

Stereochemically-Defined Supramolecular Architectures: Diastereomerically-Pure Multi-Ru^{II} Complexes

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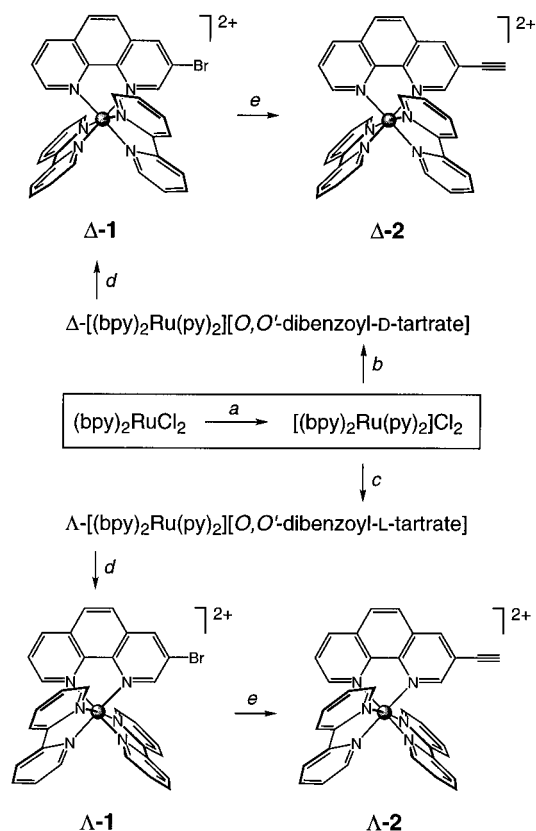
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Inspired by the structural and functional sophistication of photosynthetic light-harvesting complexes, chemists have been attempting to fabricate devices capable of performing light-induced functions.¹ Multimetallic assemblies, many of them containing Ru^{II} polypyridyl complexes, have become an integral part of such systems due to their chemical stability, redox properties, and favorable photophysical characteristics.² These multinuclear Ru^{II} complexes have been predominantly constructed by a stepwise synthesis of the multitopic ligands followed by metal complexation.^{2,3} While the natural photobiological assemblies have no stereochemical ambiguity, the synthetic systems are formed as diastereomeric mixtures. The functions of these stereochemically heterogeneous systems are not well defined, and their characterization is limited.⁴ Having control over the absolute stereochemistry at each metal center is therefore of ultimate importance for the design and synthesis of functional supramolecular architectures.

Some effort has been devoted to solving the stereochemical problems in the construction of multimetallic complexes.⁵ In particular, stereospecific complexations of multitopic ligands with enantiomerically-pure complexes containing labile ligands have been employed.^{6,7} These approaches do not overcome a key difficulty (*i.e.*, the need to selectively coordinate a metal center into one of a few available binding sites of a multitopic ligand). We report a novel and versatile approach for the efficient synthesis of diastereomerically-pure multi-Ru^{II} arrays using enantiomerically-pure chiral coordination complexes as building blocks. Palladium-mediated cross-coupling reactions between bromo- and ethynyl-functionalized octahedral Ru^{II} complexes afford di- and trinuclear complexes with predetermined chirality at the metal centers. To the best of our

Scheme 1^{a,b}



^a Reagents: (a) pyridine, MeOH, H₂O, reflux; (b) disodium (+)-*O,O'*-dibenzoyl-D-tartrate; (c) disodium (–)-*O,O'*-dibenzoyl-L-tartrate; (d) (i) 3-bromo-1,10-phenanthroline, ethylene glycol, 120 °C, (ii) NH₄PF₆, H₂O; 87% yield; (e) (i) TMS–C≡CH, (dppf)PdCl₂, CuI, DMF, Et₃N, 96% yield, (ii) K₂CO₃, MeOH, 82% yield. ^b All complexes were isolated as their PF₆[–] salts.

knowledge, this is the first *controlled synthesis* of stereochemically-defined multinuclear Ru^{II} complexes.

The enantiomerically-pure Ru^{II}-containing building blocks were prepared as shown in Scheme 1. The commercially available (bpy)₂RuCl₂ was treated with pyridine to give the racemic complex [(bpy)₂Ru(py)₂]Cl₂. Addition of disodium (–)-*O,O'*-dibenzoyl-L-tartrate led to selective crystallization of Δ-[(bpy)₂Ru(py)₂][(-)-*O,O'*-dibenzoyl-L-tartrate]·12H₂O.^{7,8} Treating this chiral precursor with 3-bromo-1,10-phenanthroline⁹ followed by exchanging the tartrate counterions with PF₆[–] gave Δ-[(bpy)₂Ru(3-bromo-1,10-phenanthroline)]²⁺(PF₆[–])₂ (Δ-1). The enantiomeric Δ-[(bpy)₂Ru(3-bromo-1,10-phenanthroline)]²⁺(PF₆[–])₂ (Δ-1) was obtained by replacing the dibenzoyl-L-tartrate with dibenzoyl-D-tartrate. The CD spectra of the enantiomerically-pure complexes exhibit typical excitonic interactions of the π–π* transitions¹⁰ and the expected two Cotton effects of the metal-to-ligand charge-transfer bands in the visible region (Figure 1).¹¹ Cross-coupling reactions of building blocks Δ-1 and Δ-1 with (trimethylsilyl)acetylene followed by desilylation proceeded in high yields to afford the enantiomerically-pure 3-ethynyl-1,10-phenanthroline complexes Δ-2 and Δ-2, respectively (Scheme 1).^{12,13}

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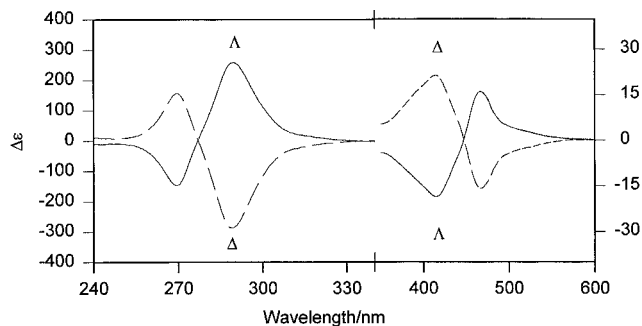
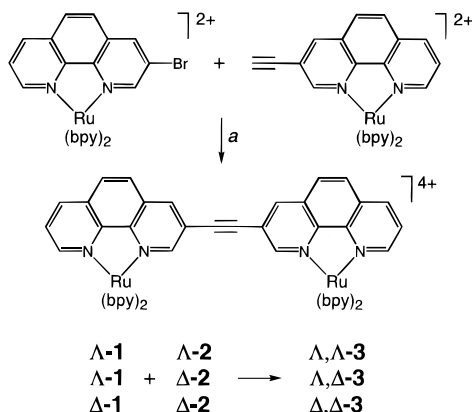


Figure 1. CD spectra of Λ -1 (solid line) and Δ -1 (dashed line) in acetonitrile.

Scheme 2^a



^a Reagents: (a) $(\text{Ph}_3\text{P})_2\text{PdCl}_2$, CuI, DMF, Et_3N . Typical yields: 70–85%.

Palladium-mediated cross-coupling reactions between the enantiomerically-pure bromo-containing complexes **1** and the ethynyl-containing complexes **2** gave the diastereomerically-pure bimetallic complexes Λ,Λ -**3**, Δ,Δ -**3**, and Λ,Δ -**3** in good yields (Scheme 2).¹² Comparing the CD spectra of the dinuclear Ru^{II} complexes Λ,Λ -**3** and Δ,Δ -**3** to the CD spectra of their corresponding mononuclear precursors confirmed the absolute configuration at the metal centers (Figures 1 and 2). As expected, no CD spectrum is observed for the meso dinuclear complex Λ,Δ -**3**.¹⁴

Complexes of higher nuclearity can be made from multifunctional building blocks. The enantiomerically-pure difunctional Λ - $[(\text{bpy})_2\text{Ru}(3,8\text{-dibromo-1,10-phenanthroline})]^{2+}(\text{PF}_6^-)_2$ **Λ-4** has been prepared from Λ - $[(\text{bpy})_2\text{Ru}(\text{py})_2][(-)\text{-}O,O'$ -dibenzoyl-L-tartrate] $\cdot 12\text{H}_2\text{O}$ and 3,8-dibromo-1,10-phenanthroline⁹ following the same procedure utilized for the monofunctional complexes. Cross-coupling with (trimethylsilyl)acetylene followed by desilylation gave the diethynyl derivative Λ - $[(\text{bpy})_2\text{Ru}(3,8\text{-diethynyl-1,10-phenanthroline})]^{2+}(\text{PF}_6^-)_2$ **Λ-5**. Cross-coupling reactions of **Λ-5** and 2 equiv of **Λ-1** or **Δ-1** afforded the diastereomerically-pure trinuclear complexes Λ,Λ,Λ -**6** and Δ,Δ,Δ -**6**, respectively (Scheme 3).¹²

In conclusion, we have demonstrated that monofunctionalized as well as difunctionalized coordination Ru^{II} complexes can be

(14) Residual optical activity (5–10%) is sometimes observed due to the presence of the butadiyne-linked binuclear complex. This byproduct results from the oxidative-dimerization of the enantiomerically-pure ethynyl-containing component and can be removed by chromatography.

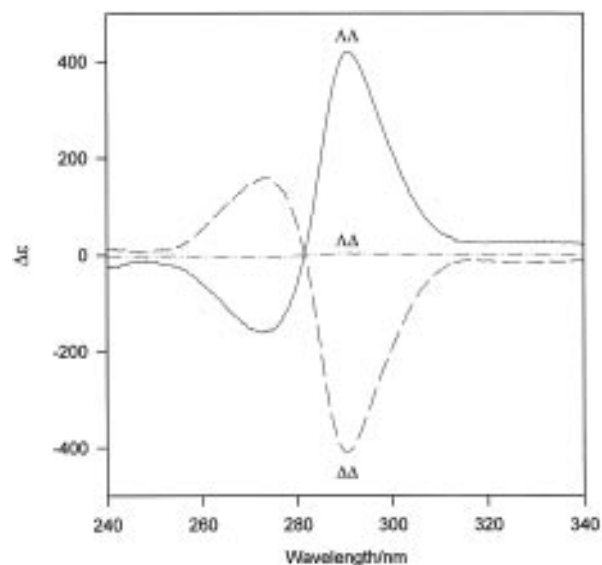
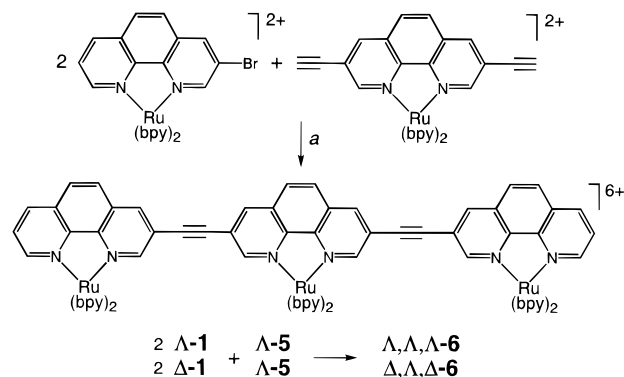


Figure 2. CD spectra of Λ,Λ -**3** (solid line), Δ,Δ -**3** (dashed line) and Λ,Δ -**3** (dash-dot line) in acetonitrile.

Scheme 3^a



^a Reagents: (a) $(\text{Ph}_3\text{P})_2\text{PdCl}_2$, CuI, DMF, Et_3N . Typical yields: 60–80%.

used as enantiomerically-pure building blocks and cross-coupled to one another to give conjugated multi- Ru^{II} complexes. The ease of preparation of these building blocks together with the availability of various cross-coupling reactions makes this strategy extremely powerful. Our simple and modular methodology opens new routes for the fabrication of multimetallic supramolecular assemblies with unique architectures and predetermined absolute configurations of the metal centers.

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Supporting Information Available: Complete experimental procedures as well as spectroscopic (^1H NMR, IR, MS, UV-vis, CD) and cyclic voltammetry data for all new compounds (6 pages). See any current masthead page for ordering and Internet access information.