Metal Complexes with Tetrapyrrole Ligands, LXXIII[◇]

Oxidation and Reduction of Cerium(IV) Sandwich Complexes with Porphyrin Ligands Linked by Aliphatic Diether Bridges of Variable Chain Length

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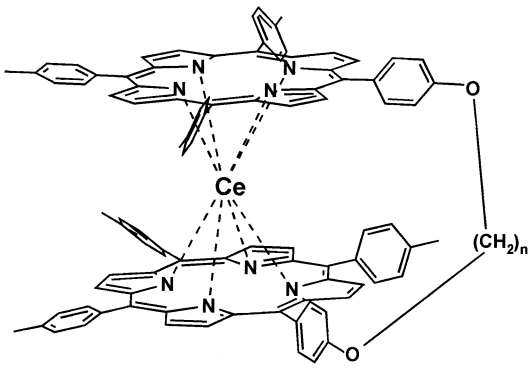
Starting from 5-(4-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin (**2a**), the new bis(porphyrinyloxy)alkanes **4a** and **4d** were synthesized by ether formation with the α,ω-dibromoalkanes $Br(CH_2)_nBr$ (n = 8, 11; **3a**, **3d**). **4a** was obtained by a two-step reaction with the 5-[4-(8-bromooctyloxy)phenyl]-10,15,20-tris(4-methylphenyl)porphyrin (**2b**) as an intermediate. The diporphyrins **4a** and **4d** were metalated with cerium(III) acetylacetonate to yield the new (porphyrin)-cerium sandwich complexes **1a** and **1d** which were characterized by UV/Vis, IR, ^{1}H-NMR, ^{13}C-NMR spectroscopy and cyclic voltammetry. The mono- and dications and the cerium(III) bisporphyrinate anions of **1a-d** were produced by electrochemical oxidation and reduction, respectively, and were examined by UV/Vis/NIR spectroscopy. The length of the lateral chains does not have a specific effect on the first and second oxidation potentials of the porphyrin rings and the reduction potentials of the cerium ions in the bisporphyrinate systems, and on the energy of the NIR bands of the monocations.

Synthetic aggregates of porphyrins or metalloporphyrins and quinones are presently being studied in order to understand the elementary steps of light-induced charge separation in photosynthesis. Most of these contain covalent links between the individual functional groups or chromophores[1]. The (porphyrin-quinone)zinc systems prepared by Staab et al.[2] were especially stimulating for our work devoted to (porphyrin)cerium(IV) double-deckers in which the two porphyrin systems were linked by a quinone-containing bridge[3]. In the course of that work, cerium(IV) double-deckers of the type $Ce[ttpO(CH_2)_nOttp]$ (**1**)[4], namely **1b** and **1c**, were constructed in which the two porphyrin rings are bridged by aliphatic diether chains containing 9 or 10 methylene groups (n = 9 or 10), respectively. Since **1c** had shown unexpectedly high oxidation potentials at the porphyrin rings, the investigation was extended to the double-deckers **1a** and **1d** which have either a somewhat shorter (8 methylene groups, n = 8) or a longer "ansa" chain (11 methylene groups, n = 11). The electrochemical oxidations and reductions of all four species **1a**−**d** were coherently followed by cyclic voltammetry and digital coulometry[5]. The results are reported below.

Very recently, novel species have been added to those bisporphyrinate double-deckers of tetravalent metal ions mentioned[3] so far: Aida et al.[6] have obtained chiral zirconium(IV) and cerium(IV) bisporphyrinates and succeeded in the separation of their enantiomers.



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No.	1a	1b	1c	1d
n	8	9	10	11

Synthesis

The cerium double-deckers **1b** and **1c** had been prepared starting from the monofunctionalized tetraarylporphyrin H_2(HOttp) (**2a**) which is easily accessible from a mixed condensation-oxidation reaction of pyrrole, *p*-tolualdehyde, and *p*-hydroxybenzaldehyde[7] and can be transformed into a diporphyrin by ether formation with α,ω-dibromoalkanes, e. g. 1,9-dibromononane (**3b**) and 1,10-dibromodecane (**3c**),

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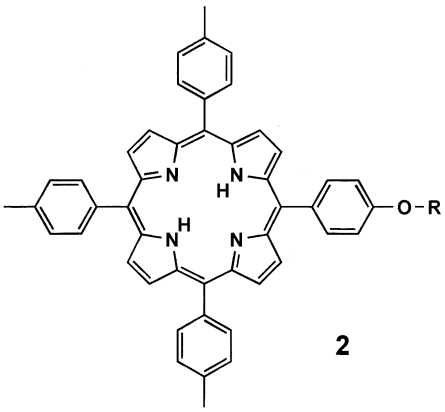
respectively[3][7]. Although sandwich formation leading to $Ce(HOttp)_2$ is possible with **2a**[8], the application of lateral bridges was unsuccessful because $Ce(HOttp)_2$ exists as a mixture of vicinal and transversal isomers. Thus, sandwich formation had been performed[3] starting from the respective diporphyrins **4b** or **4c** obtained from **2a** and **3b** or **3c**, respectively, and the new sandwiches **1a** and **1d** had to be prepared starting from **2a** by the diporphyrin route as well.



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No.	R
2a	H
2b	$(CH_2)_8Br$
2c	$(CH_2)_9Br$
2d	$(CH_2)_{10}Br$
2e	$(CH_2)_{11}Br$

$Br—(CH_2)_n—Br$ **3** For n see **1**

Indeed, the diporphyrin **4d** could be made by directly coupling two equivalents of **2a** with **3d** in the presence of cesium carbonate in dimethylformamide at 100°C (see Experimental Section, protocol 1; 93%). The monofunctionalized porphyrin **2e** was also formed as a byproduct as already observed for **2c** and **2d**[3] and could be separated by column chromatography. However, because of the formation of many decomposition products, the former procedure failed for **4a** which then was prepared stepwise[5] by first, formation of the [(bromoalkoxy)phenyl]porphyrin **2b** (protocol 2; 89%) from **2a** and **3a**, and then coupling of the resulting **2b** with another equivalent of **2a** (protocol 3; 28%).

The formation of the double-deckers **1a** (11%) and **1d** (15%; protocol 4) was managed as described previously[3] for **1b** (24%) and **1c** (11%), by lithiation of the diporphyrins **4a** and **4d**, respectively, with *n*-butyllithium and subsequent addition of cerium(III) acetylacetonate in trichlorobenzene (TCB). The yields (given above in parentheses) were comparably small for all four double-deckers with a small preference for the chain length $n = 9$. Thus, all these lateral chains appear to fit the gap between the vicinal pair of phenolic oxygen atoms in the cerium double-decker system of **1a–d**.

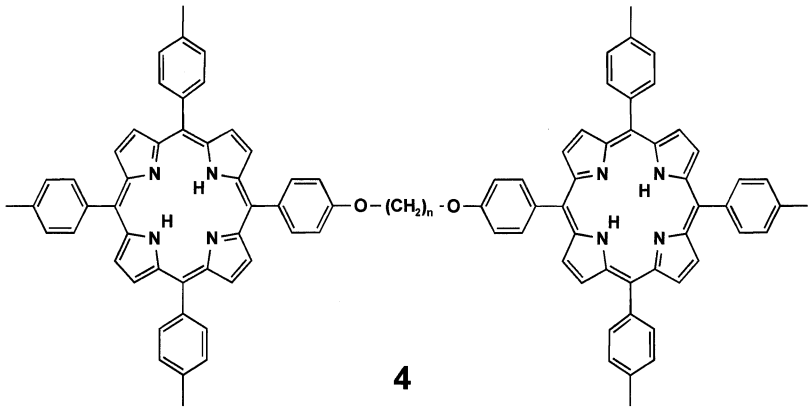
Analytical Characterization

All the new compounds were identified by their UV/Vis, ^{1}H-NMR, IR, and mass spectra (for individual data, see protocols 1–4). The new diporphyrins **4a** and **4d** were prepared in the same manner as the known[3] species **4b** and **4c**. An additional identification came from the determination of their R_f values which increase in the series **4a** < **4b** < **4c** < **4d** (see Experimental Section, Table 4) indicating a decrease in polarity as the chain length of the diether bridge increases.

The new double-deckers **1a** and **1d**, as well as newly prepared[5] samples of **1b** and **1c**, which otherwise showed spectra identical with those of the original samples[3], were additionally characterized by ^{13}C-NMR data which are compiled in Table 1. The assignments were corroborated by DEPT experiments.

UV/Vis Spectra

The UV/Vis spectra of the new alkane-bridged double-deckers **1a** and **1d** resemble those of their unbridged analogs $Ce(ttp)_2$[9] and $Ce(HOttp)_2$[8] as much as the spectra of the double-deckers **1b** and **1c**, see Table 2a. All complexes show the typical Soret (B) band and four characteristic Q



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For n see **1**

Table 1. ^{13}C-NMR data of **1a–d** (δ values at 25°C in $CDCl_3$)

	CH_3[a]	CH_2[b]	CH_2[c]	CH_2–O[d]	C=C[e]	=C–O[f]
1a	21.59	25.44–28.06	28.86	68.41	123.88–153.34	158.18
1b	21.59	25.67–29.16	29.81	68.70	123.78–153.25	158.34
1c	21.59	25.89–29.34	29.81	68.41	123.72–153.43	158.55
1d	21.59	26.00–29.50	29.81	68.52	123.69–153.24	158.58

[a] CH_3, tolyl. – [b] $C_{aliphat.}$. – [c] $C_{aliphat.}$. – [d] $C_{aliphat.}$–O. – [e] $C_{arom.}$, $C_{heteoarom.}$. – [f] $C_{arom.}$–O.

bands which are labeled as discussed for cofacial porphyrin ligands in sandwich complexes[3][10]. The lateral aliphatic chain connecting the porphyrin ligands in the cerium sandwiches does not have any effect on the intensity and the location of the B and the Q bands (for data, see Experimental Section, protocol 4).

Table 2. UV/Vis/NIR data (λ_{max} [nm], lg ε in parentheses, at 25°C in CH_2Cl_2) of a) the double-deckers **1a–d**, b) the radical cations formed from **1a–d**, c) the dications formed from **1a–d** and d) the bisporphyrinate anions formed from **1a–d**

Table 2a

	B (Soret)	Q″	Q(1,0)	Q(0,0)	Q′
1a	398 (5.27)	483 (4.04)	544 (3.91)	586 (3.37)	647 (3.34)
1b	398 (5.27)	483 (4.04)	544 (3.91)	586 (3.37)	647 (3.34)
1c	398 (5.12)	480 (3.92)	544 (3.80)	582 (3.33)	648 (3.30)
1d	398 (5.29)	478 (4.09)	545 (3.94)	584 (3.42)	648 (3.40)

Table 2b

	E [V]	UV/Vis/NIR absorbance {λ_{max} [nm], (lg ε)}
1a	0.9	393 (5.28), 673 (3.90), 801 (3.57), 1386 (3.94)
1b	0.9	393 (5.13), 678 (3.69), 805 (3.45), 1385 (3.95)
1c	0.9	393 (5.04), 679 (3.80), 794 (3.66), 1383 (3.79)
1d	0.9	394 (5.21), 678 (3.67), 806 (3.40), 1383 (3.75)

Table 2c

	E [V]	UV/Vis/NIR absorbance {λ_{max} [nm], (lg ε)}
1a	1.3	389 (5.23), 668 (4.15), 802 (3.94), 1049 (3.97)
1b	1.3	389 (5.07), 675 (3.96), 805 (3.79), 1043 (3.85)
1c	1.3	388 (4.96), 678 (3.97), 802 (3.75), 1046 (3.75)
1d	1.3	389 (5.15), 674 (4.02), 801 (3.75), 1046 (3.77)

Table 2d

	E [V]	UV/Vis absorbance {λ_{max} [nm], (lg ε)}
1a	–0.6	415 (5.71), 515 (4.09), 555 (4.13), 646 (3.82)
1b	–0.6	415 (5.74), 518 (4.10), 558 (4.16), 643 (3.92)
1c	–0.6	415 (5.47), 515 (3.82), 556 (3.88), 643 (3.55)
1d	–0.6	415 (5.78), 519 (4.01), 554 (4.05), 643 (3.86)

Cyclic Voltammetry

In dichloromethane, cerium(IV) bisporphyrinates $Ce^{IV}(p)_2$ [e. g. $Ce(tpp)_2$, $Ce(ttp)_2$, or $Ce(oep)_2$] usually show two reversible oxidations (E_1, E_2) occuring at the porphyrin system and producing the π cation $[Ce(p)_2]^+$ and the π dication $[Ce(p)_2]^{2+}$, respectively[11]. The first quasireversible reduction (E_3) occurs at the metal center[11a] and generates a cerium(III) double-decker anion, $[Ce^{III}(p)_2]^-$. These essential processes are characterized in Eq. (1) by their respective reduction steps.

$$[Ce^{IV}(p^\bullet)(p^\bullet)]^{2+} + e^- \rightarrow [Ce^{IV}(p^\bullet)(p)]^+ + e^- \rightarrow Ce^{IV}(p)_2 + e^- \rightarrow [Ce^{III}(p)_2]^- \quad (1)$$

In order to clarify whether the previously found abnormally high oxidation potential of **1b** could be reproduced, and if it existed, were due to some steric abnormity of **1b**, the whole series **1a–d** was studied by cyclic voltammetry. New samples of **1b** and **1c** were prepared[5] as previously described[3] and measured anew. To our disappointment, all the double-deckers **1a–d** showed the three redox steps E_1, E_2, and E_3 at potentials very close to those of the reference compound $Ce(ttp)_2$ (see Table 3). A typical voltammogram is shown in Figure 1.

Figure 1. Cyclic voltammogram of the bridged double-decker **4a** (CH_2Cl_2, room temperature, NBu_4PF_6 as supporting electrolyte, calomel electrode)

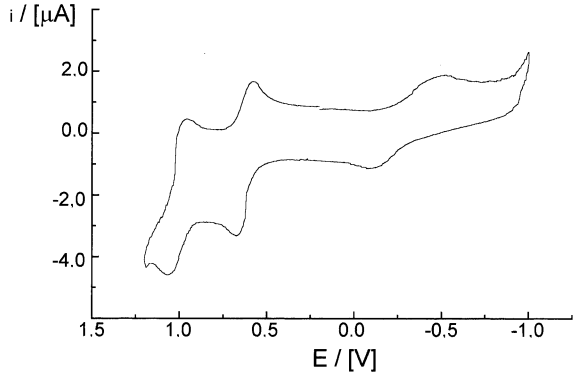

Table 3. Comparison of the redox potentials of the double-deckers $Ce(ttp)_2$ and **1a–d** (CH_2Cl_2, room temperature, NBu_4PF_6 as supporting electrolyte, saturated calomel electrode)

	E_1 [V]	E_2 [V]	E_3 [V]
$Ce(ttp)_2$	1.000	0.620	–0.290
1a	1.000	0.605	–0.300
1b	1.019	0.632	–0.303
1c	1.018	0.627	–0.310
1d	1.020	0.630	–

The similarity of all the redox potentials implies that the variation of the chain length ($8 < n < 11$) in the four double-deckers does not alter the mutual π-π interactions of the two porphyrin rings in these double-deckers. Thus, contrary to our previous speculation, the relative orientation of the two porphyrin ligands may not be altered by this variation of the length of the lateral chain.

Oxidation and Reduction

In order to record the UV/Vis/NIR spectra of the species connected by the redox processes defined by Eq. (1), the laterally bridged sandwich complexes **1a–d** were subjected

to electrolysis at controlled potentials (see protocol 5). The oxidations occurring at the porphyrin system produce the π radical-cation $[Ce(p^{\bullet}-p)]^{+}$ and the π dication $[Ce[p^{\bullet}-p^{\bullet})]^{2+}$, respectively, $(p-p)^{2-}$ symbolizing the diporphyrinate ligands derived from **3a**−**d**. The reduction takes place at the metal center and generates the double-decker anion $[Ce^{III}(p-p)]^{-}$.

On oxidation, the UV/Vis/NIR spectra show a hypsochromic shift of the B band from 398 via 393 (π radical-cation) to 389 nm (π dication; see Tables 2b and 2c). The typical feature of the π radical-cations $[Ce^{IV}(p^{\bullet})(p)]^{+}$ is a broad NIR band, found at 1350 nm for $[Ce^{IV}(tpp^{\bullet})(tpp)]^{+}$.[12] For $[Ce(p^{\bullet}-p)]^{+}$ it appears at 1383 nm. For the π dications $[Ce^{IV}(tpp^{\bullet})(tpp^{\bullet})]^{2+}$ and $[Ce^{IV}(p^{\bullet}-p^{\bullet})]^{2+}$, similar bands are observed at 1017[12] and 1044 nm, respectively. Reduction at the cerium ion yielding the double-decker anions $[Ce^{III}(p-p)]^{-}$ is indicated by a bathochromic shift of the B band to 415 nm (Table 2d), as found earlier for a series of lanthanoid(III) bisporphyrinate anions $[Ln(tpp)_2]^{-}$[13] An NIR band does not appear.

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Experimental Section

Spectrometers and chemicals used were specified in a previous paper of this series[8]. − Electrochemistry: Princeton Applied Research potentiostat M 173 contolled by an interface M 175 with the software M 270/250. − 1,8-Dibromooctane, 1,11-dibromoundecane, Cs_2CO_3, and DMF were obtained from Fluka Chemie AG, *n*-butyllithium (1.6 M in *n*-hexane) from Acros, and $Ce(acac)_3 \times H_2O$ from Aldrich. − *p*-(Hydroxyphenyl)tris(*p*-tolyl)porphyrin[7] (**2a**) was prepared by a literature method. − Elemental analyses were performed by Analytical Laboratories, P.O.B. 1106, D-51779 Lindlar. − Analytical thin layer chromatography was performed on commercial aluminium sheets coated with silica gel 60 F_{254} (Merck). A comparison of the R_f values found for the diporphyrins **4a**−**4d** is given in Table 4.

Table 4. Comparison of the R_f values of the diporphyrins **4a**−**d** determined by thin-layer chromatography (silica gel, toluene, room temperature)

4a	**4b**	**4c**	**4d**
0.50	0.55	0.59	0.64

Protocol 1: 1,11-Bis[4-{10,15,20-tris(4-methylphenyl)porphyrin-5-yl}phenoxy]undecane (**4d**): To a solution of 310 mg (0.46 mmol) of **2a** and 1.3 g (3.99 mmol) of anhydrous cesium carbonate in 15 ml of DMF a solution of 339 mg (1.08 mmol) of **3d** in 25 ml of DMF was added dropwise under nitrogen at 100°C. After cooling and filtration, the solvent was removed in vacuo. The residue was treated with 10 ml of toluene and chromatographed on an alumina column (II, neutral, 15 × 3.5 cm). Fractions were obtained as follows: with toluene a violet forerun of the monofunctionalized [(ω-bromoundecyloxy)phenyl]porphyrin **2e** and with CH_2Cl_2 the violet fraction of the diporphyrin **4d**. Evaporation of the solvent in vacuo and crystallization from CH_2Cl_2/MeOH (1:1) yielded the diporphyrin **4d** as a violet powder. 319 mg (93%). − MS; *m/z* (%): 748 (100) $[M^{2+}]$, 1496 (69) $[M^{+}]$. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 420 nm (5.78), 517 (4.36), 553 (4.15), 592 (3.93), 648 (3.93). − IR (KBr), 6 most intensive bands and NH band: $\tilde{\nu}$ [cm^{-1}] = 803, 970, 1247, 1470, 1512, 2925, 3314 (NH). − ^1H NMR (CD_2Cl_2): δ = −2.84 (s, 4 H, NH), 1.55−1.70 [m, 14 H, $OCH_2CH_2(CH_2)_7CH_2CH_2O$], 1.97−2.02 [m, 4 H, $OCH_2CH_2(CH_2)_7CH_2CH_2O$], 2.66−2.68 (m, 18 H, CH_3, tolyl), 4.24 [t, *J* = 8 Hz, 4 H, $OCH_2CH_2(CH_2)_7CH_2$-CH_2O], 7.26 (d, *J* = 8 Hz, 4 H, *m*-phenoxy-H), 7.51−7.56 (m, 12 H, *m*-tolyl-H), 8.04−8.09 (m, 16 H, *o*-tolyl- and *o*-phenoxy-H), 8.84−8.88 (m, 16 H, pyrrole-H).

Protocol 2: 5-[4-(8-Bromooctyloxy)phenyl]-10,15,20-tris(4-methylphenyl)porphyrin (**2b**): 1.68 g (6.2 mmol) of **3a** were added under nitrogen to a solution of 424 mg (0.63 mmol) of **2a** and 1.74 g (5.34 mmol) of anhydrous cesium carbonate in 50 ml of DMF. After stirring at 50°C for 5 h, the solution was filtered and the solvent removed in vacuo. 484 mg (89%) of the porphyrin **2b** were obtained as a violet powder after chromatography on an alumina column (II, neutral, 15 × 3.5 cm, isolation of the first violet fraction) with toluene and crystallization from CH_2Cl_2/MeOH (1:1). − MS; *m/z* (%): 863 (100) $[M^{+}]$. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 420 nm (5.64), 517 (4.23), 553 (3.98), 592 (3.70), 648 (3.70). − IR (KBr), 6 most intensive bands and NH band: $\tilde{\nu}$ [cm^{-1}] = 801, 967, 1177, 1246, 1472, 1506, 3319 (NH). − ^1H NMR (CD_2Cl_2): δ = −2.79 (s, 2 H, NH), 1.49−1.63 [m, 8 H, $OCH_2CH_2(CH_2)_4CH_2CH_2Br$], 1.70−2.00 [m, 4 H, $OCH_2CH_2(CH_2)_4CH_2CH_2Br$], 2.69 (s, 9 H, CH_3, tolyl), 3.40 [t, *J* = 8 Hz, 2 H, $OCH_2CH_2(CH_2)_4CH_2CH_2Br$], 4.23 [t, *J* = 8 Hz, 2 H, $OCH_2CH_2(CH_2)_4CH_2CH_2Br$], 7.27 (d, *J* = 8 Hz, *m*-phenoxy-H), 7.55 (m, 6 H, *m*-tolyl-H), 8.08 (m, 8 H, *o*-tolyl- and *o*-phenoxy-H), 8.85 (m, 8 H, pyrrole-H).

Protocol 3: 1,8-Bis{4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]phenoxy}octane (**4a**): A suspension of 172 mg (0.20 mmol) of **2b**, 316 mg (0.47 mmol) of **2a** and 1.3 g (3.99 mmol) of Cs_2CO_3 in 25 ml of DMF was stirred for 5 h under nitrogen at 100°C. After cooling, 100 ml of water was added and the mixture was filtered. The violet residue was dried at 100°C and chromatographed on an alumina column (II, neutral, 15 × 3.5 cm). Fractions were obtained as follows: with toluene a violet forerun of the remaining monofunctionalized [(8-bromooctyloxy)phenyl]porphyrin **2b** and with CH_2Cl_2 the violet fraction of the diporphyrin **4a**. Evaporation of the solvent in vacuo and crystallization of the residue from CH_2Cl_2/MeOH (1:1) yielded 82 mg (28%) of **4a** as a violet powder. − MS; *m/z* (%): 1454 (100) $[M^{+}]$. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 420 nm (5.66), 517 (4.25), 553 (4.01), 592 (3.74), 648 (3.74). − IR (KBr), 6 most intensive bands and NH band: $\tilde{\nu}$ [cm^{-1}] = 801, 969, 1179, 1245, 1472, 1508, 3320 (NH). − ^1H NMR (CD_2Cl_2): δ = −2.78 (s, 4 H, NH), 1.59−1.76 [m, 8 H, $OCH_2CH_2(CH_2)_4CH_2$-CH_2O], 2.02−2.09 [m, 4 H, $OCH_2CH_2(CH_2)_4CH_2CH_2O$], 2.67−2.69 (m, 9 H, CH_3, tolyl), 4.29 [t, *J* = 8 Hz, 4 H, $OCH_2CH_2(CH_2)_4CH_2CH_2O$], 7.29 (d, *J* = 8 Hz, *m*-phenoxy-H), 7.51−7.56 (m, 12 H, *m*-tolyl-H), 8.06−8.13 (m, 16 H, *o*-tolyl- and *o*-phenoxy-H), 8.84−8.88 (m, 16 H, pyrrole-H).

Protocol 4: General procedure of the metalation of the diporphyrins **4a** and **4d** with $Ce(acac)_3 \times H_2O$: A solution of 1.6 mmol of BuLi in 0.25 ml of *n*-hexane was added to a solution of 100 mg of **4a** (0.069 mmol) or **4d** (0.067 mmol) in 50 ml of TCB under nitrogen. The resulting solution was stirred for 10 min at room temperature. After the addition of 313 mg (0.69 mmol) or 303 mg (0.67 mmol) of $Ce(acac)_3 \times H_2O$, the solution was heated at reflux for 6 h. After cooling and filtration, the solvent was evaporated in vacuo. The residue was purified on an alumina column (II, neutral,

15 × 3.5 cm) with toluene. The first brown fraction contained the double-decker followed by the second violet fraction of the corresponding diporphyrin. After evaporation of the solvent from the first fraction and recrystallization of the residue from CH_2Cl_2/MeOH (1:1) the following double-deckers were isolated as brown powders:

1,8-Bis{4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]-phenoxy}octanatocerium(IV) (**1a**): 9 mg (11%). − MS; *m/z* (%): 1590 (100) [M^+]. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 399 nm (5.38), 478 (4.14), 545 (4.02), 584 (3.52), 646 (3.45). − IR (KBr), 9 most intensive bands: $\tilde{\nu}$ [cm^{-1}] = 802, 983, 1023, 1096, 1178, 1263, 1325, 1511, 2930. − ^{1}H NMR ($CDCl_3$): δ = 1.77−1.82 [m, 8 H, $OCH_2CH_2(CH_2)_4CH_2CH_2O$], 2.11−2.25 [m, 4 H, $OCH_2CH_2(CH_2)_4CH_2CH_2O$], 2.72−2.74 (m, 18 H, CH_3, tolyl), 4.46/4.58 [m, 4 H, $OCH_2CH_2(CH_2)_4CH_2CH_2O$], 6.29 (m, 8 H, *exo* *o*-tolyl- and *o*-phenoxy-H), 6.50 (m, 2 H, *exo* *m*-phenoxy-H), 7.07 (m, 6 H, *exo* *m*-tolyl-H), 7.50 (m, 2 H, *endo* *m*-phenoxy-H), 7.93 (m, 6 H, *endo* *m*-tolyl-H), 8.15−8.54 (m, 16 H, pyrrole-H), 9.48 (m, 8 H, *endo* *o*-tolyl- and *o*-phenoxy-H). − ^{13}C NMR ($CDCl_3$): δ = 21.59 (CH_3, tolyl), 25.44−28.06 [$OCH_2CH_2(CH_2)_4CH_2CH_2O$], 28.86 [$OCH_2CH_2(CH_2)_4CH_2CH_2O$], 68.42 [$OCH_2CH_2(CH_2)_4CH_2CH_2O$], 123.88−153.34 ($C_{arom.}$, $C_{heteroarom.}$), 158.18 ($C_{arom.}$−O). − CV (CH_2Cl_2/NBu_4PF_6): *E* = 1.000 V, 0.605, −0.300. − $C_{102}H_{82}CeN_8O_2 \times 4\ H_2O$ (1664.00): calcd. C 73.62, H 5.45, N 6.73; found C 73.95, H 5.82, N 6.26.

1,11-Bis{4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]-phenoxy}undecanatocerium(IV) (**1d**): 16 mg (15%). − MS; *m/z* (%): 1632 (100) [M^+]. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 398 nm (5.29), 478 (4.09), 545 (3.94), 584 (3.42), 638 (3.40). − IR (KBr), 9 most intensive bands: $\tilde{\nu}$ [cm^{-1}] = 801, 981, 1026, 1100, 1178, 1261, 1326, 1512, 2970. − ^{1}H NMR ($CDCl_3$): δ = 1.64−1.80 [m, 14 H, $OCH_2CH_2(CH_2)_7CH_2CH_2O$], 2.03−2.15 [m, 4 H, $OCH_2CH_2(CH_2)_7CH_2CH_2O$], 2.71−2.72 (m, 18 H, CH_3, tolyl), 4.34/4.48 [m, 4 H, $OCH_2CH_2(CH_2)_7CH_2CH_2O$], 6.28 (m, 8 H, *exo* *o*-tolyl- and *o*-phenoxy-H), 6.50 (m, 2 H, *exo* *m*-phenoxy-H), 7.05 (m, 6 H, *exo* *m*-tolyl-H), 7.60 (m, 2 H, *endo* *m*-phenoxy-H) 7.93 (m, 6 H, *endo* *m*-tolyl-H), 8.17−8.41 (m, 16 H, pyrrole-H), 9.48 (m, 8 H, *endo* *o*-tolyl- and *o*-phenoxy-H). − ^{13}C NMR ($CDCl_3$): δ = 21.59 (CH_3, tolyl), 26.00−29.50 [$OCH_2CH_2(CH_2)_4CH_2CH_2O$], 29.81 [$OCH_2CH_2(CH_2)_4CH_2CH_2O$], 68.52 [$OCH_2CH_2(CH_2)_4CH_2CH_2O$], 123.69−153.24 ($C_{arom.}$, $C_{heteroarom.}$), 158.58 ($C_{arom.}$−O). − CV (CH_2Cl_2/NBu_4PF_6): *E* = 1.020 V, 0.630, −0.305. − $C_{105}H_{88}CeN_8O_2 \times 5\ H_2O$ (1724.10): calcd. C 73.15, H 5.73, N 6.50; found C 73.40, H 5.68, N 6.04.

Protocol 5: General procedure for the electrochemical oxidations and reductions of the cerium(IV) bisporphyrinates **1a**−**d**: A solution of 1.40 mg (8.8×10^{-4} mmol) of **1a**, 1.45 mg (9.04×10^{-4} mmol) of **1b**, 1.63 mg (1.01×10^{-3} mmol) of **1c**, or 1.64 mg (1.01×10^{-3} mmol) of **1d** in 60 ml of a 0.1 M solution of NBu_4PF_6 in CH_2Cl_2 was electrolyzed by a three-potential cycle. Along the first two oxidations at +0.9 V and +1.3 V, charges of about 81 to 95 mC and 87 to 95 mC, respectively, were transferred while the solutions changed their colors from orange/brown via yellow to yellow/green. Thereafter, the solutions were reduced by a constant potential at −0.6 V. During this three-step reduction of the dications to the double-decker anions the color changes reversed with the appearance of orange/brown and then yellow/green for the last reduction step with total charges between 200 and 254 mC being transferred. After the first two oxidations and the total reduction, samples were taken, appropriately diluted, and placed into cuvettes for UV/Vis/NIR spectroscopy producing the spectral data given in Tables 2b−d.

[1] H. Kurreck, M. Huber, *Angew. Chem.* **1995**, *107*, 929−947; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 849−866 and references cited therein.

[2] T. Häberle, J. Hirsch, F. Pöllinger, H. Heitele, M. E. Michel-Beyerle, C. Anders, A. Döhling, C. Krieger, A. Rückemann, H. A. Staab, *J. Phys. Chem.* **1996**, *100*, 18269−18274 and references cited therein.

[3] J. W. Buchler, G. Heinz, *Chem. Ber.* **1996**, *129*, 1073−1081.

[4] Abbreviations used: M, metal; $(p)^{2-}$, $(ttp)^{2-}$, $(Hottp)^{2-}$, dianions of general porphyrin, 5,10,15,20-tetrakis(methylphenyl)-porphyrin, 5-hydroxyphenyl-10,15,20-tritolylporphyrin (**1a**); $[ttpO(CH_2)_nOttp]^{4-}$, tetraanion of a diporphyrin (see **4**); H(acac), acetylacetone; TCB, 1,2,4-trichlorobenzene.

[5] T. Dippell, Diplomarbeit, Technische Universität Darmstadt, **1996**.

[6] K. Tashiro, K. Konishi, T. Aida, *Angew. Chem.* **1997**, *109*, 882−884; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 856−858.

[7] R. G. Little, *J. Heterocycl. Chem.* **1978**, *15*, 203−208.

[8] J. W. Buchler, V. Eiermann, H. Hanssum, G. Heinz, H. Rüterjans, *Chem. Ber.* **1994**, *127*, 589−595.

[9] J. W. Buchler, H. G. Kapellmann, M. Knoff, K. L. Lay, S. Pfeifer, *Z. Naturforsch., B* **1983**, *38B*, 1339−1345.

[10] [10a] O. Bilsel, J. W. Buchler, P. Hammerschmitt, J. Rodriguez, D. Holten, *Chem. Phys. Lett.* **1991**, *182*, 415−421. − [10b] O. Bilsel, J. Rodriguez, S.N. Milam, P.A. Gorlin, G. S. Girolami, K. S. Suslick, D. Holten, *J. Am. Chem. Soc.* **1992**, *114*, 6528−6538. − [10c] K. M. Kadish, G. Moninot, Y. Hu, D. Dubois, A. Ibnlfassi, J.-M. Barbe, R. Guilard, *J. Am. Chem. Soc.* **1993**, *115*, 8153−8166.

[11] [11a] J. W. Buchler, K. Elsässer, M. Kihn-Botulinski, B. Scharbert, *Angew. Chem.* **1986**, *98*, 257−258; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 286−287. − [11b] J. W. Buchler, *Comments Inorg. Chem.* **1987**, *6*, 175−191. − [11c] J. W. Buchler, B. Scharbert, *J. Am. Chem. Soc.* **1988**, *110*, 4272−4276.

[12] J. W. Buchler, A. De Cian, J. Fischer, P. Hammerschmitt, R. Weiss, *Chem. Ber.* **1991**, *124*, 1051−1058.

[13] J. W. Buchler, P. Hammerschmitt, I. Kaufeld, J. Löffler, *Chem. Ber.* **1991**, *124*, 2151−2159.

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