Stereoselective synthesis of linear bipyridyl–phenylene based ruthenium rods from enantiopure building blocks

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Extended stereochemically pure C_2-symmetric diruthenium rods, Λ,Λ-1, Δ,Δ-1, Λ,Λ-2 and Δ,Δ-2, have been synthesized from enantiomerically pure building blocks.

The synthesis of nanosize-components for potential applications in electronic or optical systems is a central theme in current material science.[1] The design of molecular counterparts to macroscopic electronic components has largely focussed on molecular wires.[2]

In a molecular approach to microscopic semiconductor technology, we are interested in finding molecular counterparts to doped material. Conjugated π-systems such as rods consisting of linear phenylene chains could function as molecular wires. In principle, electronic conductivity along the axis of the rods in the form of photo- or electro-chemically generated positive hole doping may be achieved by incorporation of photo- and redox-active metal centres, such as Ru^{II}, into the periphery of the rods. The ruthenium doping would be expected to change the conductivity and optical properties of the phenylene chain and add signal reading abilities to it.

Directly connected or phenylene bridged 2,2′-bipyridyl (bpy) units may be regarded as phenylene chains that contain sites for metal coordination. The 4′,4″-linkage between two 2,2′-bipyridyl (bpy) units in [{(bpy)$_2$Ru}$_2$(LL)][PF$_6$]$_4$ (LL = 2,2′ : 4,′4″ : 2″,2‴-quaterpyridine) gives the complex a transoid overall conformation and mediates a weak metal-to-metal interaction.[3] However, to construct a linear molecular wire containing ruthenium centres, the bpy units must be linked in the 5-position either directly or by a linker such as phenylene. In addition, the electronic transitions that are the most intense in the bpy and phen (phen = 1,10-phenanthroline) rings take place along the longer axis of these ligands making linkages of bpy or phen units in the 5,5′- and 3,8-positions, respectively, attractive.[4]

We herein present the synthesis of the shortest constituents of a series of linear π-conjugated phenylene type ruthenium rods **1** and **2** (Fig. 1) in which bpy units are linked directly, dmqtby‡ (**3**), or *via* a *para*-phenylene bridge, bmbpyb‡ (**4**), to each other in the 5-position.§

The incorporation of more than one [(phen)$_2$Ru]$^{2+}$ unit into the molecular wire of bpy-type will give rise to diastereoisomers since each unit may have Λ- or Δ-configuration at the ruthenium centre. Enantiomerically pure (ep) and diastereomerically pure (dp) syntheses of various polypyridine ruthenium complexes using the appealing concept of ep building blocks have been successfully pursued by several groups.[5]

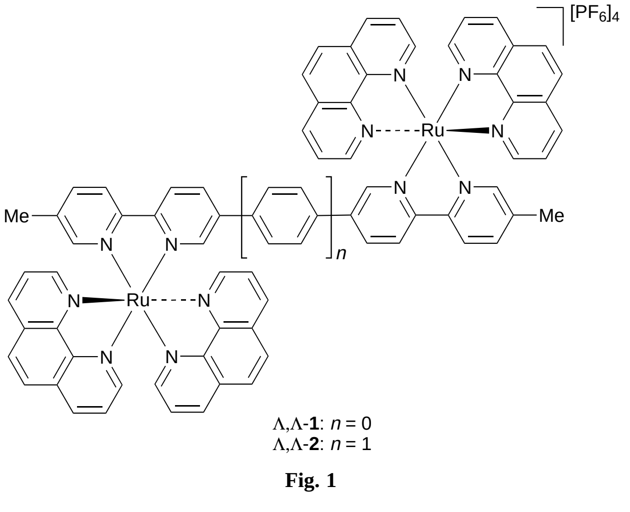
Ligands **3** and **4**, respectively, were reacted with 2.2 equiv. of ep Λ-**5** and Δ-**5**,¶ respectively, giving Λ,Λ-**1**, Δ,Δ-**1**, Λ,Λ-**2** and Δ,Δ-**2**, respectively [58% yield of **1** and 49% yield of **2** after purification on a Bio-Beads S-X1 (Bio-Rad laboratories) size-exclusion column, MeCN–toluene (1 : 1)].‖ Ligands **3** and **4**, respectively, were also reacted with 2.2 equiv. of racemic **5**, giving the mixture of all stereoisomers Λ,Λ-**1**, Δ,Δ-**1**, Δ,Λ-**1** (mix-**1**) and Λ,Λ-**2**, Δ,Δ-**2**, Δ,Λ-**2** (mix-**2**), respectively.

The ligand **3** and the phenylene-bridged homologue **4** were synthesized by a Pd(PPh$_3$)$_4$ catalysed Stille cross-coupling protocol[6] between respectively, the dibrominated bridging units 6,6′-dibromo-3,3′-bipyridyl and 1,4-bis[5-(2-bromopyridyl)]benzene and two equiv. each of 2-trimethylstannyl-5-methylpyridine.

The ^{1}H NMR spectrum of Λ,Λ-**1** (and Δ,Δ-**1**) is much less complicated than the ^{1}H NMR spectrum of mix-**1**. Obviously, the short distance between the asymmetric ruthenium centres in **1** leads to large enough differences in ^{1}H NMR shifts for the diastereoisomers Λ,Λ-**1** (Δ,Δ-**1**) and Δ,Λ-**1** to be observable. For **2** in contrast, where the asymmetric ruthenium centres are further apart (by a *para*-phenylene unit), the ^{1}H NMR spectrum of Λ,Λ-**2** (and Δ,Δ-**2**) is identical to the ^{1}H NMR spectrum of mix-**2**.

That Λ,Λ-**1**, Δ,Δ-**1**, Λ,Λ-**2** and Δ,Δ-**2** are essentially ep and dp as demonstrated by the fact that in the circular dichroism spectra, Λ,Λ-**1** and Δ,Δ-**1** as well as Λ,Λ-**2** and Δ,Δ-**2**, respectively, are almost perfect mirror images (Fig. 2). For Λ,Λ-**1** and Δ,Δ-**1** the diastereomeric excess could be determined to $>98.5\%$ by ^{1}H NMR spectroscopy because of the differences in ^{1}H NMR chemical shifts between Λ,Λ-**1** (Δ,Δ-**1**) and mix-**1**.

One measure of the degree of electronic communication between metal centres in symmetrical dimers is the separation of the oxidation potential between the two centres. The results from cyclic voltammetry (CV) of the linear complexes **1** show only one reversible oxidative wave at 1.31 V *vs.* SCE in MeCN, indicating no communication between the ruthenium centres.** Furthermore, one reversible reductive wave at −1.11 V *vs.* SCE in DMF and two reductive cathodic waves at −1.32 and −1.49 V appeared (the corresponding anodic waves could not be detected because of extensive adsorption). The first reductive wave is assigned to ligand **3** and the two others most likely to the phenanthroline ligand in analogy with the assignments of the



Λ,Λ-**1**: *n* = 0
Λ,Λ-**2**: *n* = 1

Fig. 1

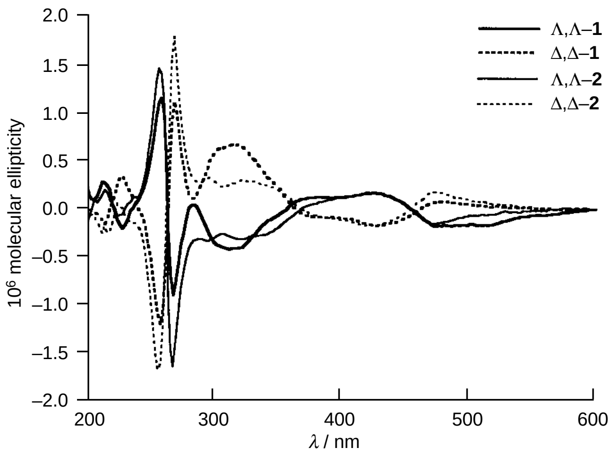


Fig. 2 Circular dichroism spectra of Λ,Λ-**1**, Δ,Δ-**1**, Λ,Λ-**2** and Δ,Δ-**2** in MeCN

CV of the analogue $[\{(bpy)_2Ru\}_2(LL)][PF_6]_4$, bridged in the 4′,4″-position (reversible reductive waves at −1.10, −1.44, −1.57 V *vs*. SCE in MeCN).[3] The CV of the phenylene-bridged linear complexes **2** shows also only one reversible 2e oxidative wave at 1.29 V *vs*. SCE in MeCN, one reversible reductive wave at −1.19 and one reductive cathodic wave at −1.36 V *vs*. SCE in DMF (a third reductive wave could not be observed). The reductive waves in complex **2** are assigned in analogy with complex **1** to ligands **4** and phen, respectively.

The complexes **1** and **2** have almost identical electronic spectra in MeCN. Only one flat MLCT band could be detected [λ = 450 (ε = 2.54 × 10^4), 448 nm (2.98 × 10^4 dm^3 mol^{-1} cm^{-1}), respectively] demonstrating that the Ru–dmqtpy and Ru–bmbpyb transitions are of similar energy as for Ru–phen and being almost identical to the monoruthenium complex $[Ru(bpy)_3]^{2+}$ [λ = 452 nm (ε = 1.45 × 10^4 dm^3 mol^{-1} cm^{-1})].[7] Thus the red-shift for the Ru–(bridging ligand) MLCT band, observed in the analogue $[\{(bpy)_2Ru\}_2(LL)][PF_6]_4$ and indicating a weak metal–metal interaction,[3] seems to be absent in complexes **1** and **2**. The π–π* transitions for compounds **1** [λ = 265 (ε = 1.52 × 10^5), 224 nm, (1.13 × 10^5 dm^3 mol^{-1} cm^{-1})] and **2** [λ = 263 (ε = 1.69 × 10^5), 223 nm, (1.22 × 10^5 dm^3 mol^{-1} cm^{-1})] are located almost at the same wavelength as for $[Ru(phen)_3]^{2+}$ [λ = 263 (ε = 1.13 × 10^5), 224 nm (8.03 × 10^4 dm^3 mol^{-1} cm^{-1})].[8] The values of the absorption coefficients indicate that these π–π* transitions in complexes **1** and **2** are phenanthroline based. More difficult is the assignment of Ru–(bridging ligand) π–π* transitions.

The excitations of compounds **1** and **2** in the MLCT band resulted in intense emission at 639 and 613 nm, respectively, being somewhat red-shifted compared to $[\{(bpy)_2Ru\}_2(LL)][PF_6]_4$. Excitation in the phenanthroline π–π* bands leads to an intense emission at 735 and 417 nm for each of the two complexes **1** and **2**.

In conclusion stereoisomerically pure linear bipyridyl–phenylene based ruthenium rods, **1** and **2**, have been synthesized from ep building blocks. By the methods used in this work no electronic communication between the two halves of the rods could be detected. Oxidation or reduction at a given centre may however be expected to delocalize over the whole system and provides means for p and n doping of such types of inorganic molecular rods.

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Notes and References

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‡ dmqtpy = 5,5‴-dimethyl-2,2′ : 5′,5″ : 2″,2‴-quaterpyridine and bmbpyb = 1,4-bis[5-(5′-methyl)-2,2′-bipyridyl)]benzene.

§ Linear oligoruthenium rods have also been constructed with ethynyl linkers between phen or bpy.[5*h*,9]

¶ Prepared by several resolutions following a literature procedure;[10] ep **5** reacts with bidentate ligands with retention of configuration.[5*a*,*b*]

‖ Complexes **1** and **2** were characterised by ^{1}H NMR spectroscopy, elemental analysis and electrospray MS {**1**: *m/z* 315.9 [**1** − $4PF_6$]$^{4+}$, 469.5 [**1** − $3PF_6$]$^{3+}$, 776.4 [**1** − $2PF_6$]$^{2+}$ and 1696.1 [**1** − PF_6]$^{+}$ and **2**: *m/z* 333.9 [**2** − $4PF_6$]$^{4+}$, 493.9 [**2** − $3PF_6$]$^{3+}$ and 813.7 [**2** − $2PF_6$]$^{2+}$}.

** Cyclic voltammetry was performed with 0.1 M Bu_4PF_6 as electrolyte and Ag/AgCl as reference electrode. The Ag/AgCl electrode is −50 mV *vs*. SCE.

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