

(Pentamethylcyclopentadienyl)ruthenium π -Complexes of Metalloporphyrins: Platforms with Novel Photo- and Electrochemical Properties

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Porphyrins and metalloporphyrins provide an extremely versatile synthetic base for a variety of materials applications.^[1] In particular, porphyrin–metallocene conjugates have a great potential in such areas as solar energy conversion,^[2] activation of small molecules,^[3] porphyrin-assisted electron transfer,^[4] or development of molecular devices.^[5] While extensively studied in these various contexts, one potential limitation of porphyrins and metalloporphyrins in photoinduced electron-transfer reactions is that they generally act as electron donors rather than acceptors.^[6] Although there have been some studies involving electron-transfer-derived reduction of metalloporphyrins,^[7,8] in most cases the site of electron capture is not the porphyrin ring but rather a coordinated redox active metal center.^[7,8] This limitation can be overcome by using strong electron donors, such as metallocenes, that may permit the porphyrin-ring-centered

reduction of metalloporphyrins by photoinduced electron transfer. However, for this strategy to be effective a strong electronic interaction between the metallocene and porphyrin units is required and this has rarely been observed. In most cases, the metallocene is simply linked to the macrocycle through different spacers at the porphyrin *meso* or β positions,^[9] through direct linkages through C–C bonds at the *meso* positions,^[10] or by axial coordination of pyridylferrocene.^[11] A more effective strategy might involve direct fusion of a metallocene complex onto the porphyrin π -electron framework and while such compounds have been known synthetically for a decade, little has been done to expand this synthetic approach or investigate the electronic communication between the metal centers.^[12] Recently, the fusion of a cyclopentadiene ring onto one of the pyrroles of a porphyrin was studied in an effort to enhance such electronic communication, and yielded encouraging results.^[13] However, the photoinduced electron transfer of this or other metallocene–porphyrin complexes has yet to be explored.^[14] It thus remains an open question whether the direct fusion strategy can be used to “convert” a porphyrin ring from a photodonor into a photoacceptor.

Here we report the synthesis and characterization of three new hybrid metalloporphyrin–ruthenocene compounds, in which a metal–cyclopentadienyl fragment is linked to a porphyrin core by direct coordination, and by using a combination of cyclic voltammetry, UV/Vis spectroelectrochemistry, ESR spectroscopy, and femtosecond and nanosecond laser flash photolysis analyses, we show that photoinduced electron transfer from the ruthenocene moiety (acting as a donor) to the singlet excited state of metalloporphyrins (acting as an acceptor) takes place efficiently following photoexcitation.

Recently, we found that $[\text{Ru}(\text{CH}_3\text{CN})_3(\text{Cp}^*)][\text{PF}_6]$ ($\text{Cp}^* =$ pentamethylcyclopentadienyl) is an excellent precursor for the formation of multi-metallocene species based on non-

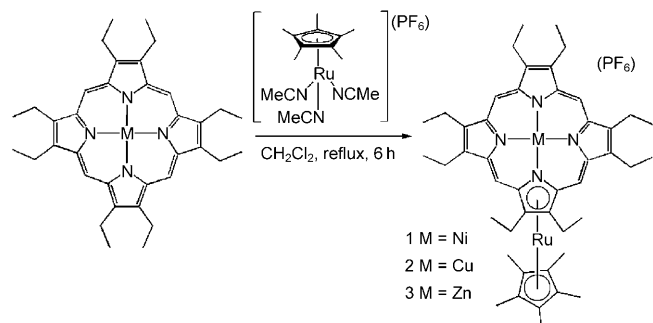
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conjugated tetrapyrrolic ligands.^[15] The reaction between this semi-sandwich complex and the zinc(II), copper(II), or nickel(II) metalloctaethylporphyrins provides the corresponding mixed porphyrin–metallocene compounds in good yields (see Scheme 1 and the Supporting Information for details).



Scheme 1. Synthesis of bimetallic complexes **1**, **2**, and **3**.

The new bimetallic complexes were isolated as air-stable dark green solids and characterized by elemental analysis, mass spectrometry, and NMR or EPR spectroscopies; in addition, complexes **2** and **3** were characterized by means of X-ray diffraction in the solid state (see Figure 1).^[16] The single-crystal X-ray analyses of **2** and **3** support the proposed formation of sandwich-type structures, and further reveal that the Cp* ligand and the porphyrin rings are

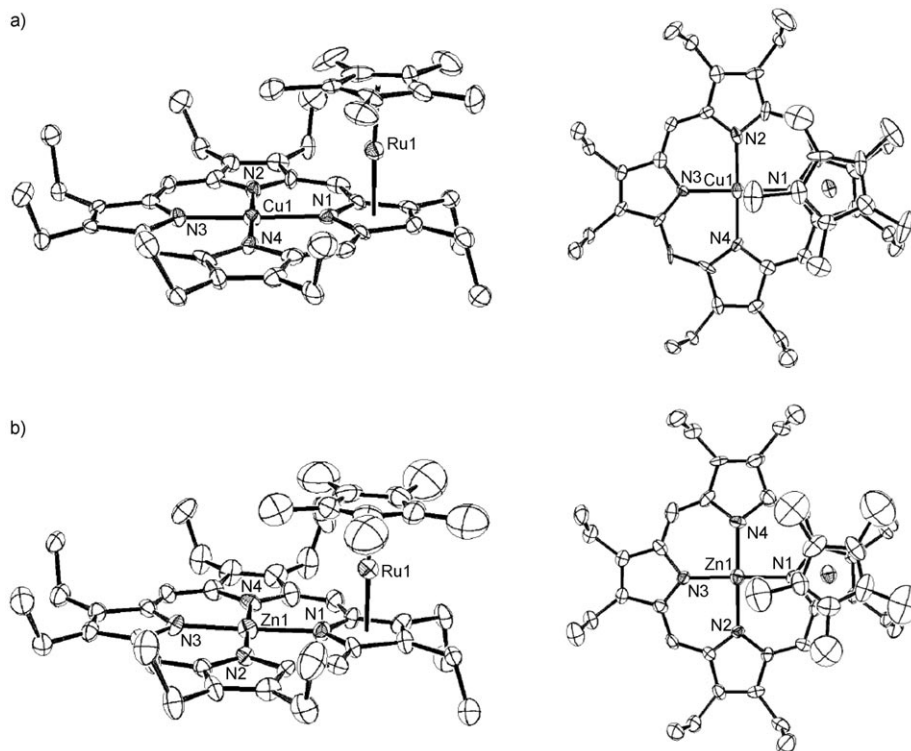


Figure 1. Side and top views of a) **2** and b) **3**, showing partial atom labeling schemes. Displacement ellipsoids are scaled to the 30% probability level. Hydrogen atoms and PF₆ counterions have been removed for clarity.

almost parallel. This latter finding stands in contrast with the previous ruthenium–arene–porphyrin complexes reported by Rauchfuss, systems in which the [Ni(OEP)] macrocycle (OEP=octaethylporphyrin) was found to be severely nonplanar upon coordination, whereas the [Zn(OEP)] macrocycle was found to be closer to planarity.^[12]

The UV/Vis spectra of these bimetallic compounds display bands that are broadened and redshifted relative to those for the respective metalloporphyrins. Although a number of factors could contribute to this, it is a potential indication of effective electronic communication between the organometallic moieties and the macrocyclic cores. Further evidence of a possibly strong electronic perturbation caused by π -complexation to the porphyrin core is the fact that all the “mixed” ruthenocene–porphyrin molecules give rise to only very weak fluorescence (see Figure S1 in the Supporting Information). The presumption that this coupling was indeed strong led us to propose that porphyrinic cores in systems **1–3** would act as electron acceptors following photoexcitation. As described below, this was established through photophysical analyses.

As a prelude to the photophysical analyses, the electrochemical properties of system **1–3** were examined by cyclic voltammetry (Figure 2). Ni^{II} compound **1** shows three well-resolved oxidations located at $E_{1/2}$ =1.08, 1.23, and E_p =1.51 V and two reductions located at $E_{1/2}$ =−0.78 (E_p =−0.83 V) and $E_{1/2}$ =−1.34 V. A comparison of these data with the electrochemical behavior of [Ni^{II}(OEP)] (Figure S2 in the Supporting Information) reveals that fusion of the organometallic fragment results in a dramatic change in the electronic properties of the macrocycle, as judged by the increase in the number of electrochemical events and the evident shifts in the potentials.

The UV/Vis spectral changes observed during the oxidation or reduction of metalloporphyrins have been often used to determine the site of electron transfer. If the intensity of the Soret band is strongly affected, the process is generally ring-centered; if the absorptivity of the Soret band undergoes little or no change, the electron-transfer reactions can be assigned as metal-centered.^[17] Changes in the Soret band upon oxidation and reduction (Figures S3 and S4, respectively, in the Supporting Information) were monitored by spectroelectrochemistry. These analyses revealed virtually no change and thus provided support for the

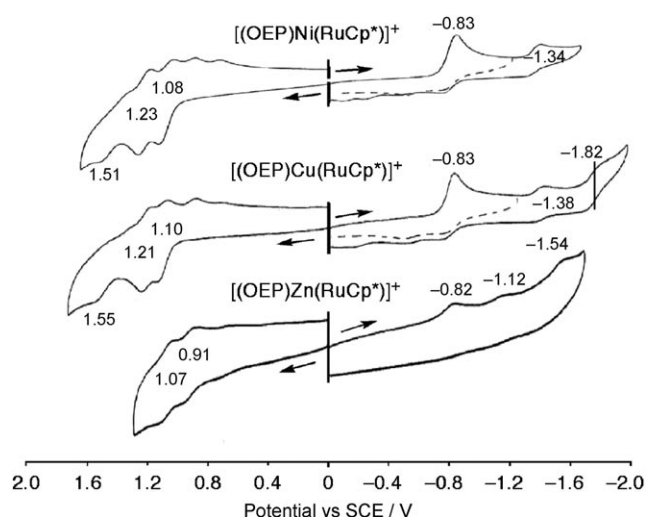


Figure 2. Cyclic voltammograms of the investigated compounds in CH_2Cl_2 , with 0.1 M TBAPF₆ (TBA=tetrabutylammonium) as the supporting electrolyte.

conclusion that the first two oxidations and the second reduction at **1** are metal-centered.^[18] Accordingly, the third oxidation and the initial reduction must be localized on the porphyrin π -system. The first metal-centered oxidation can be assigned to the ruthenocene moiety; this assignment is consistent with the ESR spectroscopy result described below. It is also in good agreement with the results found by Kadish, Smith, and co-workers for β,β' -fused ruthenocenceporphyrins^[13] and with the fact that ruthenocene itself undergoes an initial one-electron oxidation.^[19]

Cu^{II} complex **2** undergoes three well-resolved oxidations located at $E_{1/2}=1.10$, 1.21, and $E_p=1.55$ V. Three reductions located at $E_p=-0.83$, $E_{1/2}=-1.38$, and -1.82 V are also observed (see Figure 2). These data reveal a considerable difference between this compound and its precursor [Cu^{II}(OEP)] (Figure S2 in the Supporting Information), which gives evidence for the important effect caused by the incorporation of the [Ru(Cp*)]⁺ fragment in the system. Analyses of the UV/Vis spectral changes during time-resolved controlled potential oxidation and reduction (see Figures S5 and S6 in the Supporting Information) leads us to suggest that the first oxidation is metal-centered; in analogy to compound **1**, they have been ascribed to the ruthenium center.

Zn^{II} complex **3** also displays a rich electrochemistry, namely, two oxidations and three reductions; unfortunately, these processes lack electrochemical reversibility on the time scale of cyclic voltammetry (see Figure 2).

Complex **2** and its one-oxidation product were further characterized by ESR spectroscopy. The original spectrum of **2** shows the typical pattern and g values of a Cu^{II} porphyrin,^[20] whereas the ESR spectrum of the mono-oxidized species with [Ru(bpy)₃][PF₆]₃ (Figure 3; bpy = 2,2'-bipyridine) provides clear evidence for the presence of strong electronic communication between the two electroactive fragments, as judged by the large spin-spin coupling observed between the Cu^{II} and Ru^{III} centers. Because the zero-field splitting

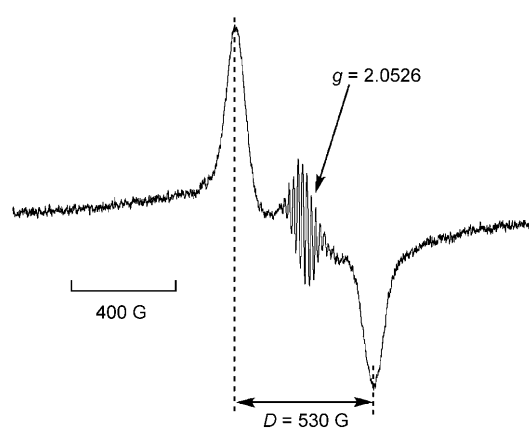


Figure 3. ESR spectrum of **2** produced by oxidation using [Ru(bpy)₃][PF₆]₃ in frozen CH_2Cl_2 at -150°C .

constant ($D=530$ G)^[21] depends on the distance between two electrons with parallel spins, the distance between the two spins can be evaluated from the D value to be 3.74 \AA .^[22] This is in close agreement with the separation between the Cu^{II} and Ru^{III} centers as revealed by X-ray diffraction analysis (i.e., $3.732(2) \text{ \AA}$).

Femtosecond laser excitation of **2** afforded the transient absorption spectra with absorption bands at $\lambda=510$, 650, and 720 nm, as shown in Figure 4, whereas no transient absorption was observed for [Cu(OEP)] at 2.5 ns after the laser excitation (see Figure S7 in the Supporting Information). The transient absorption bands at $\lambda=650$ and 720 nm with bleaching at $\lambda=750$ nm can clearly be assigned to the [Cu(OEP)] radical anion after comparison with the spectrum of the one-electron reduced species of **2** (see Figure S5 in the Supporting Information). The transient absorption band at $\lambda=510$ nm is assigned to the one-electron oxidized species of **2** in which the Ru center is oxidized (Figure S6 in the Supporting Information).^[23] Thus, photoinduced electron transfer occurs to produce a charge-separated (CS) state. The lifetime of this CS state was determined to be 63 ns by

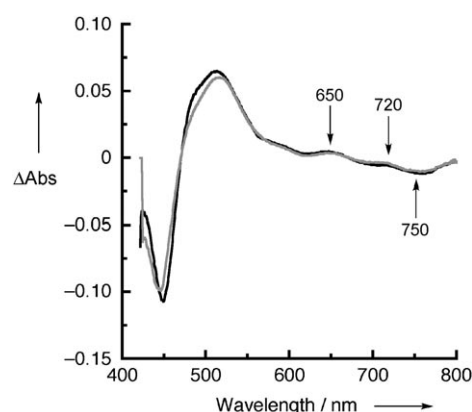


Figure 4. Transient absorption spectra of **2** in THF, taken 50 (—) and 2500 ps (---) after femtosecond laser pulse irradiation by a 410 nm laser at 298 K.

monitoring the single exponential decay of the transient absorption at $\lambda = 510$ nm produced as the result of nanosecond laser flash photolysis (Figure 5).

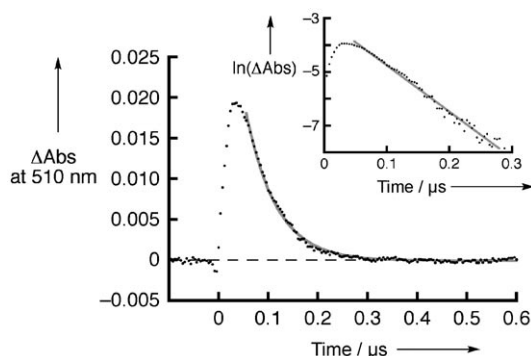


Figure 5. Decay time profile of the absorbance feature at 510 nm observed after nanosecond laser photoexcitation of **2** in THF. Inset: First-order plot.

Similar transient absorption spectra were observed after femtosecond laser excitation of **1** and **3**; once again, a CS state that involved the porphyrin acting as a photoacceptor was produced (see Figure S8 in the Supporting Information).^[24] The lifetime of the CS state of **1** was determined to be 180 ps (Figure S9 in the Supporting Information). In the case of **3**, the CS state decays to the triplet excited state of [Zn(OEP)], a species in which the characteristic features were detected by nanosecond laser flash photolysis of **3** (Figure S10 in the Supporting Information).

In summary, a series of fused metalloporphyrin–ruthenocene compounds has been synthesized by direct coordination of a [Ru(Cp*)]⁺ fragment to the π -electron “face” of several metalloctaethylporphyrins. The optical and electrochemical properties of this new family of compounds are consistent with the presence of a strong electronic interaction between the fused organometallic moiety and the porphyrin core. These strong interactions, in turn, allow for efficient photoinduced electron transfer from the ruthenocene unit to the singlet excited state of the metalloporphyrin after laser flash photolysis. The result is a CS state in which the porphyrin macrocycle acts as an electron acceptor and the ruthenocene moiety acts as a donor. Because this approach allows for an effective “reversal” of the normal character of metalloporphyrins, we think it provides a promising new approach to the creation of photovoltaic devices that could prove useful in a number of areas.

Experimental Section

Detailed synthetic procedures and characterization of **1–3** are given in the Supporting Information.

Cyclic voltammetry was carried out by using an EG&G Princeton Applied Research (PAR) 173 potentiostat/galvanostat. A homemade three-electrode cell was used for cyclic voltammetric measurements and con-

sisted of a glassy carbon working electrode, a platinum counter-electrode, and a homemade saturated calomel reference electrode (SCE). UV/Vis spectroelectrochemical experiments were performed by using a homemade thin-layer cell with a light-transparent platinum net working electrode. Potentials were applied and monitored by using an EG&G PAR Model 173 potentiostat.^[25] Time-resolved UV/Vis spectra were recorded by using a Hewlett-Packard Model 8453 diode array spectrophotometer. Femtosecond laser flash photolysis was conducted by using a Clark-MXR 2010 laser system and an optical detection system provided by Ultrafast Systems (Helios). Typically, 5000 excitation pulses were averaged to obtain the transient spectrum at a set delay time. The kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Nanosecond time-resolved transient absorption measurements were carried out by using the laser system provided by UNISOKU Co. The photodynamics were monitored by continuous exposure to a xenon lamp (150 W) as a probe light and a photomultiplier tube (Hamamatsu 2949) as a detector. Transient spectra were recorded by using fresh solutions in each laser excitation. The solution was deoxygenated by argon purging for 15 min prior to measurements.

The ESR spectrum of oxidized **2** was recorded by using a JEOL JES-RE1XE spectrometer. The singly oxidized products were produced by a one-electron oxidation of the **2** with [Ru(bpy)₃](PF₆)₃. The *g* value and zero-field splitting constant were calibrated by using Mn²⁺ markers.

The X-ray data were collected at 153 K on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoK α radiation ($\lambda = 0.71073$ Å) and equipped with an Oxford Cryostream low temperature device.

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- [1] *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, Boston, **2000**, 1–10.
- [2] a) K. Uosaki, T. Kondo, X.-Q. Zhang, M. Yanagida, *J. Am. Chem. Soc.* **1997**, *119*, 8367–8368; b) H. Nakagawa, K. Ogawa, A. Sakate, Y. Kobuk, *Chem. Commun.* **2006**, 1560–1562; c) D. Kalita, M. Mourise, Y. Kokube, *New J. Chem.* **2006**, *30*, 77–92.
- [3] P. D. Beer, M. G. B. Drew, D. Hesk, R. Jagessar, *J. Chem. Soc. Chem. Commun.* **1995**, 1187–1189.
- [4] a) P. M. Hoffman, J. A. Ibers, *Acc. Chem. Res.* **1983**, *16*, 15–21; b) B. Koszarna, H. Butenschoen, D. T. Gryco, *Org. Biomol. Chem.* **2005**, *3*, 2640–2645.
- [5] a) N. B. Thornton, H. Wojtowicz, T. Netzel, D. W. Zixon, *J. Phys. Chem. B* **1998**, *102*, 2101–2110; b) C. Bucher, C. H. Devillers, J.-C. Moutet, G. Royal, E. Saint-Aman, *Chem. Commun.* **2003**, 888–889.
- [6] a) S. Fukuzumi, H. Imahori in *Electron Transfer in Chemistry, Principles, Theories, Methods, and Techniques, Vol. 2* (Eds.: V. Balzani, P. Piotrowiak, M. A. J. Rodgers, J. Mattay, D. Astruc, H. B. Gray, J. Winkler, S. Fukuzumi, T. E. Mallouk, Y. Haas, A. P. de Silva, I. Gould), Wiley-VCH, Weinheim, **2001**, pp. 927–975; b) D. Gust, T. A. Moore in *The Porphyrin Handbook, Vol. 8* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, p. 153.

- [7] Protonated porphyrins can act as good electron acceptors, see: T. Kojima, T. Nakanishi, R. Harada, K. Ohkubo, S. Yamauchi, S. Fukuzumi, *Chem. Eur. J.* **2007**, *13*, 8714–8725.
- [8] S. Fukuzumi, K. Ohkubo, W. E. Z. Ou, J. Shao, K. M. Kadish, J. A. Hutchison, K. P. Ghiggino, P. J. Sentic, M. J. Crossley, *J. Am. Chem. Soc.* **2003**, *125*, 14984–14985.
- [9] a) R. W. Wagner, T. E. Johnson, J. S. Lindsey, *Tetrahedron* **1997**, *53*, 6755–6790; b) H. Imahori, K. Tamaki, D. M. Guldi, C. Luo, M. Fujitsuka, O. Ito, Y. Sakata, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 2607–2617; c) A. K. Burrell, W. M. Campbell, D. L. Officer, S. M. Scott, K. C. Gordon, M. R. McDonald, *J. Chem. Soc. Dalton Trans.* **1999**, 3349–3354; d) D. Curriel, K. Ohkubo, J. R. Reimers, S. Fukuzumi, M. J. Crossley, *Phys. Chem. Chem. Phys.* **2007**, *9*, 5260–5266.
- [10] a) P. D. W. Boyd, A. K. Burrell, W. M. Campbell, P. A. Cocks, K. C. Gordon, G. B. Jameson, D. L. Officer, Z. Zhao, *Chem. Commun.* **1999**, 637–638; b) S. W. Rhee, Y. H. Na, Y. Do, J. Kim, *Inorg. Chim. Acta* **2000**, *309*, 49–56; c) J. Rochford, A. D. Rooney, M. T. Pryce, *Inorg. Chem.* **2007**, *46*, 7247–7249; d) V. A. Nadtochenko, N. N. Denisov, V. Y. Gak, N. V. Abramova, N. M. Loim, *Russ. Chem. Bull.* **1999**, 1900–1903.
- [11] Y. Kashiwagi, H. Imahori, Y. Araki, O. Ito, K. Yamada, Y. Sakata, S. Fukuzumi, *J. Phys. Chem. A* **2003**, *107*, 5515–5522.
- [12] a) K. K. Dailey, G. P. A. Yap, A. L. Rheingold, T. B. Rauchfuss, *Angew. Chem.* **1996**, *108*, 1985; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1833; b) K. K. Dailey, T. B. Rauchfuss, *Polyhedron* **1997**, 3129; c) R. G. Wollmann, D. N. Hendrickson, *Inorg. Chem.* **1977**, *16*, 3079–3089.
- [13] H. J. H. Wang, L. Jaquinod, M. M. Olmstead, M. G. H. Vicente, K. M. Kadish, Z. Ou, K. M. Smith, *Inorg. Chem.* **2007**, *46*, 2898–2913.
- [14] Although photoinduced electron transfer from the ferrocene moiety to metalloporphyrins in ferrocene–metalloporphyrin complexes has been postulated, no charge-separated state has so far been detected (see ref. [11]).
- [15] L. Cuesta, D. Gross, V. M. Lynch, Z. Ou, W. Kajonkijya, K. Ohkubo, S. Fukuzumi, K. M. Kadish, J. L. Sessler, *J. Am. Chem. Soc.* **2007**, *129*, 11696–11697.
- [16] Crystallographic data for **2**: triclinic, $P\bar{1}$ (No. 2); $a=10.191(2)$, $b=15.570(2)$, $c=17.858(3)$ Å; $\alpha=110.550(6)$, $\beta=105.170(7)$, $\gamma=90.970(7)^\circ$; $V=2542.2(7)$ Å³; $Z=2$; $T=-120^\circ\text{C}$; $R=0.0907$, $R_w=0.1175$; $\text{GOF}=1.217$. Crystallographic data for **3**: triclinic, $P\bar{1}$ (No. 2); $a=10.4590(5)$, $b=15.7622(7)$, $c=18.152(1)$ Å; $\alpha=112.100(2)$, $\beta=93.280(2)$, $\gamma=105.280(2)^\circ$; $V=2633.3(17)$ Å³; $Z=2$; $T=-120^\circ\text{C}$; $R=0.0802$, $R_w=0.1470$; $\text{GOF}=1.106$. CCDC-693147 (**2**) and -693148 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [17] K. M. Kadish, E. V. Caemelbecke, G. Royal in *The Porphyrin Handbook, Vol. 8* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard.), Academic Press, Boston, **2000**, Chapter 55, pp. 1–260.
- [18] The metal-centered reduction is assigned to the ruthenium fragment because numerous Ni^{II} porphyrins have been electrochemically characterized and invariably the reductions do not involve the Ni center; see: K. M. Kadish, E. Van Caemelbecke, G. Royal in *The Porphyrin Handbook, Vol. 8* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, chap. 55, pp. 66–72.
- [19] The electrochemical oxidation of ruthenocene was reported to afford the dimer dication; see: S. Trupia, A. Nafady, W. E. Geiger, *Inorg. Chem.* **2003**, *42*, 5480–5482.
- [20] K. L. Cunningham, K. M. McNett, R. A. Pierce, K. A. Davis, H. H. Harris, D. M. Falck, D. R. McMillin, *Inorg. Chem.* **1997**, *36*, 608–613.
- [21] The outer line of the $\Delta MS=1$ transition along the z axis is not seen due to the broadening of the small signal. However, the signal perpendicular to z is clearly observed, and affords the D value. A doublet species is observed at the center of the ESR spectrum, however, the amount is negligible.
- [22] J. E. Wertz, J. R. Bolton, *Electron Spin Resonance: Elementary Theory and Practical Applications*, McGraw-Hill, New York, **1972**, pp. 223–257.
- [23] The absorption spectrum of $[\text{Ru}(\text{Cp})_2]^+$ was reported to exhibit a shoulder absorption at around 500 nm; see: M. S. Rodriguez-Morgade, T. Torres, C. Atienza-Castellanos, D. M. Guldi, *J. Am. Chem. Soc.* **2006**, *128*, 15145–15154. An increase in absorbance around 500 nm due to the oxidized $[\text{Ru}(\text{Cp}^*)]^+$ unit is also observed in the electrochemical oxidation of **2** (Figure S4 in the Supporting Information).
- [24] A distinctive transient absorption maximum is observed at 770 nm in the femtosecond laser flash photolysis of **1** (Figure S9 in the Supporting Information), a spectral feature that is assigned to a $[\text{Ni}(\text{OEP})]^-$ π -radical anion based on the spectroelectrochemical data obtained following the first reduction of **1** (Figure S7 in the Supporting Information).
- [25] X. Q. Lin, K. M. Kadish, *Anal. Chem.* **1985**, *57*, 1498–1501.

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