# Photochemical Reduction of Cerium(IV) Porphyrin Sandwich Complexes

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Irradiation of cerium(IV) complexes of 5,10,15,20-tetraphenyl- and 2,3,7,8,12,13,17,18-octaethylporphyrin ($H_2$tpp and $H_2$oep, respectively) with visible light, in the presence of triethylamine as an electron donor, leads to their photoreduction. The process was followed using electron absorption and ESR spectroscopies. Photoirradiation of $[Ce^{IV}\{tpp(-2)\}_2]$ resulted in the formation of $[Ce^{III}\{tpp(-2)\}\{tpp(-2)\}]^-$. The reverse oxidation of this compound with chloroform as an electron acceptor was also observed. The photoreduction of $[Ce^{IV}\{oep(-2)\}\{oep(-2)\}]$ was more complicated, giving rise to the photoreduced neutral complex $[Ce^{III}\{oep(-1)\}\{oep(-2)\}]$ which exhibits an ESR spectrum typical of lanthanoid(III) bis(porphyrinates).

The lanthanoid porphyrin sandwich complexes are of growing interest since their first synthesis in 1985 by Buchler, Weiss and co-workers.[1,2] In a series of papers they characterized bis(octaethylporphyrin) sandwich compounds of $Ce^{IV}$ and all the trivalent rare-earth elements, with the exception of $Ce^{III}$ and radioactive Pm.[3–6] Similar sandwiches have been prepared with tetraphenyl- and tetratolyl-porphyrins[7–9] and complexes containing different porphyrin rings[9–12] or porphyrin and phthalocyanine rings are also known.[13,14] It is believed that such closely coupled dimeric porphyrins of magnesium (distance between the rings is $\approx$3–4 Å) can play a significant role in the bacterial photosynthetic reaction centres.[13–17]

A schematic view of the ring arrangements in the sandwich 2,3,7,8,12,13,17,18-octaethylporphyrin ($H_2$oep) and 5,10,15,20-tetraphenylporphyrin ($H_2$tpp) complexes is shown in Fig. 1. The cerium 4+ cation is located between two porphyrin dianions and has a co-ordination number of eight, characteristic for the rare-earth-metal complexes. Inasmuch as the most common oxidation state for other lanthanoids is +3, Buchler, Weiss and co-workers[1,3,4,6] have proposed that the +3 ion is encompassed by one normal dianion and a second radical $\pi$ cation, similar to the analogous bis(phthalocyaninato)-lanthanoid(III) compounds.[18,19] According to the nomenclature originally used for the phthalocyanines,[20] in which the dianion is written as P(−2) and the cation radical as P(−1), the formula of the cerium(IV) and other trivalent lanthanoid sandwiches can be written as $Ce^{IV}[P(-2)]_2$ and $Ln^{III}[P(-2)P(-1)]$.

Much interest has been focused on the redox reactions of lanthanoid porphyrin sandwich complexes. Radical $\pi$ cations $[Ce^{IV}P(-2)P(-1)]^+$ and $[Ln^{III}P(-1)(-1)]^+$ were formed in electrochemical and chemical ways.[6,8,10,21,22] Reduced cerium(IV) sandwich porphyrin anions had initially been observed by cyclic voltammetry and have recently been isolated as the tetrabutylammonium salts.[23]

The photooxidation of bis(octaethylporphyrinato)cerium(IV) in toluene solution in the presence of an electron acceptor such as $CCl_4$ has recently been reported.[22] In this paper we present results of the photoreduction of cerium(IV) octaethyl- and tetraphenyl-porphyrin sandwich complexes in the presence of an electron donor. Steady-state photolysis of the complexes in triethylamine or toluene–triethylamine solutions was monitored by absorption spectroscopy and electron spin resonance. We have considered the question of whether one-electron reduction takes place on the ligand or on the cerium centre of the sandwich.

## Experimental

*Materials.*—5,10,15,20-Tetraphenylporphyrin and 2,3,7,8,-12,13,17,18-octaethylporphyrin (Aldrich) were used without additional purification. Cerium(III) acetylacetonate hydrate was purchased from Strem Chemicals, triethylamine of highest available purity from Fluka. Basic aluminium oxide (activity 60, 70–230 mesh, Merck) was used for the column chromatography. All the solvents were certified as purex for analysis grade [Solvents, Documentation, Syntheses (SDS)] and were kept over 3 Å molecular sieves. Toluene was additionally dried by distillation over $CaH_2$.

*Synthesis.*—Cerium(IV) bis(octaethylporphyrinate) and bis(tetraphenylporphyrinate) were prepared by prolonged heating (24 h) at reflux of mixtures of cerium(III) acetylacetonate hydrate and $H_2$oep or $H_2$tpp respectively in 1,2,4-trichlorobenzene under an argon atmosphere, according to the procedure described by Buchler and co-workers.[1,6,9] After completion of the reaction the 1,2,4-trichlorobenzene was removed by evaporation under reduced pressure. The residue was vacuum dried overnight, dissolved in $CH_2Cl_2$ and applied to the top of a basic $Al_2O_3$ column. The toluene-eluted fractions of the pure compounds (purity was checked by absorption spectroscopy and TLC) were pooled. The solvent was removed by vacuum evaporation. The final products, after being vacuum-dried overnight, were obtained as amorphous powders {Found: C, 68.70; H, 7.05; N, 7.95. Calc. for $[Ce(oep)_2]\cdot 4H_2O$ ($C_{72}H_{96}CeN_8O_4$): C, 67.70; H, 7.55; N, 8.75%. UV/VIS (chloroform) [$\lambda_{max}$(log $\varepsilon$)]: 377.6 (4.89), 472 (3.74), 529.6 (3.51), 572.4 (3.94) and 658 (2.97). Found: C, 76.60; H, 5.40; N, 7.85. Calc. for $[Ce(tpp)_2]$ ($C_{88}H_{56}CeN_8$): C, 77.40; H, 4.15; N, 8.20%) UV/VIS (toluene) [$\lambda_{max}$(log $\varepsilon$)]: 396.2 (5.30), 486.0 (4.09), 540.7 (3.98) and 631 (3.41)}.

*Measurements.*—Absorption spectra were taken with a Perkin Elmer Lambda 5 spectrophotometer, using 1 cm quartz cells to record in the 300–900 nm region at a temperature of 21 ± 1 °C. The ESR spectra were run on Bruker ER-420 and ESP-300 spectrometers operating with 100 kHz field modulation, fitted with an ER-400-X-RL cavity and B-V-T variable-temperature controller and ESR-900 (Oxford) liquid-helium facilities, respectively. The elemental analysis was performed by Service Central des Microanalyses du CNRS.

*Method.*—Steady-state photolysis of the argon-purged

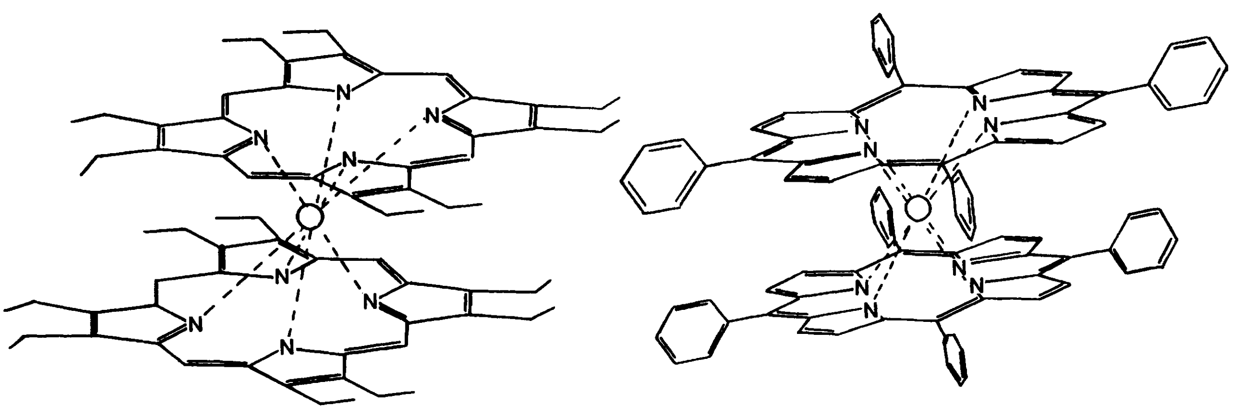


Fig. 1 Molecular structure of [Ln(oep)$_2$] and [Ln(tpp)$_2$] complexes

solutions was carried out at 21 ± 1 °C up to the moment when decomposition of the compound was detected by a decrease in all the bands without any change in their relative intensities. The electron donor (triethylamine) was added to the solutions immediately before the start, as in previous studies.[22,24–26] A 250 W THORN halogen projector lamp was used for the sample irradiation. The light was filtered to remove UV ( < 400 nm) radiation.

## Results and Discussion

The changes in the absorption spectrum during photolysis of a $6.8 \times 10^{-6}$ mol dm$^{-3}$ [Ce(tpp)$_2$] solution in toluene containing 0.3 mol dm$^{-3}$ triethylamine are shown in Fig. 2. Two sharp isosbestic points are present at 400 and 550 nm. The B band of the starting solutions at 395 nm shifts to 410.5 nm and the Q band shifts as well, from 541.2 to 560 nm. The band at 486 nm fades and a new band at 610 nm appears. The weak band at 652 nm present for the starting solutions is due to the tiny contamination of the [Ce(tpp)$_2$] by tetraphenylchlorin.[27,28] The tetraphenylchlorin is formed during the synthesis as a by-product of the oxidation of Ce$^{\text{III}}$ to Ce$^{\text{IV}}$. Despite repeating the column chromatography purification we were not able to remove the chlorin completely. After 7 min of photolysis, a black solid was precipitated. This product proved highly sensitive and our attempts to isolate it were unsuccessful, despite the use of a dry-box and an argon atmosphere. When the precipitate is dissolved in chloroform the resulting absorption spectrum is either that of [Ce(tpp)$_2$] or a mixture of the two B bands: 395 and 410 nm.

To check whether the photoreduction of [Ce(tpp)$_2$] is reversible, 5% (v/v) of chloroform was added to the final product of photoreduction, at the end of precipitation. After the precipitate had dissolved, the mixture was irradiated again. Fig. 3 clearly shows that photoreduction is fully reversible. Following initial irradiation, two sharp isosbestic points can be seen at the same wavelengths as previously observed for the reduction process. The spectrum of the final solution is the same as that of [Ce(tpp)$_2$]. Longer irradiation (more than 5 min) leads to the formation of a new band at 445 nm (last dotted line in Fig. 3). This band has recently been reported for the first time.[22] The important red shift of the B band suggests major structural changes. This phenomenon might be connected with demetallation of the complex and dication [H$_4$tpp(−2)]$^{2+}$ formation.

The photoreduction of [Ce(oep)$_2$] does not run so smoothly as that of the tetraphenyl sandwich, regardless of an increased concentration of triethylamine and prolonged irradiation. Reduction occurred when [Ce(oep)$_2$] was dissolved in pure triethylamine (Fig. 4). Isosbestic points were not observed, as a flocky red-brown precipitate appeared before the reaction was complete. Formation of this precipitate is responsible for the rapid decrease in the B band (Fig. 4). However, a significant change in spectrum can be observed. The B band at 377.2 nm shifts to 393.5 nm. The components of the Q band are shifted from 472.0, 529.6 and 572.4 to 488.0, 546.2 and 589.1 nm, respectively. As for the tetraphenylporphyrin sandwich, we were not able to isolate the product of reduction. The back oxidation to [Ce(oep)$_2$] is almost instantaneous.

Scheme 1 shows possible one-electron transfer reactions of the lanthanoid sandwich porphyrins. The electronic absorption spectral distribution and the intensity of bands due to the metal and ring-oxidized or -reduced porphyrins arise from the combination of $\pi$–$\pi^*$ and metal-to-ligand or ligand-to-metal charge transfer inside the 18$\pi$-electron ring.[26,29,30] It has been demonstrated that if the symmetry of the porphyrin complex does not change (all sandwiches considered here have approximate $D_{4d}$[31,32]) the spectra should be analogous for the compounds with the same $\pi$-electron distribution on the porphyrin rings. It has clearly been demonstrated using UV, IR and magnetic circular dichroism (MCD) spectroscopy that the spectrum of the $\pi$-radical cation [Ce$^{\text{IV}}$P(−1)P(−2)]$^+$ is essentially the same as that of the neutral trivalent lanthanoid complexes [Ln$^{\text{III}}$P(−1)P(−2)].[6,10,12,22,31] The same resemblance is observed when one compares the spectrum of the [Ce$^{\text{IV}}${tpp(−2)}{tpp(−2)}] photoreduction product with that of the product of [Ln$^{\text{III}}${tpp(−1)}{tpp(−2)}] electroreduction in the presence of tetrabutylammonium bromide, recently published by Buchler *et al.*[23] These spectra are basically indentical and we can assume that as a result of the Ce(tpp)$_2$ sandwich photoreduction, [Ce$^{\text{III}}${tpp(−2)}{tpp(−2)}]$^-$ is formed. The absence of intense broad bands in the region 600–800 nm, characteristic for radical $\pi$ anions,[6,33,34] excludes the possibility of formation of the $\pi$-anion radical [Ce$^{\text{IV}}${tpp(−3)}{tpp(−2)}]$^-$. The possibility of an electron transfer from the metal to the ring, leading to a $\pi$-radical anion [Ce$^{\text{IV}}$P(−3)P(−2)]$^-$ has to be taken into consideration. In such a compound the electron possibly delocalized over two porphyrin rings could modify the electronic absorption spectrum. However, the formation of such a radical is not supported by ESR measurements (see below).

The photoreduction of the [Ce$^{\text{IV}}${oep(−2)}{oep(−2)}] sandwich is different. Surprisingly, the final spectrum is not that of [Ce$^{\text{III}}${oep(−2)}{oep(−2)}]$^-$, but it is essentially the same as the spectra of the neutral trivalent lanthanoid complexes [Ln$^{\text{III}}${oep(−1)}{oep(−2)}].[6] The photoreduction of the octaethylporphyrin complex to [Ce$^{\text{III}}${oep(−2)}{oep(−2)}]$^-$ is probably almost immediately followed by a one-electron oxidation. In the latter process, contrary to cerium tetraphenylporphyrinate oxidation, not a Ce$^{\text{III}}$ but the octaethylporphyrin ring is oxidized to form a neutral sandwich [Ce$^{\text{III}}${oep(−1)}{oep(−2)}] and the process is rapidly reversible to the initial [Ce(oep)$_2$] complex. The formation of the neutral sandwich [Ce$^{\text{III}}${oep(−1)}{oep(−2)}] is confirmed by the presence of a near-IR band (about 1400 nm), characteristic for the sandwich species containing one normal and one oxidized ring, *e.g.*

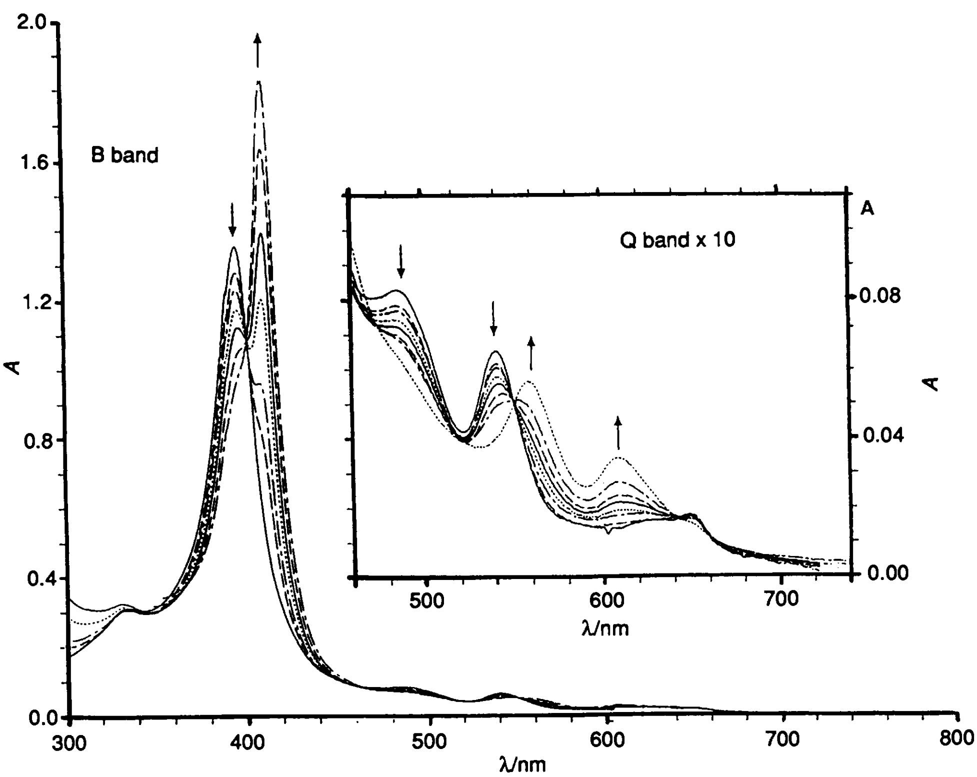


**Fig. 2** Evolution of the absorption spectra of a [Ce$^{IV}${tpp(−2)}{tpp(−2)}] (6.8 × $10^{-6}$ mol dm$^{-3}$) solution in toluene containing 0.3 mol dm$^{-3}$ triethylamine, upon photoreduction. Spectra are shown for 0, 0.5, 1, 2, 3, 5 and 7 min of irradiation

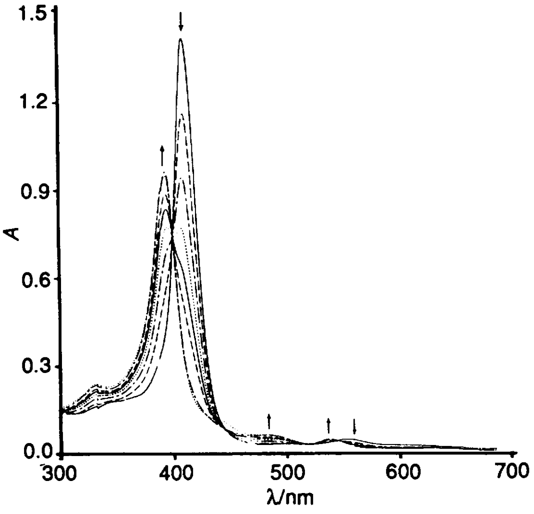


**Fig. 3** Evolution of the absorption spectra of [Ce$^{III}${tpp(−2)}{tpp(−2)}]$^-$ in toluene containing 0.3 mol dm$^{-3}$ triethylamine and 5% (v/v) chloroform, upon photooxidation. Spectra were taken for 0, 0.25, 0.5, 0.75, 1, 2, 3 and 5 min of irradiation

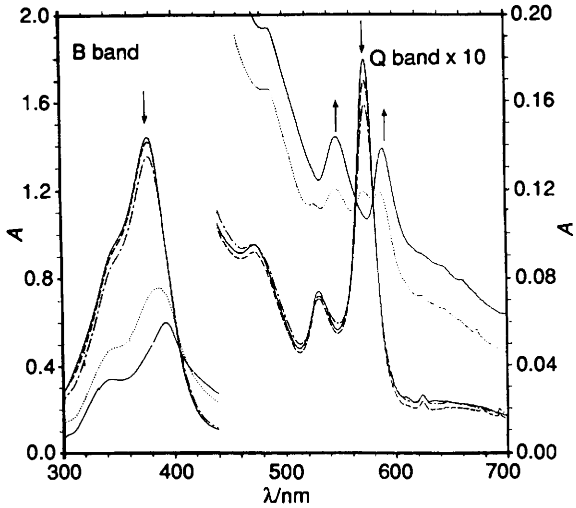


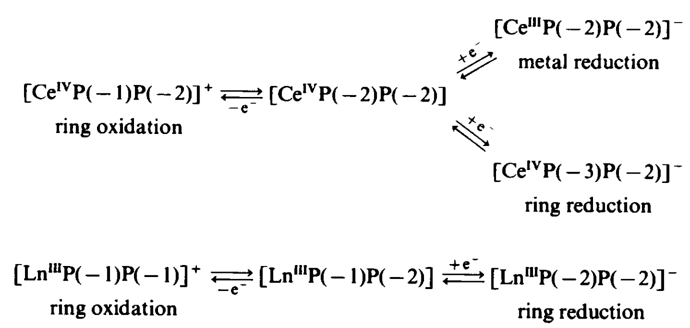
**Fig. 4** Evolution of the absorption spectra of [Ce$^{IV}${oep(−2)}{oep(−2)}] (1.8 × $10^{-5}$ mol dm$^{-3}$) in triethylamine solution upon photoreduction. Spectra are shown for 0, 1, 3, 6 and 9 min of irradiation

oep(−2) and oep(−1). Such a near-IR band was found for all [Ln$^{III}${oep(−1)}{oep(−2)}] complexes,[6] and for the π-cation radical [Ce$^{IV}${oep(−1)}{oep(−2)}]$^+$.[8,10]

The ESR spectra support our conclusions. For the ESR experiments saturated and helium-purged solutions of [Ce(tpp)$_2$] and [Ce(oep)$_2$] were prepared in toluene containing 5% (v/v) triethylamine and pure triethylamine, respectively. An ESR signal was not observed before irradiation. The spectra depicted in Fig. 5 appeared after 5 min of irradiation. Longer irradiation leads to disappearance of the signal from the octaethylporphyrin complex and apparently does not affect that arising from the tetraphenylporphyrin complex.

Whereas the Ce$^{4+}$ ion is diamagnetic, Ce$^{3+}$ ion with a $^2F_{5/2}$ ground state is paramagnetic. The ESR spectrum of Ce$^{III}$ in the organic compound described in the literature[35] is the same as that we have obtained for CeCl$_3$. The trivalent cerium signal is not found for the product of photoreduction of either the octaethyl or tetraphenyl sandwich. This is probably due to the low concentration of the compounds, although for the ESR study saturated solutions were used. Instead, for the photoreduction product of [Ce(oep)$_2$] a signal typical of an organic radical ($g$ = 2.0188 ± 0.0002) is observed, similar to those for neutral yttrium and europium octaethylporphyrinate complexes.[3,4] This confirms our conclusion that photoreduction leads to the formation of an unstable neutral complex [Ce$^{III}${oep(−1)}{oep(−2)}].

For the photoreduction product of [Ce(tpp)$_2$], a signal with



**Scheme 1**

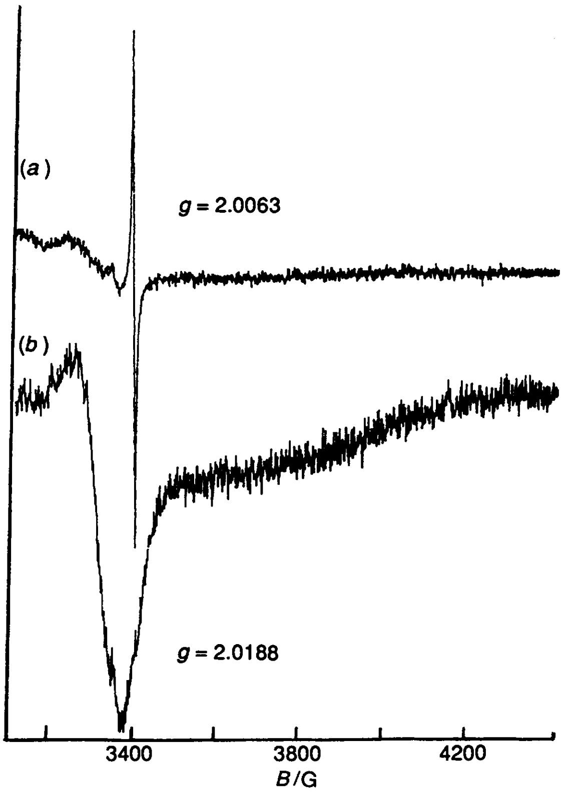


**Fig. 5** Electron spin resonance spectra of saturated solutions of (*a*) [Ce(tpp)$_2$] in toluene containing 5% (v/v) triethylamine and (*b*) [Ce(oep)$_2$] in pure triethylamine, after 5 min of photoirradiation ($T$ = 3.5 K); G = $10^{-4}$ T

$g$ = 2.0063 ± 0.0002 is found, but this signal is different from that of the octaethyl complex. It comes from the photogenerated radical $Et_3N^{\cdot +}$, which also can play the role of counter ion in the [Ce$^{III}$P(−2)P(−2)]$^-$ complex. These types of amine radicals and their role in electron-transfer processes involving porphyrin rings have been the subject of numerous studies.[36–38]

## Conclusion

It has been demonstrated that photoirradiation of the cerium(IV) tetraphenyl- and octaethyl-porphyrin sandwiches, in the presence of triethylamine as an electron acceptor, leads to reduction of the metal. Reduction of the ring and π-anion radical formation is not observed. Both sandwiches have the same symmetry, but owing to the different spatial arrangements of the ring substituents, the products of photochemical reduction are different. Reduction of [Ce$^{IV}${tpp(−2)}{tpp(−2)}] yields [Ce$^{III}${tpp(−2)}{tpp(−2)}]$^-$. The different photoreduction pathways of [Ce(tpp)$_2$] and [Ce(oep)$_2$] can also be related to the different redox properties of the porphyrin ligands. The first redox potential of [Ce(tpp)$_2$] is only 0.17 V.[21] The photoreduction of [Ce(oep)$_2$] needs a longer irradiation time than photoreduction of [Ce(tpp)$_2$]. The reverse process in the presence of an electron acceptor has also been demonstrated. The photoreduction of [Ce$^{IV}${oep(−2)}{oep(−2)}] is more complicated. The absorption spectrum of the neutral sandwich [Ce$^{III}${oep(−1)}{oep(−2)}] is reported here for the first time. However, the compound cannot be isolated as it rapidly reverts to the starting sandwich of tetravalent cerium.

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