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Orthogonal $Ru^{II}(bpy)_3$ complexes in *meso*-substituted porphyrins

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Abstract

The synthesis and characterization of mono- and bis-*meso*-substituted porphyrins, where the substituents are bipyridine (bpy) groups are described. Treatment of these new porphyrins with an excess of *cis*-$RuCl_2(bpy)_2$ gives rise to their respective mono- and bis-$Ru^{II}(bpy)_3$ complexes. These ruthenium porphyrin complexes all exist as a number of structural isomers and this is reflected in both the proton and carbon NMR spectra. The cyclic voltammetry of these redox active systems was examined and is reported herein. The cyclic voltammetry for the ruthenium porphyrins is complex, with the usual two oxidation and two reduction waves of porphyrins mixing with the three reduction waves of the porphyrin bound $Ru^{II}(bpy)_3$ and the single oxidation wave seen for the Ru^{II}/Ru^{III} couple. In the case of the mono-ruthenium porphyrin, this complex redox chemistry results in the presence of a reversible two-electron reduction, along with the other redox processes. The bis-ruthenium porphyrin has an even more complex redox chemistry. However, the first ligand-based reduction wave in both the mono- and bis-substituted complexes, occur at more negative potentials than those in, simple free, $Ru^{II}(bpy)_3$.

Introduction

The degree of electronic communication through chemical and biochemical systems is largely dependent upon the nature of the bridge connecting the two interacting centers. Similarly, the environment between and around redox-active prosthetic groups is responsible for the directionality and efficiency of long-range electron transfer in biological systems. For instance, a particularly important role in mediating electron transfer in light harvesting proteins is played by the chlorophyll prosthetic group [1, 2]. For some years, therefore, we [3, 4] and others [5] have been interested in the synthesis and optical properties of porphyrin-bridged donor acceptor complexes as models for understanding the possible mediating role of this particular prosthetic group. For much of this work we have relied on the use of porphyrins or metalloporphyrins as donors and quinones as acceptors [3]. Recently, however, we have become interested in the consideration of more elaborate systems that do not rely on the use of these particular donors and acceptors [4]. One such approach could be to use redox active metal centers. Given the well known metal-to-ligand charge transfer (MLCT) properties of $Ru^{II}(bpy)_3$ [6], we set out to examine the role, if any, a porphyrin macrocycle might play in bridging, or mediating, electronic interaction(s) between the two metal centers. Presented here are the synthesis, conformational properties and electrochemistry of the porphyrin-bridged binuclear complex **1** and its mononuclear control compound **2** shown in Fig. 1. It should be noted that during the course of this work Sauvage and coworkers [7] reported a similar porphyrin system using terpyridine groups as the ancillary coordinating ligands [8].

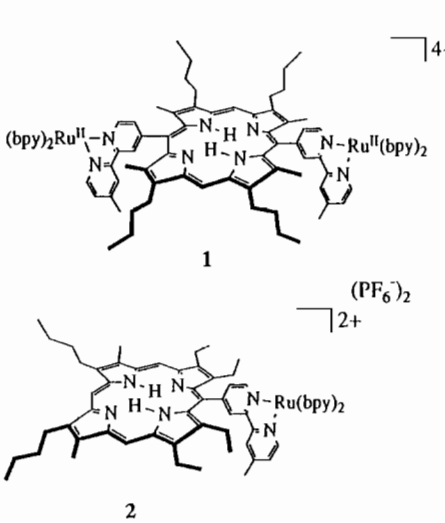

Fig. 1. Orthogonal $Ru^{II}(byp)_3$ complexes **1** and **2**.

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Experimental

General information

All solvents and chemicals were of reagent grade quality, purchased commercially and used without further purification except as noted below. CH_3CN or CH_2Cl_2 when used as solvents or in electrochemical studies were heated at reflux with and distilled from CaH_2. Column chromatography was performed on Merck type 60 (230–400 mesh) silica gel. Thin layer chromatography (TLC) was performed on commercially prepared silica gel plates purchased from Analtech, Inc. or Whatman International, Inc.

Electronic spectra were recorded on a Beckman DU-7 spectrophotometer. Proton and ^{13}C NMR spectra were obtained in $CDCl_3$ or CD_3CN with either Me_4Si or the solvent as an internal standard. Proton NMR spectra were recorded on a General Electric QE-300 (300 MHz) spectrometer. The peak assignments given were made on the basis of integrations and spectral comparisons with similar compounds. Carbon spectra were measured at 75 or 125 MHz with use of either a General Electric QE-300 or Nicolet NT-500 spectrometer, respectively. Low resolution mass spectra were measured with either a Finnigan-MAT 4023 or Bell and Howell 21-491 instrument. Fast atom bombardment mass spectra (FAB-MS) were determined with a Finnigan-MAT TSQ-70 instrument and 3-nitrobenzyl alcohol (NBA) matrix. High resolution mass spectra were obtained with a Bell and Howell 21-110B instrument.

Cyclic voltammetry was performed on a Pine Instruments Company model RDE4 potentiostat/galvanostat. A solvent saturated argon purge and a three-electrode configuration were used throughout. The working electrode was platinum and a platinum wire was used as the counter electrode. The reference electrode was Ag/AgCl, which was separated from the bulk solution by a fritted glass bridge containing the supporting electrolyte (0.1 M $TBAPF_6$) in the appropriate solvent (either CH_3CN or CH_2Cl_2). In order to eliminate junction potentials and to facilitate comparisons with other solvent systems, potentials are reported versus ferrocene/ferricinium [9] and all potentials are reported relative to SCE with $E_{1/2}$ (Fc/Fc^+) = 0.41 V versus SCE.

4-Formyl-4'-methyl-2,2'-bipyridyl

A 200 ml round-bottomed flask was charged with 4,4'-dimethyl-2,2'-bipyridyl (5 g, 0.025 mol), selenium dioxide (3.02 g, 0.025 mol) and 100 ml of diglyme. The flask was flushed with nitrogen and equipped with a reflux condensor. The reaction was then heated at reflux for 24 h. The mixture was filtered while hot to remove the precipitated selenium. After cooling the solution was again filtered and the solvent removed *in vacuo*. The residue was then extracted with acetone. The acetone was subsequently removed *in vacuo*. The residue consisted of a mixture of bipyridines that was separated by column chromatography (silica, CH_3CN:$CHCl_3$, 9:1, vol.:vol.). On TLC, with the same eluent, the three bipyridines (4,4'-dimethyl-2,2'-bipyridyl, $R_f = 0.75$; 4-formyl-4'-methyl-2,2'-bipyridyl, $R_f = 0.5$; 4,4'-diformyl-2,2'-bipyridyl, $R_f = 0.3$) can be identified by final treatment of the TLC plate with a solution of Fe^{2+}. Upon spraying with the Fe^{2+} solution, the spots on the TLC plate turn red or purple (4,4'-dimethyl-2,2'-bipyridyl, red; 4-formyl-4'-methyl-2,2'-bipyridyl, purple; 4,4'-diformyl-2,2'-bipyridyl, red). The 4-formyl-4'-methyl-2,2'-bipyridyl was finally obtained as a colorless solid in 30% yield and had spectral properties identical to those previously reported [10].

5-(4'-(4''-Methyl)-2',2''-bipyridyl)-2,3,7,8-tetraethyl-13,17-dibutyl-12,18-dimethylporphyrin (4)

A 25 ml round-bottomed flask was charged with 4-formyl-4'-methyl-2,2'-bipyridyl (182 mg, 0.943 mmol), **6** (568 mg, 0.943 mmol) [12] and 15 ml of propionic acid. The flask was covered with aluminum foil and equipped with a reflux condensor. The reaction was then heated at reflux for 2 h. After cooling to room temperature the reaction mixture was carefully poured into a separatory funnel containing equal portions of $CHCl_3$ and Na_2CO_3 (aq.). The organic portion was extracted, washed several times with Na_2CO_3 (aq.) and dried over Na_2SO_4. The $CHCl_3$ solution was filtered and the solvent removed on a rotary evaporator. The crude porphyrin was loaded onto a silica gel column and eluted with 5% MeOH in $CHCl_3$ to yield 222 mg (0.304 mmol, 32% yield) of product. UV–Vis ($CHCl_3$): $\lambda_{max} = 406$, 504, 538, 574, 624 nm. ^1H NMR (300 MHz, $CDCl_3$): δ −3.06 (1H, br. s, NH), −2.92 (1H, br. s, NH), 1.22 (6H, t ($J = 7.4$ Hz), 13,17-$CH_2CH_2CH_2CH_3$), 1.31 (12H, m, 2,3,7,8-CH_2CH_3), 1.86 (4H, m ($J = 7.5$ Hz), 13,17-$CH_2CH_2CH_2CH_3$), 2.35 (4H, m ($J = 7.4$ Hz), 13,17-$CH_2CH_2CH_2CH_3$), 2.59 (3H, s, 4''-CH_3), 2.99 (4H, q ($J = 7.5$ Hz), 3,7-CH_2CH_3), 3.68 (6H, s, 13,17-CH_3), 4.13 (8H, m, 2,8-CH_2CH_3 and 13,17-$CH_2CH_2CH_2CH_3$), 7.19 (1H, d ($J = 4.7$ Hz), 6''-*H*), 8.33 (1H, d ($J = 5.0$ Hz), 6'-*H*), 8.57 (1H, d ($J = 4.8$ Hz), 5''-*H*), 8.69 (1H, s, 3''-*H*), 9.13 (1H, d ($J = 4.9$ Hz), 5'-*H*), 9.52 (1H, s, 3'-*H*), 9.95 (1H, s, 15-*H*), 10.25 (2H, s, 10,20-*H*) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 11.7, 14.2, 17.7, 18.6, 19.8, 21.2, 23.1, 26.1, 35.2, 95.8, 96.9, 115.8, 122.2, 124.8, 126.1, 128.7, 136.3, 140.4, 141.9, 142.4, 143.9, 144.6, 146.2, 147.2, 148.1, 149.2, 149.3, 151.3, 154.2, 155.7 ppm. FAB-MS (NBA, 70 eV): *m/z* (relative intensity, %) 731 (M^+, 44); 733 ($M^+ + 2$, 16). Exact mass for $C_{49}H_{59}N_6$: calc. 731.4801, found 731.4818. *Anal.* Calc. for $C_{49}H_{59}N_6 \cdot \frac{1}{3}CHCl_3$: C, 76.77; H, 7.75; N, 10.89. Found: C, 76.50; H, 7.54; N, 10.92%.

5,15-Bis(4'-(4''-methyl)-2',2''-bipyridyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin (3)

In a three-necked, 100 ml, round-bottomed flask **5** (168 mg, 0.587 mmol) and 4-formyl-4'-methyl-2,2'-bipyridyl (116 mg, 0.587 mmol) were added to 59 ml of 1:1 CH_2Cl_2:MeOH which was previously bubbled with argon for 15 min. The flask was covered with foil and 500 μl trifluoroacetic acid was added. The reaction was allowed to stir in the dark for 4 h after which time 216 mg of *o*-chloranil was added to effect oxidation. The oxidation was allowed to proceed for 5 h. At this time the contents were poured into CH_2Cl_2. The organic solution was then washed with K_2CO_3 (aq.) and dried over Na_2SO_4. The dark reaction product was chromatographed on silica gel eluting first with 5% MeOH/$CHCl_3$ and then with 7% MeOH/$CHCl_3$. The main, pale burgundy fraction was collected and dried *in vacuo* to give 256 mg of **3** (0.276 mmol, 47% yield). λ_{max} = 409, 507, 538, 574, 625 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ −2.29 (2H, br. s, N*H*), 1.15 (12H, t (J = 7.3 Hz), 2,8,12,18-$CH_2CH_2CH_2CH_2$), 1.79 (8H, sextet (J = 7.4 Hz), 2,8,12,18-$CH_2CH_2CH_2CH_3$), 2.21 (8H, quintet (J = 6.9 Hz), 2,8,12,18-$CH_2CH_2CH_2CH_3$), 2.58 (6H, s, 4''-CH_3), 2.61 (12H, s, 3,7,13,17-CH_3), 3.99 (8H, t (J = 7.6 Hz), 2,8,12,18-$CH_2CH_2CH_2CH_3$), 7.20 (2H, d (J = 4.1 Hz), 6''-*H*), 8.01 (2H, br. s, 6'-*H*), 8.54 (2H, d (J = 4.3 Hz), 5''-*H*), 8.64 (2H, s, 3''-*H*), 9.07 (2H, d (J = 4.3 Hz), 5'-*H*), 9.31 (2H, s, 3'-*H*), 10.29 (2H, s, 10, 20-*H*) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.18, 15.32, 21.26, 23.37, 26.47, 35.46, 97.41, 115.07, 122.32, 124.94, 125.70, 128.22, 135.53, 141.63, 143.87, 144.18, 148.20, 148.29, 149.24, 151.67, 155.46, 155.50, 155.90 ppm. FAB-MS (NBA, 70 eV) *m/z* (relative intensity, %) 927 (M^+, 47); 928 ($M^+ + 1$, 100); 929 ($M^+ + 2$, 68); 930 ($M^+ + 3$, 25). Exact mass for $C_{62}H_{71}N_8$: calc. 927.5802, found 927.5786. *Anal.* Calc. for $C_{62}H_{71}N_8$: C, 80.22; H, 7.71; N, 12.07. Found: C. 79.39; H, 7.71; N, 11.92%.

Ru(5-(4'-(4''-methyl)-2',2''-bipyridyl)-2,3,7,8-tetraethyl-13,17-dibutyl-12,18-dimethylporphyrin)(2,2'-bipyridyl)$_2^{2+}$(PF_6^-)$_2$ (2)

A 25 ml round-bottomed flask was charged with **4** (35 mg, 0.048 mmol), *cis*-Ru(bpy)$_2$Cl$_2$ (92 mg, 0.191 mmol) and 10 ml of EtOH. The system was heated at reflux with stirring for 48 h. The EtOH was removed *in vacuo* and the dark solid dissolved in CH_3CN:H_2O:KNO_3(sat., aq.) (3:3:1) and loaded onto a silica gel column. The product was obtained by elution with this solvent mixture ($R_f \sim 0.5$). After collection of the major reddish fraction the volume of eluent was reduced to ~5 ml on a rotary evaporator. This yielded a dark sludge. A copious amount (~250 ml) of dry acetone was added to the flask containing the sludge and the solid KNO_3 precipitate that resulted removed by filtration and washed several times with acetone. The acetone washings were taken to dryness *in vacuo* and the resulting red solid taken up in H_2O. The desired product was obtained by addition of a saturated aqueous solution of KPF_6 to this H_2O solution. This induced an orange-red precipitate (the final complex) which was collected by slow filtration through a medium porosity fitted glass funnel. The yield was 34 mg (0.0237 mmol, 49%). UV–Vis ($CHCl_3$): λ_{max} (ϵ) 400 (140 000), 460 (27 000), 502 (20 000), 538 (8 500), 572 (7 400), 624 (3 100) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ −3.4 (1H, br. s, N*H*); −3.2 (1H, br. s, N*H*); 0.74 (3H, t (J = 7.2 Hz), 2-CH_2CH_3); 1.13 (6H, T (J = 7.4 Hz), 13,17-$CH_2CH_2CH_2CH_3$); 1.34 (3H, t (J = 7.3 Hz), 8-CH_2CH_3); 1.80 (4H, sextet, 13,17-$CH_2CH_2CH_2CH_3$); 1.90 (6H, t, 3,7-CH_2CH_3): 2.24 (4H, quintet, 13,17-$CH_2CH_2CH_2CH_3$); 2.38 (3H, s, 4''-CH_3); 3.0–3.3 (4H, m, 3,7-CH_2CH_3); 3.60 (3H, s, 12-CH_3); 3.62 (3H, s, 18-CH_3); 4.03 (2H, q, 2-CH_2CH_3); 4.13 (2H, q, 8-CH_2CH_3); 7.30–9.48 (22H, m, bipyridine-*H*); 10.01 (1H, s, 15-*H*); 10.25 (1H, s, 10-*H*); 10.31 (1H, s, 20-*H*) ppm. FAB-MS (NBA, 70 eV): *m/z* (relative intensity, %) 1144 (M^+, 85); 1145 ($M^+ + 1$, 79); 1146 ($M^+ + 2$, 62). Exact mass for $C_{69}H_{74}N_{10}Ru^{2+}$: calc. 1144.5141, found 1144.5127. *Anal.* Calc for $C_{69}H_{74}N_{10}RuP_2F_{12} \cdot 2H_2O$: C, 56.36; H, 5.35; N, 9.53. Found: C, 56.01; H, 5.15; N, 9.30%.

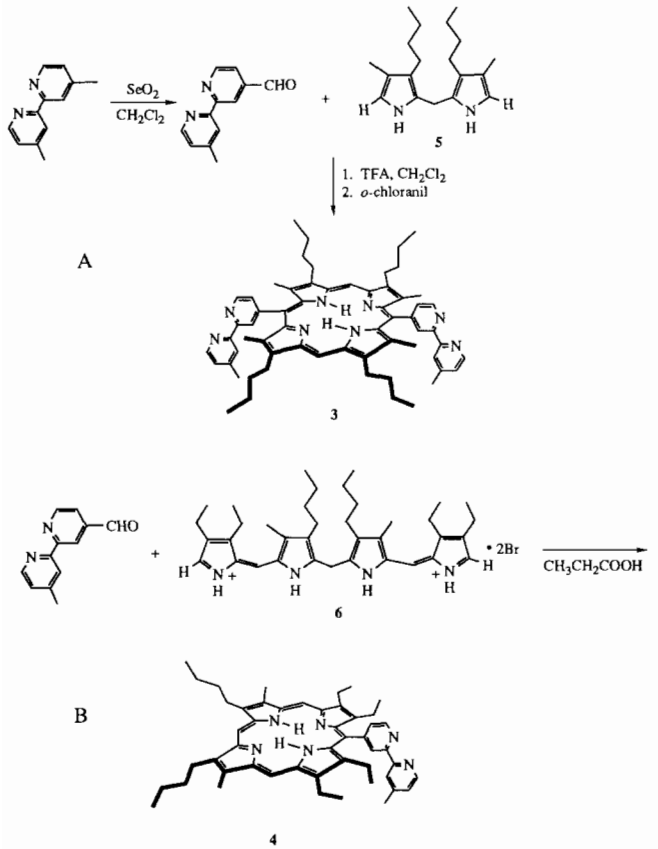
Bis-Ru(5,15-bis-4'(4''-methyl-2',2''-bipyridyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin)-bis(2''',2''''-bipyridyl)$_2^{4+}$(PF_6^-)$_4$ (1)

A 100 ml round-bottomed flask was charged with **3** (133 mg, 0.143 mmol), *cis*-Ru(bpy)$_2$Cl$_2$ (210 mg, 0.43 mmol) and 40 ml of EtOH. The reaction mixture was heated at reflux with stirring for 48 h. After this time, the EtOH was removed *in vacuo* and the resulting dark solid residue redissolved in CH_3CN:H_2O:KNO_3(aq.) (3:3:1) and loaded onto a silica gel column. The complex was obtained by elution with this solvent system. After collection of the main red band, the solvent volume was reduced to *c.* 5 ml *in vacuo* and 200 ml of acetone added to the resulting, thick slurry in order to precipitate out the undesired KNO_3. The KNO_3 precipitate was removed by vacuum filtration with the resulting filter cake being washed extensively with dry acetone. The acetone washings were then combined with the original filtrate, dried over Na_2SO_4 and evaporated to dryness *in vacuo*. The resulting orange–red residue was then redissolved in H_2O and a saturated aqueous solution of KPF_6 was added. After *c.* 20 min. the desired product **1** precipitated as the (PF_6^-)$_4$ salt. The solid was collected by filtration through a fine glass frit and then washed several times with H_2O. This gave, after drying, product **1** in 19% yield (51 mg, 0.021 mmol). UV–Vis ($CHCl_3$): λ_{max} (ϵ) 407 (150 000), 463 (51 000), 503 (20 000), 538 (8 700), 569 (7 200), 624 (3 400) nm. ^{1}H NMR (300

MHz, $CDCl_3$): δ −2.56 (2H, br. s, N*H*); 1.12 (6H, t, 2,8,12,18-$CH_2CH_2CH_2CH_3$); 1.15 (6H, t, 2,8,12,18-$CH_2CH_2CH_2CH_3$); 1.81 (8H, m, 2,8,12,18-$CH_2CH_2CH_2CH_3$); 2.18 (8H, m, 2,8,12,18-$CH_2CH_2CH_2CH_3$); 2.82 (6H, s, 4″-CH_3); 3.95 (4H, m, 2,8,12,18-$CH_2CH_2CH_2CH_3$); 4.09 (4H, m, 2,8,12,18-$CH_2CH_2CH_2CH_3$); 7.29–9.26 (52H, m, bipyridine-*H*); 10.31 (1H, s, *meso*-H); 10.36 (2H, s, *meso*-H); 10.41 (1H, s, *meso*-H) ppm. Mass spectrum (FAB-MS, 70 eV): *m/z* (relative intensity, %) 1793 (M^+, 29); 1794 ($M^+ + 1$, 36). Exact mass for $C_{102}H_{103}N_{16}Ru_2F_2$: calc. 1793.6595, found 1793.6614. *Anal.* Calc. for $C_{102}H_{103}N_{16}Ru_2P_4F_{24} \cdot 4H_2O$: C, 50.90; H, 4.65; N, 9.31. Found: C, 51.05; H, 4.45; N, 9.42%.

Results and discussion

The ligands required for the construction of the desired target metal complexes, compounds **1** and **2**, are the bypyridine-substituted porphyrins **3** and **4**. These, previously unknown materials were prepared according to the synthetic procedures summarized in Scheme 1. The SeO_2 oxidation of 4,4′-dimethyl-2,2′-bipyridyl provided the starting aldehyde for the porphyrin syntheses.



Scheme 1. Synthetic sequence for the construction of *meso*-substituted bipyridyl functionalized porphyrins.

Reaction of this aldehyde under Lindsey-modified conditions [11] with the α-free dipyrrylmethane **5** [3] provided the 5,15-bis(4′-(2′,2″-bipyridyl))porphyrin (**3**) (Scheme 1, Part A). Here, it proved necessary to increase the acid concentration to 2.1×10^{-2} M from the optimized 10^{-3} M concentration used by Lindsey [11] in order to account for the basic pyridine nitrogen lone pairs. After chromatographic purification on silica gel (eluent 5% MeOH/$CHCl_3$) and two-solvent recrystallization ($CHCl_3$/MeOH), porphyrin **3** could be isolated in *c.* 40% yield. Compound **4** was synthesized using a modification of the basic method of Johnson and Gaete-Holmes [12]. Specifically, reaction of the 1,19-dideoxy-*ac*-biladiene dihydrobromide (**6**) [12] with the bipyridine aldehyde in propionic acid yielded **4** in *c.* 20–25% yield, after chromatographic purification on silica gel using 7% MeOH/$CHCl_3$ as the eluent and two-solvent recrystallization from $CHCl_3$/MeOH (Scheme 1, Part B).

Complexation of ruthenium(II) into the available porphyrin-bound bipyridine sites was achieved by the reaction of an excess of *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) dihydrate in absolute ethanol at reflux. The resulting complexes **1** and **2** were then purified as their nitrate salts by chromatography on silica gel using CH_3CN:H_2O:KNO_3(sat., aq.), 3:3:1 (vol.:vol.:vol.), as the eluent. These materials are stable complexes of ruthenium(II) and can be handled without any special precautions.

The presence of bulky substituents at the *meso* positions in complexes **1** and **2** was expected by analogy to earlier work (cf, for example, ref. 3a), to enforce hindered rotation about the porphyrin-to-bipyridine bond. This in turn was expected to give rise to the presence of several isomers and to a more complex NMR pattern than would be expected for a non-isomeric, freely rotating system. The *meso*-H region of the ^{1}H NMR spectrum of complex **2** is shown in Fig. 2. Inequivalencies in the *meso* (10- and 20-H) signals are observed in this complex. These are reflective of the relative influences of the bipyridyl ligands on each side of the porphyrin plane. In particular, the expected restricted rotation about the porphyrin–bipyridyl bond is sufficient to create a situation in which one side of the porphyrin plane experiences a pyridine ligand *edge*, while the other is influenced by a pyridine ligand *face*. This then gives rise to the observed three *meso*-H signals.

This symmetry-breaking inequivalence is also reflected in the splitting of the ^{1}H NMR signals for the 12- and 18-CH_3 as well as the 2,3,7 and 8-CH_2CH_3 protons of complex **2**. It is also reflected in the ^{1}H NMR spectrum of complex **1**. In this doubly functionalized case, hindered rotation gives rise to a mixture of four diastereoisomers and to the observation of three *meso*-H signals in the ^{1}H NMR spectrum. These three

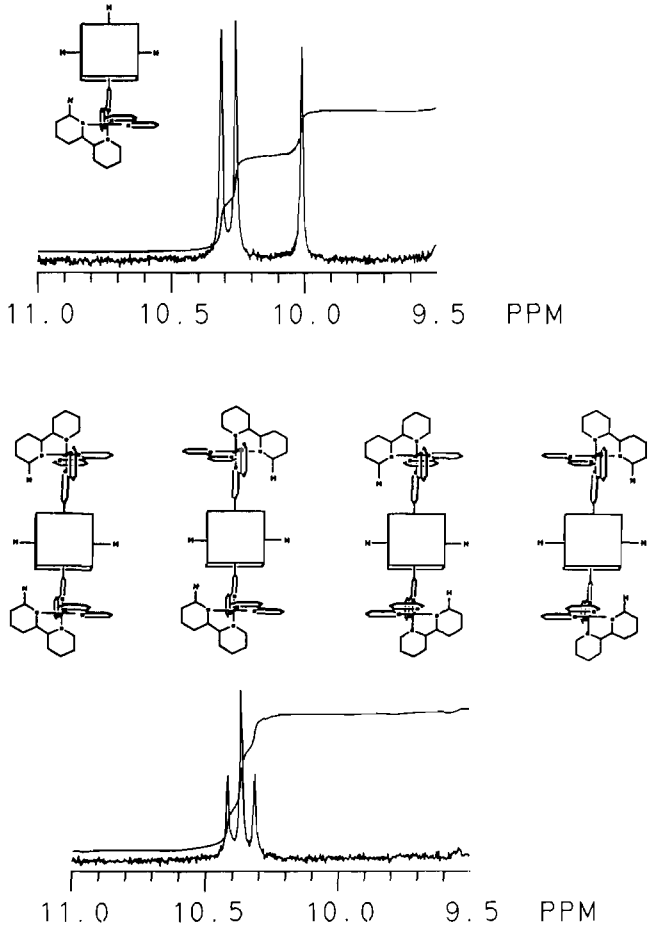


Fig. 2. 300 MHz ^{1}H NMR spectra recorded in CH_3CN for the *meso*-H region of $Ru^{II}(bpy)_3$-porphyrins **1** (lower trace) and **2** (upper trace).

signals, which are observed in the 1:2:1 ratio expected for a statistical ratio of diastereoisomers, are reproduced in the lower frame of Fig. 2.

Absorption spectra recorded in CH_3CN reveal a characteristic $Ru^{II}(bpy)_3$ metal-to-ligand charge transfer (MLCT) band along with Q and B porphyrin bands for complexes **1** and **2**. These are shown in Fig. 3 along with the absorption spectrum for the ruthenium free porphyrin **4**. Excitation into the MLCT band at single wavelengths from 450–470 nm failed to give rise to emission from this state, but rather, produced only emission from the porphyrin. While this may indicate a new non-radiative decay channel for the MLCT state due to the porphyrin linkage (i.e. via an intramolecular electron transfer), it is more likely a result of direct porphyrin excitation into the B band which has a finite absorbance between 450–470 nm. The latter explanation is further supported by fluorescence excitation spectra which indicate that porphyrin fluorescence is due only to direct porphyrin excitation and does not emanate from excitation into the MLCT band.

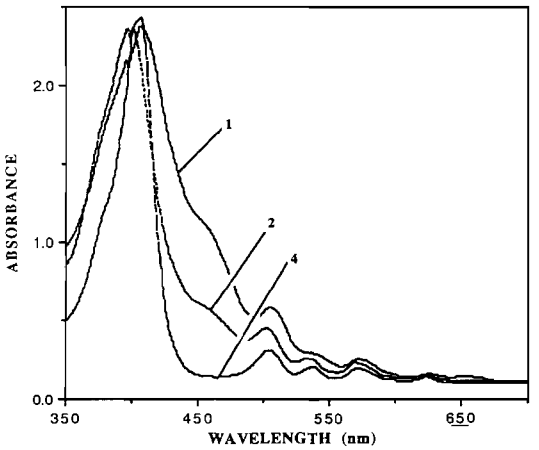


Fig. 3. Visible absorption spectra in CH_3CN for compounds **1**, **2** and **4**.

Cyclic voltammograms (CVs) for porphyrins **3** and **4** recorded in CH_2Cl_2*, 0.1 M $TBAPF_6$ over the region 1.5 to −1.8 V versus SCE are given in Figs. 4 and 5. As can be seen by the relative peak positions and the obtainable $E_{1/2}$ values (see Table 1) both **3** and **4** have essentially the same redox properties. In general porphyrins display two oxidation peaks in the region 0.5 to 1.4 V versus SCE and two reduction peaks in the region −1 to −1.8 V versus SCE [13]. The presence of what appears to be a third reduction peak in both **3** and **4** is attributed to the presence of the bipyridyl group.

The cyclic voltammograms for the ruthenium complexes **1** and **2** recorded in CH_2Cl_2*, 0.1 M $TBAPF_6$ (Figs. 6 and 7) exhibit a more complex redox chemistry. This is especially noticeable in the region −1 to −1.8 V versus SCE where both porphyrins [13] and $[Ru(bpy)_3]^{2+}$ [14] display multiple reduction peaks. Despite the complexity of the reduction region (see also below), the oxidation portion of the cyclic voltammogram for complex **2** is relatively straightforward. Observable are two porphyrin oxidation peaks similar to those observed for **4** (at $E_{1/2}=1.23$ V versus SCE and $E_{1/2}=0.83$ V versus SCE, see Table 1), along with one other reversible oxidation. This new oxidation peak occurs at $E_{1/2}=1.41$ V versus SCE and is assigned to the Ru^{II}/Ru^{III} couple, being only slightly shifted from the value observed for the Ru^{II}/Ru^{III} couple in $Ru(bpy)_3^{2+}$ (see Table 1).

While the oxidation region of **2** is readily understood, the reduction region is somewhat more confusing. It

*In general CH_3CN is considered to be a better solvent for electrochemistry, especially for potentials < -1.5 V. However, the porphyrins **3** and **4** were not soluble in CH_3CN. Thus, to enable a more accurate comparison between the porphyrins and the ruthenium complexes, all potential and figures result from the use of CH_2Cl_2 as a solvent unless otherwise stated.

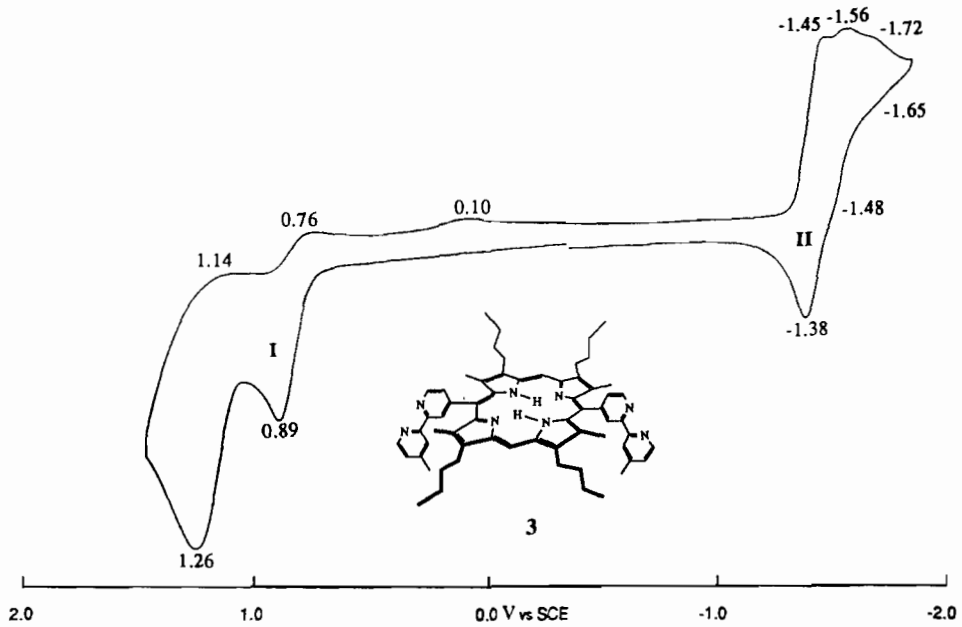


Fig. 4. Cyclic voltammogram of **3** in CH_2Cl_2/0.1 M $TBAPF_6$ at a Pt electrode with a sweep rate of 50 mV/s.

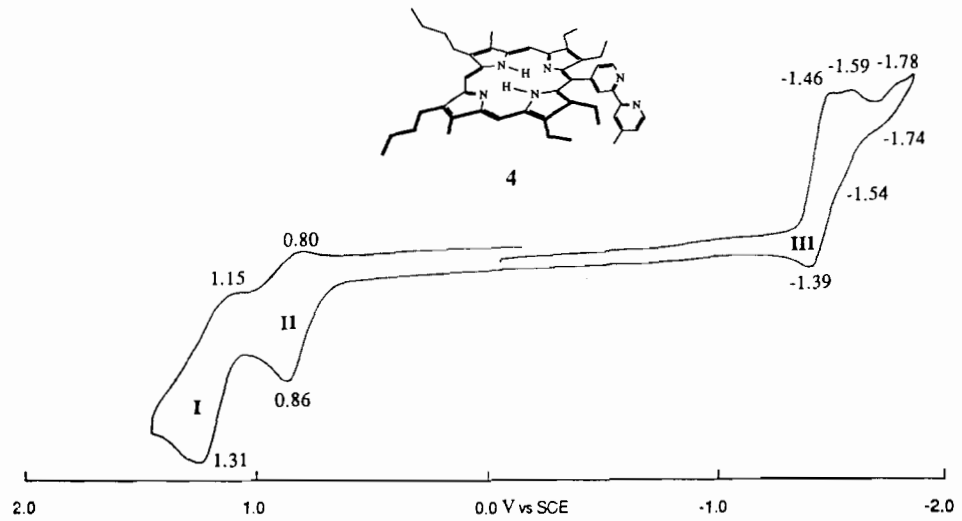


Fig. 5. Cyclic voltammogram of **4** in CH_2Cl_2/0.1 M $TBAPF_6$ at a Pt electrode with a sweep rate of 50 mV/s.

is noticeably the superposition of an expected porphyrin reduction peak at $E_{1/2} = -1.15$ V versus SCE and three characteristic, ligand-based, $Ru(bpy)_3^{2+}$ reduction peaks at $E_{1/2} = -1.22$*, -1.54 and -1.73 V versus SCE that make this region so interpretatively complex. The presence of a reversible two-electron reduction peak ($\Delta E_p = 30$ mV) at $E_{1/2} = -1.15$ is worthy of note. Nonetheless, the first ligand-based reduction of **2** ($E_p = -1.22$ V versus SCE)* is significantly easier to achieve than the corresponding reduction for the metal free systems **3** and **4** ($E_{1/2} = -1.42$ V versus SCE). In fact, it is also easier than that observed in $Ru(bpy)_3^{2+}$ ($E_{1/2} = -1.32$ V versus SCE).

This latter finding, which is expected for a ligand with an extended conjugation framework, is reflective, perhaps, of an influence of the porphyrin on this bipyridine centered redox potential. The addition of a second ruthenium complex to the porphyrin, as in **1**, serves to increase further the complexity of the redox chemistry. Instead of the two porphyrin oxidation peaks observed in the cyclic voltammograms of **2–4**, the CV of complex **1** (in CH_2Cl_2) shows four oxidation waves with limited chemical reversibility, that are tentatively assigned to what are considered as being primarily porphyrin-centered oxidation processes. By contrast and

*While the actual $E_{1/2}$ value could not be obtained due to the overlap of redox peaks in this region the E_p value is quoted to give a reference for comparison.

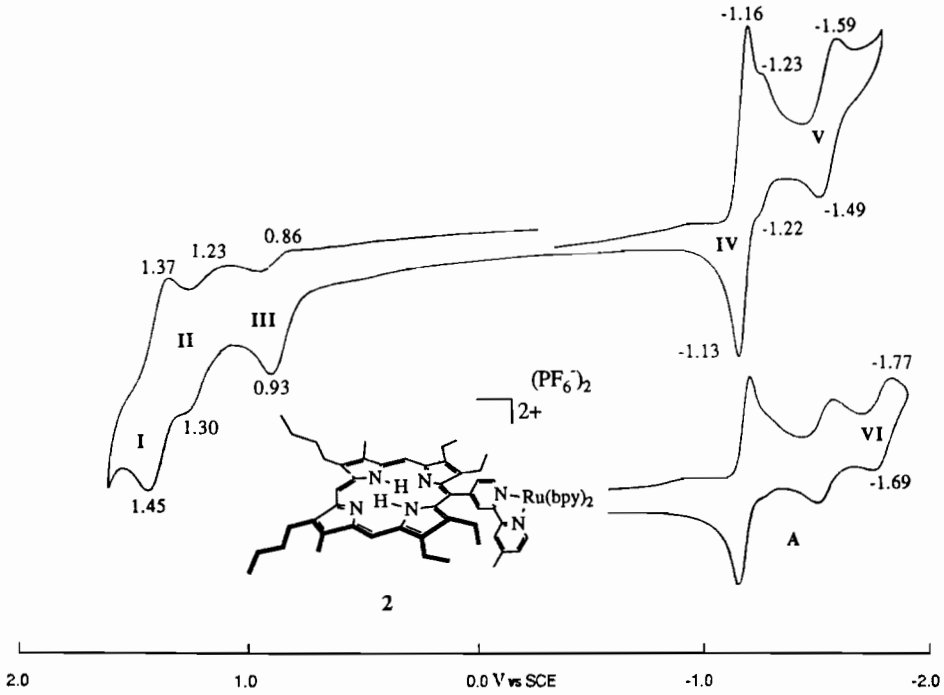


Fig. 6. Cyclic voltammogram of **2** in CH_2Cl_2/0.1 M $TBAPF_6$ at a Pt electrode with a sweep rate of 50 mV/s. Inset A was recorded in CH_3CN/0.1 M $TBAPF_6$ at a Pt electrode with a sweep rate of 50 mV/s and reported relative to SCE.

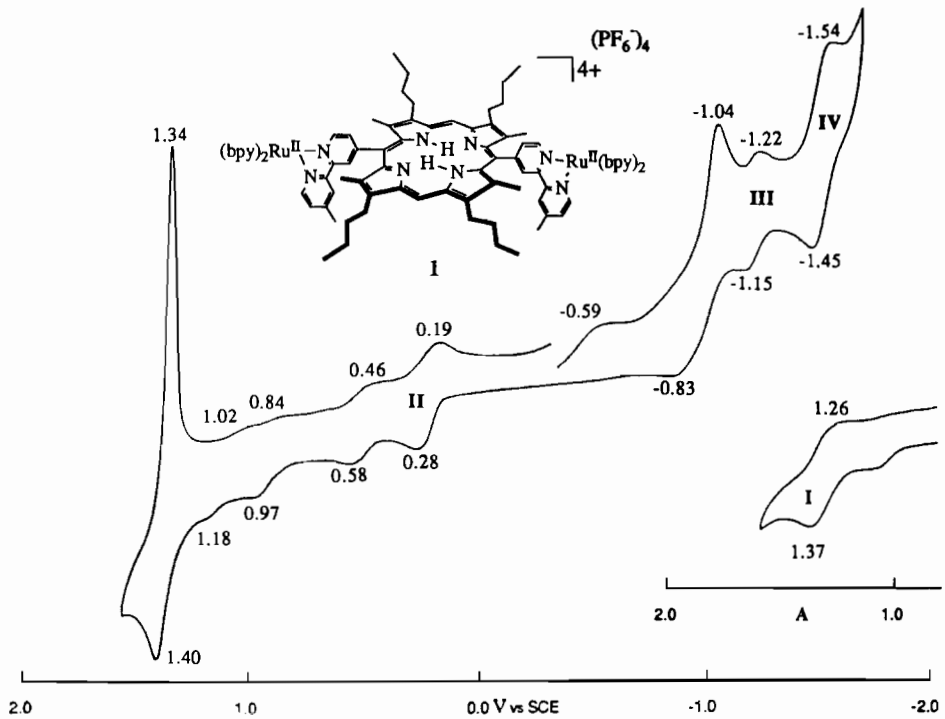


Fig. 7. Cyclic voltammogram of **1** in CH_2Cl_2/0.1 M $TBAPF_6$ at a Pt electrode with a sweep rate of 50 mV/s. Inset A was recorded in CH_3CN/0.1 M $TBAPF_6$ at a Pt electrode with a sweep rate of 50 mV/s and reported relative to SCE for the region 1–2 V and is shown as confirmation that the Ru(III) species precipitates on the electrode as it is formed when CH_2Cl_2 is used as a solvent.

interestingly, the Ru^{II}/Ru^{III} couple, on the other hand, is still observed as a single peak at $E_{1/2} = 1.32$ V versus SCE. The $E_{1/2}$ value for this Ru^{II}/Ru^{III} couple is reported using CH_3CN as a solvent as the $E_{1/2}$ value for this couple could not be accurately determined from the data obtained using CH_2Cl_2 as a solvent. When CH_2Cl_2

TABLE 1. Cyclic voltammetric peak potentials ($E_{1/2}$) for bipyridine functionalized porphyrins and their ruthenium complexes in 0.1 M $TBAPF_6$–dichloromethane solutions at a platinum electrode and a sweep rate of 50 mV/s

Species	V vs. SCE																	
	Oxidations								Reductions									
	$E_{1/2}$	ΔE_p	i_{pa}/i_{pc}[a]	$E_{1/2}$	ΔE_p	i_{pa}/i_{pc}[a]	$E_{1/2}$	ΔE_p	i_{pa}/i_{pc}[a]	$E_{1/2}$	ΔE_p	$E_{1/2}$	ΔE_p	i_{pa}/i_{pc}[a]	$E_{1/2}$	ΔE_p	i_{pa}/i_{pc}[a]
$Ru(bipy)_3^{2+}$	1.35[d]	0.07										−1.32[d]	0.07		−1.51[d]	0.07		
1	1.32[d]	0.11	0.90[c]	0.52			0.24	0.09	0.93[c]			−1.19	0.07		−1.50	0.09	0.91[c]	
2	1.41	0.08	0.98[c]	1.27	0.70		0.89	0.13	0.80[c]	−1.15	0.03	−1.22			−1.54	0.10	0.92[c]	−1.73	0.08	0.96[c]
3	1.20						0.83	0.13	0.78[b]			−1.42	0.07		−1.52			
4				1.23	0.16	0.82[b]	0.83	0.06				−1.43	0.07		−1.56			
Ferrocene	0.41	0.07																

[a]Ref. 15. [b]Recorded in CH_2Cl_2 0.1 $TBAPF_6$ with a sweep rate of 500 mV/s. [c]Recorded in CH_3CN 0.1 $TBAPF_6$ with a sweep rate of 500 mV/s. [d]Recorded in CH_3CN 0.1 $TBAPF_6$ with a sweep rate of 50 mV/s.

was used as the solvent, a Ru(III) species precipitates on the electrode. This results in the very intense reduction peak on the reverse sweep clearly seen in Fig. 7.

In the doubly substituted system **1**, as was true for complex **2**, the complexity of the reduction region makes assignments of the half-wave potentials difficult. In addition, trace amounts of H_2O, presumably arising from hydration of the cationic (+4) porphyrin complex, made the detection of the third ligand-based reduction impossible. However, the first ligand-based reduction wave was easily detected and found, as in the mono-substituted complex **2**, to be relatively anodic ($E_{1/2}$ = −1.19 V versus SCE).

The synthesis of the Ru(II) complexes **1** and **2** is a multistep process. The overall yield is relatively modest. Nonetheless, the procedure allows for the preparation of several tens of milligrams per experiment. Their static absorption and emission spectra are essentially a superposition of non-interacting chromophores, due in part to the constrained orthogonality at the porphyrin–bipyridyl linkage. The more conjugated nature of the first ligand-based reduction for complexes **1** and **2** could lead to an overall orbital pathway for interaction between the two metal centers. We are currently exploring this interaction with mixed-metal complexes and porphyrins that allow for greater overlap between the individual sub units.

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