

Stepwise Syntheses of Mono- and Di-nuclear Ruthenium tpphz Complexes [(bpy)₂Ru(tpphz)]²⁺ and [(bpy)₂Ru(tpphz)Ru(bpy)₂]⁴⁺ {tpphz = tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]phenazine}

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The complex [(bpy)₂Ru(tpphz)]²⁺ (tpphz = tetrapyrrophenazine), is obtained by reaction of [(bpy)₂Ru(phendione)]²⁺ with 5,6-diamino-1,10-phenanthroline; upon reaction with [(bpy)₂Ru(Me₂CO)₂]²⁺, the fully conjugated dimer [(bpy)₂Ru(tpphz)Ru(bpy)₂]⁴⁺ is obtained.

One of the main goals of molecular electronics is the mastery of intramolecular electron transfer over long distances. Although interesting results have been obtained with polyenes¹ or phenyl groups² as bridging units between metallic centres, a class of molecules exhibiting simultaneously: (i) a large defined length, allowing connection to ultrasmall metallic structures;³ (ii) conjugated character, to ensure efficient electron transfer; (iii) rigid structure, to avoid conformational problems and (iv) good stability (at least more stable than carotene derivatives) is still lacking.

Ladder oligomers⁴ offer an attractive possibility for fulfilling these requirements. However, the main drawback associated with these structures is their poor solubility. Since they are built from fused aromatic rings, they exhibit a tendency for strong π - π intermolecular interactions which counterbalance solute-solvent interactions. The obvious way to overcome this effect is to prepare ligands with either bulky substituents or long flexible chains.⁵

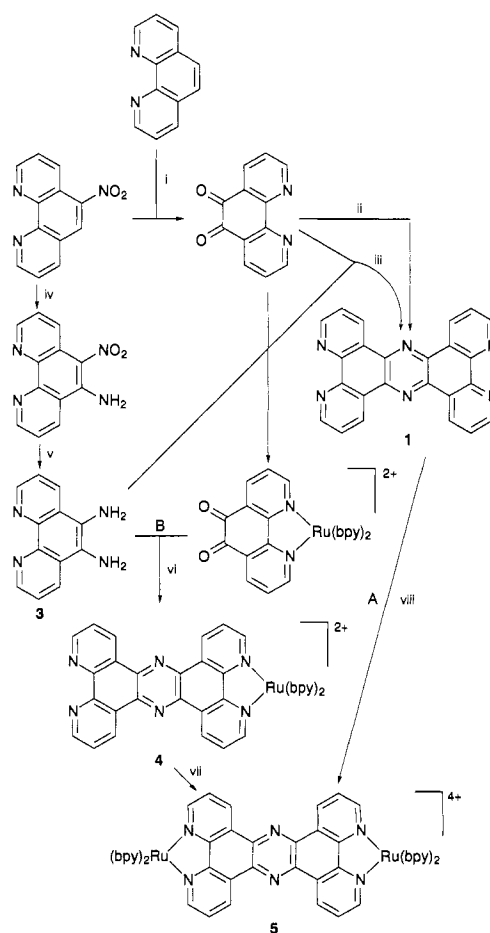
Another possibility would be to build up the bridging ligand from a soluble monomer precursor, and in particular to use the reaction of pre-coordinated ligands. This would also allow the preparation of soluble mononuclear and asymmetric binuclear complexes bridged by poorly soluble or fully insoluble ligands.

Using these latter principle, we describe here the syntheses of the poorly soluble tetrapyrro[3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]phenazine (tpphz) ligand, which contains bipyridine 'ends' with a central pyrazine skeleton, and the corresponding mono- and di-nuclear Ru(bpy)₂ complexes (bpy = 2,2'-bipyridine). Related mononuclear complexes [(bpy)₂M(dppz)]²⁺ [dppz = dipyrro[3,2-a:2',3'-c]phenazine, M = Ru, Os] and [(tpy)RuO(dppz)]²⁺ have already been used as molecular light-switches for DNA⁶ and micellar solutions,⁷ or for DNA cleavage.⁸

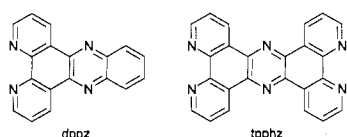
Routes to the mono- and di-nuclear complexes [(bpy)₂Ru(tpphz)]²⁺ **4** and [(bpy)₂Ru(tpphz)Ru(bpy)₂]⁴⁺ **5** are shown in Scheme 1. Complex **5** can be prepared in a classical way (route A) by reaction of the bridging ligand tpphz **1** with [(bpy)₂RuCl₂]²⁺. The tpphz ligand was prepared by condensation of 1,10-phenanthroline-5,6-dione (phendione) in molten ammonium acetate or by condensation of 5,6-diamino-1,10-phenanthroline **3** with phendione. 5-Amino-6-nitro-1,10-phenanthroline **2** was prepared by direct nucleophilic amination of the corresponding nitrophenanthroline with hydroxylamine in the presence of KOH.⁹ Reduction of **2** by hydrazine/palladium on carbon gave 5,6-diamino-1,10-phenanthroline **3**. The poor solubility of **1** precluded efficient synthesis of the mononuclear complex **4** which was obtained in 80% yield by reaction of 5,6-diamino-1,10-phenanthroline **3** with the complex [(bpy)₂Ru(phendione)]²⁺. The dimer **5** was then obtained by reaction of **4** with [(bpy)₂Ru(Me₂CO)₂]²⁺.

Unexpectedly, the ¹H NMR spectra of **4** in CD₃CN were very sensitive to concentration. Although the bpy ligands are only slightly affected, the tpphz proton chemical shifts can be shifted to higher field by up to 0.6 ppm with increasing concentration. This suggests that, in concentrated solutions, the complexed tpphz ligands aggregate, probably in a way similar to that found in the crystal packing of [(tpy)-RuOH₂(dppz)]²⁺,⁸ π - π interactions between close tpphz molecules causes an electronic shielding of their protons. As expected, this shielding decreases with increasing temperature.

Irradiation at 447 nm of dry acetonitrile solutions of **4** caused intense luminescence at 636 nm (intensity = 0.7 relative to [Ru(bpy)₃]²⁺ under the same conditions). Addition of water led to a significant decrease of intensity and the complex did not



Scheme 1 Routes to complexes **4** and **5**. Reagents and conditions: i, HNO₃-H₂SO₄; ii, MeCO₂NH₄, 180 °C, 2 h, 47%; iii, DMF, 70%; iv, NH₂OH·HCl (7 equiv.) KOH (10 equiv.), EtOH, reflux, 1 h, 33%; v, NH₂NH₂·H₂O (10 equiv.) 10% Pd/C, 83%; vi, MeCN-MeOH, 65 °C, 4 h; vii, [Ru(bpy)₂Cl₂], AgCF₃SO₃ (2.1 equiv.), MeCN, reflux, 3 h, 80%; viii, [Ru(bpy)₂Cl₂]²⁺·2H₂O (2.5 equiv.), EtOH-H₂O, reflux, 48 h, NH₄PF₆, 84%.



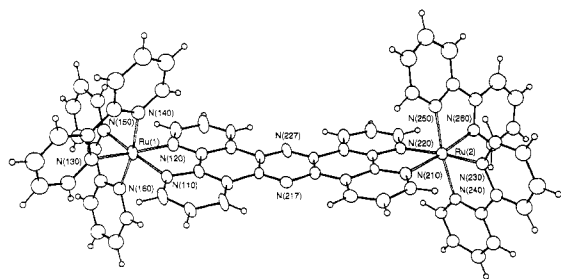


Fig. 1 Structure of one of the two cations **5**; for clarity, the hydrogen atoms have been drawn with arbitrary low isotropic thermal parameters (1 \AA^2)

luminesce at all in aqueous solution. These luminescence properties are very similar to that of the molecular 'light-switches' $[(\text{bpy})_2\text{Ru}(\text{dppz})]^{2+}$ and derivatives.⁶ This phenomenon has been suggested¹⁰ to be related to proton quenching of the MLCT luminescence by protonation (although hindered) at the basic phenazine nitrogen atoms.

Apart from the $\text{tpphz } n-\pi^*$ absorptions in the range 300–400 nm, the UV–vis spectra of **4** and **5** are very similar to that of $[\text{Ru}(\text{bpy})_3]^{2+}$. The absence of a red shift for the MLCT band, despite the better π -accepting character of tpphz vs bpy has also been observed in $[(\text{bpy})_2\text{Ru}(\text{dppz})]^{2+}$. In contrast, the first reduction processes of the complexes **4** and **5** (-0.965 and -0.785 V) occur at potentials which are markedly less cathodic than $[\text{Ru}(\text{bpy})_3]^{2+}$ (-1.33 V), or $[(\text{bpy})_2\text{Ru}(\text{dppz})]^{2+}$ (-1.02 V), due to the more pronounced π -accepting character of tpphz . As emphasized by Kaim and coworkers for dppz complexes,¹⁰ this discrepancy between the redox behaviour and the absorption spectra results probably from the low intensity of the $\text{Ru}^{\text{II}}-\text{tpphz}$ type LUMO absorption band which is overlapped by the more intense $\text{Ru}^{\text{II}}-\text{bpy}$ type π^* (LUMO + 1 and LUMO + 2). Indeed, the LUMO is mainly localized on the pyrazine part of tpphz with only small coefficients at the metal-bound nitrogen atoms while the LUMO + 1 and LUMO + 2 involve the bpy ends of tpphz .

The nitrate salt of complex **5** was crystallized from water and its structure was determined by X-ray crystallography.[†] The asymmetric unit contains two independent $[(\text{bpy})_2\text{Ru}(\text{tpphz})-\text{Ru}(\text{bpy})_2]^{4+}$ cations, eight nitrate anions and ten water molecules. Fig. 1 shows the structure of one of the two complex cations. In this asymmetric unit and for both cations, each $(\text{bpy})_2\text{Ru}(\text{tpphz})$ fragment is right-handed. The space group being centrosymmetric, the unit cell contains only $\Delta\Delta$ and $\Lambda\Lambda$ complexes but no $\Delta\Lambda$ complex. As the two terminal $\text{Ru}(\text{bpy})_2$ moieties are well separated [intramolecular $\text{Ru}\cdots\text{Ru}$ distances: $\text{Ru}(1)\cdots\text{Ru}(2)$ 12.735(1), $\text{Ru}(3)\cdots\text{Ru}(4)$ 12.776(1) Å], it is very likely that the synthesis yields a statistical distribution of $\Delta\Delta$, $\Lambda\Lambda$ and $\Delta\Lambda$ complexes 1 : 1 : 2 ratio. All the crystals isolated in several crystallizations were isostructural. Complete evaporation of the mother-liquor gave only a non-crystalline residue, which suggests a higher solubility of the $\Delta\Lambda$ nitrate salt in water. The geometry around each $(\text{bpy})_2\text{Ru}(\text{tpphz})$ fragment is very similar to that found in $[\text{Ru}(\text{bpy})_3]^{2+}$.¹¹ The ruthenium–nitrogen distances of 2.028(9)–2.131(1) Å and the bite angles of 77.8(4)–79.8(4)° are in the normal range for bipyridine-like ligands.¹² The bridging tpphz ligand is not fully planar, being at the same time bent and twisted with a maximum distance between the centre of tpphz and the direct $\text{Ru}\cdots\text{Ru}$ vector of 0.57 Å. In one of the complexes, the twist angle between the tpphz ends is 18°, which would correspond in longer polyquinoxalines to half a turn each 100 Å. This distortion, very likely caused by packing forces, illustrates a relative lack of rigidity of this type of fully aromatic ladder.

Further developments involve stepwise syntheses of mono-, di- and poly-nuclear complexes bridged by longer fully insoluble polyquinoxaline ligands and the determination of their physicochemical properties.

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[†] Crystal data for **5** $[\text{NO}_3]_4 \cdot 5\text{H}_2\text{O}$, $\text{C}_{64}\text{H}_{54}\text{N}_{18}\text{O}_{17}\text{Ru}_2$, $M = 1549.39$, triclinic, space group $P\bar{1}$, $a = 19.455(3)$, $b = 21.388(4)$, $c = 21.582(4)$ Å, $\alpha = 96.36(2)$, $\beta = 94.16(2)$, $\gamma = 98.02(2)^\circ$, $U = 8847(3)$ Å³, $Z = 4$, $D_c = 1.16$, $F(000) = 3152$. Addition of NBu_4Br to a solution of the PF_6 salt of dimer **5** in acetone precipitated the bromide salt, which was then dissolved in a minimum of warm water. Addition of AgNO_3 , filtration of AgBr and slow evaporation gave crystals suitable for X-ray diffraction. A dark red prism ($650 \times 500 \times 400 \mu\text{m}$) was mounted in a capillary containing mother-liquor on an Enraf-Nonius CAD4-F diffractometer at 297 K, with Mo-K α radiation ($\lambda = 0.71069$ Å, graphite monochromator), $\omega-2\theta$ scans, $4 < 2\theta < 44^\circ$, variable speed, no significant decay, 22 365 reflections collected. Data were corrected for Lorentz polarization, and absorption using DIFABS ($\mu = 3.94 \text{ cm}^{-1}$, min., max. transmission 0.92, 1.17).¹³ The positions of the ruthenium atoms were found using SHELXS86¹⁴ and all subsequent calculations were performed using CRYSTALS.¹⁵ Final refinement of 1360 parameters (348 atomic positions) in 9 blocks, using 10 917 reflections with $I > 3\sigma(I)$ converged at $R = 0.090$ and $R_w = 0.103$. The high values for R are not only due to the poor crystallinity of the sample and the large number of parameters refined (1360) but also to the higher disorder of the NO_3^- counter-ions and water molecules. The final difference maps showed some residual peaks around disordered atoms with max., min. residual electron density of 0.9, -0.5 e \AA^{-3} . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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