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Structure and photochemical properties of ruthenium complexes having dimethyl-substituted DPPZ or TPPHZ as a ligand†

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Novel ruthenium complexes having 4,7-dimethyl-substituted DPPZ or TPPHZ as a ligand have been synthesized: the methyl groups on the ligands exert a shielding effect on the phenazine nitrogens which prevents solvent-quenching.

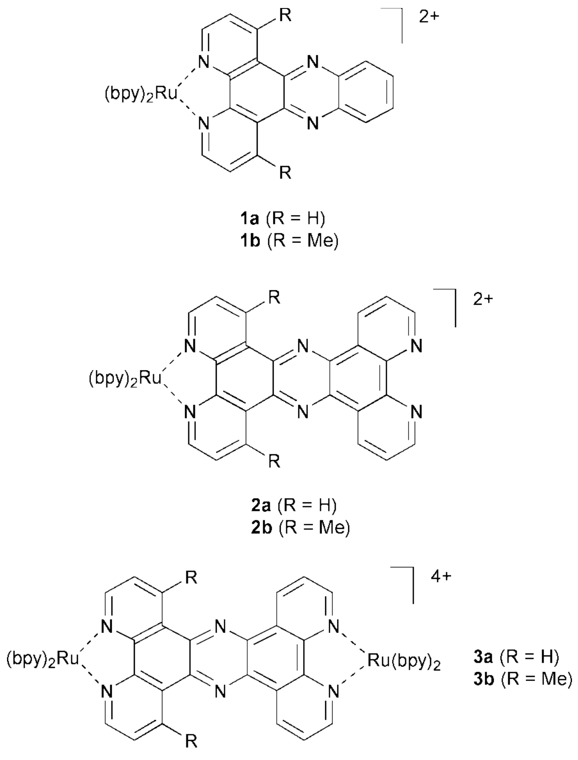
The ruthenium complexes having DPPZ (dipyrido[3,2-*a*:2′,3′-*c*]-phenazine)[1] or TPPHZ (tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine)[2] as a ligand have been of much interest because of their unique emission properties arising from extended aromatic structures incorporating a phenazine moiety. In particular, the most remarkable feature is the high sensitivity towards their environment.[3,4,5] In highly polar protic solvents such as water and MeOH, the emission intensities, *i.e.* the emission lifetimes of the complexes, decrease considerably due to the deactivation of the excited state by hydrogen bonding or proton transfer to the phenazine nitrogens. By contrast, in hydrophobic media rather strong emissions are observed.[6] This makes the complexes potentially useful as luminescence probes for DNA[5,7] and micelles.[4] However, this unique character also limits the utility of the complexes as a photo-sensitizer.

We were interested in controlling the solvent-dependence of the emission properties of the complexes. For this purpose, we newly synthesized ruthenium complexes having 4,7-dimethyl-substituted DPPZ (dmDPPZ) or TPPHZ (dmTPPHZ) as a ligand (**1b**, **2b** and **3b**), expecting that the hydrophobic methyl groups on the new ligands would shield the phenazine nitrogens from the environment, and thereby effectively preventing the solvent-quenching (Fig. 1). ‡

For the synthesis of the complexes **1b**–**3b**,§ [Ru(bpy)$_2$L]$^{2+}$ (L = 4,7-dimethyl-1,10-phenanthroline-5,6-dione) was prepared at first from Ru(bpy)$_2$Cl$_2$ and L, which was obtained by oxidation of 4,7-dimethyl-1,10-phenanthroline according to the reported method.[8] Condensation[5,9] of [Ru(bpy)$_2$L]$^{2+}$ with the appropriate 1,2-diaminobenzene derivatives yielded **1b** and **2b** in only modest yields (30–40%), which may be caused by steric hindrance of the methyl groups.

The crystal structure of **1b** clearly shows the close vicinity of the methyl groups to the phenazine nitrogens (Fig. 2).¶ The average bond distances and angles of **1b** are comparable to typical values for similar ruthenium polypyridine complexes.[10] Two methyl carbon atoms and the DPPZ framework lie on an essentially perfect plane. The two dmDPPZ ligands are packed in a head-to-tail fashion as observed in the crystal structure of [Ru(OH$_2$)(DPPZ)(tpy)]$^{2+}$ (tpy = terpyridine),[11] although their planes are not superposed on each other owing to the presence of the methyl groups.

Table 1 summarizes the electrochemical data of **1a**,**b**–**3a**,**b** as well as those of DPPZ and dmDPPZ. All the oxidation and reduction potentials of the complexes **1b**–**3b** are shifted to more negative values by the introduction of the methyl groups. This tendency is consistent with the previous observations in the ruthenium complexes having dimethyl-substituted 2,2′-bipyridine or 1,10-phenanthroline derivatives as ligands.[12,13]



1a (R = H)
1b (R = Me)

2a (R = H)
2b (R = Me)

3a (R = H)
3b (R = Me)

Fig. 1

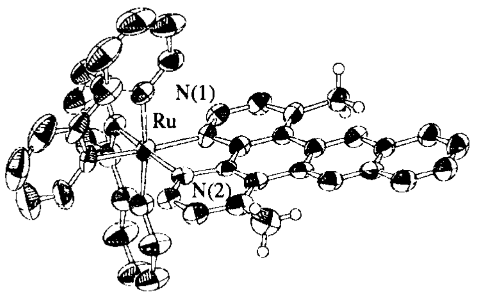


Fig. 2 The ORTEP[16] view of **1b**. Hydrogen atoms and anions are omitted for clarity. Selected bond lengths (Å) and angle (°): Ru–N(1) 2.050(7), Ru–N(2) 2.049(7); N(1)–Ru–N(2) 78.6(3).

The photochemical properties of **1a**,**b**–**3a**,**b** in MeCN and MeOH are summarized in Table 2. As almost no solvent-dependence was observed in the absorption spectra for all of the complexes, only the data in MeCN are depicted in the table. The peak positions and intensities of the MLCT absorption bands of the complexes are not changed markedly by the introduction of the methyl groups. The emission maxima

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† Electronic supplementary information (ESI) available: unit cell of **1b**. See http://www.rsc.org/suppdata/dt/b0/b005428n/

Table 1 Electrochemical data ($E_{1/2}$/V *vs.* Fc/Fc$^+$)[a]

Compound	Oxidation	Reduction 1	Reduction 2	Reduction 3
DPPZ		−1.62		
dmDPPZ		−1.76		
1a	+0.91	−1.36	−1.79	−2.00
1b	+0.85	−1.48	−1.80	−2.03
2a	+0.91	−1.26	[b]	[b]
2b	+0.89	[b]	[b]	[b]
3a	+0.92	−1.19	[b]	[b]
3b	+0.89	−1.25	[b]	[b]

[a] The cyclic voltammetry was conducted with glassy C, Pt and Ag/Ag$^+$ as working, counter and reference electrodes, respectively, under a N_2 atmosphere. The concentration was kept at 1 mM in DMF (DPPZ, dmDPPZ) or MeCN (**1a**,**b**–**3a**,**b**) with 0.1 M TBAP. Scan rate = 100 mV s^{-1}. [b] These values were not determined due to broad or irreversible peaks.

Table 2 Photochemical data

	Absorption[a] in MeCN λ_{max}/nm (ε/10^4 M^{-1} cm^{-1})	Emission[b] in MeCN λ_{max}/nm	τ/ns	in MeOH λ_{max}/nm	τ/ns
1a	450 (1.8)	625	740	619	30
1b	450 (1.7)	625	1160	619	820
2a	450 (2.1)	620	930	619	580
2b	451 (2.2)	624	1100	623	920
3a	444 (3.5)	680	90	671	30
3b	445 (3.6)	682	180	678	100

[a] MLCT absorptions were measured in MeCN at room temperature. [b] Emission spectra excited at 450 nm were recorded at room temperature and corrected for spectral response by calibrating the fluorimeter with a standard lamp. The concentrations of all measured samples were 1.0 × 10^{-5} M.

of **1b**–**3b** are almost the same or slightly red-shifted as compared with those of **1a**–**3a** respectively. These observations indicate that the methyl substitution on the ligands does not alter the relative energies of the excited states of the complexes appreciably.[13]

The effect of the methyl groups on the emission lifetimes of the complexes is obvious. Even in MeCN, **1b**–**3b** exhibit increased lifetimes, as observed for the ruthenium complexes with 4,7- or 5,6-dimethyl-1,10-phenanthroline as ligands.[12,14] In MeOH, the presence of the methyl groups effects emission lifetimes more profoundly. The lifetime of **1b** is 27 times longer than that of **1a**, while **2b** and **3b** show moderate increase (2–3 times). This result can be interpreted by the difference in the steric environments around the phenazine nitrogens between DPPZ and TPPHZ. As pointed out already,[5] the phenazine nitrogen atoms of the DPPZ ligand are more exposed to the outer environment than those of TPPHZ, in which the space around the phenazine nitrogens is inherently sterically crowded. This makes the solvent-interaction of the phenazine nitrogens more difficult for TPPHZ than for DPPZ and results in the relatively longer emission lifetime of **2a** in MeOH compared to that of **1a**.

In the cases of **3a** and **3b**, the emissions are considerably red-shifted and the lifetimes are rather short regardless of solvent as already reported for **3a**.[15] These facts suggest that the solvent-interaction may not be the main factor for the deactivation of the excited states in **3a** and **3b**. Consequently, the shielding effect of the methyl groups on the phenazine nitrogens is more profound in **1b** than in **2b** and **3b**. A similar increase in the emission lifetime was observed for **1b** in MeCN containing 10% water (**1a**: τ = 35 ns, **1b**; τ = 835 ns), although the emission of **1b** was quenched in 100% water.

Thus, we have succeeded in controlling the solvent-dependence of the emission properties of the ruthenium complexes having the DPPZ or TPPHZ ligand by the introduction of methyl groups on the ligands. The present results may increase the utility of these complexes as a photo-sensitizer and also contribute to the further understanding of the photochemical properties of the complexes.

Notes and references

‡ Barton and Hartshorn have already reported on the photochemical properties of the ruthenium complexes with derivatives of the DPPZ ligand and discussed the effect of peripheral substitution.[9]

§ Selected data for [Ru(bpy)$_2$L][ClO$_4$]$_2$ (L = 4,7-dimethyl-1,10-phenanthroline-5,6-dione): Anal. Found: C, 46.80; H, 3.13; N, 9.48%. Calcd for $C_{34}H_{26}N_6Cl_2O_{10}Ru\cdot H_2O$: C, 47.01; H, 3.25; N, 9.68%. ES-MS: 750 [M − ClO$_4$]$^+$. For **1b**: Anal. Found: C, 51.33; H, 3.37; N, 11.66%. Calcd for $C_{40}H_{30}N_8Cl_2O_8Ru\cdot H_2O$: C, 51.07; H, 3.43; N, 11.91%. ES-MS: 822 [M − ClO$_4$]$^+$. For **2b**: Anal. Found: C, 51.04; H, 3.15; N, 13.10%. Calcd for $C_{46}H_{32}N_{10}Cl_2O_8Ru\cdot 3H_2O$: C, 51.21; H, 3.55; N, 12.98%. ES-MS: 924 [M − ClO$_4$]$^+$. For **3b**: Anal. Found: C, 47.85; H, 2.91; N, 11.60%. Calcd for $C_{66}H_{48}N_{14}Cl_4O_{16}Ru_2\cdot H_2O$: C, 47.89; H, 3.04; N, 11.85%. ES-MS: 1537 [M − ClO$_4$]$^+$. The new ligand L was characterized by ^{1}H-NMR and used in the next reaction without further purification due to its instability.

¶ Crystal data for $C_{40}H_{30}N_8O_8Cl_2Ru$ **1b**: M = 922.70, Triclinic, a = 15.799(8), b = 15.86(1), c = 17.17(1) Å, α = 89.17(3), β = 89.64(4), γ = 76.57(5)°, V = 4183(4) Å^3, T = 223 K, space group $P\bar{1}$, Z = 4, D_c = 1.47 g cm^{-3}, μ(Mo-K) = 5.63 cm^{-1}, R = 0.074 and Rw = 0.093 for 9199 unique reflections with $I > 3\sigma(I)$. CCDC reference number 186/2134. See http://www.rsc.org/suppdata/dt/b0/b005428n/ for crystallographic files in .cif format.

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