A functionalized ruthenium(II)-bis-terpyridine complex as a rod-like luminescent sensor of zinc(II)

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The nearly non-luminescent ruthenium(II)-terpyridine chromophore, functionalized with an uncoordinated terpyridine fragment, 2, undergoes Zn(II)-induced association leading to a luminescent rod-like 2 : Zn^{2+} : 2 species with a luminescence enhancement factor, EF ⩾ 10.

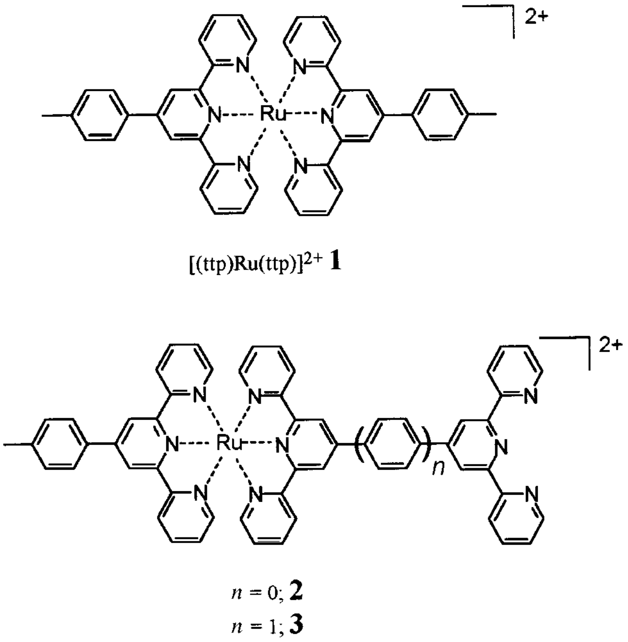
In the field of transition metal chemistry the assembly of Ru(II), Os(II), and Re(I) complexes to yield polymetallic species is being pursued both for fundamental and practical reasons.[1–4] Examples include (i) the investigation of energy and electron transfer processes in geometrically well defined systems where the metal-based components are held together by covalent bonds,[5–7] (ii) the exploitation of spectroscopic properties (particularly luminescence) for testing the sensing ability of appended groups towards protons, cations, and anions,[1–3] and (iii) the building up of dendritic species comprising tens of metal centres for light-harvesting and energy-collection purposes.[8,9]

An interesting Ru-based chromophore to be employed in such type of assemblies is $[Ru(tpy)_2]^{2+}$ {tpy is 2,2′:6′,2″-terpyridine; Scheme 1 shows the related complex $[(ttp)Ru(ttp)]^{2+}$ **1**, containing the 4′-tolyl-tpy ligand, ttp}.[10] This is because substitution at the 4′ position of tpy allows the construction of geometrically well-defined rod-like rigid species.[11] The luminescence properties of both $[Ru(tpy)_2]^{2+}$ and **1** are rather poor (their room temperature luminescence quantum yield and lifetime in acetonitrile solvent are $\Phi \approx 10^{-5}$ and $\tau < 1 \times 10^{-9}$ s, respectively[10]) but the incorporation of these or related complexes in polynuclear species may result in significant luminescence improvements.[7,12]

By using luminescence spectroscopy we have investigated the properties of acetonitrile–water solutions of the complexes $[(ttp)Ru(tpy\text{-}tpy)]^{2+}$ **2** and $[(ttp)Ru(tpy\text{-}ph\text{-}tpy)]^{2+}$ **3**, Scheme 1,† in the presence of Zn^{2+} [ph = 1,4-phenylene]. We found that Zn^{2+} coordination of the free tpy fragments of **2**[13] is accompanied by a substantial enhancement of luminescence intensity; by contrast no such effect is observable for **3**. Luminescence results are collected in Table 1. In addition we could use luminescence spectroscopy to monitor the formation of the tripartite species, **2 :** Zn^{2+} **: 2**.

The absorption spectra of **2** and **3** in acetonitrile–water (1 : 1 v/v) display intense absorption bands in the UV region (250–350 nm, $\varepsilon \approx 10^5$ M^{-1} cm^{-1}) and moderately intense bands in the visible region (450–550 nm, $\varepsilon \approx 10^4$ M^{-1} cm^{-1}). The former bands are due to ligand centered (^1LC) transitions and those occurring in the visible are due to metal-to-ligand charge-transfer (^1MLCT) transitions, of Ru→L electronic configuration.[6,11] Owing to the presence of the uncoordinated tpy fragment in **2** and **3,** addition of Zn^{2+} causes[13] some changes in the absorption features. These changes are only modest in the region of the ligand-centred transitions of both complexes; however, for **2** the longest-wavelength band maximum (MLCT region) undergoes a bathochromic shift from 491 to 498 nm (for **3** the corresponding absorption maximum at 491 nm is not affected by the presence of Zn^{2+}). This indicates that for **2**, the Zn^{2+} ion causes stabilization of the lowest-lying Ru→L CT energy level, which involves the tpy-tpy fragment, Scheme 1. For **3** no such effect is apparent.

The excited states responsible for the luminescence, Table 1, are formally triplet levels of Ru→L CT nature, and involve in



$[(ttp)Ru(ttp)]^{2+}$ **1**

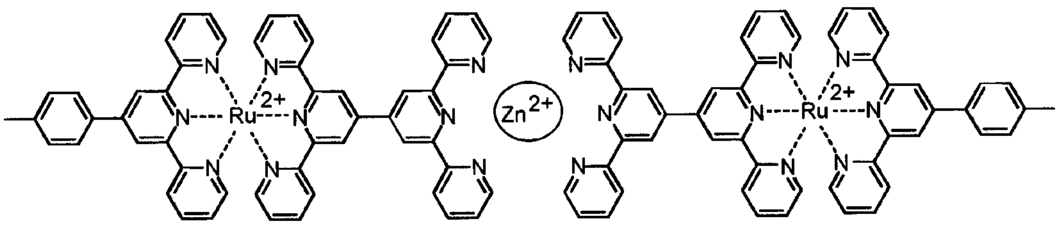
$n = 0$; **2**
$n = 1$; **3**

Scheme 1

Table 1 Luminescence properties[a]

				In the presence of Zn^{2+b}		
	$\lambda_{max}{}^c$/nm	τ/ns	$10^4\Phi^d$	$\lambda_{max}{}^c$/nm	τ/ns	$10^4\Phi^d$
$[(ttp)Ru(ttp)]^{2+}$ (**1**)[e]	640	0.9	0.32			
$[(ttp)Ru(tpy\text{-}tpy)]^{2+}$ (**2**)	660	6.3	1.6	710	84	16
$[(ttp)Ru(tpy\text{-}ph\text{-}tpy)]^{2+}$ (**3**)	648	2.4	0.6	650	3.3	0.9

[a] Room temperature aerated acetonitrile–water (1 : 1 v/v). [b] More than 3 equiv. [c] Band maxima for uncorrected spectra. [d] From corrected spectra. [e] Acetonitrile solvent, ref. 10.



2:Zn^{2+}:2

Scheme 2

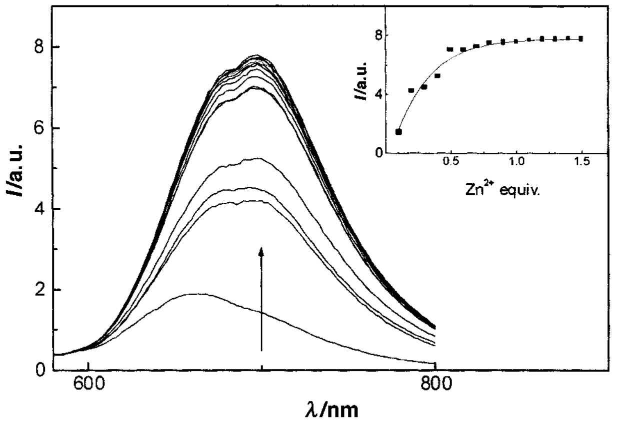


Fig. 1 Luminescence spectrum of complex **2** after Zn^{2+} addition. Excitation wavelength is at 494 nm, where the changes in absorbance intensity are within 5%. The inset shows the luminescence intensity taken at 700 nm *vs.* the added Zn^{2+} equivalents.

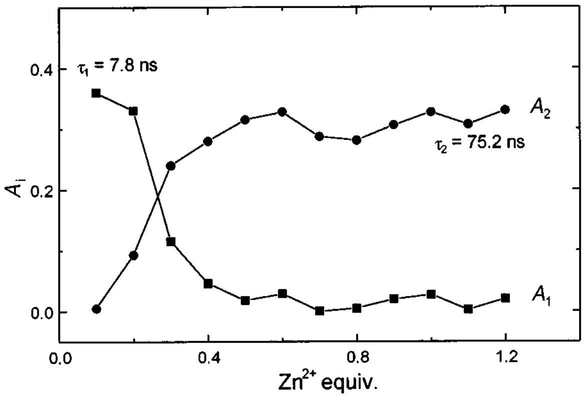


Fig. 2 Changes in the relative amplitudes A_1 and A_2 for the dual luminescence decay of complex **2** (concentration 1×10^{-5} M) upon Zn^{2+} addition. The decays are monitored over the full emission range.

each case the larger size ligand present on either side of the Ru(II) centre, *i.e.* tpy-tpy and tpy-ph-tpy for **2** and **3**, respectively.[10] The luminescence properties gathered in Table 1 indicate that Zn^{2+} remarkably affects the luminescence band maximum, intensity and lifetime for the case of **2**. In contrast, for **3** no substantial changes can be registered. This different behaviour may be understood in terms of the role of the phenylene group in decoupling the Ru-based chromophore and the tpy appended site.[14]

The results of a titration experiment on the luminescence intensity of **2** are illustrated in Fig. 1. For this complex, subsequent additions of Zn^{2+} cause gradual shifts of the band maximum from 660 to 700 nm, with a concomitant increase of the luminescence intensity. The inset of Fig. 1 shows that the change in luminescence intensity at 700 nm *vs.* the Zn^{2+} concentration is consistent with formation of a **2** : Zn^{2+} : **2** species.

The same conclusion is supported by the time resolved luminescence properties exhibited upon titration of complex **2** with Zn^{2+}. The luminescence decayed according to a dual exponential law, $I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$, and a global analysis as performed on 12 decay profiles gave $\tau_1 = 7.8$ ns and $\tau_2 = 75.2$ ns, with varying amplitudes (A) depending on the added equivalents of Zn^{2+}, see Fig. 2. Comparison of the results depicted in Fig. 2 with the luminescence properties reported in Table 1 suggests that the two species responsible for the dual exponential behavior are **2** and **2** : Zn^{2+} : **2**. Based on the coordination number of 6 for the Zn(II) centre and on the geometry of the tpy coordination site,[7,13] the **2** : Zn^{2+} : **2** complex is most likely linearly arranged with an estimated Ru–Ru distance of 2.2 nm, Scheme 2.

With respect to the starting complex **2**, it is noteworthy that the **2** : Zn^{2+} : **2** complex exhibits improved luminescence properties, EF = 10 (with respect to **2** in neat acetonitrile, EF ≈ 50). This is due to the delocalizing ability of the tpy-tpy ligand[12] combined with the stabilizing effect of the Zn^{2+} centre. Our results, which are in line with those of a recent report on polynuclear complexes where the bridging ligands contain the highly delocalizing ethynyl group,[7] suggest that it is possible to use Ru(II)-terpyridine derivatives both to develop Zn^{2+} luminescent sensors and to construct nanometric rod-like assemblies with tuneable luminescence properties.

Notes and references

† The synthesis and characterization of complexes **1**, **2**, and **3** were described previously.[11] Absorption and luminescence spectra of dilute solutions (≈ 10^{-5} M) in acetonitrile–water (1 : 1 v/v) were recorded with a Perkin Elmer Lambda 5 spectrophotometer and with a Spex Fluorolog II spectrofluorimeter, respectively. Uncorrected luminescence band maxima are used throughout the text. In order to determine corrected band maxima and luminescence quantum yields we followed a procedure described in ref. 12. Luminescence lifetimes were obtained with an IBH single-photon-counting apparatus. The titration experiments were conducted with Gilson P20 Pipetman microburettes by using concentrated solutions (10^{-3} M) of $ZnCl_2$.

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