 130.87, 132.35, 132.87, 133.76, 136.92, 150.03, 152.84, 170.95, 175.00.

Anal. calcd. C<sub>23</sub>H<sub>15</sub>N<sub>5</sub>·H<sub>2</sub>O: C 72.8, H 4.5, N 18.5; found: C 72.6, H 4.6, N 18.5.

## L4

As per the general procedure using *n*-BuLi (1.6 mol/L in hexanes, 5.1 mL, 8.1 mmol), HNMe<sub>2</sub> (2 mol/L in THF, 4.1 mL, 8.1 mmol), 1-cyanopyrene (1.68 g, 7.42 mmol), and 2-cyanopyridine (1.44 mL, 15.0 mmol) in 150 mL anhyd. ether. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 9.51 (d, J = 10 Hz, 1H) H<sub>py</sub>; 9.12 (d, J = 8 Hz, 1H), H<sub>py</sub>; 9.06 (d, J = 4 Hz, 2H) H<sub>6,6</sub>"; 8.94 (d, J = 8 Hz, 2H) H<sub>3,3</sub>"; 8.39–8.07 (m, 7H) 7H<sub>py</sub>; 8.05 (td, J = 2 Hz, 8 Hz, 2H) H<sub>4,4</sub>"; 7.61 (dd, J = 5 Hz, 6 Hz, 2H) H<sub>5,5</sub>". <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 124.19, 124.49, 124.65, 124.84, 125.56, 125.82, 125.89, 126.09, 127.07, 128.90, 129.07, 129.33, 129.73, 130.27, 130.30, 130.84, 133.63, 136.82, 150.22, 153.13, 171.15, 175.46, 176.75. Anal. calcd. C<sub>29</sub>H<sub>18</sub>N<sub>5</sub>·0.5H<sub>2</sub>O: C 78.4, H 4.1, N 15.8; found: C 78.7, H 3.3, N 15.5.

#### Ruthenium triazine complexes 2b and 2d

RuCl<sub>3</sub>·3H<sub>2</sub>O (0.032 g, 0.12 mmol) was added to a stirred solution of the appropriate ligand (0.24 mmol) in EtOH (15 mL). The mixture was stirred at RT for 15 min and then heated to reflux for 1 h. The reaction mixture was cooled and satd. KPF<sub>6</sub> (aq., 5 mL) was added. The solution was diluted with a 100 mL of water and the red solid collected and injected onto a silica column and eluted with acetone/water/KNO<sub>3</sub>(satd.) 9:0.9:0.1. The nitrate salt was metathesized to the PF<sub>6</sub> salt by the addition of NH<sub>4</sub>PF<sub>6</sub> and the solvent removed under reduced pressure. The product was collected by dissolving the solid in acetonitrile and precipitated by addition to water and recrystallized from acetonitrile/ether to afford **2b** and **2d** as red solids.

#### 2b

Red solid, 56%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): 9.68 (d, J = 9 Hz, 2H) H<sub>nap</sub>; 9.11 (d, J = 7 Hz, 4H) H<sub>3,3</sub>"; 9.09 (m, 2H) H<sub>nap</sub>; 8.40 (d, J = 8 Hz, 2H) H<sub>nap</sub>; 8.23 (d, J = 8 Hz, 2H) H<sub>nap</sub>; 8.17 (td, J = 8 Hz, 1 Hz, 4H) H<sub>4,4</sub>"; 7.90–7.98 (m, 4H) H<sub>nap</sub>; 7.88 (d, J = 6 Hz, 4H) H<sub>6,6</sub>"; 7.81 (t, J = 8 Hz, 2H) H<sub>nap</sub>; 7.46 (td, J = 6, 2Hz, 4H) H<sub>5,5</sub>". HR-MS: M<sup>2+</sup> (–2PF<sub>6</sub>) = 462.0845. Anal. calcd. C<sub>46</sub>H<sub>30</sub>N<sub>10</sub>RuP<sub>2</sub>F<sub>12</sub>·4H<sub>2</sub>O: C 46.6, H 3.2, N 11.8; found: C 46.4, H 2.7, N 11.7.

#### 2d

Red solid, 11%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): 10.03 (d, J = 10 Hz, 2H) H<sub>pyrene</sub>; 9.52 (d, J = 8.3 Hz, 2H) H<sub>pyrene</sub>; 9.18 (d, J = 8 Hz, 4H) H<sub>3,3</sub>"; 8.66 (d, J = 8 Hz, 2H) H<sub>pyrene</sub>; 8.60 (d, J = 9.3 Hz, 2H) H<sub>pyrene</sub>; 8.38–8.53 (m, 8H) 4H<sub>pyrene</sub>; 8.25 (t, J = 7 Hz, 2H) H<sub>pyrene</sub>; 8.19 (t, J = 8 Hz, 4H) H<sub>4,4</sub>";7.92 (d, J = 5 Hz, 4H) H<sub>6,6</sub>"; 7.47 (dd, J = 6 Hz, 6Hz, 4H) H<sub>5,5</sub>". Anal. calcd. C<sub>58</sub>H<sub>38</sub>N<sub>10</sub>RuP<sub>2</sub>F<sub>12</sub>·2H<sub>2</sub>O: C 53.7, H 2.9, N 10.8; found: C 53.7, H 2.4, N 10.2.

#### Zinc triazine complexes 3a, 3b, and 3d

 $Zn(ClO_4)_2$ · $GH_2O$  (0.05 mmol, 0.018 g) was added to a stirred solution of the appropriate ligand (0.1 mmol) in MeCN (15 mL). The mixture was refluxed for 15 min, cooled, and the solvent removed under reduced pressure. The solid was recrystallized from ethanol, followed by pre-

cipitation in acetonitrile/diethyl ether to yield complexes **3a**-**3d**.

## 3a

White solid, 68%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): 9.14 (d, J = 8Hz, 2H) H<sub>2'</sub>, "; 9.05 (d, J = 7 Hz, 2H) H<sub>3,3</sub>"; 8.31 (t, J = 8 Hz, 2H) H<sub>4,4</sub>"; 8.24 (d, J = 4 Hz, 2H) H<sub>6,6</sub>"; 7.93 (t, J = 7 Hz, 1H) H<sub>4</sub>, "; 7.80 (t, J = 7 Hz, 2H) H<sub>3</sub>, "; 7.64 (dd, J = 6 Hz, 7 Hz, 2H) H<sub>5,5</sub>". Anal. calcd. C<sub>38</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>10</sub>O<sub>8</sub>Zn: C 51.5, H 3.0, N 15.8; found: C 51.7, H 3.2, N 16.1.

## *3b*

Yellow solid, 55%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): 9.50 (d, J = 9 Hz, 1H) H<sub>nap</sub>; 9.09 (d, J = 8 Hz, 2H) H<sub>3,3</sub>"; 9.05 (d, J = 7 Hz, 1H) H<sub>nap</sub>; 8.43 (d, J = 8 Hz, 1H) H<sub>nap</sub>; 8.30–8.34 (m, 4H) H<sub>4,4</sub>", H<sub>66</sub>"; 8.20 (d, J = 8 Hz, 1H) H<sub>nap</sub>; 7.90–7.93 (m, 2H) 2H<sub>nap</sub>; 7.78 (t, J = 7 Hz, 1H) H<sub>nap</sub>; 7.69 (dd, J = 5 Hz, 6 Hz, 2H) H<sub>5,5</sub>". Anal. calcd. C<sub>46</sub>H<sub>30</sub>C<sub>12</sub>N<sub>10</sub>O<sub>8</sub>Zn·H<sub>2</sub>O: C 55.0, H 3.2, N 13.9; found: C 55.1, H 3.6, N 14.1.

# 3d

Orange solid, 84%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): 9.93 (d, J = 9 Hz, 1H) H<sub>pyrene</sub>; 9.49 (d, J = 9 Hz, 1H) H<sub>pyrene</sub>; 9.19 (d, J = 8 Hz, 2H) H<sub>3,3</sub>"; 8.60–8.63 (m, 2H) 2H<sub>pyrene</sub>; 8.47– 8.54 (m, 3H) 3H<sub>pyrene</sub>; 8.35–8.41 (m, 5H) H<sub>pyrene</sub>, H<sub>4,4</sub>", H<sub>6,6</sub>"; 7.72 (dd, J = 6 Hz, 6Hz, 2H) H<sub>5,5</sub>". Anal. calcd. C<sub>58</sub>H<sub>34</sub>Cl<sub>2</sub>N<sub>10</sub>O<sub>8</sub>Zn·H<sub>2</sub>O: C 60.4, H 3.2, N 12.2; found: C 60.5, H 3.4, N 12.3.

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# References

- 1. X.-Y. Wang, A. Del Guerzo, and R.H. Schmehl. J. Photochem. Photobiol. C, 5, 55 (2004).
- J.P. Sauvage, J.P. Collin, J.C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, and L. Flamigni. Chem. Rev. 94, 993 (1994).
- 3. E. Baranoff, J.-P. Collin, L. Flamigni, and J.-P. Sauvage. Chem. Soc. Rev. 33, 147 (2004).
- (a) J.H. Alstrum-Acevedo, M.K. Brennaman, T.J. Meyer. Inorg. Chem. 44, 6802 (2005); (b) M. Grätzel. Inorg. Chem. 44, 6841 (2005).
- (a) V. Balzani, A. Juris, M. Venturi, S. Campagna, and S. Serroni. Chem. Rev. 96, 759 (1996); (b) S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, and V. Balzani. Top. Curr. Chem. 280, 117 (2007).

- (a) E.A. Medlycott and G.S. Hanan. Coord. Chem. Rev. 250, 1763 (2006); (b) E.A. Medlycott and G.S. Hanan. Chem. Soc. Rev. 34, 133 (2005).
- 7. T.J. Rutherford, D.A. Reitsma, and F.R. Keene. J. Chem. Soc. Dalton Trans. 3659 (1994).
- 8. F.M. MacDonnell and S. Bodige. Inorg. Chem. 35, 5758 (1996).
- A.I. Baba, J.R. Shaw, J.A. Simon, R.P. Thummel, and R.H. Schmehl. Coord. Chem. Rev. 171, 43 (1998).
- A.C. Benniston, A. Harriman, D.J. Lawrie, and A. Mayeux. Phys. Chem. Chem. Phys. 6, 51 (2004).
- S. Baitalik, X.-Y. Wang, and R.H. Schmehl. J. Am. Chem. Soc. 126, 16304 (2004).
- W. Leslie, R.A. Poole, P.R. Murray, L.J. Yellowlees, A. Beeby, and J.A.G. Williams. Polyhedron, 23, 2769 (2004).
- J.F. Michalec, S.A. Bejune, and D.R. McMillin. Inorg. Chem. 39, 2708 (2000).
- J.F. Michalec, S.A. Bejune, D.G. Cuttell, G.C. Summerton, J.A. Gertenbach, J.S. Field, R.J. Haines, and D.R. McMillin. Inorg. Chem. 40, 2193 (2001).
- G. Albano, V. Balzani, E.C. Constable, M. Maestri, and D.R. Smith. Inorg. Chim. Acta, 277, 225 (1998).
- 16. X.-Y. Wang, A. Del Guerzo, and R.H. Schmehl. Chem. Commun. 2344 (2002).
- H. Krass, E.A. Plummer, J.M. Haider, P.R. Barker, N.W. Alcock, Z. Pikramenou, M.J. Hannon, and D.G. Kurth. Angew. Chem., Int. Ed. 40, 3862 (2001).
- K.K. Patel, E.A. Plummer, M. Darwish, A. Rodger, and M.J. Hannon. J. Inorg. Biochem. 91, 220 (2002).
- H.-S. Chow, E.C. Constable, C.E. Housecroft, M. Neuburger, and S. Schaffner. Dalton Trans. 2881 (2006).
- 20. E.A. Medlycott and G.S. Hanan. Inorg. Chem. Commun. **10**, 229 (2007).
- (a) E.A. Medlycott, G.S. Hanan, F. Loiseau, and S. Campagna. Chem. Eur. J. 13, 2837 (2007); (b) M.I.J. Polson, E.A. Medlycott, G.S. Hanan, L. Mikelsons, N.J. Taylor, M. Watanabe, Y. Tanaka, F. Loiseau, R. Passalacqua, and S. Campagna. Chem. Eur. J. 10, 3640 (2004); (c) M.I.J. Polson, N.J. Taylor, and G.S. Hanan. Chem. Commun. 1356 (2002).
- N.W. Alcock, P.R. Barker, J.M. Haider, M.J. Hannon, C.L. Painting, Z. Pikramenou, E.A. Plummer, K. Rissanen, and P. Saarenketo. Dalton–Trans. 1447 (2000).
- M. Klissinger and J. Michl. Excited states and photochemistry of organic molecules. VCH. New York. 1995.
- Handbook of photochemistry. 3rd ed. *Edited by* M. Montalti, A. Credi, L. Prodi, and M.T. Gandolfi. CRC. Boca Raton, FL. 2006.
- 25. G.P. Bluemer and M. Zander. Z. Naturforsch. 34A, 909 (1979).
- 26. M. Zander. Z. Naturforsch. 33A, 998 (1978).
- 27. However, we cannot exclude that an ILCT emission also takes place in L4, obscured by the more intense excimeric emission.
- 28. T.J. Meyer. Pure Appl. Chem. 58, 1193 (1986) and refs. cited therein.
- 29. G.A. Crosby. Acc. Chem. Res. 8, 231 (1975).
- 30. (*a*) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, and A. von Zelewsky. Coord. Chem. Rev. **84**, 85 (1988); (*b*) Y. Chen and T.J. Meyer. Chem. Rev. **98**, 1439 (1998).
- G. Guglielmo, V. Ricevuto, A. Giannetto, and S. Campagna. Gazz. Chim. Ital. 119, 457 (1989).