Stereoisomerically controlled inorganic architectures: synthesis of enantio- and diastereo-merically pure ruthenium–palladium molecular rods from enantiopure building blocks

Kenneth Wärnmark, Jim A. Thomas, Olga Heyke and Jean-Marie Lehn*

Laboratoire de Chimie Supramoléculaire, Institut Le Bel, Université Louis Pasteur, 4 rue Blaise Pascal, F-67000 Strasbourg, France

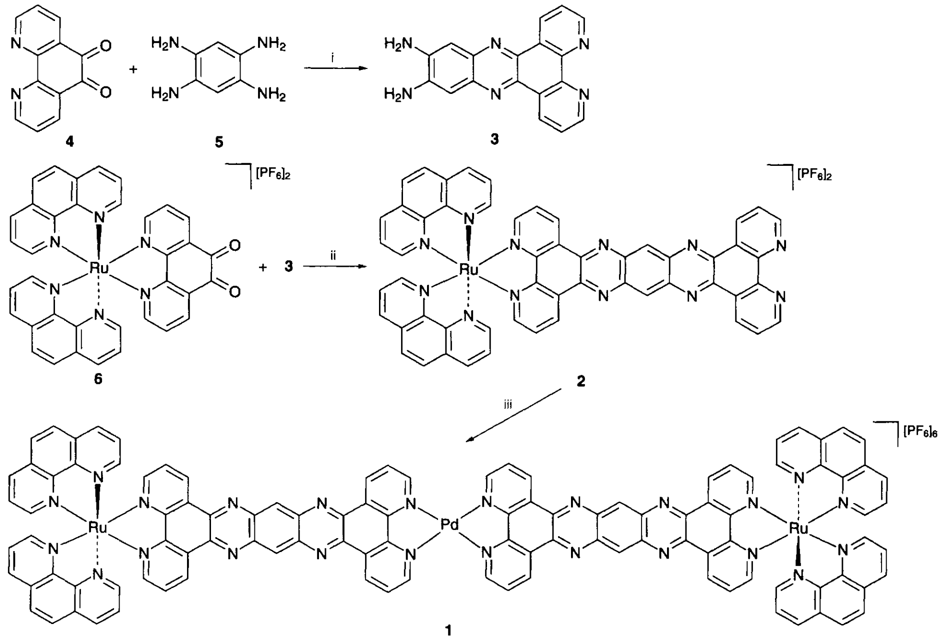
The construction of nanometre scale $\mathrm{Ru^{II}Pd^{II}Ru^{II}}$ π-conjugated molecular rods, Λ,Λ-1 and Δ,Δ-1, from enantiomerically pure building blocks, provides a method for obtaining enantio- and diastereo-merically pure $\mathrm{Ru^{II}}$-based molecular architectures.

Rigid π-conjugated molecular rods not only present a synthetic challenge and an appealing architecture, but they also constitute components for the construction of functional nanometre scale devices, such as molecular wires of photonic and electronic nature. Their extension into two or three dimensions makes them suitable candidates for the construction of photochemical antennas. The interest in molecular wires has resulted in a variety of approaches to their fabrication.[1–3]

Linear architectures, 'molecular wires', containing photoactive and/or redoxactive metal centres may present a range of interesting features based on energy and electron transfer processes involving communication along and between the two ends of the wires. Such is the case for the actively studied ruthenium(II)–diimine centres. However, structures containing more than one octahedral metal ion coordinated to three bidentate ligands give rise to diastereoisomers, as each metal centre will have Λ- or Δ-configuration. This situation is commonly encountered with ruthenium(II)–2,2-bipyridyl or –1,10-phenanthroline based polynuclear complexes, molecular wires, and photochemical antennae.[2–4] It is of interest to obtain diastereomerically pure (dp) compounds, both for structural and functional reasons. To this end, two main strategies can be envisaged: (*i*) separation of the diastereoisomeric mixture generated upon *in situ* formation of the metal centres,[5] or (*ii*) the use of enantiomerically pure (ep) building blocks containing the desired metal centre. The latter strategy has been successfully employed in the synthesis of ep and dp bimetallic ligand-bridged ruthenium complexes using, for example, ep $\mathrm{[Ru(bpy)_2(py)_2]^{2+}}$[6] and $\mathrm{[Ru(phen)_2(CO)_2]^{2+}}$ (bpy = 2,2′-bipyridine, py = pyridine, phen = 1,10-phenanthroline).[7]

The condensation of aromatic *o*-diamines and *o*-quinones provides a convenient entry to aromatic ligands suitable for ruthenium coordination.[8,9] Extended ligands of this type, with two available coordinating sites, would be promising building blocks for extended π-conjugated multi-metal molecular rods or wires.

We here report the application of the appealing synthon strategy mentioned above for the construction of ep and dp $\mathrm{Ru^{II}}$-based molecular architectures by using ep building blocks formed by the condensation of aromatic *o*-diamines and *o*-quinones. We have thus synthesized ep and dp pure π-conjugated molecular rods $\mathrm{[Pd\{LRu(phen)_2\}_2][PF_6]_6}$ {L = 9,11,20,22-tetraazatetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-1:2‴,3‴-*n*]-pentacene} Λ,Λ-1 and Δ,Δ-1 from two ep building blocks $\mathrm{[Ru(phen)_2][PF_6]_2}$ Λ-2 and Δ-2, respectively (Scheme 1), connected through a $\mathrm{Pd^{II}}$ linkage.† The rods Λ,Λ-1 and Δ,Δ-1



Scheme 1 *Reagents and conditions*: i, EtOH, 78 °C, 5 min; ii, deaerated MeCN–thf–HOAc (1 : 1 : 1), 90 °C, 5 h; iii, $\mathrm{[(Pd(MeCN)_4[BF_4]_2}$, MeCN, ambient temperature then $\mathrm{NH_4PF_6}$

each consist of two enantiomerically pure octahedral Ru^{II} centres located at a distance of 35 Å‡ and separated by a PdL_2 unit containing a square-planar Pd^{II} site (Fig. 1).§

The synthetic sequence leading to Λ,Λ-**1** and Δ,Δ-**1** is shown in Scheme 1.¶ Diamine **3** was obtained from 1,10-phenanthroline-5,6-dione **4**[8e] and freshly prepared 1,2,4,5-tetraaminobenzene **5**|| in 79% yield after purification on a neutral Al_2O_3 column [MeOH–DMF(4 : 1)]. The key ep building blocks Λ-**2** and Δ-**2** were constructed by condensation of 11,12-diaminodipyrido[3,2-*a*:2′,3′-*c*]phenazine (dadppz) **3** and ep [Ru(phen)$_2$(phen-5,6-dione)][PF_6]$_2$ Λ-**6** and Λ-**6**,[8e] respectively [40% yield after purification on a Bio-Beads SX-1 size-exclusion column, MeCN–toluene (1 : 1)]. The compounds Λ-**2** and Δ-**2** contain, in addition to the metal centre, a free coordinating site, making them suitable building blocks for stepwise construction of inorganic molecular architectures. The molecular rods Λ,Λ-**1** and Δ,Δ-**1** were synthesized by stirring 2 equiv. of Λ-**2** and Δ-**2**, respectively, and 1 equiv. of [Pd(MeCN)$_4$][BF_4]$_2$ in MeCN at ambient temperature. They were isolated in 55–65% yield by treatment with NH_4PF_6 and repeated precipitation with MeCN–Et_2O and $MeNO_2$–Et_2O. In a MeCN solution of 2 equiv. of **2** and 1 equiv. of Pd^{II} only the dimer **1** is formed, giving a well resolved ^1H NMR spectrum.** The circular dichroism spectra of Λ,Λ-**1** and Δ,Δ-**1** as well as of Λ-**2** and Δ-**2** (Fig. 2) are almost perfect mirror images with the CD intensities of **1** twice that of **2**. This means most probably that Λ,Λ-**1** and Δ,Δ-**1** are ep as well as dp and that there is no communication between the centres in the $Ru^{II}Ru^{II}$ state.

The ep and dp compounds Λ,Λ-**1** and Δ,Δ-**1** are promising candidates for molecular wires due to their nanometer scale dimension, rigid linear structure and extended π-system possessing redox-active Ru^{II} centres. The present methodology may be extended to more elaborated molecular architectures opening new possibilities for the design of stereochemically well defined inorganic superstructures.

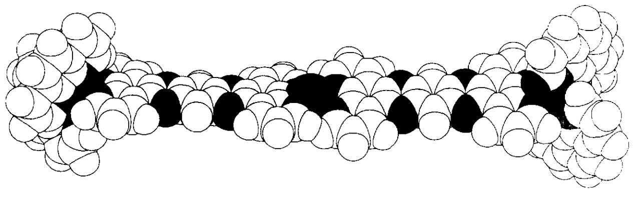


Fig. 1 Space-filling representation of the inorganic architecture **1** based on the crystal structure geometries for [Ru(bipy)$_3$]$^{2+}$ and [Pd(phen)$_2$]$^{2+}$ centres

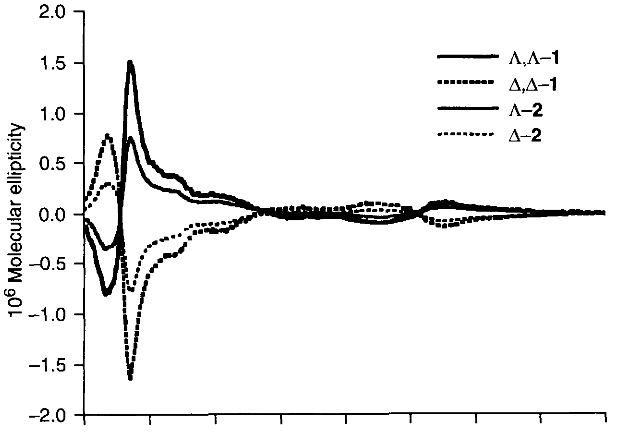


Fig. 2 Circular dichroism spectra of Λ,Λ-**1**, Δ,Δ-**1**, Δ-**2** and Δ-**2** in MeCN

We thank Nèija Boumédiène, Laboratoire de Spectrométrie de Masse Bio-Organique for electrospray-MS measurements as well as the Swedish Natural Science Research Council and the Wenner-Gren Center Foundation for Scientific Research (K. W.), the Royal Society European Exchange Programme (J. A. T.) and the Fonds des Verbandes der Chemichen Industrie e.V. (O. H.) for postdoctoral fellowships.

Footnotes

† Molecular rods have been constructed by coordination of tetrahedral Cu^I or Zn^{II} to phenanthroline appended porphyrins.[10]

‡ From an MM2 calculation using standard parameters and frozen metal centres.

§ The PdL_2 unit is believed to be slightly twisted from planarity in analogy with a X-ray structure analysis of [(Pd(phen)$_2$][PF_6]$_2$.[11]

¶ Compounds **1** and **2** were characterised by ^1H NMR spectroscopy, elemental analysis, UV–VIS spectroscopy, and cyclic voltammetry. In addition **1** was characterised by electrospray MS {major peaks: *m/z* 333.6 [**1** − 6PF_6]$^{6+}$ ands 474.0 [**2** − 2PF_6]$^{2+}$} and **2** by FABMS {*m/z* 1093.1 [**2** − PF_6]$^+$ and 948.2 [**2** − 2PF_6 + e]$^+$}. Compound **3** was characterised by ^1H NMR spectroscopy and FABMS.

|| Compound **5** was prepared by reducing 1,3-diamino-4,6-dinitrobenzene[12] with phenylhydrazine (120 °C, 1 h, then 160 °C, 4 h).

** ^1H NMR titrations shows that peaks associated with L of **1** broaden upon addition of an excess of **2**. Thus, extensive ligand exchange takes place when an excess of **2** is present, as expected for an associative exchange mechanism.[13] Furthermore, within the detection limit of ^1H NMR, all of **2** is coordinated to Pd^{II} at 1 equiv. of **2**, as well as at 2 equiv. of **2**, thus forming strong 1 : 1 and 2 : 1 complexes (**1**), respectively.

References

1 J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995, pp. 89–138.
2 M. D. Ward, *Chem. Soc. Rev.*, 1995, **24**, 121.
3 P. J. Steel, *Coord. Chem. Rev.*, 1990, **106**, 227.
4 G. Denti, S. Serroni, S. Campagna, A. Juris, M. Ciano and V. Balzani, in *Perspective in Coordination Chemistry*, ed. A. F. Williams, VCH, VHCA, Basel, 1992, pp. 153–164; A. J. Downard, G. E. Honey, L. F. Phillips and P. J. Steel, *Inorg. Chem.*, 1991, **30**, 2259; R. Sahai, D. A. Baucom and D. P. Rillema, *Inorg. Chem.*, 1986, **25**, 3843; G. F. Strouse, J. R. Schoonover, R. Duesing, S. Boyde, W. E. Jones and T. J. Meyer, *Inorg. Chem.*, 1995, **34**, 473; J. R. Shaw, R. T. Webb and R. S. Schmehl, *J. Am. Chem. Soc.*, 1990, **112**, 1117; A. C. Benniston, V. Goulle, A. Harriman, J.-M. Lehn and B. Marczinke, *J. Phys. Chem.*, 1994, **98**, 7798; S. Serroni and G. Denti, *Inorg. Chem.*, 1992, **31**, 4251.
5 D. A. Reitsma and F. R. Keene, *J. Chem. Soc., Dalton Trans.*, 1993, 2859.
6 X. Hua and A. Von Zelewsky, *Inorg. Chem.*, 1991, **30**, 3796; 1995, **34**, 5791.
7 T. J. Rutherford, M. G. Quagliotto and F. R. Keene, *Inorg. Chem.*, 1995, **34**, 3857.
8 (*a*) J.-C. Chambron, J.-P. Sauvage, E. Amouyal and P. Koffi, *Nouv. J. Chim.*, 1985, **9**, 527; (*b*) A. E. Friedman, J.-C. Chambron, J.-P. Sauvage, N. J. Turro and J. K. Barton, *J. Am. Chem. Soc.*, 1990, **112**, 4960; (*c*) R. M. Hartshorn and J. K. Barton, *J. Am. Chem. Soc.*, 1992, **114**, 5919; (*d*) N. Gupta, N., Grover, G. A. Neyhart, W. Liang, P. Singh and H. H. Thorp, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1048; (*e*) C. Hiort, P. Lincoln and B. Nordén, *J. Am. Chem. Soc.*, 1993, **115**, 3488.
9 J. Bolger, A. Gourdon, E. Ishow and J.-P. Launay, *J. Chem. Soc., Chem. Commun.*, 1995, 1799.
10 M. J. Crossley, P. L. Burn, S. J. Langford and J. K. Prashar, *J. Chem. Soc., Chem. Commun.*, 1995, 1921.
11 S. Geremia, L. Randaccio, G. Mestroni and B. Milani, *J. Chem. Soc., Dalton Trans.*, 1992, 2117.
12 R. Nietzki and A. Schedler, *Chem. Ber.*, 1897, **30**, 1666.
13 P. M. Maitlis, P. Espinet and M. J. H. Russel, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1982, vol. 6, p. 235.

Received, 6th December 1995; Com. 5/07944F