New luminescent ruthenium complexes with extended π systems

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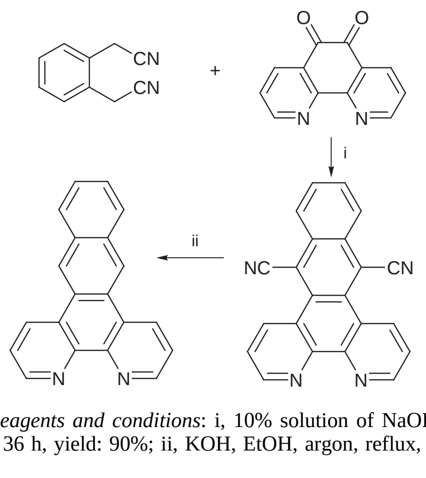
New Ru(II) complexes are presented as potential luminescent sensors, fluorescent labels and DNA photoprobes.

Owing to their remarkable properties, Ru(II) polypyridyl complexes are used in several areas.[1,2,3] The chelating ligands play an important role in determining the properties of such systems.[4] In $[Ru(dppz)(bpy)_2]^{2+}$ the dppz (dipyrido[3,2-*a* : 2,3-*c*]phenazine) ligand is suitable for the direct formation of a charge transfer excited state,[5] which is an important requirement for solar energy conversion. Furthermore dppz contains an extended aromatic system which can bind *via* π–π interaction to the DNA helix.[6] Along this line, two novel phenanthroline-type ligands, CN_2-np (naphtho[2,3-*f*][1,ω]phenanthroline-9,14-dicarbonitrile) and np (naphtho[2,3-*f*][1,ω]phenanthroline) have been prepared, which present some structural features similar to those of dppz. Fukui function calculations[7] indicate that, dppz, CN_2-np and, to a minor extent, np can be considered as comprising a bpy chelating subunit anchored to a remote accepting anthracene-type site (9,10-anthracenedicarbonitrile and anthracene respectively). One could therefore expect that the photophysical and electrochemical properties of $[Ru(CN_2\text{-}np)(bpy)_2]^{2+}$ and $[Ru(np)(bpy)_2]^{2+}$ would be related to those of $[Ru(dppz)(bpy)_2]^{2+}$, however, we have found some new different interesting features. Since the system of $[Ru(dppz)(bpy)_2]^{2+}$ is still the subject of controversial discussion, the following results will help in the understanding of such complexes.

The CN_2-np ligand was synthesized by condensation of *o*-xylylene dicyanide and 1,10-phenanthroline-5,6-dione in basic conditions. Successive decarboxylation of CN_2-np in basic conditions gives the np ligand (Scheme 1). $[Ru(np)(bpy)_2](PF_6)_2$ was prepared by heating the np ligand with 1 equiv. of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ in methoxyethanol at 120 °C under argon for 15 h (yield after chromatographic plate purification: 19%). $[Ru(CN_2\text{-}np)(bpy)_2](PF_6)_2$ was prepared by heating the CN_2-np ligand with 1 equiv. of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ in ethylene glycol for 6 min in a microwave oven (yield after chromatographic plate purification: 26%).[8]



Scheme 1 *Reagents and conditions*: i, 10% solution of NaOEt in EtOH, room temp., 36 h, yield: 90%; ii, KOH, EtOH, argon, reflux, 12 h, yield: 57%.

Electrochemical data (Table 1) show that oxidation is a reversible metal centered Ru(III)/Ru(II) process for both $[Ru(CN_2\text{-}np)(bpy)_2]^{2+}$ and $[Ru(np)(bpy)_2]^{2+}$ and the $E_{1/2}$ values obtained are very similar to those reported for $[Ru(bpy)_3]^{2+}$. This suggests that CN_2-np and np are similar to bpy with respect to their coordination ability to ruthenium: the σ donating properties of the two ligands are the same as those of bpy and the back donation from the Ru(II) ion is localized on bpy orbitals having π* character and does not involve the anthracene-type fragment of the two ligands. For $[Ru(CN_2\text{-}np)(bpy)_2]^{2+}$, owing to the presence of withdrawing groups (CN), the added electron in the first reduction product and the lowest excited state are expected to be localized on CN_2-np. The first reduction wave of $[Ru(CN_2\text{-}np)(bpy)_2]^{2+}$ occurs at a potential (−0.75 V in MeCN) very close to that of the free ligand (−0.79 V in DMSO, identical to that of 9,10-anthracenedicarbonitrile) and 0.27 V less negative than that of $[Ru(dppz)(bpy)_2]^{2+}$, in agreement with a stronger electron accepting character of 9,10-anthracenedicarbonitrile with respect to phenazine (Table 1). The further three monoelectronic reduction steps in $[Ru(CN_2\text{-}np)(bpy)_2]^{2+}$ occur close to those of the three first reduction waves of $[Ru(bpy)_3]^{2+}$. This indicates that, after reduction of the anthracenedicarbonitrile fragment, reduction at the two chelating bpy ligands and at the bpy part of the CN_2-np ligand takes place. The last reduction step (−1.67 V) is localized on the bpy moiety of CN_2-np, since it occurs at a potential value less negative than the third reduction wave of $[Ru(bpy)_3]^{2+}$, as expected for bpy connected to an acceptor unit. The first two reduction potentials of $[Ru(np)(bpy)_2]^{2+}$ are very similar to those for $[Ru(bpy)_3]^{2+}$. The reduction potential of the free ligand np (−1.86 V) is similar to that of anthracene (−1.90 V).

Preliminary photophysical measurements show that $[Ru(CN_2\text{-}np)(bpy)_2]^{2+}$ and $[Ru(np)(bpy)_2]^{2+}$ behave very differently from each other. The photophysical data are reported in Table 2 where values for $[Ru(bpy)_3]^{2+}$ and $[Ru(dppz)(bpy)_2]^{2+}$ are also listed. The photophysical properties of $[Ru(np)(bpy)_2]^{2+}$ resemble those of $[Ru(bpy)_3]^{2+}$ despite the presence of

Table 1 Electrochemical data[a]

	$E_{1/2}(Ru^{II/III})$/V	E_{red}/V			
			'bpy' centered		
$[Ru(CN_2\text{-}np)(bpy)_2]^{2+}$	1.25	−0.75	−1.30	−1.50	−1.67
$[Ru(dppz)(bpy)_2]^{2+}$	1.24	−1.02	−1.44	−1.67	
$[Ru(np)(bpy)_2]^{2+}$	1.24		−1.38	−1.55	
$[Ru(bpy)_3]^{2+}$	1.29		−1.33	−1.52	−1.76
CN_2-np		−0.79[b]			
9,10-anthracenedicarbonitrile		−0.79[b]			
dppz		−1.11[b]			
Phenazine		−0.77[c]			
np		−1.86[b]			
Anthracene		−1.90[b]			

[a] Unless otherwise noted, redox potentials were measured in MeCN *vs.* SCE at room temp.; $NBu^t_4PF_6$ as supporting electrolyte. [b] In DMSO. [c] In DMF, ref. 5.

Table 2 Photophysical data[a]

	Absorption	Emission (298 K)		Emission (77 K)
	λ_{max}/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})	λ_{max}/nm (τ/ns)	$10^{-3}\phi_{em}$	λ_{max}/nm (τ/μs)
$[Ru(CN_2\text{-np})(npy)_2]^{2+}$	439 (1.46), 398 (1.26), 380 (1.19), 309 (5.44), 290 (8.42), 256 (3.67), 228 (3.66)	700^b (120) 610^{b,c} (1700, 185)	0.5 2.0^c	587 (7.1), 660 (464)
$[Ru(ddpz)(bpy)_2]^{2+}$	448 (1.57), 366 (1.55), 357 (1.56), 352 (sh) 315 (sh), 284 (9.36), 255 (4.18), 212 (5.00)	667 (229) 610^c (260)	390	624 (2.6)
$[Ru(np)(bpy)_2]^{2+}$	452 (1.51), 292 (6.68), 256 (3.13)	610 (170) 610^c (834)	16 82^c	578 (6.6)
$[Ru(bpy)_3]^{2+}$	452 (1.45), 345 (sh), 323 (sh), 285 (8.71), 250 (2.51), 238 (2.95), 208 (sh), 185 (8.91)	611 (190) 611^c (1000)	12 60^c	600 (4.1)

[a] Unless otherwise noted, photophysical measurements were made in MeCN and emission spectra at 77 K were recorded in butyronitrile. [b] Maximum value of a multicomponent band. [c] De-aerated solution.

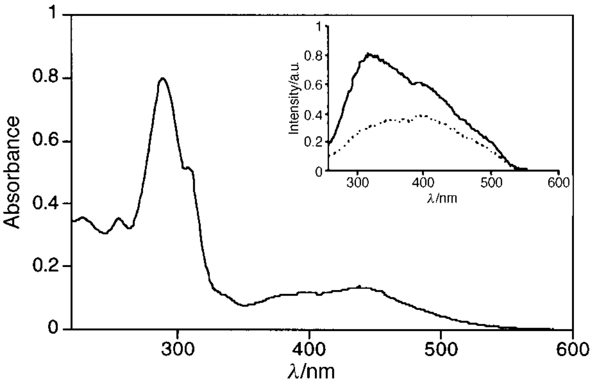


Fig. 1 Absorption spectrum of $[Ru(CN_2\text{-np})(bpy)_2]^{2+}$ in MeCN solution (1.5×10^5 M). Inset: luminescence spectra in aerated (----), and de-aerated (—), MeCN solution.

an extended π system condensed with the bpy ligand. For $[Ru(CN_2\text{-np})(bpy)_2]^{2+}$ the absorption spectrum, recorded in acetonitrile solution, shows the visible region broad bands due to absorption to different ^{1}MLCT excited states, involving both the bpy (higher energy) and the CN_2-np (lower energy) ligands (Fig. 1). It is interesting that CN_2-np shows rather low energy π–π* transitions (350–400 nm), that are also present in the complex, while the higher energy absorption bands are attributed to bpy π–π* transitions. In CH_2Cl_2 solution fluorescence of the free ligand occurs at 427 nm, while no phosphorescence emission was detected even at low temperature. We expect, however, a separation between the singlet and the triplet excited states very similar to that reported for the 9,10-anthracenedicarbonitrile,[9] and therefore a triplet state falling in the 700 nm region. The emission spectrum of $[Ru(CN_2\text{-np})(bpy)_2]^{2+}$ at room temperature in an aerated MeCN solution shows a very broad, multicomponent and weak band centered at 700 nm (Fig. 1). In deaerated solution however the maximum of this band shifts to higher energy and has two different excited state lifetimes (Table 2, and Fig. 1). Such photophysical investigation suggests the presence of two non-equilibrated charge transfer excited states; one state localized on the bpy moiety and the other lower energy state involving the anthracenedicarbonitrile unit. They appear to show different sensitivity to dioxygen, as reflected in their different lifetimes.

At low temperature the excited state lifetime (Table 2) for the lowest energy emitting state of $[Ru(CN_2\text{-np})(bpy)_2]^{2+}$ is far too long (464 μs) to be assigned to a pure ^{3}MLCT excited state. The long lived luminescence at low temperature could be attributed to a smaller degree of excited state distortion owing to the greater delocalization of the excited electron in the CN_2-np π* system as similarly reported by Meyer and coworkers[10] for a series of ruthenium complexes. However, for $[Ru(CN_2\text{-np})(bpy)_2]^{2+}$ the effect is really drastic, and in the absence of the CN groups, no effect due to delocalization is observed. Therefore the presence of a low lying triplet state centered on the CN_2-np ligand, close in energy to the lowest ^{3}MLCT excited state, should play an important role. When the solution is frozen, the ^{3}MLCT excited states move to higher energy and the intraligand (IL) state becomes the low lying excited state with a longer lifetime (Table 2). Such intraligand excited states have been previously observed in transition metal complexes.[11] The extremely long excited state lifetime is of course a very appealing property for the use of such a complex as a luminescent sensor or fluorescent label.

As mentioned above, $[Ru(np)(bpy)_2]^{2+}$ in MeCN shows emission properties similar to those of $[Ru(bpy)_3]^{2+}$. However in aqueous buffered solution an enhancement of the luminescence quantum yield in the presence of DNA, is observed as reported for $Ru(dppz)(phen)_2]^{2+}$.[12] With respect to $[Ru(dppz)(phen)_2]^{2+}$, $[Ru(np)(bpy)_2]^{2+}$ is already strongly luminescent in aqueous solution (in the absence of DNA), the quantum yield of luminescence is increased only by a factor of 2.5 ($\geqslant 10^6$ for $[Ru(dppz)(phen)_2]^{2+}$) and a simple monoexponential decay is observed in presence of increasing amounts of DNA. $[Ru(CN_2\text{-np})(bpy)_2]^{2+}$ shows, under the same conditions as above, a lowering of the absorption coefficient in the presence of DNA. In particular the bands at 350–400 nm corresponding to π–π* transitions of CN_2-np are diminished with increasing DNA concentration. This suggests binding of the anthracenedicarbonitrile unit of the ligand to the DNA helix.

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