

## Formation of Supramolecular Complexes of Tris(6,6'-oligoethyleneglycol-3,3'-bipyridazine)ruthenium(II) Dichloride with Alkali and Alkaline Earth Metal Ions

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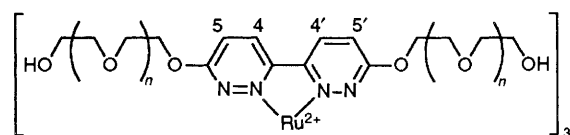
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The new tris(6,6'-oligoethyleneglycol-3,3'-bipyridazine)Ru<sup>II</sup>-dichlorides **1**, **2** form binuclear metal complexes with alkali and alkaline earth ions with high selectivity and these complexes show increased fluorescence quantum yields and lifetimes.

Metal complexes including additional metal ion binding sites provide interesting molecular networks for the production of supramolecular multi metal assemblies.<sup>1,2</sup> These provide means to mimic the electron transfer and light harvesting processes of the photosynthetic reaction centre.<sup>3-6</sup>

Recently some interesting supramolecular structures on the basis of photoactive Ru-complexes covalently linking the components were prepared and studied.<sup>7-9</sup> These assemblies once prepared, however, cannot be modified owing to their excited state properties. Also, solubility problems, due to their high molecular mass, can occur in water. We therefore developed a new concept of attaching a sensitizer-relay and potential donor by non-covalent hydrophobic interactions.<sup>10</sup>

Here, we report (i) the first highly water soluble Ru-complexes **1**, **2** (Scheme 1) having polyether chains which allow supramolecular assemblies to be formed and (ii) tuning of excited state properties.<sup>†</sup> To test the binding ability of these new Ru-complexes **1**, **2** and the changes produced in the excited state, electron and energy transfer processes were excluded. As models, guests of **1** and **2** alkali and alkaline earth ions were selected.

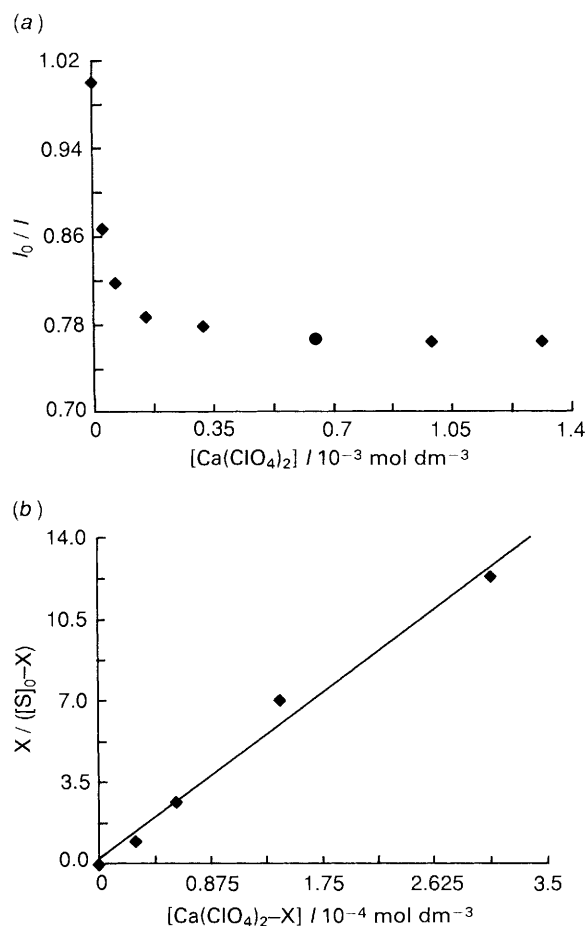


**1**;  $n = 2$ : Ru(33bpdz)<sub>3</sub><sup>2+</sup>

**2**;  $n = 3$ : Ru(44bpdz)<sub>3</sub><sup>2+</sup>

<sup>†</sup> Compounds **1** and **2** were prepared from the corresponding free ligands (3 equiv.) with Ru(Me<sub>2</sub>SO)<sub>4</sub>Cl<sub>2</sub> (1 equiv.); the new compounds have been characterised by UV, NMR and mass spectroscopy.

*Selected spectroscopic data:* <sup>1</sup>H NMR (400 MHz; D<sub>2</sub>O) **1** δ 8.46 (d, 6H, <sup>3</sup>J<sub>4,5</sub> = <sup>3</sup>J<sub>4',5'</sub> 9.5 Hz, H<sup>4,4'</sup>) 7.49 (d, 6H, <sup>3</sup>J<sub>5,4</sub> = <sup>3</sup>J<sub>5',4'</sub> 9.5 Hz, H<sup>5,5'</sup>) 3.4–4.1 (m, 78H, glycol-H); **2** δ 8.43 (d, 6H, <sup>3</sup>J<sub>4,5</sub> = <sup>3</sup>J<sub>4',5'</sub> 9.5 Hz, H<sup>4,4'</sup>) 7.37 (d, 6H, <sup>3</sup>J<sub>5,4</sub> = <sup>3</sup>J<sub>5',4'</sub> 9.5 Hz, H<sup>5,5'</sup>) 3.4–4.1 (m, 102H, glycol-H).



**Fig. 1** (a) Fluorescence enhancement of **2** at different concentrations of added Ca(ClO<sub>4</sub>)<sub>2</sub>. (b) Analysis of the association constant of Ca(ClO<sub>4</sub>)<sub>2</sub> to **2** using the fluorescence enhancement data: Fox X insert  $\Delta I/\Delta I_{\max}$ . [S]<sub>0</sub>.

**Table 1** Lifetime and association constants of alkali and alkaline earth cations with **1** and **2**

		$\tau^a/\text{ns}$	$K_a^b$				
			Li <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Ba <sup>2+</sup>
Ru(33bpdz) <sub>3</sub> <sup>2+</sup>	<b>1</b>	3136	170	—	200	2200	2500
Ru(44bpdz) <sub>3</sub> <sup>2+</sup>	<b>2</b>	3310	300	—	420	41000	330

<sup>a</sup> Acetonitrile. <sup>b</sup> Values of association constants  $\pm 10\%$ .

Addition of alkali or alkaline earth ions to an acetonitrile solution of **1** and **2** results in an increase in the fluorescence intensity of **1** and **2**. Fig. 1(a) exemplifies the fluorescence increase of **2** upon addition of Ca<sup>2+</sup>. It is evident that the fluorescence enhancement reaches a saturation value, implying that formation of an intramolecular complex between **2** and Ca<sup>2+</sup> results in an increase in the fluorescence intensity of the chromophore. Similar fluorescence enhancements are observed with other alkali and alkaline earth ions, yet the increase in the fluorescence intensities differs for the various ions and depends on their concentrations.<sup>8</sup>

Assuming that a 1 : 1 complex between **1** or **2** and alkali and alkaline earth metals is formed, the association constants of the ions to **1** and **2** can be calculated on the basis of  $\Delta I$ , the relative fluorescence increase of the chromophore at an added concentration of the metal ion,  $\Delta I_{\text{max}}$ , the relative fluorescence increase,  $[S]_0$  the initial concentration of **1** and **2** and  $[M]$  the concentration of the added ions. Analysis of the experimental fluorescence intensity plots as a function of added alkali or alkaline earth ions results in a linear relationship, Fig. 1(b), implying that indeed the supramolecular complexes correspond to a 1 : 1 stoichiometry. Table 1 summarizes the derived association constants of alkali and alkaline earth cations with **1** and **2**. It is evident, that with Na<sup>+</sup> no binding and with Li<sup>+</sup> weak binding takes place. In turn, high selectivity in the binding of alkali earth cations to **2** is observed and the binding constant of Ca<sup>2+</sup> is *ca.* 100-fold higher than those of Mg<sup>2+</sup> and Ba<sup>2+</sup>. Similarly, the association constant of Ca<sup>2+</sup> to **1** is *ca.* 20-fold lower as compared to **2**. Interestingly, the association constant of Ba<sup>2+</sup> to **1** is *ca.* 10-fold higher than that of Mg<sup>2+</sup>, while similar binding constants are found for the two ions to **2**.

Alkali and alkaline earth ions cannot participate in any intramolecular electron or energy transfer processes involving the excited state of **1** or **2**. Thus, the fluorescence intensity changes upon addition of the cations can only originate from alterations of the photophysical properties of **1** and **2** in the presence of alkali and alkaline earth ions. We find that addition of the ions results in an increase in the fluorescence quantum yield as well as an increase in the fluorescence lifetime of **1** and **2**.

Thus, the enhanced steady-state fluorescence of **1** and **2**

upon addition of alkali and alkaline earth cations originates from two complementary contributions: increase of the fluorescence quantum yield of the chromophores and longer lifetimes of their excited states. In fact, the changes of each of these factors could provide the basis for calculating the association constants of the ions to the chromophores. We have examined in detail the changes in the lifetime,  $\Delta\tau$ , and fluorescence quantum yield  $\Delta\phi$  of **1** upon addition of different concentrations of Ba<sup>2+</sup>. Using the fluorescence quantum yield and lifetime changes, the derived association constants correspond to  $K_a = 2450 + 10\% \text{ dm}^3 \text{ mol}^{-1}$  (based on  $\Delta\phi$ ) and  $K_a = 2750 + 10\% \text{ dm}^3 \text{ mol}^{-1}$  (based on  $\Delta\tau$ ), respectively. These values are in excellent agreement with the association constant derived from steady-state fluorescent studies  $K_a = 2500 + 10\% \text{ dm}^3 \text{ mol}^{-1}$  (Table 1).

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- For weak complexation constants ( $K_a < 5000 \text{ dm}^3 \text{ mol}^{-1}$ ) only the region where 20–80% of the Ru-complex being in the associated form is taken for calculation of the association constants; cf. D. A. Deranleau, *J. Am. Chem. Soc.*, 1969, **91**, 4044.