

Stereoselective synthesis of chiral coordination polymers with partial control of the rigid main chain topology

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The condensation polymerization between the appropriate enantiomers of $[\text{Ru}(1,10\text{-phenanthroline-5,6\text{-dione})}_2\text{(bpy)}]^{2+}$ **1** and $[\text{Ru}(1,10\text{-phenanthroline-5,6\text{-diamine})}_2\text{(bpy)}]^{2+}$ **2** in *meta*-cresol gave the homochiral coordination polymers Δ -**3** and Λ -**3** as well as the *meso* polymer, $\Delta\Lambda$ -**3**, which exhibit rigid, ribbon-like structures with different main chain topologies.

Ruthenium(II) polypyridine complexes have been incorporated into oligomers, dendrimers and polymers because they combine considerable thermal and chemical stability with advantageous catalytic, luminescent and redox properties.¹ Recently, through the work of the groups of Lehn² and Tor³ and ourselves,⁴ it has been shown that substitutionally inert, enantiopure derivatives of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{phen})_3]^{2+}$ are robust chiral synthons for the synthesis of oligomeric and dendritic polynuclear assemblies. The use of enantiopure monomers permits stereospecific synthesis of a particular diastereomer (in most cases) and allows detailed study of the properties and topology of individual isomers.⁵

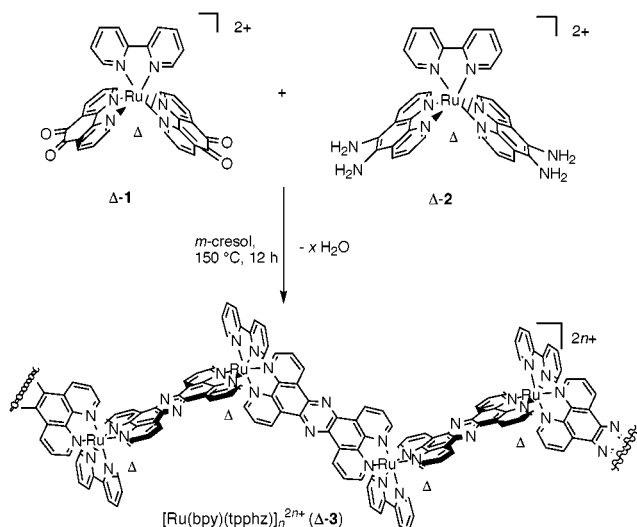
Rehahn and coworkers have shown that coordination polymers of the type $[\text{Ru}(\text{bpy})(\text{tpphz})]_n^{2n+}$ (tpphz = tetrapyrido[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*j*]phenazine) can be synthesized with P_n ranging from 11 to 30.⁶ These polymers have a conformationally rigid main chain and high overall charge, yet remain readily soluble and easily characterized by NMR. Owing to the synthetic approach, however, the absolute stereochemistry at each ruthenium site is random which also significantly affects the main-chain topology.

We have developed a stereospecific synthesis of this polymer as shown in Scheme 1. Chiral monomers Δ -**1** $[\text{PF}_6]_2$ and Λ -**1** $[\text{PF}_6]_2$ are prepared from oxidation of Δ - and Λ - $[\text{Ru}(\text{phen})_2(\text{bpy})]^{2+}[\text{PF}_6]_2$, respectively, and are converted to Δ -**2** $[\text{PF}_6]_2$ and Λ -**2** $[\text{PF}_6]_2$,[†] as described for related compounds in the literature.⁷ By using comonomers, it is possible to prepare

three isomeric condensation polymers:[‡] the enantiomeric homochiral polymers Δ -**3** and Λ -**3** and the alternating Δ - Λ 'copolymer', $\Delta\Lambda$ -**3**, which is a *meso* structure. This, to the best of our knowledge, is the first example of a soluble, chiral coordination polymer in which the chirality is centered at the metal sites.[§]

The absorption and ¹H NMR spectra for all three isomers are indistinguishable and match that observed for polymer assembled from racemic monomers. All three are also luminescent at room temperature in MeCN with an emission maximum (λ_{em} = 675 nm) comparable to related multinuclear compounds.⁸ Rehahn and coworkers had noted that the presence of diastereomers in their 'racemic' polymers apparently did not complicate the NMR spectrum, presumably owing to the large distance (12.7 Å) between stereocenters.⁶ Our results here and with dendritic assemblies bridged by tpphz ligands confirm this hypothesis. End-group analysis of the ¹H NMR spectrum give a minimum P_n of 13–15 for all three isomers of **3** which corresponds to M_n of ca. 12 000–14 000 (as the PF_6^- salt). *meta*-Cresol was the only solvent that gave a reasonable degree of polymerization with common solvents (H_2O , MeCN, EtOH) yielding only oligomers (P_n = 3–5). Similar solvent effects had been reported in the synthesis of organic ladder polymers.⁸

The stereochemistry of the monomers is retained despite the harsh polymerization conditions, as determined by CD. The CD of the polymers, Δ -**3**, Λ -**3** and $\Delta\Lambda$ -**3**, are displayed in Fig. 1 where the $\Delta\epsilon$ is reported on a per mole repeating unit. As found with related tpphz bridged dimers, tetramers, hexamers and decamers,⁴ the chromophores are not significantly electronically coupled and the CD intensity in the visible region is close to that calculated on a per chromophore basis. The enantiomeric Δ -**3** and Λ -**3** exhibit strong Cotton effects and show the expected mirror image relationship. The $\Delta\Lambda$ -**3** (*meso*) polymer is achiral and not expected to show any CD however a small Cotton effect is observed. We have observed a side reaction in our studies of related ruthenium dimers, tetramers, hexamers and decamers⁴ which is most likely responsible for the observed CD. Coordinated phenidone can undergo a two electron–two proton reduction with coordinated phendiamine to yield a coordinated catechol and phendiimine, respectively. The phendiimine is able to further react with coordinated phendiamine to form a tpphz bridge with expulsion of NH_3 . The net



Scheme 1 Reagents and conditions: *meta*-cresol, 150 °C, 12 h, N_2 atm.

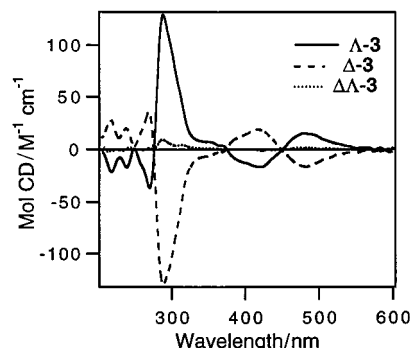


Fig. 1 CD of Δ -**3**, Λ -**3** and $\Delta\Lambda$ (*meso*)-**3** in MeCN.

result here would be the occasional incorporation (*ca.* 7%) of adjacent monomers **2** into the polymer and formation of chain terminating catechol species. Several lines of evidence support this. The sign of the CD found in the *meso* polymer always corresponds to the sign of the **2** monomer used in the reaction. Ammonia, in the form of ammonium ion, is observed to appear in the NMR of model complexes prepared from monomers in a NMR tube experiment in CD₃CN. Oligomers of **3** can be formed upon reaction of **2** with *para*-tetrachloroquinone. It is also possible that the observed CD is due to end-group effects, however, we note that the redox reaction described above would likely enrich the end-groups with the catechol terminated product which would likely give a CD of the opposite sign.

Rehahn and coworkers observed that the topology of the rigid, ribbon-like main chain will be dependent on the absolute configuration of the individual ruthenium centers.⁶ In our system it is possible to control this variable, however, this alone does not permit complete topochemical control of the resulting polymer chain. Four 'locked' torsional isomers are possible for this polymer, two for the *meso* and two for the homochiral structures. Every four-metal unit can exhibit a form of *syn* and *anti* stereochemistry of which the torsional angle (Θ for Ru₁-Ru₂-Ru₃-Ru₄) is dependent on the chirality of the individual metal centers. Newman projections for the *meso* (Fig. 2, left) and homochiral (Fig. 2, right) polymers viewed down the Ru₂-Ru₃ axis (with the intervening tpphz parallel with the horizontal axis) show the orientation of the remaining chelate rings (bpy or bridging tpphz) on the front and back rutheniums. If the polymer chain is oriented such that the link to the front Ru₁ comes in at the b quadrant, we can denote each isomer by which quadrants the entering (Ru₁-Ru₂; dark arrow) and leaving (Ru₃-Ru₄; gray arrow) tpphz ligands are in (quadrants labeled in Fig. 2). For the *meso* polymer, only the *syn*-(b,b)-isomer and the *anti*-(b,d)-isomer are allowed, which have torsional angles (Θ) of 0° and 180°, respectively. The descriptors, *syn* and *anti*, are determined relative to the horizontal tpphz plane. Importantly, the homochiral polymers have different torsional angles for the *syn*-(b,a)-isomer ($\Theta = 72^\circ$) and *anti*-(b,c)-isomer ($\Theta = 108^\circ$) which will dramatically affect the overall main chain configuration. The torsional angles were determined from molecular modeling of related dendrimer systems in conjunction with crystallographic data for Λ -[Ru(phen)₃][PF₆]₂¹⁰ and the dimer $\Delta\Delta$ -[(bpy)₂Ru(tpphz)Ru(bpy)₂][NO₃]₄.¹¹

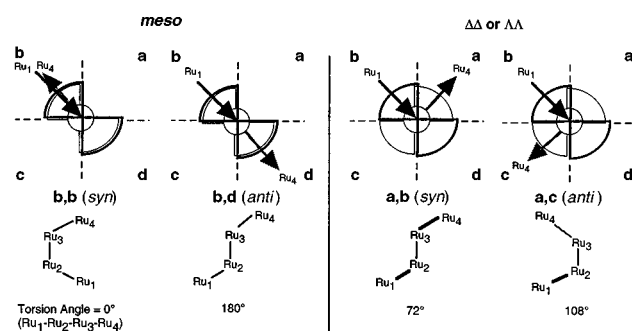


Fig. 2 Newman projections and torsional angle data for the various torsional isomers of the polymer **3**.

From the above considerations, we can predict that the *meso* polymer has a zigzag structure containing only b,b and b,d-isomers (excepting redox related defects as described above) and therefore a structure in which all the Ru atoms are approximately coplanar. On the other hand, the homochiral polymers will form random coil structures owing to the presence of only b,c- and b,a-isomers. Currently, the use of enantiopure monomers only permits partial control of the main chain topology, however steric bulk has been used with some

success to favor the more expanded chain structures (in racemic polymers)^{6c} and may be useful here to further direct the stereochemical outcome of this reaction.

In conclusion, we have developed a new route to coordination polymers containing chiral ruthenium trisdiimine complexes in the main chain backbone which we can use to partially control the topology of the rigid polymer main-chain. Together these results show that it is possible to exert considerable control over both the local and global polymer stereochemistry. Ultimately materials such as these may be useful in a variety of chiral technologies including chiral sensing, catalysis and separations.

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Notes and references

† The enantiomers of **1** and **2** were characterized by ¹H and ¹³C NMR, elemental analyses, UV-VIS and CD spectroscopy. CD (Λ -**1**) [$\lambda_{\text{max}}/\text{nm}$ ($\Delta\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 242 (-39.8), 260 (+45.5), 283 (-39.0), 307 (+128), 328(sh) (+12.4), 350 (-9.05), 411 (-30.6), 461 (+12.5), 507(sh) (+8.23). CD (Λ -**2**) [$\lambda_{\text{max}}/\text{nm}$ ($\Delta\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 236 (-12.7), 259 (+8.48), 268(sh) (+7.20), 283 (-14.3), 307 (+87.2), 350 (-2.29), 418 (-16.2), 483 (+11.5).

‡ Polymers Λ -**3**, Δ -**3** and $\Delta\Delta$ -**3** were characterized by ¹H and ¹³C NMR, elemental analyses, UV-VIS and CD spectroscopy. Typical yield was 65%.

§ A coordination polymer is defined as requiring coordinate bonds to form the polymer main chain.¹¹ Several examples of chiral complexes coordinated to an organic polymer chain or metallation of a chiral main-chain are known.^{3a,13} Non-racemic helical coil oligomers and polymers have also been reported.¹⁴

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