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Enhanced stereoselectivity in a di-Ru(II) complex of an achiral bis-bidentate ligand†

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The diastereoselective formation of a *meso*-dinuclear Ru(II) complex of a novel bis-bidentate ligand is reported along with its electrochemical and photophysical properties. The design of the ligand, with its parallel coordination vectors, induces a diastereoselectivity of 1 : 13 : 1 [ΛΛ : (ΛΔ or ΔΛ) : ΔΔ] for the dinuclear complex.

Ru(II)–polypyridyl complexes have attracted much attention due to their tunable electrochemical and photophysical properties,[1a–c] which allows them to find applications in light-harvesting systems.[2] One simple approach to produce multinuclear Ru(II)-based chromophores is to design ligands with more than one chelating site.[3] In this context, Ru(II)–bpy (bpy = 2,2′-bipyridine) based scaffolds are photophysically more useful synthons as opposed to the synthetically and structurally more appealing tpy (tpy = 2,2′;6′,2″-terpyridine) based scaffolds.[4] Polynuclear Ru(II) complexes of bidentate ligands often require purification of stereoisomers, and this stereochemical complexity increases with the addition of each metal ion.[5] Nonetheless, owing to their stereoselective interactions with DNA, the isomerically pure Ru(II) complexes with bidentate ligands have shown potential as DNA probes.[6] They can also be used as enantiopure building blocks in supramolecular assemblies.[7]

Many attempts have been made to separate enantiomers and diastereomers of Ru–polypyridyl complexes. Although the pioneering work of chromatographic separation based on cation exchange and ion pairing using non-chiral anionic additives, such as toluene-4-sulfonate, developed by Keene and co-workers, has been proven to work, the major drawback of this method is that relatively long separation times are sometimes required.[8a,b] Chiral resolution using capillary electrophoresis[9] and capillary zone electrophoresis with enantiopure tartrate salts[10] and chiral DNA[9] have also been proven to be useful. Chiral discrimination of Ru complexes on silica columns using Δ or Λ-P(V)catecholato complexes could also be achieved, as shown by Lacour[11] and Gruselle.[12] Recently, Vos and Macdonnell *et al.* have developed enantiomeric separations of Ru(II)–polypyridyl complexes using HPLC with teicoplanin[13] and cyclodextrin[6] chiral stationary phases (CSPs).

In order to control the stereoselectivity of the final product, we introduced parallel coordination vectors into the bridging ligand (BL) such that adjacent [Ru(bpy)$_2$] units could only enter the coordination site in opposite enantiomeric forms. Although ligands **L2**, **L3** and **L4** in Chart 1 possess parallel coordination vectors, **L2** doesn't form dinuclear complexes chelated by the N-atoms due to steric hindrance. In **L3** and **L4**, the coordination vectors are antiparallel, so they also afford mixtures of *rac* and *meso*-dinuclear complexes. BLs with angular coordinated vectors, for *e.g.*, **L5–L11**, have been shown to afford a mixture of *rac*-(ΛΛ or ΔΔ) and *meso*-(ΛΔ or ΔΛ) dinuclear complexes upon complexation with the [Ru(bpy)$_2$] unit. Thus, we designed a bis-bidentate ligand that can (i) accommodate two [Ru(bpy)$_2$] units, (ii) offer parallel coordination vectors with larger bite angles compared to **L2–L11** that force coordinated complexes into close proximity.

We present herein a novel bis-bidentate ligand, **dgpm** (**L1**) (dgpm = diguanidinepyrimidine) (Chart 1), in which the two coordination vectors are parallel. The dinuclear Ru(II) complex of **dgpm** has been synthesized and characterized by solution NMR spectroscopy, UV-vis absorption spectroscopy, cyclic voltammetry, and XRD analysis. Also, due to the unique design

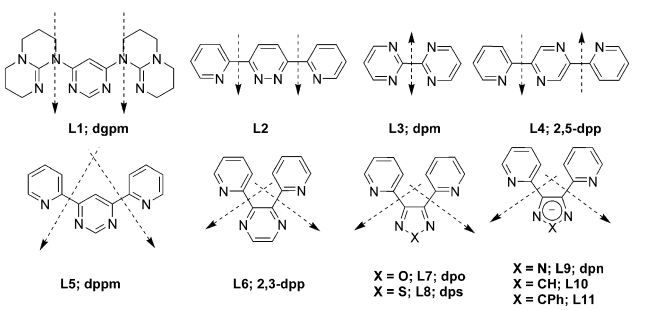

Chart 1 Ligands with different coordination vectors, as shown by dashed arrows, in their bis-bidentate chelating mode.

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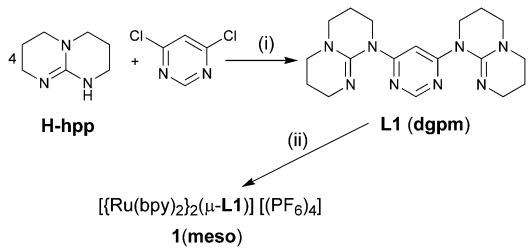

Scheme 1 Syntheses of ligand **L1** and complex **1**(***meso***). (i) toluene, microwave at 160 °C; 90%; (ii) *cis*-Ru(bpy)$_2$Cl$_2$ (3.5 eq.) in *n*-butanol at reflux followed by the addition of KPF$_6$; 65%.

of **dgpm**, the *meso*-dinuclear complex is formed with high diastereoselectivity.

The bis-bidentate chelating ligand, **L1** (diguanidinepyrimidine; **dgpm**), could be synthesized conveniently by microwave-assisted heating using 4 equivalents of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido-[1,2-α]pyrimidine (**H-hpp**), in 90% yield (Scheme 1). Complex **1**(***meso***) ([{Ru(bpy)$_2$}$_2$(μ-**L1**)] [(PF$_6$)$_4$]) was synthesized by refluxing a butanol mixture of **L1** and *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O in a 1 : 3.5 molar ratio. A satisfactory yield was obtained after purification by column chromatography, followed by anion metathesis. For reaction (ii) the product is a heterochiral *meso*-diruthenium complex, **1**(***meso***), which can be isolated in a 1 : 13 : 1 (ΛΛ : ΛΔ (or ΔΛ) : ΔΔ) (see Fig. S4 in ESI†) ratio over its homochiral form using a simple silica column chromatography without using a chirally pure [Ru]-precursor or chiral ion-exchange chromatography.[14] The coordination vectors in **L1** are parallel and it forms six-membered ring cycles upon coordination (Chart 1), which in turn precludes the formation of sterically demanding ΛΛ or ΔΔ *rac* isomers and maximize the possibility of π–π interactions between the bpy units of each Ru centre in complex **1**(***meso***).

The ^{1}H NMR spectrum of **L1** is symmetric in nature and exhibits two aromatic and six aliphatic peaks. This symmetric nature suggests a fast equilibrium between the equatorial and axial protons residing on the same carbon atom in the unsaturated **hpp** backbone. Attaching a heterocycle at the guanidine N*H*-position of **H-hpp** renders the six annular methylene units nonequivalent, as observed by both ^{1}H and ^{13}C NMR spectroscopies, in contrast to free **H-hpp**.[15] Based on the racemic Ru(bpy)$_2$Cl$_2$ starting material, the helicity of bpy ligands induces stereogenecity in the two Ru centres in **1**(***meso***), with the possibility of Λ and Δ-enantiomers. However, the relatively simple ^{1}H and ^{13}C NMR spectra of **1**(***meso***) suggest a favorable formation of ΛΔ (or ΔΛ) diastereomers over (also revealed by crystallography) a possible statistical combination of 1 : 2 : 1 = ΛΛ : ΛΔ : ΔΔ. In the ^{1}H NMR spectrum of the complex, the farthest upfielded singlet peak is at 6.1 ppm, which may be attributed to the 5-pyrimidyl proton due to the shielding by adjacent **hpp** moieties. Based on the ^{1}H NMR assignment, Polson *et al.* had previously reported a diastereoselectivity of 4 : 9 : 1 = ΛΛΛ : ΛΛΔ(=ΔΛΛ) : ΛΔΛ in a triruthenium complex.[14] The existence of a singlet peak at 6.1 ppm in the ^{1}H NMR spectrum of reaction (ii) (Fig. S2 in ESI†), albeit with a very minor impurity, suggests the exclusive formation of the *meso*-isomer.

The single crystal X-ray structure of **1**(***meso***) confirms the *meso*-structure and reveals two coordinatively saturated Ru(II) ions in a distorted octahedral geometry. The Ru–N bonds in bpy nitrogens were found to be shorter than those in pyrimidines and **hpp**-nitrogens, which in turn suggest strong σ-donation from **hpp** units and back π-bonding to the bpy moieties (Table S2 in ESI†). Although the two Ru-atoms are perfectly planar with the central pyrimidine ring, thereby increasing the possibility of better electronic communication through the BL, the overall C_2-symmetry of this cation is lost in the solid state due to spatial arrangement of the bpy units which are bowed towards one another, forming effective offset face-to-face π–π interactions.[16] This deformation is due to the flexible alkyl linkers which allow the non-planar chair conformation of the BL.[17a,b] As a consequence the parallel coordination vectors in **L1** maximize of π–π interactions (Fig. 1).‡

The electrochemical behaviour of crystallized complex **1**(***meso***) was examined by cyclic voltammetry, which exhibits two and five monoelectronic quasi-reversible oxidations and reductions, respectively. Despite the short intermetallic distance of 5.903 Å, the metal-based oxidations indicate weak communication (ΔE_{ox} = 160 mV) in the acetonitrile solution as shown by a small comproportionation constant (K_c) value equal to 506. This value is identical to what is found for the dinuclear complex containing ligand **L5** (or dppm) (Table S3 in ESI†) and related compounds such as the pyrimidine BLs.[18] Key factors like the metal–metal distance, the electron density of the LUMO at the coordinating centres,[19a,b] and the nature of the bridge can influence the M–M interaction. With short internuclear metal–metal separations and **L3** as a BL, it has been proposed that electron transfer may be through the direct orbital overlap of the metal d orbitals,[19a,20] and may be the same in

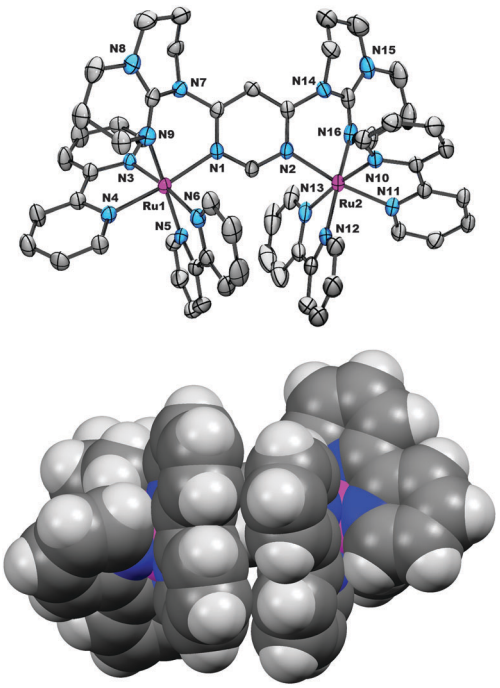

Fig. 1 Perspective views of complex **1**(***meso***), (i) with partial labelling (top), (ii) spacefill model of **1**(***meso***), along the plane of central pyrimidine ring, showing the π–π interaction of the bpy units, favoring the diastereoselective formation of ΛΔ (or ΔΛ)-isomers over ΔΔ or ΛΛ-isomers (bottom). Hydrogen atoms, anions and solvated acetonitrile molecules are not shown for clarity; the ellipsoids correspond to a 50% probability level.

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this study. In the cathodic region, among five quasi-reversible reductions, the first four reductions are bpy based, while the last one is pyrimidine based. Although, theoretically, in dinuclear Ru-complexes, bearing electron deficient diazine BLs (for *e.g.* **L3**, **L5** and **L6**), the first reduction usually involves electron transfer into the BL,[1a,3,21] due to strong σ-donation from the **hpp** units, the BL is now difficult to reduce. A relative comparison of the oxidation potentials among **1**(***meso***) and dinuclear Ru-complexes comprising anionic BLs **L9** and **L10**, suggests that **L1** is the strongest donor.

The electronic absorption spectra of crystallized **L1** and **1**(***meso***) were recorded in dry, degassed acetonitrile (Fig. S6 and Table S4 in ESI†). Five main transitions are observed in the electronic absorption spectra of complex **1**(***meso***), where the first two high-energy transitions at 244 and 289 nm are essentially LC transitions. The transitions at 368 and 470 nm have been ascribed to MLCT, with non-negligible contributions from LC transitions as suggested by TD-DFT calculations of similar compounds.[22] So, these transitions may be assigned to ^{1}(ML)LCT (singlet metal–ligand to ligand charge transfer) transitions.

The spectral progression accompanying the oxidation of **1**(***meso***)$^{4+}$ to **1**(***meso***)$^{5+}$ and **1**(***meso***)$^{6+}$ in 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$–$CH_3CN$ at ambient temperature was monitored (Fig. S8 in ESI†). The lowest energy absorption band at 368 nm decreased in energy and intensity following one-electron oxidation to mixed valence (5+) species on changing the potential from 600 mV to 700 mV and collapsed completely at 800 mV. The fate of the other low energy absorption band at 470 nm is similar, but the decrease is gradual with increasing applied potential. New bands appear at 316 nm and 600 nm (16 700 cm^{-1}), with continued oxidation from 4+ to 5+ to 6+ species, which could be assigned to LC and ligand-to-metal charge transfer (LMCT) transitions, respectively, and the latter is consistent with the π(bpy) → dπ(Ru^{III}) LMCT transition at 17 160 cm^{-1} in $[Ru^{III}(bpy)_3]^{3+}$.[23] A similar LMCT band is also observed in the mixed valence species upon oxidation by an equimolar amount of cerium ammonium nitrate (CAN) (Fig. S7 in ESI†).

In conclusion, a novel bis-bidentate ligand, **dgpm** was attached with two $[Ru(bpy)_2]^{2+}$ units. The predominant diastereoselective formation of the *meso*-isomer, without using the enantiopure [Ru]-precursor or chiral chromatographic separation, is facilitated by three factors (i) a rigid and thermodynamically stable chair conformation of the BL, which offers parallel coordination vectors (ii) stable six-membered chelate ring formation upon complexation and (iii) maximum possible π–π interaction between the bpy units of each Ru-centre. Complex **1**(***meso***) oxidizes at a low positive potential, thus confirming the high σ-donating nature of **dgpm**. This complex also exhibits LMCT absorption upon gradual one-electron oxidation, chemically or spectroelectrochemically, without any intervalence charge transfer (IVCT) band when scanned up to 3000 nm, which suggests that the oxidation states of the two metal sites are distinct and do not readily interconvert. The overall stereoselectivity could be increased by adding steric bulk to the periphery of the bpy units. The ensuing increase in unfavourable steric interactions between the bpy units in the *rac*-isomer would disfavor formation. Alternatively, by increasing the π-surface of the bpy units that are involved in face-to-face π-interactions or changing these bpy units with 1,10-phenanthroline, with higher degree of planar π-interactions, the diastereoselectivity may be increased even more, and these investigations are underway.

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Notes and references

‡ Crystal data for **1**(***meso***): $[C_{58}H_{58}N_{16}Ru_2][4(PF_6)][2(C_2H_3N)]$, M = 1843.33, monoclinic, a = 22.038(2) Å, b = 14.0363(13) Å, c = 25.925(3) Å, α = 90°, β = 112.384(2)°, γ = 90°, V = 7415.2(13) Å^3, T = 150(2) K, space group Cc, Z = 4, 108217 reflections measured, 13 608 independent reflections (R_{int} = 0.0597). The final R_1 value is 0.0382 ($I > 2\sigma(I)$). The final w$R(F^2)$ value is 0.1008 ($I > 2\sigma(I)$). The final R_1 value is 0.0384 (all data). The final w$R(F^2)$ value is 0.1011 (all data); (CCDC 964842).

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