Metal Complexes with Tetrapyrrole Ligands, LXXII[◇]

Cerium(IV) Sandwich Complexes with Porphyrin Ligands Linked by Aliphatic and Quinone-Containing Bridges

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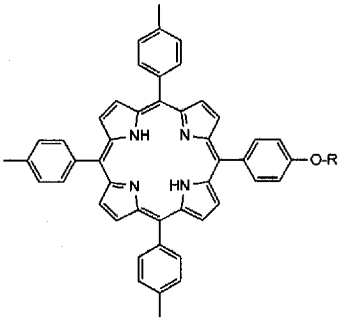
Starting from 5-(4-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin (**1a**), the new bis(porphyrinylphenoxy)alkanes **4a–c** were synthesized by ether formation with the α,ω-dibromoalkanes $Br(CH_2)_nBr$ (n = 9,10; **3a**, **b**) and 1,4-bis(3-bromopropyl)-2,5-dimethoxybenzene (**3c**). The bis[(porphyrinylphenoxy)propyl]hydroquinone dimethyl ether **4c** derived from **3c** was converted into the diporphyrin-quinone **4e** by methyl ether cleavage with BBr_3 and subsequent oxidation with ammonium cerium(IV) nitrate. The bisporphyrins **4a–c**, **e** were metalated with cerium(III) acetylacetonate to yield the new cerium porphyrin sandwich complexes **5a–c**, **e** which carry the alkane links in vicinal positions at the porphyrin rings. **5a–c**, **e** were characterized by UV/Vis, IR, ^{1}H-NMR spectroscopy and cyclic voltammetry. The quinone-bridged cerium sandwich complex **5e** contains the quinone moiety in a distinct non-coplanar orientation relative to the porphyrin ligands of the double-decker system. The length of the lateral chains may have a dramatic effect on the first and second oxidation potentials, E_3 and E_2, of the porphyrin rings: for **5b** having 10 aliphatic C atoms in the chain, E_3 and E_2 are higher by 0.26 and 0.24 V, respectively, as compared with **5a** having only 9 aliphatic C atoms. E_3 and E_2 for the latter are rather close to values for species with dipropylbenzene chains (i.e. in **5c** and **5e**) or without lateral bridges.

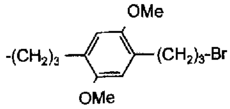
Synthetic aggregates of porphyrins, carotenoids, and quinones were prepared and studied in order to understand the elementary steps of light-induced charge separation in photosynthesis. Most of these contain covalent links between the individual functional groups or chromophores[2], but other binding forces are also used for aggregate formation[1,3]. A notable example of covalent aggregates are the porphyrin-quinone cyclophanes prepared by Staab et al.[4].

With the synthesis of metalloporphyrin double-deckers $M(ttp)_2$[5,6], another approach to this field was found. Two porphyrin ligands are held together by coordinative bonds. These sandwich-like compounds might be regarded as models[7,8] of the special pair of bacteriochlorophyll b molecules, the central unit of the bacterial reaction center, because they display structural, spectroscopic, and electrochemical analogies to the latter. Especially those double-deckers that contain a tetravalent central metal ion which is not easily oxidized itself, e.g. Ce(IV)[6,9], Th(IV)[10], Zr(IV)[11,12], or Hf(IV)[11,12], are candidates for an investigation because photoionization of the coupled system of porphyrin ligands would just concern the porphyrin ligands as in the special pair and not the metal. Strong π-π interactions between the closely arranged porphyrin rings give rise to a facilitated oxidation of the porphyrin π systems as compared with the appropriate monoporphyrinates, an observation that might be called "double-decker effect"[7]. The oxidized porphyrin sandwich systems show a characteristic near infrared absorption[7–12]. A similar absorption band is also found for the oxidized special pair[13].

Scheme 1. Monofunctionalized porphyrins 1



1

No.	R
1a	H
1b	$-(CH_2)_9-Br$
1c	$-(CH_2)_{10}-Br$
1d	

In order to check whether a metalloporphyrin double-decker could perform anything special in an aggregate devised to perform light-induced charge separation, the synthesis of a double-decker with an appended quinone moiety was undertaken. Having at hand a series of cerium(IV) double-deckers in which each of the porphyrin ligands, e.g. **1a**, is monofunctionalized[14], it seemed worthwhile to construct a bridge between the hydroxy functions found in the double-decker **2A** (Scheme 2, R = H) and to insert a quinone moiety into this bridge. This bridge then would serve to keep the quinone moiety in a fixed, probably noncoplanar

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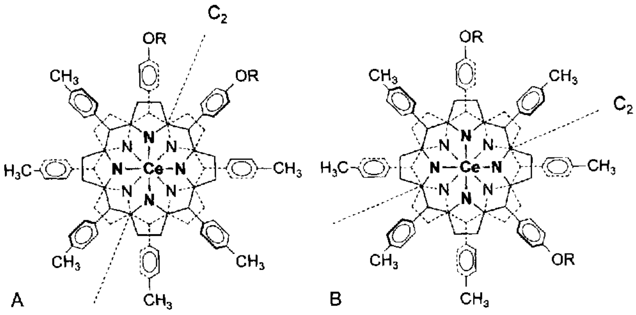
Scheme 2. **A**: Vicinal, **B**: transversal isomer of the bisfunctionalized cerium double-deckers **2** (derived from the porphyrins **1a** or **1c**)



2

orientation with respect to the porphyrin planes of the double-decker, an aspect which might be important for the interpretation of any photophysical measurements. The bridge approach developed by Staab and coworkers[4] was favorably applied to the porphyrin-quinone cyclophanes in which the porphyrin and quinone units are linked in a rigid and well-defined manner. This was confirmed by their crystal structures and ^{1}H-NMR studies in solution[15]. Especially noteworthy is a porphyrin-porphyrin-quinone triad[16] which contains two anthracene-bridged porphyrins besides the quinone unit in a cyclophane chain. In a metalloporphyrin double-decker, an even closer distance between the porphyrin rings could be achieved which would be minimal in the respective zirconium or hafnium derivatives due to the small ionic radii of these quadrivalent ions. However, up to now, all our attempts to prepare zirconium bisporphyrinates from any monofunctionalized porphyrin with substituents containing oxygen or nitrogen atoms failed. While this work was finished[17], Suslick et al. succeeded in obtaining a zirconium bisporphyrin sandwich complex[18] connected with an anthraquinone part via a single amide bond which does not put the quinone moiety in a fixed position. Their synthesis involved a tricky nitration of Zr(tpp)$_2$ yielding a mixture of mono- and dinitrated products[19]. The effect of the appended quinone was indeed a quenching of the fluorescence of the bisporphyrinate which is thought to be diagnostic of a photoinduced charge transfer from the porphyrin to the quinone.

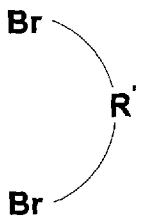
In this paper the synthesis is described of cerium sandwich complexes formally derived from **2A** by introduction of lateral chains, i.e. coupling the oxy substituents in the adjacent porphyrin rings with suitable *n*-nonane, *n*-decane, or dipropylbenzene derivatives; the latter were already known as precursors of quinone units within cyclophane chains[20].

Synthesis

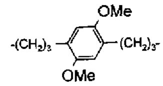
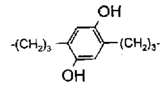
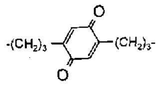
The synthesis of cerium double-deckers derived from monofunctionalized tetraarylporphyrins has already been described[14]. Reaction of Ce(acac)$_3$ with the monohydroxyporphyrin **1a**[21] gave a mixture of a vicinal (**2Aa**) and a transversal (**2Ba**) isomer of a difunctionalized cerium double-decker (Scheme 2). It was not possible to separate these isomers by chromatography due to their very similar chemical and physical properties. From this result the idea arose to separate the two isomers by a chemical reaction which can take place only at one isomer. The two isomers differ from each other in the distance of the two phenolic hydroxyl groups. From simple molecular modeling calculations it can be estimated that the distance of the hydroxyl groups is about 9 Å in the vicinal isomer (**2Aa**) and about 17 Å in the transversal isomer (**2Ba**)[22]. An intramolecular connection of the two hydroxyl groups by reaction with a difunctionalized tether of a length between 9 and 17 Å should only be successful in the case of the vicinal isomer **2Aa**. Attempts to realize an intramolecular connection by reaction of the dihydroxy double-decker mixture of **2Aa** and **2Ba** with dibromononane **3a** or dibromodecane **3b** failed. They yielded a mixture of different sandwich complexes and porphyrins which could not be separated.

Therefore, it was intented to prepare a bisporphyrin with a quinone precursor in its bridging unit and to introduce the cerium at a later stage, thus avoiding any problems arising from the unfavorable configurations **B** (Scheme 2) or the lability of the cerium double-deckers towards acids.

Scheme 3. Dibromoalkanes **3**



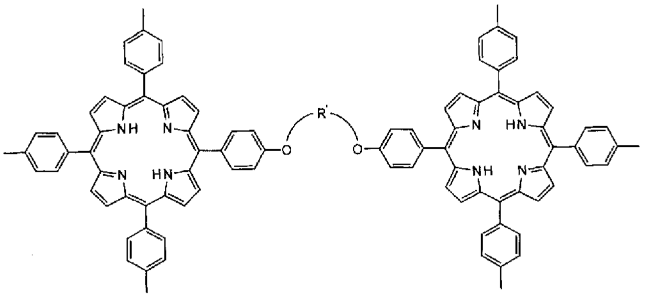
3

No.	R
3a	-(CH$_2$)$_9$-
3b	-(CH$_2$)$_{10}$-
3c	
3d	
3e	

Synthesis of the Diporphyrins: A general synthesis of bisporphyrins derived from **1a** has already been described[23]. Reaction of dibromoalkanes with **1a** yielded ω-bromoalkyl porphyrinyl ethers. The latter compounds were then allowed to react in a second step with another phenolic porphyrin to give bisporphyrins. This synthesis was improved to a one-step reaction by slow addition of the dibromoalkane to a solution of **1a** in DMF in the presence of Cs$_2$CO$_3$. From the reaction of the porphyrin **1a** with the dibromoalkanes **3a–c** the bisporphyrins **4a–c** were obtained (eq. 1; protocol 1, see Experimental).

$$\underset{2\cdot\mathbf{1a}}{2\ \mathrm{H_2(HOttp)}} + \underset{\mathbf{3a-c}}{\mathrm{Br{-}R'{-}Br}} \xrightarrow{\mathrm{Cs_2CO_3/DMF/100\,^\circ C}} \underset{\mathbf{4a-c}}{\mathrm{H_4(ttpOR'Ottp)}} \qquad (1)$$

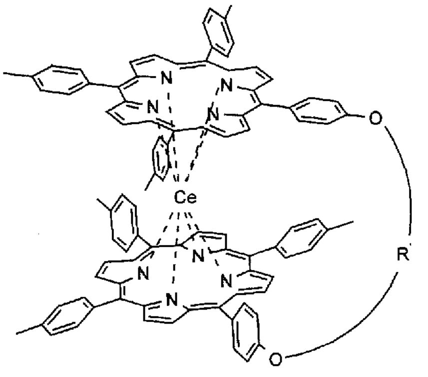
Scheme 4. Covalently linked diporphyrins **4**



4

For R' see **3**

Scheme 5. Covalently bridged double-deckers **5**



5

For R' see **3**

The monofunctionalized porphyrins **1b–d** were formed only as byproducts and could be separated by column chromatography. They are available as main products by addition of an excess of the bromides to the hydroxyporphyrin **1a**. Thus, the monofunctionalized porphyrin **1c** was obtained which was required as a reference compound for the bridged diporphyrins (protocol 2). The diether bridges of the diporphyrins **4a–c** were chosen with such a length that the sandwich complex formation can only lead to the isomer derived from the dihydroxy double-decker **2Aa** with the vicinal arrangement of the ether bridge. The dibromide **3c**[20] was chosen because it contains a 1,4-dimethoxy-2,5-phenylene fragment in its chain which could be used to generate a *p*-quinone entity in the product. To obtain the quinone bisporphyrin **4e**, in a first step the bisporphyrin **4c** was demethylated with boron tribromide[24] (protocol 3). During this procedure a large excess of boron tribromide must be avoided because the reagent may also cleave the two phenyl propyl ether bonds of the bisporphyrin **4c**, which results in the degradation of the latter. Therefore, boron tribromide was added dropwise to a solution of **4c** in dichloromethane (40 °C). During workup of this reaction mixture partial oxidation of the hydroquinone diporphyrin **4d** to the quinone diporphyrin **4e** occurred due to the contact with air. The resulting porphyrin mixture of **4d** and **4e** was not separated, but treated with ammonium cerium(IV) nitrate in dichloromethane/acetonitrile[25] to obtain only the quinone diporphyrin **4e** which was purified by column chromatography.

Synthesis of the Double-Deckers: For the preparation of the cerium sandwich complexes **5a–c, e** the diporphyrins **4a–c, e** were treated with *n*-butyllithium and then heated at reflux with Ce(acac)$_3$ in 1,2,4-trichlorobenzene (TCB) (eq. 2; protocol 4).

$$\underset{\textbf{4a–c, e}}{\mathrm{H_4(tppOR'Ottp)}} \xrightarrow{\substack{\text{1. 4 } n\text{-BuLi; } -4 \text{ BuH} \\ \text{2. Ce(acac)}_3\text{; } -3 \text{ Li(acac),} \\ \text{3. 1/4 O}_2\text{; } -1/2 \text{ Li}_2\text{O}}} \underset{\textbf{5a–c, e}}{\mathrm{Ce(ttpOR'Ottp)}} \qquad (2)$$

The double-deckers were separated from residual diporphyrins by chromatography. Autoxidation of Ce(III) to Ce(IV) occurred during the purification. The preparation of the non-bridged double-decker **2c** (a mixture of the vicinal and transversal isomer, see **2Ac** and **2Bc**, respectively, Scheme 2) from the monofunctionalized porphyrin **1c** was realized in the same way (protocol 4). The reaction conditions for the preparation of the quinone-bridged double-decker **5e** starting from the diporphyrin **4e** must be controlled carefully due to the lability of the quinone moiety. A large excess of *n*-butyllithium destroys the diporphyrin and leads to unidentified decomposition products. The longer the reaction mixture was heated, the less of the double-decker could be isolated (a reaction time of about 3 h was the best). The formation of the hydroquinone diporphyrin **4d** was observed by thin-layer chromatography after the addition of Ce(acac)$_3$ and heating for about 15 min (see protocol 4). Obviously, **4e** was partially reduced to **4d** either by the alkyllithium or the cerium(III) acetylacetonate or by both compounds. Whether **4d** was totally decomposed under the basic reaction conditions or metalated to **5d** and oxidized to **5e** during workup could not be decided because it was not possible to separate any **5d** from the decomposition products which accumulated at later stages of the procedure. Due to the rather small amounts of **5e** that were obtained a reduction of **5e** to **5d** was not investigated.

In order to avoid any deleterious effect of the butyllithium during the insertion of cerium, a variant of protocol 4 was used in which BuLi was replaced by anhydrous cesium carbonate as a base. Likewise, a reduction of **4e** to **4d** was observed. However, the yields of **5e** were lower. It was tried to extract any **5d**, which could have been enriched in the mixture of polar decomposition products due to its high polarity, by oxidation of **5d** to the less polar **5e**. Treatment of the polar decomposition products with ammonium cerium(IV) nitrate or dichlorodicyano-*p*-benzoquinone and subsequent thin-layer chromatography did not show any formation of **5e**.

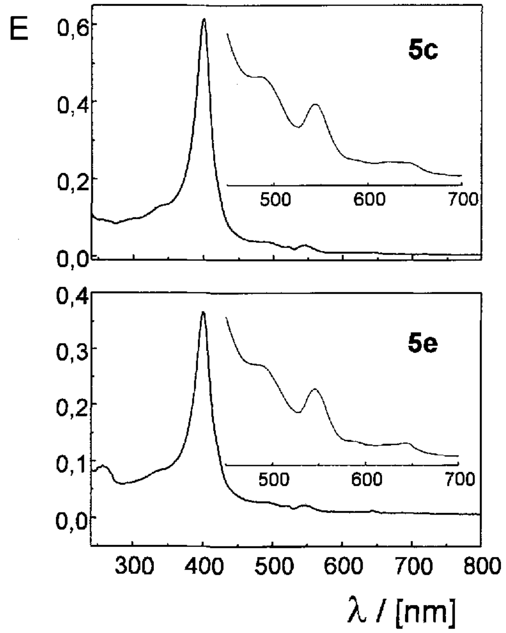
2,5-Bis(3-bromopropyl)quinone (**3e**) was prepared as a reference compound for the bisporphyrin quinone **4e** and the quinone-bridged double-decker **5e**. It was obtained by methyl ether cleavage of **3c** and oxidation with ammonium cerium(IV) nitrate according to standard literature procedures[24,25].

Analytical Characterization

UV/Vis Spectra: The UV/Vis spectra of the new double-deckers **5a**–**c**, **e** and **2c** resemble their non-functionalized symmetric analog $Ce(ttp)_2$[5,6]. All new complexes show the B band and four characteristic Q bands which are labeled as discussed for cofacial porphyrin ligands in sandwich complexes[26]. All bands of the double-decker **2c** are found in the reference spectrum of $Ce(ttp)_2$ with almost identical wavelength and intensity. The UV/Vis spectrum of **2c** does neither show any difference as compared with the spectra of $Ce(ttp)_2$ reflecting the presence of monofunctionalized porphyrin ligands nor a distinction of the two isomers **2Ac** and **2Bc**. The spectra of the bridged double-deckers **5a**–**c**, **e** are very close to those of $Ce(ttp)_2$ and **2c** as well. Nevertheless, they differ slightly in the location of the Q′ band. The Q′ bands of all bridged double-deckers **5a**–**c**, **e** are hypsochromically shifted as compared with the non-bridged double-deckers $Ce(ttp)_2$ and **2c**. This might be a result of a forced deviation of the parallel arrangement of the two porphyrin ligands and/or a distortion from the square antiprismatic geometry by the bridging tethers.

The quinone and the porphyrin chromophore each contribute individually to the UV/Vis spectrum of the quinone bridged double-decker **5e** (Figure 1). Neither the absorptions of the quinone nor those of the porphyrin chromophore show any mutual influence. This can be seen by comparison of the quinone absorptions of the double-decker **5e** and the isolated quinone **3e** as well as the double-decker absorptions of the sandwich complexes **5e** and **5a**–**c**.

Figure 1. UV/Vis spectra of the bridged double-deckers **5c** and **5e** (CH_2Cl_2, room temperature)



Cyclic Voltammetry: In dichloromethane, cerium sandwich complexes $Ce(p)_2$ usually show three redox steps in their cyclic voltammograms[7a,c,27]. Oxidations occur at the porphyrin system and produce the π cation $[Ce(p)_2]^+$ and the π dication $[Ce(p)_2]^{2+}$. Reduction generates a double-decker anion, $[Ce(p)_2]^-$ containing a Ce(III) ion. All new complexes show these three redox steps. The redox potentials of the non-bridged double-decker **2c** and the alkoxy-bridged double-decker **5a** are rather close to that of the reference compound $Ce(ttp)_2$ (Table 2, redox potentials are labeled according to eq. 3).

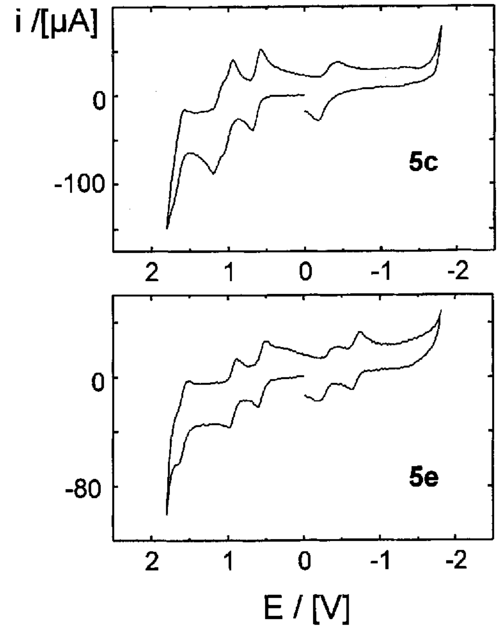
$$[Ce(p_2)]^{3+} \underset{E_1}{\overset{e}{\rightleftharpoons}} [Ce(p_2)]^{2+} \underset{E_2}{\overset{e}{\rightleftharpoons}} Ce(p_2)^{+} \underset{E_3}{\overset{e}{\rightleftharpoons}} [Ce(p_2)] \underset{E_4}{\overset{e^-}{\rightleftharpoons}} [Ce(p_2)]^{-} \underset{E_5}{\overset{e^-}{\rightleftharpoons}} [Ce(p_2)]^{2-} \qquad (3)$$

5b having 10 aliphatic C atoms in its bridge shows dramatically (and reproducibly) higher values of its first and second oxidation potential as compared with all other cerium double-deckers listed in Table 2. In fact, E_2 and E_3 are higher by 0.26 and 0.24 V, respectively, as compared with **5a** having only 9 aliphatic C atoms. Contrary to previous experience with cerium(IV) bisporphyrinates[7a], it appears that the rings in **5b** are not easier oxidized as compared with a corresponding monoporphyrin, e.g. the zinc porphyrin Zn(MeOttp)[5] which is derived from $H_2(HOttp)$ (**1a**) by ether formation yielding $H_2(MeOttp)$ and metalation with $Zn(OAc)_2$. For Zn(MeOttp), E_2 and E_3 amount to 1.035 and 0.722 V, respectively[28]. Thus, the beforementioned "double-decker effect" is abolished, if not even overcompensated by the formal insertion of one additional methylene group into the lateral C_9 chain of **5a**. The reason of this is not clear.

The double-decker **2c** and all the bridged double-deckers **5a**–**c**, **e** closely resemble each other in the electronic effect of the substituents in the *meso* positions of the porphyrin rings. Each of these substituents can be considered as an aryl alkyl ether so that the electronic effects contributing to the net electron density of the porphyrin system should be similar as well. Therefore, as long as purely aliphatic bridges are concerned, differences in the redox behavior of the laterally bridged double-deckers should only arise from a different relative orientation of their porphyrin systems enforced by the bridging units which vary in chain length. This could lead to an alteration of the π-π overlap of the porphyrin systems in the complexes facilitating or impeding their redox processes, either by tilting of the two parallel porphyrin planes or by deviating considerably from the relative rotation of the two porphyrin rings from the angle of 45° with respect to their eclipsed position which is usually observed in cerium(IV) bisporphyrinates[9]; both movements would effect a distortion of the square-antiprismatic geometry of the central coordination group. Further efforts are needed to obtain crystals of **5a** and **5b**, to prepare further alkylbridged metal bisporphyrinates with other metals and alkyl chains (e.g. $n = 8$ or 11), and to do molecular modeling experiments as long as X-ray crystallography is precluded due to lack of sufficiently large crystals. Furthermore, it will be worthwhile to look at the variation of the near infrared absorption energies of the radical cations derived from the double-deckers with $8 < n < 11$, respectively; these energies are known to be dependent on the ring-ring distance in the unconstrained double-decker complexes[7].

The first and second oxidation potential of the double-deckers **5c** and **5e** are in the typical range of cerium sandwich complexes derived from tetraarylporphyrins. However, **5c** and **5e** are the first cerium porphyrin sandwich complexes which show a third oxidation potential at 1.67 and 1.651 V, respectively, generating a $[Ce(p_2)]^{3+}$ trication (see Figure 2). The cyclic voltammogram of the sandwich complex **5e** exhibits a second reduction step which is not observed in that of complex **5c**. The second reduction of **5e** at −0.682 V (E_5, Table 2) can be identified as a redox process occurring at the quinone system by comparing its value with the reduction potential of the isolated quinone **3e** at −0.675 V. Both reductions are reversible and differ only by 0.007 V. A reversible one-step reduction of quinones to semiquinones was found for other substituted benzoquinones in dichloromethane as well[29]. For cerium(IV) bisporphyrinates devoid of a quinone unit, E_5 would be the first reduction of the porphyrin ring which is expected below −1.6 V[11a]; this would be safely observed only in dimethylformamide[30] and was not studied here.

Figure 2. Cyclic voltammograms of the bridged double-deckers **5c** and **5e** (CH_2Cl_2, NBu_4PF_6 as supporting electrolyte, calomel electrode)



The reduction of the cerium(IV) ions (E_4, see Table 2), does not depend so strongly on the chain length of the lateral bridges. It appears to vary with the substituents present in the chain (or at the phenoxide oxygen atoms in **2c**) in a manner which cannot be explained at present. Nevertheless, the reduction of **5b** at the cerium(IV) ion is more easy by about 0.05 V as compared with **5a**, in line with the impeded oxidation of the former.

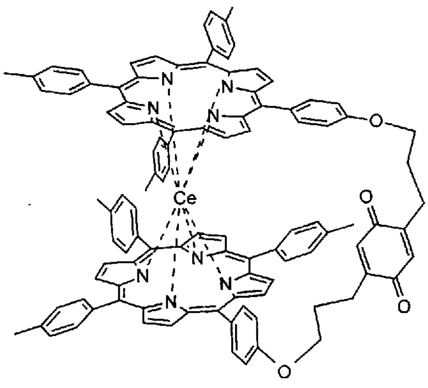
Another observation being irregular for cerium porphyrin sandwich complexes is made in the cyclic voltammogram of **5c**. The anodic or cathodic waves of the second oxidation step show a "shoulder" which is shifted to higher or lower potential, respectively, as compared with the corresponding peak maximum (see Figure 2). The shoulders are not seen in the case of any other cerium double-decker, especially not in **5e**. The question arose wether these shoulders might be caused by oxidation of the dimethoxybenzene group in **5c**. Assuming a reversible oxidation for the two redox waves, we calculated a redox potential of 1.053 V (not given in Table 2). This is almost 0.2 V higher than the oxidation potential of the isolated dihalide **3c** showing an irreversible oxidation at 0.86 V. On the other hand, no irreversible oxidation of the dimethoxybenzene moiety can be observed for the double-decker **5c** in the range of 0.86 V. Thus, the redox waves centered at 1.053 V could belong to the oxidation of the dimethoxyphenylene moiety. The observed anodic shift of about +0.2 V with respect to **3c** could then be caused by the vicinity of the cerium cation in a species which as a whole is already positively charged.

If the incorporation of the redox center into a charged surrounding plays any role at all, the reduction of the quinone unit of **5e** occurring in an anion, the cerium(III) double-decker $[\mathbf{5e}]^-$, should occur at a more negative potential as compared with **3c**. Since this is not the case, the reduction of the quinone moiety in **5e** might be influenced at the same time by the positive cerium cation in its proximity.

Conclusions

A general synthesis of cerium sandwich complexes derived from covalently linked bisporphyrins was developed. Using the bridging units of the bisporphyrin ligand with appropriate lengths of the tethers, only the isomers derived from the vicinal isomer **2A** were obtained. The incorporation of a 1,4-dimethoxy-2,5-phenylene unit into the linking alkylidene chain of the diporphyrin ligand allows the preparation of the quinone-bridged porphyrin sandwich complex **5e**. The insertion of cerium into the hydroquinone **4d** and the concomitant aerial oxidation of the hydroquinone **5d** (or its unmetalated precursor **4d**) are certainly a delicate procedure, but cleavage of the dimethyl ether **5c** with BBr_3 and subsequent oxidation to **5e** are precluded by the acid lability of the cerium bis(porphyrinates) which lose the metal in weakly acidic media.

Scheme 6. Quinone-bridged double-decker **5e**



5e

Table 1. UV/Vis spectra of the cerium(IV) bisporphyrinates $Ce(ttp)_2$ (**2c** and **5a**–**c**, **e** and the quinone **3e** (λ_{max} [nm], lg ε in parentheses, at 25 °C in CH_2Cl_2)

	bq [a]	B	Q"	Q(1,0)	Q(0,0)	Q'
$Ce(ttp)_2$ [b]		396.0	486.0	540.0		630.0
		(5.35)	(4.15)	(4.03)		(3.49)
2c		398.9	479.8	543.0	583.6	629.2
		(5.49)	(4.27)	(4.13)	(3.30)	(3.61)
5a		398.9	485.7	543.6	586.4	649.2
		(5.12)	(3.95)	(3.83)	(3.44)	(3.27)
5b		399.1	478.6	543.8	585.9	648.2
		(5.43)	(4.20)	(4.10)	(3.39)	(3.56)
5c		398.9	485.7	543.6	587.0	649.2
		(5.12)	(3.95)	(3.83)	(3.47)	(3.27)
5e	258.0	399.8	488.2	545.6	586.4	648.5
	(3.38)	(5.32)	(4.04)	(3.92)	(3.52)	(3.38)
3e	258.3					
	(3.84)					

[a] bq indiates the absorption band of the quinone part. – [b] Most recent UV/Vis spectrum (Bruins Omega 10).

Table 2. Comparison of the redox potentials of the double-deckers $Ce(ttp)_2$ **2c**, and **5a**–**c**, **e**, and the dihalides **3c**, **e** (CH_2Cl_2), NBu_4PF_6 as supporting electrolyte, calomel electrode)

	E_1	E_2	E_3	E_4	E_5
$Ce(ttp)_2$		1.000	0.620	-0.29 [a]	
2c		0.997	0.673	-0.394	
5a		0.984	0.617	-0.278	
5b		1.220	0.882	-0.222	
5c	1.670	1.070	0.618	-0.294	
5e	1.651	0.935	0.555	-0.326	-0.682
3c			0.86 [b]		
3e					-0.675

[a] Ref.[28]. – [b] Irreversible (anodic peak given).

In **5e** two porphyrin ligands are connected via a dialkyl-substituted quinone. The stable square antiprismatic coordination geometry of the cerium sandwich complex effects a well-defined although not yet exactly known non-coplanar orientation of the quinone moiety relative to the porphyrin ligands of the double-decker system. The presence of a double-decker and a quinone unit in the same molecule does not seem to influence the UV/Vis spectra or the redox potential of the individual chromophores. Thus, no donor-acceptor interactions are detectable. Studies of the fluorescence quenching of **5e** have not yet been made because the cerium(IV) double-deckers are nonluminescent[31]. Formal replacement of cerium(IV) in **5e** by lanthanum(III) would lead to a fluorescent lanthanum(III) bisporphyrinate anion[32], but attempts to prepare such species came to a halt at the anionic La(III) analog of **5c**[28].

Nevertheless, the synthesis of **5a** and **5b** and the discovery of the remarkable difference of their ring oxidation potentials E_2 and E_3 revealed the possibility of tuning the redox potentials of cofacial bisporphyrins by adjusting their relative orientations by steric modification of electronically inactive substituents of the porphyrin systems, an aspect which is being further pursued.

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Experimental

Spectrometers, sources of analytical data and other chemicals used were specified in a previous paper of this series[14]. 1,9-Dibromononane, 1,10-dibromodecane, Cs_2CO_3, and DMF were obtained from Fluka Chemie AG. 1,4-Bis(3-bromopropyl)-2,5-dimethoxybenzene[20] (**3c**) and (*p*-hydroxyphenyl)tri-*p*-tolylporphyrin[23] **1a** were prepared by literature methods.

Protocol 1: General procedure of the preparation of the diporphyrins **4a**–**c** from **1a** and 1,9-dibromononane (**3a**), 1,10-dibromodecane (**3b**), 1,4-bis(3-bromopropyl)-2,5-dimethoxybenzene (**3c**), respectively. – To a solution of 310 mg (0.46 mmol) of **1a** and 1.3 g (3.99 mmol) of anhydrous cesium carbonate in 15 ml of DMF a solution of 309 mg of **3a**, 324 mg of **3b**, or 410 mg of **3c** (1.08 mmol) 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-bromoalkoxy)phenyl]porphyrins **1b**–**d** and with CH_2Cl_2 the violet fraction of the diporphyrins **4a**–**c**. Evaporation of the solvent in vacuo and crystallization of the residue from CH_2Cl_2/MeOH (1:1) yielded the following diporphyrins **4a**–**c** as violet powders:

1,9-Bis{4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]phenoxy}nonane (**4a**): Yield 190 mg (56%). – MS, *m/z* (%): 1468 (100) [M^+]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 420 nm (5.84), 517.2 (4.40), 553.6 (4.16), 592.3 (3.88), 648.2 (3.88). – IR (KBr), 7 most intense bands: $\tilde{\nu}$ = 800 cm^{-1}, 965, 1240, 1465, 2920, 1510, 3320 (NH). – ^1H NMR ($CDCl_3$): δ = −2.81 (s, 4H, NH), 1.53–1.58 [m, 10H, $OCH_2CH_2(C\mathit{H}_2)_5CH_2CH_2O$], 2.02 [m, 4H, $OCH_2C\mathit{H}_2(CH_2)_5C\mathit{H}_2CH_2O$], 2.65 (m, 18H, CH_3, tolyl), 4.28 [t, *J* = 8 Hz, 4H, $OC\mathit{H}_2CH_2(CH_2)_5CH_2C\mathit{H}_2O$], 7.28 (d, *J* = 8 Hz, 4H, oxyphenyl 3,5-H), 7.55 (m, 12H, tolyl 3,5-H), 8.09 (m, 16H, tolyl and oxyphenyl 2,6-H), 8.85 (m, 16H, pyrrole H).

1,10-Bis{4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]phenoxy}decane (**4b**): Yield 240 mg (70%). – MS, *m/z* (%): 741 (100) [M^{2+}], 1482 (35) [M^+]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 420 nm (5.96), 516.7 (4.51), 552.9 (4.27), 592.4 (3.99), 648.6 (4.00). – IR (KBr), 7 most intense bands: $\tilde{\nu}$ = 795 cm^{-1}, 970, 1240, 1170, 1470, 2920, 3320 (NH). – ^1H NMR ($CDCl_3$): δ = −2.80 (s, 4H, NH), 1.53–1.59 [m, 12H, $OCH_2CH_2(C\mathit{H}_2)_6CH_2CH_2O$], 2.01 [m, 4H, $OCH_2C\mathit{H}_2(CH_2)_6C\mathit{H}_2CH_2O$], 2.64 (m, 18H, CH_3, tolyl), 4.28 [t, *J* = 8 Hz, 4H, $OC\mathit{H}_2CH_2(CH_2)_6CH_2C\mathit{H}_2O$], 7.28 (d, *J* = 8 Hz, 4H, oxyphenyl 3,5-H), 7.55 (m, 12H, tolyl 3,5-H), 8.09 (m, 16H, tolyl and oxyphenyl 2,6-H), 8.85 (m, 16H, pyrrole H).

1,4-Dimethoxy-2,5-bis{3-[4-[10,15,20-tris(4-methylphenyl)-porpyhrin-5-yl]phenoxy]propyl}benzene (**4c**): Yield 307 mg (85%). – MS, *m/z* (%): 1562 (100) [M^+], 781 (85) [M^{2+}]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 420.3 nm (5.91), 516.7 (4.52), 552.6 (4.29), 592.7 (4.04), 648.6 (4.03). – IR (KBr), 7 most intense bands: $\tilde{\nu}$ = 799 cm^{-1}, 1507, 1469, 1245, 1215, 1469, 1178, 3317 (NH). – ^1H NMR ($CDCl_3$): δ = −2.75 (s, 4H, NH), 2.31 (m, 4H, dimethoxybenzene-$CH_2C\mathit{H}_2CH_2O$), 2.67 (m, 18H, CH_3, tolyl), 2.99 [t,

J = 8 Hz, 4H, dimethoxybenzene-$C\mathit{H}_2CH_2CH_2O$], 3.89 (s, 6H, OCH_3), 4.28 (t, J = 8 Hz, 4H, dimethoxybenzene-$CH_2CH_2C\mathit{H}_2O$), 6.88 (s, 2H, dimethoxybenzene 3,6-H), 7.28 (d, J = 8 Hz, 4H, oxyphenyl 3,5-H), 7.53 (m, 12H, tolyl 3,5-H), 8.08 (m, 16H, tolyl and oxyphenyl 2,6-H), 8.85 (m, 16H, pyrrole H). – CV (CH_2Cl_2/NBu_4PF_6): 1.269 V, 0.863, −1.261.

Protocol 2. – 5-[4-(10-Bromodecyloxy)phenyl]-10,15,20-tris(4-methylphenyl)porphyrin (**1c**): 1.85 g (6.2 mmol) of **3b** was added under nitrogen to a solution of 424 mg (0.63 mmol) of **1a** and 1.74 g (5.34 mmol) of anhydrous cesium carbonate in 50 ml DMF. After stirring at 100 °C for 5 h, the solution was filtered and the solvent removed in vacuo. 456 mg (81%) of the porphyrin **1c** was 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* (%): 810 (100) [M$^+$ – HBr], 890 (28) [M$^+$]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 419.7 nm (5.64), 516.5 (4.1), 553.1 (3.96), 592.7 (3.69), 647.2 (3.70). – IR (KBr), 7 most intense bands: $\tilde{\nu}$ = 800 cm^{-1}, 965, 1245, 1175, 1470, 1505, 2960, 3320 (NH). – ^{1}H NMR ($CDCl_3$): δ = −2.83 (s, 2H, NH), 1.30–1.64 [m, 12H, $OCH_2CH_2(C\mathit{H}_2)_6CH_2CH_2Br$], 1.84–1.99 [m, 4H, $OCH_2C\mathit{H}_2(CH_2)_6C\mathit{H}_2CH_2Br$), 2.70 (s, 9H, CH_3, tolyl), 3.46 [t, J = 8 Hz, 2H, $OCH_2CH_2(CH_2)_6CH_2C\mathit{H}_2Br$], 4.26 [t, J = 8 Hz, 2H, $OC\mathit{H}_2CH_2(CH_2)_6CH_2CH_2Br$], 7.28 (d, J = 8 Hz, 2H, oxyphenyl 3,5-H), 7.55 (m, 6H, tolyl 3,5-H), 8.09 (m, 8H, tolyl and oxyphenyl 2,6-H), 8.85 (m, 8H, pyrrole H).

Protocol 3. – 2,5-Bis{3-[4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]phenoxy]propyl}quinone (**4e**): A solution of 366 mg (0.234 mmol) of **4c** in 80 ml of CH_2Cl_2 was heated at reflux, while a solution of 1.4 mmol of boron bromide in 25 ml of CH_2Cl_2 was added dropwise. The reaction mixture was poured into 30 ml of 2 N NaOH when no starting material but the beginning formation of the monohydroxyporphyrin **1a** was observable by thin-layer chromatography (silica gel/CH_2Cl_2). After washing with 40 ml of water, the solvent of the organic layer was distilled off in vacuo. The crude product which contained a mixture of **4e** and the hydroxyquinone diporphyrin **4d** (not isolated) was dissolved in a mixture of CH_3CN (12 ml) and CH_2Cl_2 (16 ml) and the solution treated with 315 mg (0.57 mmol) of $(NH_4)_2[Ce(NO_3)_6]$ in 4 ml of water. After 90 min, 50 ml of water and 50 ml of CH_2Cl_2 were added. The solvent of the organic layer was removed in vacuo and the residue chromatographed with CH_2Cl_2 on an alumina column (II, neutral, 15 · 3.5 cm). From the first violet fraction 291 mg (81%) of **4e** was obtained after evaporation of the solvent in vacuo and recrystallization of the residue from CH_2Cl_2/MeOH (1:1). – MS, *m/z* (%): 1532 (100) [M$^+$], 766 (85) [M^{2+}]. – UV/Vis: λ_{max} (lg ε) = 261.3 nm (4.54), 419.6 (5.88), 515.8 (4.47), 552.2 (4.22), 592.4 (3.95), 647.4 (3.95). – IR (KBr), 8 most intense bands: $\tilde{\nu}$ = 801 cm^{-1}, 1257, 1023, 1101, 1653 (C=O), 1508, 1608 (C=C), 3318 (N–H). – ^{1}H NMR ($CDCl_3$): δ = −2.85 (s, 4H, NH), 2.17 (m, 4H, quinone-$CH_2C\mathit{H}_2CH_2O$), 2.61 (m, 18H, CH_3, tolyl), 2.77 (t, J = 8 Hz, 4H, quinone-$C\mathit{H}_2CH_2CH_2O$), 4.24 (t, J = 8 Hz, 4H, quinone-$CH_2CH_2C\mathit{H}_2O$), 6.74 (s, 2H, quinone 3,6-H), 7.15 (d, J = 8 Hz, 4H, oxyphenyl 3,5-H), 7.47 (m, 12H, tolyl 3,5-H), 8.01 (m, 16H, tolyl and oxyphenyl 2,6-H), 8.77 (m, 16H, pyrrole H). – CV (CH_2Cl_2/NBu_4PF_6): 1.218 V, 0.854, −0.662, −1.298.

Protocol 4: General procedure of the metalation of the diporphyrins **4a–c, e** or the monofunctionalized porphyrin **1c** with Ce(acac)$_3$ · H_2O. – A solution of 1.6 mmol of *n*BuLi in 1 ml of hexane was added to a solution of 100 mg (0.068 mmol) of **4a**, 99 mg (0.067 mmol) of **4b**, 100 mg (0.064 mmol) of **4c**, or 98 mg (0.11 mmol) of **1c** in 60 ml of TCB under nitrogen. In the case of the diporphyrin **4e** (100 mg, 0.065 mmol) only 0.4 mmol of *n*BuLi in 0.25 ml of hexane was used. The solution was stirred for 10 min at room temp. After the addition of 300 mg (0.66 mmol), 295 mg (0.65 mmol), 282 mg (0.62 mmol), 275 mg (0.60 mmol), or 255 mg (0.56 mmol) of Ce(acac)$_3$ · H_2O to the porphyrins **4a**, **4b**, **4c**, **4e**, and **1c**, respectively, the solution was heated at reflux for 3 h. After cooling and filtration the solvent was evaporated in vacuo. The reaction mixture of the diporphyrin **4e** and the double-decker **5e** was cooled in the presence of air and then evaporated to dryness. All double-deckers except **5e** were purified on an alumina column (II, neutral, 15 × 3.5 cm) with toluene. The first brown fraction contained in every case the double-decker followed by the second violet fraction of the corresponding diporphyrin or the monofunctionalized porphyrin **1c**. The double-decker **5e** was obtained as the first brown fraction by chromatography on a silica gel column (30 × 2.5) with CH_2Cl_2 followed by the second violet fraction of the diporphyrin **4e**. The double-deckers were isolated as brown powders after evaporation of the solvent and recrystallization from CH_2Cl_2/MeOH.

{1,9-Bis[4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]phenoxy]nonanato}cerium(IV) (**5a**): Yield 26 mg (24%). – MS, *m/z* (%): 1604 (100) [M$^+$]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 398.9 nm (5.12), 485.7 (3.95), 543.6 (3.83), 586.4 (3.44), 649.2 (3.27). – IR (KBr), 7 most intense bands: $\tilde{\nu}$ = 800 cm^{-1}, 975, 1240, 1170, 1320, 1500, 2960. – ^{1}H NMR ($CDCl_3$): δ = 1.69/1.76 [m, 10H, $OCH_2CH_2(C\mathit{H}_2)_5CH_2CH_2O$], 2.15/2.25 [m, 4H, $OCH_2C\mathit{H}_2(CH_2)_2C\mathit{H}_2CH_2O$], 2.72 (m, 18H, CH_3, tolyl), 4.41/4.52 [m, 4H, $OC\mathit{H}_2CH_2(CH_2)_5CH_2C\mathit{H}_2O$], 6.28/9.50 (m, 8H/8H, *endo* and *exo* tolyl and oxyphenyl 2,6-H), 6.51/7.62 (m, 2H/2H, *endo* and *exo* oxyphenyl 3,5-H), 7.06/7.94 (m, 6H/6H, *endo* and *exo* tolyl 3,5-H), 8.13–8.49 (m, 16H, pyrrole H). – CV (CH_2Cl_2/NBu_4PF_6): 0.984 V, 0.617, −0.278. – $C_{103}H_{84}CeN_8O_2$ (1606.0): calcd. C 77.03, H 5.27, N 6.98; found C 74.48, H 5.09, N 6.28.

{1,10-Bis[4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]phenoxy]decanato}cerium(IV) (**5b**): Yield 75 mg (68%). – MS, *m/z* (%): 1618 (100) [M$^+$]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 399.1 nm (5.43), 478.6 (4.20), 543.8 (4.10), 585.9 (3.39), 648.2 (3.56). – IR (KBr), 6 most intense bands: $\tilde{\nu}$ = 800 cm^{-1}, 980, 1170, 1240, 1340, 1510. – ^{1}H NMR ($CDCl_3$): δ = 1.62/1.71 [m, 12H, $OCH_2CH_2(C\mathit{H}_2)_6CH_2CH_2O$], 2.11 [m, 4H, $OCH_2C\mathit{H}_2(CH_2)_6C\mathit{H}_2CH_2O$], 2.71 (m, 18H, CH_3, tolyl), 4.39/4.51 [m, 4H, $OC\mathit{H}_2CH_2(CH_2)_6CH_2C\mathit{H}_2O$], 6.35/9.49 (m, 8H/8H, *endo* and *exo* tolyl and oxyphenyl 2,6-H), 6.84–7.76 (m, 2H/2H, *endo* and *exo* oxyphenyl 3,5-H), 7.12/7.96 (m, 6H/6H, *endo* and *exo* tolyl 3,5-H), 8.10–8.50 (m, 16H, pyrrole H). – CV (CH_2Cl_2/NBu_4PF_6): 1.220 V, 0.882, −0.222. – $C_{104}H_{86}CeN_8O_2$ (1620.0): calcd. C 77.10, H 5.35, N 6.91; found C 77.18, H 5.53, N 6.72.

{1,4-Dimethoxy-2,5-bis[3-[4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]phenoxy]propyl]benzenato}cerium(IV) (**5c**): Yield 61 mg (56%). – MS, *m/z* (%): 849 (100) [M^{2+}]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 398.9 nm (5.12), 485.7 (3.95), 543.6 (3.83), 587.0 (3.47), 649.2 (3.27). – IR (KBr), 6 most intense bands: $\tilde{\nu}$ = 800 cm^{-1}, 980, 1508, 1215, 1245, 1178. – ^{1}H NMR ($CDCl_3$, assignment by COSY): δ = 2.39 (m, 4H, dimethoxybenzene-$CH_2C\mathit{H}_2CH_2O$), 2.72 (m, 18H, CH_3, tolyl), 3.16/2.93 (m, 2H/2H, dimethoxybenzene-$C\mathit{H}_2CH_2CH_2O$), 3.98 (s, 6H, OCH_3), 4.30/4.37 (m, 2H/2H, dimethoxybenzene-$CH_2CH_2C\mathit{H}_2O$), 6.94 (s, 2H, 3,6-dimethoxybenzene H), 6.28/9.50 (m, 8H/8H, *endo* and *exo* tolyl and oxyphenyl 2,6-H), 6.78/7.65 (m, 2H/2H, *endo* and *exo* oxyphenyl 3,5-H), 7.11/7.96 (m, 6H/6H, *endo* and *exo* tolyl 3,5-H), 8.08–8.47 (m, 16H, pyrrole H). – CV (CH_2Cl_2/NBu_4PF_6): 1.670 V, 1.070, 0.618, −0.294. – $C_{108}H_{86}CeN_8O_4$ (1700.05): calcd. C 76.30, H 5.09, N 6.59; found C 76.24, H 5.05, N 6.47.

{2,5-Bis[3-[4-[10,15,20-tris(4-methylphenyl)porphyrin-5-yl]-phenoxy]propyl]chinonato}cerium(IV) (**5e**): Yield 32 mg (29%). – MS, *m/z* (%): 1668 (100) [M^+]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 258.0 nm (4.58), 399.8 (5.32), 488.2 (4.04), 545.6 (3.92), 586.4 (3.52), 648.5 (3.38). – IR (KBr), 7 most intense bands: $\tilde{\nu}$ = 800 cm^{-1}, 980, 1654 (C=O), 1245, 1509, 1607 (C=C), 1325. – ^1H NMR ($CDCl_3$, assignment by COSY): δ = 2.31 (m, 4H, quinone-$CH_2CH_2CH_2O$), 2.66 (m, 18H, CH_3, tolyl), 2.82 (m, 4H, quinone-$CH_2CH_2CH_2O$), 4.34 (m, 4H, quinone-$CH_2CH_2CH_2O$), 6.24/9.42 (m, 6H/6H, *endo* and *exo* tolyl 2,6-H), 6.62/9.30 (m, 2H/2H, *endo* and *exo* oxyphenyl 2,6-H), 6.81 (s, 2H, quinone 3,6-H), 6.87/7.35 (m, 2H/2H, *endo* and *exo* oxyphenyl 3,5-H), 7.01/7.88 (m, 6H/6H, *endo* and *exo* tolyl 3,5-H), 8.08–8.88 (m, 16H, pyrrole H). – CV (CH_2Cl_2/NBu_4PF_6): 1.651 V, 0.935, 0.555, −0.326, −0.682. – $C_{106}H_{80}CeN_8O_4$ (1670.0): calcd. C 76.24, H 4.83, N 6.71; found C 76.13, H 5.02, N 6.57.

Bis{5-[4-(10-bromodecyloxy)phenyl]-10,15,20-tris(4-methylphenyl)porphyrinato}cerium(IV) (**2c**) (isomers **2A** and **2B**): Yield 47 mg (44%). – MS, *m/z* (%): 890 (100) [**1c**]$^+$, 958 (31) [M^{2+}]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 398.9 nm (5.49), 479.8 (4.27), 543.0 (4.13), 583.6 (3.30), 629.2 (3.61). – IR (KBr), 6 most intense bands: $\tilde{\nu}$ = 800 cm^{-1}, 970, 1245, 2920, 1175, 1325. – ^1H NMR ($CDCl_3$): δ = 1.42–1.65 [m, 24H, $OCH_2CH_2(CH_2)_6CH_2CH_2Br$], 1.80–2.13 [m, 8H, $OCH_2CH_2(CH_2)_6CH_2CH_2Br$], 2.71 (s, 18H, CH_3, tolyl), 3.45 [t, *J* = 8 Hz, 4H, $OCH_2CH_2(CH_2)_6CH_2CH_2Br$], 4.26 [t, *J* = 8 Hz, 4H, $OCH_2CH_2(CH_2)_6CH_2CH_2Br$], 6.29/9.47 (m, 8H/8H, *endo* and *exo* tolyl and oxyphenyl 2,6-H), 6.77/7.64 (m, 2H/2H, *endo* and *exo* oxyphenyl 3,5-H), 7.18/7.92 (m, 6H/6H, *endo* and *exo* tolyl 3,5-H), 8.27 (m, 16H, pyrrole H). – CV (CH_2Cl_2/NBu_4PF_6): 0.997 V, 0.673, −0.394. – $C_{114}H_{106}Br_2CeN_8O_2$ (1920.1): calcd. C 71.31, H 5.56, N 5.84; found C 71.60, H 4.16, N 5.66.

Protocol 5. – *2,5-Bis(3-bromopropyl)quinone* (**3e**): A solution of 0.2 ml (2.2 mmol) of boron tribromide in 15 ml of CH_2Cl_2 was added dropwise to a solution of 150 mg (0.39 mmol) of 1,4-bis(3-bromopropyl)-2,5-dimethoxybenzene (**2c**) in 20 ml of CH_2Cl_2. The solution was stirred overnight and then heated at reflux for 1 h. After the addition of 50 g of ice the organic layer was washed with 50 ml of 2 N NaOH and dried with $MgSO_4$. The solvent was distilled off in vacuo. The green residue and 250 mg (1.10 mmol) of DDQ were dissolved in 30 ml of CH_2Cl_2, and the solution was stirred for 1 h. Adsorptive filtration with CH_2Cl_2 on an alumina column (III, basic, 7 × 2 cm) yielded after evaporation of the solvent 121 mg (88%) of 2,5-bis(3-bromopropyl)quinone (**3e**) as yellow crystals. – MS, *m/z* (%): 348 (100) [M^+]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 258.3 nm (3.84). – IR (KBr), 7 most intense bands: $\tilde{\nu}$ = 1653 cm^{-1} (C=O), 1296, 1612 (C=C), 1210, 931, 1423, 1249. – ^1H NMR ($CDCl_3$): δ = 2.07 (m, 4H, quinone-$CH_2CH_2CH_2Br$), 2.59 (t, *J* = 8 Hz, 4H, quinone-$CH_2CH_2CH_2Br$), 3.43 (t, *J* = 8 Hz, 4H, quinone-$CH_2CH_2CH_2Br$), 6.62 (s, 2H, quinone 3,6-H). – CV (CH_2Cl_2/NBu_4PF_6): −0.675 V.

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[5] Abbreviations used: M, metal; $(p)^{2-}$, $(tpp)^{2-}$, $(ttp)^{2-}$, $(Hottp)^{2-}$, $(Meottp)^{2-}$, dianions of a general porphyrin, 5,10,15,20-tetraphenylporphyrin, 5,10,15,20-tetrakis(methylphenyl)porphyrin, 5-hydroxyphenyl-10,15,20-tritolylporphyrin (**1a**), 5-methoxyphenyl-10,15,20-tritolylporphyrin respectively; $(ttpOR'Ottp)^{4-}$, tetraanion of a diporphyrin (**4**); H(acac), acetylacetone; TCB, 1,2,4-trichlorobenzene.

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