Stereoisomerically controlled inorganic architectures: synthesis of extended enantio- and diastereo-merically pure tris-ruthenium disks from enantiopure building blocks

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Extended enantio- and diastereo-merically pure D_3-symmetric disks, $\Lambda\Lambda\Lambda$-1 and $\Delta\Delta\Delta$-1, are synthesised from enantiomerically pure building blocks.

Polymetallic molecular architectures designed for energy and electron transfer purposes are important synthetic targets in modern coordination chemistry.[1–6] Particularly interesting are systems in which the ligands connect photo- and/or redox-active metal centres through rigid π-conjugated systems, allowing


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maximal electronic communication between the active centres. Several ligands designed for multi-ruthenium(ii)–2,2'-bipyridyl (bpy), –1,10-phenanthroline (phen) and –terpyridine (terpy) complexation have been constructed.[6,7]

Compared to Ru[II]–terpy systems, Ru[II]–bpy and –phen complexes generally possess a longer excited-state lifetime and are thus better suited for the construction of photosensitisers and light-harvesting devices.[3] However, the latter systems give rise to diastereoisomers when more than one octahedral metal–tris(bidentate ligand) centre is incorporated. Obtaining diastereomerically pure (dp) compounds is important because diastereoisomers have different spatial orientations which may lead to differences in their physical properties such as rates of energy or electron transfer. The use of inorganic enantiomerically pure (ep) building building blocks allows the construction of diastereomerically pure polymetallic architectures without subsequent separation of diastereoisomers,[8–11] a task that is complicated because the number of stereoisomers increases exponentially (2^N) with the number of incorporated metal centres (N).

Our approach to ep and dp rigid π-conjugated potential antenna systems is to construct multi-metal centres around a rigid bidentate π-deficient ligand using ep building blocks. The presence of a π-deficient aromatic central ligand should faciliate the excited-state electron transfer from the metals to the central ligand. One attractive framework is 1,4,5,8,9,12-hexa-azatriphenylene (hat).[12,13] The tris-ruthenium(ii) complexes, [{L₂Ru}₃(hat)][PF₆]₆ (L = phen,[14] bpy;[15] see 2), of hat have been synthesised and they possess interesting photophysical properties.[14,15] We have recently described ep and dp rigid π-conjugated extended polymetallic rods by the use of fused phenanthroline linkers in which the ligand is constructed *in situ* by the use of the ep building-block approach.[11] Following a similar strategy, we now report the synthesis of an extended version of the hat ligand, phat† 3, and of ep and dp disks [{(phen)₂Ru}₃(phat)][PF₆]₆, $\Lambda\Lambda\Lambda$-1 and $\Delta\Delta\Delta$-1, using the ep building blocks Λ- and Δ-[Ru(phen)₂(py)₂]Cl₂,[16] Λ-4 and Δ-4, respectively, which react with retention of configuration.[8,9]

The synthetic sequence leading to $\Lambda\Lambda\Lambda$-1 and $\Delta\Delta\Delta$-1 is shown in Scheme 1.‡ Ligand 3 is best obtained in a two-step procedure: first hexaaminobenzene 5§ is condensed with 3.0 equiv. of 1,10-phenanthroline-5,6-dione 6;[17] the precipitate formed is isolated and reacted with an additional 1.4 equiv. of 6 giving 3 in 25% overall yield. Ligand 3 is then reacted with 3.3 equiv. of ep Λ-4 and Δ-4, respectively, giving ep and dp $\Lambda\Lambda\Lambda$-1 and $\Delta\Delta\Delta$-1 [10–25% yield after purification on a Bio-Beads SX-1 size-exclusion column, MeCN–toluene (1:1)]. That the compounds are ep as well as dp is demonstrated by the fact that in the circular dichroism spectra of $\Lambda\Lambda\Lambda$-1 and $\Delta\Delta\Delta$-1 are mirror images (Fig. 1).

The inorganic disk 1 resembles the multi-metal complexes [{(bpy)₂Ru}₂(tpphz)][PF₆]₂ 7[18]† and [{(phen)₂Ru(tatppe)}₂-Pd][PF₆]₂} 8[11,19]† more than 2.[14] This is presumably a result of the increased distance between the metallic centres compared to 2 as well as the close chemical resemblance between 1 and the
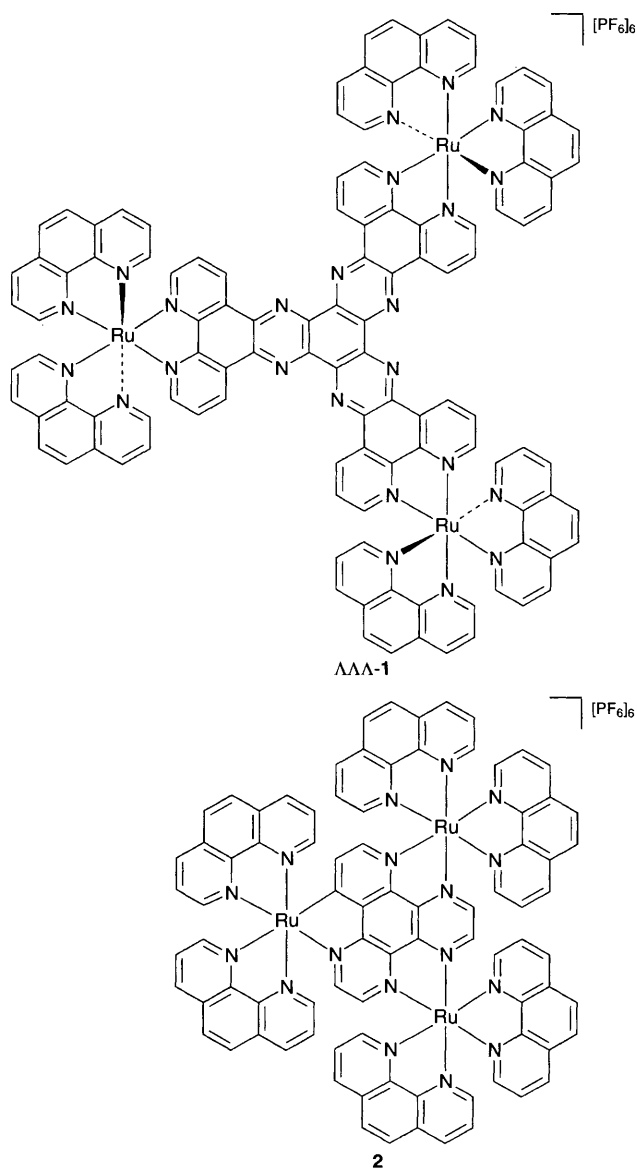
homologues **7** and **8**. Like **7** and **8**, complex **1** shows only one reversible oxidative wave (at 1.38 vs. SCE for **1** in MeCN), whereas **2** shows three waves (the first at 1.61 V). Therefore, there appears to be no large coulombic interaction between the metallic centres in **1**. Complexes **1**, **7** and **8** have the same MLCT band (at ca. 440 nm) as [Ru(phen)$_3$][PF$_6$]$_2$. A bathochromic shift of the MLCT band is present in **2** resulting from the presence of a π-accepting ligand. However, **1** has a anodic first reduction potential (−0.52 V in MeCN), as expected for a low-energy π-accepting LUMO, although not as anodic as for **2** (−0.30 V).¶ These electrochemical observations suggest that hat is a better π-acceptor than phat. Like **8**, **1** has a broad but rather weak room-temperature emission at considerably higher
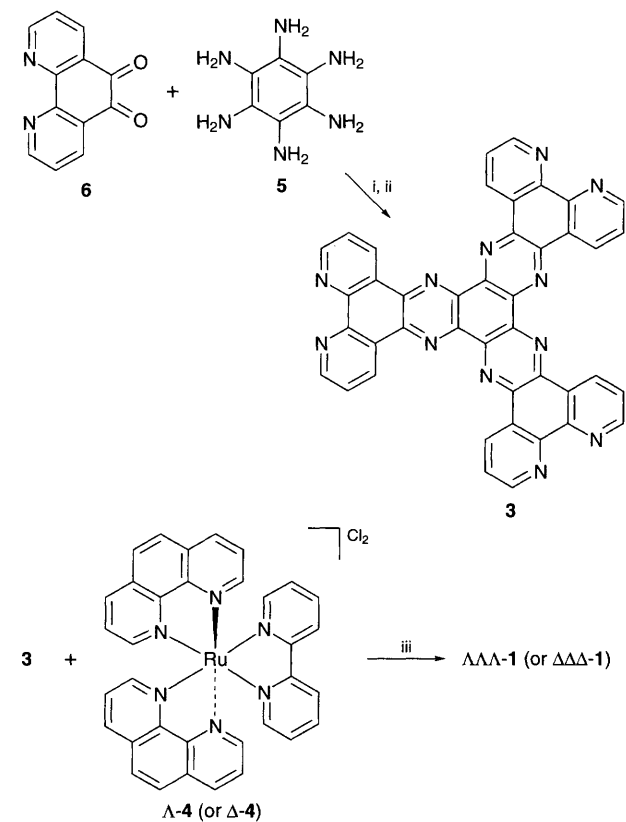
energy than **2** (630 and >800 nm, for **1** and **2**, respectively) when excited in the MLCT band. Further physicochemical studies are in progress.

In conclusion, ep and dp extended rigid disks [{(phen)$_2$-Ru}$_3$(phat)][PF$_6$]$_6$, ΛΛΛ-**1** and ΔΔΔ-**1**, have been constructed from ep building blocks. Their properties differ from those of **2**, probably due to differences in the intermetallic distances and electronic properties of the two ligands. The ligand phat and its complexes represent interesting novel components for the construction of inorganic molecular electronic devices.

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Footnotes

† phat = Phenanthroline–hat = 9,10,19,20,29,30-hexaazahexapyrido[3,2-a:2′,3-c:3″,2″-k:2‴,3‴-m:3″″,2″″-u:2″″″,3″″″-x]trinaphthylene, tpphz = tetrapyrido[3,2-a:2′,3′-c:3″,2″-h:2‴,3‴-j]phenazine and tatppe = 9,11,20,22-tetraazatetrapyrido[3,2-a:2′,3′-c:3″,2″-l:2‴,3‴-n]pentacene.

‡ Compound **1** was characterised by ¹H NMR spectroscopy, elemental analysis and electrospray MS {m/z 345.8 [**1** − 6PF$_6$]⁶⁺, 444.1 [**1** − 5PF$_6$]⁵⁺, 591.5 [**1** − 4PF$_6$]⁴⁺, 837.0 [**1** − 3PF$_6$]³⁺ and 1328.4 [**1** − 2PF$_6$]²⁺}. Compound **3** was characterised by ¹H NMR, ¹³C NMR and FABMS {m/z 691.2 [**3** + H]⁺.}

§ Freshly prepared by a modification of literature procedures.[13,20]

¶ This discrepancy can be explained by the assumption that the optical LUMO is different from the electrochemical as demonstrated for [(bipy)$_2$-Ru(dppz)]²⁺ {dppz = dipyrido[3,2-a:2′,3′-c]phenazine}[21].

Scheme 1 *Reagents and conditions*: i, deaerated EtOH–HOAc–thf (1:1:5), 90 °C, 4 h; ii, deaerated EtOH–HOAc–thf (1:3:2), 120 °C, 20 h; iii, (*a*) deaerated ethylene glycol, 120 °C, 5 d, (*b*) H$_2$O then NH$_4$PF$_6$
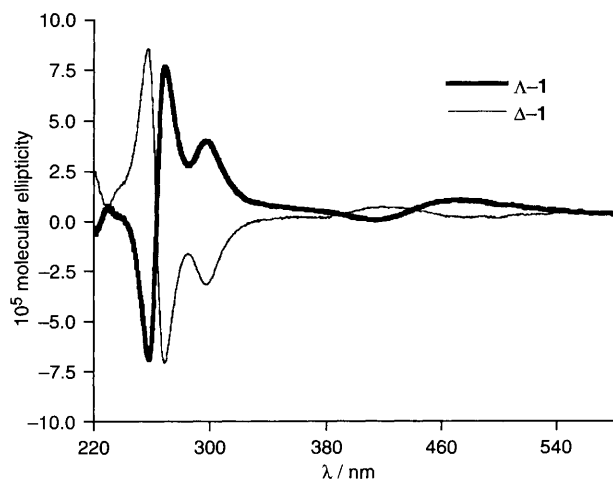

Fig. 1 Circular dichroism spectra of ΛΛΛ-**1** and ΔΔΔ-**1** in MeCN

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