Two complete stereochemical sets of dinuclear ruthenium complexes

Oma Morgan, Sihe Wang, Sung-A Bae, Robert J. Morgan, A. David Baker, Thomas C. Strekas and Robert Engel *,†

Department of Chemistry and Biochemistry, Queens College of The City University of New York, 65-30 Kissena Boulevard, Flushing, NY 11367, USA

Complete stereochemical sets of $Ru^{II}_2(bpy)_4$ (bpy = 2,2′-bipyridyl) complexes incorporating the bridging ligands 2,3-bis(2-pyridyl)pyrazine and pyrazino[2,3-*f*][4,7]phenanthroline have been prepared and characterised.

The preparation of ionic dendrimers incorporating multiple transition-metal sites has been a topic of interest of late.[1] Numerous multinuclear ruthenium(II) complexes bearing both bidentate ligands at each metal site as well as multidentate bridging ligands have been prepared; in most instances these syntheses have generated mixtures of the possible stereoisomers.[2] Stereoisomeric mixtures of the present dinuclear ruthenium(II) complexes have been reported.[2a,c]

The preparation of stereochemically pure enantiomers of the dinuclear ruthenium(II) complexes generated from the $Ru^{II}(phen)_2$ (phen = phenanthroline) building block has been reported using the bridging ligands 2,5-bis(2-pyridyl)pyrazine and 2,2′-bipyrimidine.[3] More recently, MacDonnell and Bodige[4] have reported the preparation of the complete set of stereoisomers (ΔΔ, ΔΛ, ΛΛ) based on a pair of $Ru^{II}(phen)_2$ building blocks with the bridging ligand tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2″,3″-*j*]phenazine (tpphz), and Tzalis and Tor[5] have prepared 'string-like' multiruthenium species in diastereoisomerically pure form. We herein report the first preparation of two complete sets of stereoisomers using as the bridging ligands 2,3-bis(2-pyridyl)pyrazine (dpp) and pyrazino-[2,3-*f*][4,7]phenanthroline (ppz) with $Ru^{II}(bpy)_2$ (bpy = 2,2′-bipyridine) as the metal building block. These stereochemically pure species will serve as entry points for the generation of stereochemically pure multiruthenium complexes.

Results and Discussion

The Λ and Δ isomers of $[Ru^{II}(bpy)_2(py)_2]Cl_2$ (py = pyridine) were prepared as building blocks according to the procedure of Hua and Lappin[6] by the addition of an aqueous solution of *O*,*O*′-dibenzoyl (*R*,*R*)-tartrate to racemic $[Ru^{II}(bpy)_2(py)_2]Cl_2$ in water. Upon slow evaporation, red crystals of the pure (Δ*RR*) salt Δ**1** were formed and collected by filtration. The diastereoisomeric (Λ*RR*) salt could be isolated in a relatively impure state by evaporating the mother-liquor to dryness; the pure (Λ*SS*) salt Λ**1** could be prepared by a corresponding precipitation technique using *O*,*O*′-dibenzoyl (*S*,*S*)-tartrate. Conversion of the appropriate diastereoisomeric salts into the corresponding enantiomeric Δ**1** and Λ**1** dichloride salt forms was accomplished by dissolution in acetone and precipitation with lithium chloride. As anticipated, these enantiomers exhibited equivalent, but oppositely sensed, circular dichroism (CD) curves.

Separate reaction of each of the enantiomeric $[Ru^{II}(bpy)_2(py)_2]Cl_2$ salts in equimolar amounts in ethylene glycol–water with each of the bridging ligands dpp and ppz provided the anticipated sets of enantiomers, Δ-$[Ru^{II}(bpy)_2(dpp)]Cl_2$ Δ**2** and Λ-$[Ru^{II}(bpy)_2(dpp)]Cl_2$ Λ**2** and Δ-$[Ru^{II}(bpy)_2(ppz)]Cl_2$ Δ**3** and Λ-$[Ru^{II}(bpy)_2(ppz)]Cl_2$ Λ**3**. Final purification of the individual optically pure salts was accomplished by chromatography over alumina eluting with acetonitrile–methanol (95:5). Measurements of UV/VIS and CD spectra (virtually identical but oppositely sensed for each enantiomeric pair) for each salt thus prepared indicate that these reactions proceed stereoselectively with retention of the absolute configuration about ruthenium.[7]

Table 1 The CD data for the stereoisomers (aqueous solution)

Compound	λ/nm	$\Delta\varepsilon/\text{M}^{-1}\,\text{cm}^{-1}$
Δ**1**	295	−154
Λ**1**	295	+156
Δ**2**	284	−112
Λ**2**	284	+135
Δ**3**	289	−123
Λ**3**	289	+127
ΔΔ**4**	288	−183
ΛΛ**4**	288	+177
ΔΛ**4**	Inactive	
ΔΔ**5**	288	−113
ΛΛ**5**	288	+112
ΔΛ**5**	Inactive	

Subsequent reaction of each of the optically pure materials Δ**2**, Λ**2**, Δ**3** and Λ**3** with each of Δ**1** and Λ**1** provides two complete sets of stereoisomers. After final purification using chromatography over alumina eluting with acetonitrile–methanol (95:5) the enantiomeric sets of dinuclear complexes ΔΔ**4** and ΛΛ**4** related to dpp exhibit identical UV/VIS spectra and equivalent but oppositely sensed CD spectra, again indicating that the reactions proceed in a stereospecific manner with retention of the absolute configuration about ruthenium. The UV/VIS data for newly purified stereoisomers correspond with those previously reported for stereoisomeric mixtures; appropriate CD data are summarized in Table 1. A corresponding result is observed for the enantiomeric dinuclear complexes ΔΔ**5** and ΛΛ**5** related to ppz. The *meso* species constructed ΔΛ**4** and ΔΛ**5** exhibited UV/VIS spectra corresponding to the respective enantiomeric forms, and were inactive in the CD spectrum. Schematic structural representations of one complete set of stereoisomers ΔΔ**5**, ΔΛ**5**, and ΛΛ**5** are shown in Fig. 1.

Experimental

General

All chemicals for syntheses and purifications were of commercial reagent quality and used without further purification. Alumina for column chromatography was from Aldrich (neutral, Brockmann I, 150 mesh). All NMR spectra were measured using a Brüker 400 MHz DPX400 instrument. (Notes concerning ^1H spectra and details of ^{13}C spectra are given here; details of complex ^1H NMR spectra and ^{13}C–^1H heteronuclear

---

† E-Mail: robert_engel@qc.edu

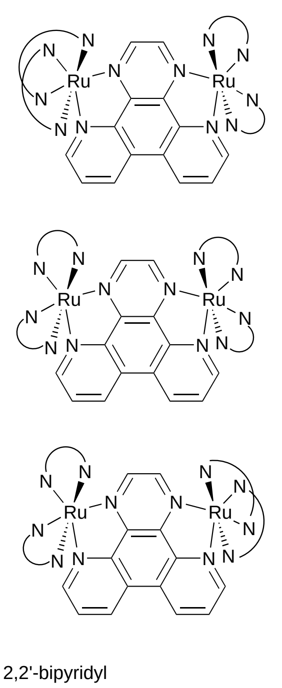

Fig. 1 Schematic structural representations of the complete set of stereoisomers of compound **5**. From top to bottom, these are: ΔΔ**5**, ΛΔ**5**, ΛΛ**5**

correlation spectra will be presented in another report concerned with NMR spectra of a range of such complexes.) The UV/VIS spectra were measured using a Hewlett-Packard 8452 Diode-Array spectrometer, and circular dichroism measurements were made in aqueous solution using a JASCO 500C CD/ORD instrument, calibrated with solutions of androsterone in 1,4-dioxane.

Preparations

(±)-$[Ru^{II}(bpy)_2(py)_2]Cl_2$. This material was prepared using a modification of a previously reported procedure.[8] A round-bottomed flask (250 cm^3) was charged with pyridine (23 cm^3), water (46 cm^3) and bis(2,2′-bipyridine)ruthenium(II) dichloride (2.00 g, 4.13 mmol). The reaction mixture was stirred while heating at reflux for 4 h, filtered while hot, and the solvent evaporated under reduced pressure. The deep red residue was dissolved in methanol (46 cm^3) and sufficient diethyl ether was added to result in the formation of a red precipitate. The mixture was allowed to stand at room temperature for 1 h, after which the precipitate was recovered by suction filtration and the crystals were washed with diethyl ether (2 × 50 cm^3). The recovered solid (1.95 g, 73.6% yield) was identical in its properties to those previously reported[8] for (±)-$[Ru^{II}(bpy)_2(py)_2]Cl_2$.

Use of disodium *O,O′*-dibenzoyl (*R,R*)-tartrate for the resolution of $[Ru^{II}(bpy)_2(py)_2]$ complexes. To an aqueous solution of disodium *O,O′*-dibenzoyl (*R,R*)-tartrate (19.50 cm^3 of 0.5 M, 9.75 mmol) was added to a solution of $[Ru^{II}(bpy)_2(py)_2]Cl_2$ (1.95 g, 3.03 mmol) in water (39 cm^3). The deep red solution was stirred for 10 min and allowed to stand at room temperature uncovered in a fumehood for 5 d. The red crystals of the pure *O,O′*-dibenzoyl (*R,R*)-tartrate salt of Δ-$[Ru^{II}(bpy)_2(py)_2]^{2+}$ Δ**1** which formed upon solvent evaporation were recovered by suction filtration and air dried (1.00 g, 71.3% yield). This material exhibited a CD spectrum (see Table 1) and a UV/VIS spectrum which corresponded to that previously reported.[6] The UV/VIS spectrum previously reported[6] was for the dichloride salt; conversion of the *O,O′*-dibenzoyl (*R,R*)-tartrate salt into the dichloride salt in the present work resulted in no change to either the CD or UV/VIS spectrum. The presently reported CD involves a greater ellipticity than that previously reported (+114 M^{-1} cm^{-1} at 295 nm for the Λ enantiomer)[6] indicating a significantly greater optical purity for the presently prepared material. Correspondingly, pure salts of Λ-$[Ru^{II}(bpy)_2(py)_2]^{2+}$ Λ**1** ($\Delta\varepsilon_{295} = +156$ M^{-1} cm^{-1}) were generated using *O,O′*-dibenzoyl (*S,S*)-tartrate as the resolving agent.

Δ-$[Ru^{II}(bpy)_2(dpp)][PF_6]_2$ Δ2. A round-bottomed flask (50 cm^3) was charged with 2,3-bis(2-pyridyl)pyrazine (52.7 mg, 0.255 mmol), Δ-$[Ru^{II}(bpy)_2(py)_2]^{2+}$, *O,O′*-dibenzoyl (*R,R*)-tartrate salt (250 mg, 0.269 mmol), and ethylene glycol–water (9:1, 7.5 cm^3). The deep red mixture was heated at reflux for 6 h, after which the solution was cooled, filtered and water (15 cm^3) added to the filtrate. To the filtrate was added ammonium hexafluorophosphate (2.0 g) which resulted in the formation of a red precipitate. The precipitate was recovered by suction filtration, dried and chromatographed over alumina, eluting with acetonitrile. The deep orange-yellow band was collected and the solvent evaporated to give pure Δ-$[Ru^{II}(bpy)_2(dpp)][PF_6]_2$ Δ**2** (155 mg, 0.165 mmol, 64.7% yield). This material exhibited a CD spectrum (see Table 1) and a UV/VIS spectrum corresponding to that previously reported for the stereoisomeric mixture.[2a,c,9] The ^1H and ^{13}C NMR spectra were measured in $(CD_3)_2SO$ solution. The ^1H spectrum exhibited a complex series of signals in the range δ 7.1–8.9. The ^{13}C spectrum exhibited 34 signals in accord with the number of unique carbon atoms in the proposed structure, eight of which were indicated by distortionless enhancement of polarisation transfer (DEPT) measurement to be devoid of attached hydrogen atoms (δ 157.45, 157.36, 157.26, 157.25, 157.00, 156.64, 156.16 and 155.19) and the remainder to be CH (δ 152.81, 152.30, 152.28, 152.27, 152.24, 152.22, 152.17, 151.93, 150.69, 146.22, 145.86, 139.54, 139.51, 139.35, 137.67, 129.06, 129.04, 128.97, 128.96, 128.82, 128.74, 128.70, 126.73, 125.79, 125.62 and 125.59). Correspondingly, pure Λ-$[Ru^{II}(bpy)_2(dpp)][PF_6]_2$ Λ**2** was prepared starting with Λ-$[Ru^{II}(bpy)_2(py)_2]^{2+}$, *O,O′*-dibenzoyl (*S,S*)-tartrate salt, exhibiting identical UV/VIS and NMR spectra, and corresponding CD spectrum.

Δ-$[Ru^{II}(bpy)_2(ppz)][PF_6]_2$ Δ3. A round-bottomed flask (50 cm^3) was charged with pyrazino[2,3-*f*][4,7]phenanthroline (104 mg, 0.448 mmol), Δ-$[Ru^{II}(bpy)_2(py)_2]^{2+}$, *O,O′*-dibenzoyl (*R,R*)-tartrate salt (250 mg, 0.269 mmol), and ethylene glycol–water (9:1, 7.5 cm^3). The deep red mixture was heated at reflux for 6 h, after which the solution was cooled, filtered and water (15 cm^3) added to the filtrate. To the filtrate was added ammonium hexafluorophosphate (2.0 g) which resulted in the formation of a red precipitate. The precipitate was recovered by suction filtration, dried and chromatographed over alumina, eluting with acetonitrile. The deep orange-yellow band was collected and the solvent evaporated to give pure Δ-$[Ru(bpy)_2(ppz)][PF_6]_2$ Δ**3** (152 mg, 0.162 mmol, 60.2% yield). This material exhibited a CD spectrum (see Table 1) and UV/VIS spectrum in accord with those of previously reported stereoisomeric mixtures.[2c] The ^1H and ^{13}C NMR spectra were measured in $(CD_3)_2SO$ solution. The ^1H spectrum exhibited a complex series of signals in the range δ 7.2–9.8. The ^{13}C spectrum exhibited 34 signals in accord with the number of unique carbon atoms in the proposed structure, ten of which were indicated by DEPT measurement to be devoid of attached hydrogen atoms (δ 156.42, 156.40, 155.99, 155.97, 155.81, 147.05, 144.76, 144.26, 144.16 and 128.44) and the remainder to be CH (δ 151.98, 151.92, 151.82, 151.16, 150.82, 148.30, 146.41, 138.10, 138.06, 138.01, 137.91, 132.90, 132.56, 127.70, 127.65, 127.53, 127.45, 127.02, 125.47, 125.26, 125.12, 124.22, 124.12 and 124.08). Correspondingly, pure Λ-$[Ru^{II}(bpy)_2(ppz)][PF_6]_2$ Λ**3** was prepared starting with Λ-$[Ru^{II}(bpy)_2(py)_2]^{2+}$, *O,O′*-dibenzoyl (*S,S*)-tartrate salt, exhibiting identical UV/VIS and NMR spectra, and corresponding CD spectrum.

ΔΔ-$[(bpy)_2Ru^{II}(dpp)Ru^{II}(bpy)_2][PF_6]_4$ ΔΔ4. A round-bottomed flask (50 cm^3) was charged with 2,3-bis(2-

pyridyl)pyrazine (30 mg, 0.14 mmol), Δ-[Ru^{II}(bpy)$_2$(py)$_2$]$^{2+}$, *O*,*O*′-dibenzoyl (*R*,*R*)-tartrate salt (250 mg, 0.27 mmol), and ethylene glycol–water (9 : 1, 7.5 cm^3). The deep red mixture was heated at reflux for 6 h, after which the solution was cooled and filtered. Water (12 cm^3) was then added to the filtrate followed by ammonium hexafluorophosphate (2.0 g). This resulted in the formation of a dark purple-red precipitate which was recovered by suction filtration and dried. Finally, this product was chromatographed over alumina, eluting with acetonitrile. The deep purple band was collected and the solvent evaporated to give pure ΔΔ-[(bpy)$_2$Ru^{II}(dpp)Ru^{II}(bpy)$_2$][PF$_6$]$_4$ ΔΔ**4** (190 mg, 0.116 mmol, 85.9% yield). This material exhibited a CD spectrum (see Table 1) and UV/VIS spectrum in accord with that observed[2a] previously for the stereoisomeric mixture. The ^{1}H and ^{13}C NMR spectra were measured in (CD$_3$)$_2$SO solution. The ^{1}H spectrum exhibited a complex series of signals in the range δ 7.1–9.1. The ^{13}C spectrum exhibited 54 signals in accord with the number of unique carbon atoms in the proposed structure, twelve of which were indicated by DEPT measurement to be devoid of attached hydrogen atoms (δ 160.83, 160.81, 160.68, 160.64, 160.54, 160.42, 160.22, 160.21, 160.17, 159.71, 159.37 and 158.27) and the remainder to be CH (δ 156.69, 156.53, 156.04, 155.68, 155.65, 155.47, 151.47, 149.80, 149.35, 143.37, 143.27, 143.20, 143.12, 143.10, 142.99, 142.92, 141.97, 141.94, 141.91, 137.83, 133.84, 133.82, 133.78, 133.75, 133.62, 133.25, 133.21, 132.81, 132.65, 132.61, 132.55, 131.98, 131.95, 129.42, 129.36, 129.32, 129.25, 129.23, 129.22, 129.20, 129.15 and 129.11). Correspondingly, pure ΛΛ-[(bpy)$_2$Ru^{II}(dpp)Ru^{II}(bpy)$_2$][PF$_6$]$_4$ ΛΛ**4** was prepared starting with Λ-[Ru^{II}(bpy)$_2$(py)$_2$]$^{2+}$, *O*,*O*′-dibenzoyl (*S*,*S*)-tartrate salt, exhibiting identical UV/VIS and NMR spectra, and corresponding CD spectrum.

ΔΛ-[(bpy)$_2$Ru^{II}(dpp)Ru^{II}(bpy)$_2$][PF$_6$]$_4$ ΔΛ4. A round-bottomed flask (50 cm^3) was charged with Δ-[Ru^{II}(bpy)$_2$(dpp)][PF$_6$]$_2$ (10 mg, 0.011 mmol), Λ-[Ru^{II}(bpy)$_2$(py)$_2$]$^{2+}$, *O*,*O*′-dibenzoyl (*S*,*S*)-tartrate salt (14 mg, 0.015 mmol), and ethylene glycol–water (9 : 1, 4 cm^3). The deep purple mixture was heated at reflux for 6 h, after which the solution was cooled, filtered and water (9 cm^3) added to the filtrate. To the filtrate was added ammonium hexafluorophosphate (1.0 g) which resulted in the formation of a dark purple-red precipitate. The precipitate was recovered by suction filtration, dried and chromatographed over alumina, eluting with acetonitrile. The deep purple-red band was collected and the solvent evaporated to give pure ΔΛ-[(bpy)$_2$Ru^{II}(dpp)Ru^{II}(bpy)$_2$][PF$_6$]$_4$ ΔΛ**4** (12 mg, 0.0073 mmol, 66.4% yield). This material was inactive in the CD spectrum and exhibited a UV/VIS spectrum corresponding to that of the previously noted ΔΔ and ΛΛ isomers and in accord with that observed[2a] for the stereoisomeric mixture. The ^{1}H and ^{13}C NMR spectra were measured in (CD$_3$)$_2$SO solution. The ^{1}H spectrum exhibited a complex series of signals in the range δ 7.1–9.4. The ^{13}C spectrum exhibited 27 signals in accord with the number of unique carbon atoms in the proposed structure, six of which were indicated by DEPT measurement to be devoid of attached hydrogen atoms (δ 157.13, 157.04, 157.01, 156.72, 156.54 and 156.52) and the remainder to be CH (δ 155.58, 154.57, 153.29, 152.96, 152.12, 151.92, 151.75, 147.54, 139.67, 139.61, 139.48, 138.44, 138.25, 132.51, 132.38, 130.43, 130.06, 129.50, 128.96, 128.89 and 125.57).

ΔΔ-[(bpy)$_2$Ru^{II}(ppz)Ru^{II}(bpy)$_2$][PF$_6$]$_4$ ΔΔ5. A round-bottomed flask (50 cm^3) was charged with pyrazino[2,3-*f*]-[4,7]phenanthroline (30 mg, 0.13 mmol), Δ-[Ru^{II}(bpy)$_2$(py)$_2$]$^{2+}$, *O*,*O*′-dibenzoyl (*R*,*R*)-tartrate salt (250 mg, 0.27 mmol), and ethylene glycol–water (9 : 1, 7.5 cm^3). The deep red mixture was heated at reflux for 6 h, after which the solution was cooled, filtered and water (12 cm^3) added to the filtrate. To the filtrate was added ammonium hexafluorophosphate (2.0 g) which resulted in the formation of a dark purple-red precipitate. The precipitate was recovered by suction filtration, dried and chromatographed over alumina, eluting with acetonitrile. The deep purple band was collected and the solvent evaporated to give pure ΔΔ-[(bpy)$_2$Ru^{II}(ppz)Ru^{II}(bpy)$_2$][PF$_6$]$_4$ ΔΔ**5** (200 mg, 0.122 mmol, 93.8% yield). This material exhibited a CD spectrum (see Table 1) and UV/VIS spectrum in accord with that observed[2c] for the stereoisomeric mixture. The ^{1}H and ^{13}C NMR spectrum were measured in (CD$_3$)$_2$SO solution. The ^{1}H spectrum exhibited a complex series of signals in the range δ 7.2–9.8. Although the structure of ΔΔ**5** contains 54 unique carbon atoms, its ^{13}C spectrum exhibited only 29 completely resolved unique signals. We could not improve the resolution to obtain fully separated signals for each unique carbon atom; it appears that in numerous instances the signals of several carbon atoms are clustered in a relatively broad unresolved band. Of the 29 signals observed, six were indicated by DEPT measurement to be devoid of attached hydrogen atoms (δ 159.24, 158.72, 158.56, 149.68, 149.14 and 131.21) and the remainder to be CH (δ 156.41, 155.14, 154.60, 154.22, 153.58, 152.13, 141.30, 141.13, 141.03, 136.36, 136.32, 130.88, 130.85, 130.70, 130.45, 130.39, 130.18, 127.93, 127.25, 127.20, 127.06, 126.98 and 126.93). Correspondingly, pure ΛΛ-[(bpy)$_2$Ru^{II}(ppz)Ru^{II}(bpy)$_2$][PF$_6$]$_4$ ΛΛ**5** was prepared starting with Λ-[Ru^{II}(bpy)$_2$(py)$_2$]$^{2+}$, *O*,*O*′-dibenzoyl (*S*,*S*)-tartrate salt. This material exhibited identical UV/VIS and NMR spectra, the latter consistent with the deficiency in number of unique carbon signals which were observed for ΔΔ**5**, and a corresponding CD spectrum (Table 1).

ΔΛ-[(bpy)$_2$Ru^{II}(ppz)Ru^{II}(bpy)$_2$][PF$_6$]$_4$ ΔΛ5. A round-bottomed flask (50 cm^3) was charged with Δ-[Ru^{II}(bpy)$_2$(ppz)][PF$_6$]$_2$ (10 mg, 0.011 mmol), Λ-[Ru^{II}(bpy)$_2$(py)$_2$]$^{2+}$, *O*,*O*′-dibenzoyl (*S*,*S*)-tartrate salt (14 mg, 0.015 mmol), and ethylene glycol–water (9 : 1, 4 cm^3). The deep purple mixture was heated at reflux for 6 h, after which the solution was cooled, filtered and water (9 cm^3) added to the filtrate. To the filtrate was added ammonium hexafluorophosphate (1.0 g) which resulted in the formation of a dark purple precipitate. The precipitate was recovered by suction filtration, dried and chromatographed over alumina, eluting with acetonitrile. The deep purple band was collected and the solvent evaporated to give pure ΔΛ-[(bpy)$_2$Ru^{II}(ppz)Ru^{II}(bpy)$_2$][PF$_6$]$_4$ ΔΛ**5** (12.2 mg, 0.0074 mmol, 67.3% yield). This material was inactive in the CD spectrum and exhibited a UV/VIS spectrum corresponding to that of the previously noted ΔΔ and ΛΛ isomers, and in accord with that observed[2c] previously for the stereoisomeric mixture. The ^{1}H spectrum exhibited a complex series of signals in the range δ 7.2–9.8. The ^{13}C spectrum exhibited only 27 signals, in accord with the number of unique carbon atoms in the proposed structure, seven of which were indicated by DEPT measurement to be devoid of attached hydrogen atoms (δ 157.78, 157.73, 157.33, 157.19, 156.93, 148.36 and 147.69) and the remainder to be CH (δ 154.79, 154.07, 153.41, 152.50, 151.97, 150.73, 139.82, 139.69, 139.67, 139.52, 130.24, 129.68, 129.39, 129.19, 128.94, 128.90, 125.68, 125.60 and 125.41).

Acknowledgements

This work was financially supported by grants from The Howard Hughes Medical Institute, The Fund for the Improvement of Post-Secondary Education and the Professional Staff Congress-Board of Higher Education Research Award Program.

References

1 R. Engel, *Adv. Dendritic Macromolecules*, 1995, **2**, 73.
2 (*a*) C. H. Braunstein, A. D. Baker, T. C. Strekas and H. D. Gafney, *Inorg. Chem.*, 1984, **23**, 857; (*b*) W. R. Murphy, K. J. Brewer, G. Gettliffe and J. D. Petersen, *Inorg. Chem.*, 1989, **28**, 81; (*c*)

Y. Fuchs, S. Lofters, T. Dieter, W. Shi, R. Morgan, T. C. Strekas, H. D. Gafney and A. D. Baker, *J. Am. Chem. Soc.*, 1987, **109**, 2691; (*d*) S. Campagna, G. Denti, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 1500; (*e*) L. De Cola, P. Belser, F. Ebmeyer, F. Barigelletti, F. Vögtle, A. von Zelewsky and V. Balzani, *Inorg. Chem.*, 1990, **29**, 495; (*f*) G. Denti, S. Serroni, S. Campagna, V. Ricevuto and V. Balzani, *Coord. Chem. Rev.*, 1991, **111**, 227; (*g*) G. Denti, S. Campagna, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *Inorg. Chem.*, 1990, **29**, 4750; (*h*) S. Campagna, G. Denti, S. Serroni, M. Ciano and V. Balzani, *Inorg. Chem.*, 1991, **30**, 3728; (*i*) G. Denti, S. Serroni, S. Campagna, V. Ricevuto, A. Juris, M. Ciano and V. Balzani, *Inorg. Chim. Acta*, 1992, **198**–**200**, 507; (*j*) S. Serroni, G. Denti, S. Campagna, M. Ciano and V. Balzani, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 944; (*k*) G. Denti, S. Campagna, S. Serroni, M. Ciano and V. Balzani, *J. Am. Chem. Soc.*, 1992, **114**, 2944; (*l*) S. Serroni, G. Denti, S. Campagna, A. Juris, M. Ciano and V. Balzani, *Angew. Chem.*, *Int. Ed. Engl.*, 1992, **31**, 1493; (*m*) G. N. A. Nallas, S. W. Jones and K. J. Brewer, *Inorg. Chem.*, 1996, **35**, 6974.

3 X. Hua and A. von Zelewsky, *Inorg. Chem.*, 1991, **30**, 3796.

4 F. M. MacDonnell and S. Bodige, *Inorg. Chem.*, 1996, **35**, 5758.

5 D. Tzalis and Y. Tor, *J. Am. Chem. Soc.*, 1997, **119**, 852.

6 X. Hua and A. G. Lappin, *Inorg. Chem.*, 1995, **34**, 992.

7 B. Bosnich, *Acc. Chem. Res.*, 1969, **2**, 266.

8 B. Bosnich and F. P. Dwyer, *Aust. J. Chem.*, 1966, **19**, 2231.

9 A. D. Baker, R. J. Morgan and T. C. Strekas, *J. Am. Chem. Soc.*, 1991, **113**, 1411.

Received 25*th April* 1997; *Paper* 7/02829F