Metal Complexes with Tetrapyrrole Ligands, LXX[◇]

# Synthesis, Characterization, and Variable-Temperature $^1$H-NMR Investigations of Cerium(IV) and Zirconium(IV) Double-Deckers Derived from 2,3,7,8,12,13,17,18-Octaethyl-5-methylporphyrin

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The synthesis of bis(2,3,7,8,12,13,17,18-octaethyl-5-methylporphyrinato)cerium(IV) and -zirconium(IV) [M(oemep)$_2$; M = Ce, Zr, respectively] is described. The complexes were characterized by UV/Vis and IR spectroscopy and cyclic voltammetry. $^1$H-NMR spectra of the new cerium and zirconium sandwich complexes show that they exist as a mixture of vicinal and transversal isomers due to the rigid square-antiprismatic coordination geometry found in metal(IV) bis(porphyrinates). From the temperature dependence of the $^1$H-NMR spectra the rotational rigidity of the double-decker system was deduced. In toluene, free rotation of the two porphyrin macrocycles with respect to each other does not occur up to 373 K.

Porphyrin sandwich complexes M(p)$_2$[1] with tetravalent metals such as cerium[2,3], uranium and thorium[4], or zirconium and hafnium[5,6] have been known for several years. They are investigated inter alia because they might be model systems of the special pair[7,8] of bacteriochlorophyll molecules in the reaction center of bacterial photosynthesis[9]. Strong $\pi,\pi$ interactions between closely arranged porphyrin rings give rise to unusual absorption, fluorescence, redox, and electron-transfer properties[10]. Although the electronic similarity of porphyrin sandwich complexes and the special pair has been doubted[11] these double-deckers can be regarded as structural and electrochemical model systems which display effective overlap of the $\pi$ electron systems of two tetrapyrrole systems resulting in a facilitated oxidation of the porphyrin ligands as compared with the appropiate monoporphyrinates[7]. This facilitation of the electron abstraction is the essential result of the close vicinity of two porphyrin rings.

In the solid state a square antiprismatic coordination geometry was found in all available crystal structures of metal bis(porphyrinates)[12]. Double-deckers derived from monosubstituted tetraarylporphyrins have a sufficiently low symmetry ($C_2$) allowing the discrimination of isomers resulting from rigid configurations in solution by $^{19}$F- and $^1$H-NMR spectroscopy. Cerium(IV) bis[(*p*-hydroxyphenyl)tri-*p*-tolylporphyrinate] and several derivates were obtained by complexation of the respective porphyrins. They exist as a mixture of vicinal and transversal isomers, each with $C_2$ symmetry and square-antiprismatic coordination geometry in a 1:1 ratio. Variable-temperature $^1$H- and $^{19}$F-NMR spectra have shown that their square antiprism is quite rigid, i. e. rotation of the two tetraarylporphyrin ligands with respect to each other does not occur up to 413 K[13]. The nitration of Zr(ttp)$_2$ in the peripheral pyrrole positions afforded a mononitro derivative Zr(ttp)(ttpNO$_2$). The $^1$H-NMR spectrum of the latter shows eight methyl signals of the *p*-tolyl groups up to 150 °C, indicating that the two porphyrin macrocycles are not rotating with respect to each other on the NMR time scale[14].

Since octaalkylporphyrins have a higher electron density at the porphyrin ring as compared with tetraarylporphyrins, it seemed worthwile to compare the structure in solution and the rigidity of cerium(IV) and zirconium(IV) bis(porphyrinates) derived from these two series of porphyrins. In this paper the synthesis, characterization, and variable-temperature $^1$H-NMR spectra of bis(2,3,7,8,12,13,17,18-octaethyl-5-methylporphyrinato)cerium(IV) and -zirconium(IV) [Ce(oemep)$_2$ and Zr(oemep)$_2$] derived from 2,3,7,8,12,13,17,18-octaethyl-5-methylporphyrin[15] [**1**, H$_2$(oemep)] are described. In these double-deckers, the *meso*-(5-)methyl groups lower the symmetry to $C_2$, hopefully allowing the observation of isomers by $^1$H-NMR spectroscopy.

## Synthesis of Cerium(IV) and Zirconium(IV) Bis(octaethyl-5-methylporphyrinates)

The preparation of the symmetrical bis(octaethylporphyrinates) Ce(oep)$_2$ and Zr(oep)$_2$ from H$_2$(oep) was already described[3–5]. The synthesis of the analogous cerium and zirconium sandwich complexes derived from **1** can be achieved in the same way. Treatment of Li$_2$(oemep) [pre-

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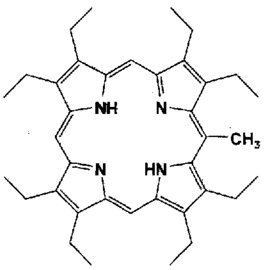


**1**: $H_2$(oemep)

pared in situ by addition of *n*-butyllithium to a solution of $H_2$(oemep) in 1,2,4-trichlorobenzene] with the acetylacetonate $Ce(acac)_3 \cdot H_2O$ in boiling 1,2,4-trichlorobenzene (TCB) yielded pure $Ce(oemep)_2$ after chromatographic workup (eq. 1) on alumina. Crystallization from $CH_2Cl_2$/MeOH afforded the cerium complex as blue-violet crystals.

$$2\ Li_2(oemep) + Ce(acac)_3 \cdot H_2O \xrightarrow[-3\ Li(acac),\ -Li^+,\ -e^-]{TCB,\ 200\,°C,\ O_2} Ce(oemep)_2 \qquad (1)$$

The new double-decker $Zr(oemep)_2$ was prepared from zirconocene dichloride, $Zr(cp)_2Cl_2$, and $Li_2$(oemep) in refluxing 1,2,4-trichlorobenzene (eq. 2) and purified by chromatography on alumina. The complex was obtained as a blue powder after crystallization from $CH_2Cl_2$/MeOH.

$$Zr(cp)_2Cl_2 + 2\ Li_2(oemep) \xrightarrow[-2\ LiCl,\ -2\ Li(cp)]{TCB,\ 200\,°C} Zr(oemep)_2 \qquad (2)$$

### Spectral Characterization of the New Double-Deckers

*UV/Vis Spectra:* The UV/Vis spectra of the new double-deckers $Ce(oemep)_2$ and $Zr(oemep)_2$ resemble their analogs $Ce(oep)_2$ and $Zr(oep)_2$, respectively. Due to the methyl substituent in *meso* position of the porphyrin system the B band and all the visible bands of $H_2$(oemep)[15] are red-shifted as compared with the appropriate bands of $H_2$(oep)[16]. This was found for the complexes $Ce(oemep)_2$ and $Zr(oemep)_2$ as compared with their analogs $Ce(oep)_2$ and $Zr(oep)_2$, respectively, for the B bands and most of the visible bands as well (Table 1, the bands were labeled as performed earlier for closely approached porphyrin ligands in sandwich complexes[17a]). The spectrum of $Ce(oemep)_2$ (Figure 1a) is just bathochromically shifted as compared with the spectrum of $Ce(oep)_2$. The effect of an introduction of *meso*-methyl groups is more complicated for zirconium: as compared with the spectrum of $Zr(oep)_2$, the spectrum of $Zr(oemep)_2$ shows bathochromic shifts only for the B, Q″, and the Q(0,0) bands, while the maxima of the Q(1,0) and Q′ bands display hypsochromic shifts. The shape of the Q(0,0) band is different (Figure 1b). This band shows two maxima for $Zr(oemep)_2$ and only one for $Zr(oep)_2$ which could express the presence of isomers in the case of $Zr(oemep)_2$.

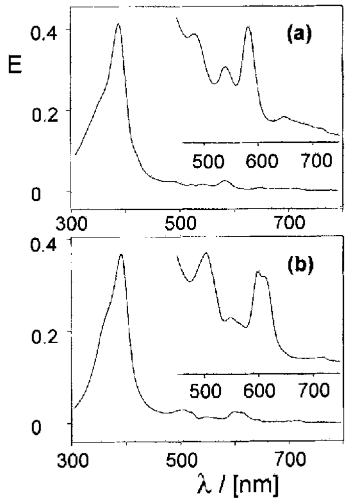
*$^1$H-NMR Spectra:* The $^1$H-NMR spectra of symmetrical $Ce(oep)_2$[3] and $Zr(oep)_2$[5] were already discussed in detail. The spectra of the corresponding *meso*-methyl derivatives differ significantly from those (see Figure 2). As typical features of $M(oep)_2$ sandwich complexes they show the splitting of the signals of the diastereotopic methylene protons for the *endo*- and *exo*-H atoms. The loss of symmetry due to the *meso*-methyl substitution leads to several signals of the methylene and methyl groups. The resolution of the spectra is not high enough to assign the methylene and methyl proton signals definitely to a fixed methylene and methyl group, respectively.

Table 1. UV/Vis spectra of metal(IV) bis(porphyrinates) $M(p)_2$ ($\lambda_{max}$ [nm], lg ε in parentheses, at 25 °C in $CH_2Cl_2$)

| $M(p)_2$ | B | Q″ | Q(1,0) | Q(0,0) | Q′ |
|---|---|---|---|---|---|
| $Ce(oep)_2$ | 378 | 467 | 530 | 573 | 646.6[a)] |
| | (5.21) | (3.92) | (3.77) | (4.24) | (3.55) |
| $Ce(oemep)_2$ | 388.9 | 482.6 | 540.2 | 581.9 | 647.0 |
| | (5.22) | (4.01) | (3.87) | (4.04) | (3.44) |
| $Zr(oep)_2$ | 383 | 490 | 550 | 592 | 750[b)] |
| | (5.22) | (4.10) | (3.78) | (4.39) | (2.72) |
| $Zr(oemep)_2$ | 391.2 | 501.9 | 546.7 | 597.6/609.9 | 719.6 |
| | (5.05) | (4.02) | (3.72) | (3.94)/ (3.91) | (3.17) |

a) Most recent UV/Vis spectrum (Bruins Omega 10). – b) Taken from ref.[6a].

Figure 1. UV/Vis spectra of $Ce(oemep)_2$ (**a**) and $Zr(oemep)_2$ (**b**) ($CH_2Cl_2$, room temperature)



If a stable square antiprismatic coordination geometry, as found for cerium bis(tetraarylporphyrinates) is assumed, two different geometrical isomers must be discussed for the $M(oemep)_2$ complexes (M = Ce, Zr) in which the *meso*-methyl groups of the two ligands adopt vicinal (**A**) or transversal (**B**) configurations (Scheme 1). Each of the two isomers has $C_2$ symmetry and hence each exists as a racemate.

The same number of diastereotopic protons results for the vicinal and transversal isomers. In each isomer there are one *meso*-methyl group, three different methyne protons, eight different methyl groups, and 16 different methylene protons (due to the diastereotopy of the methylene protons in axially dissymmetric porphyrins, there are 16 methylene groups[3,5]). The maximum number of two different *meso*-

methyl signals (singlets), six methyne proton signals (singlets), 16 methyl proton signals (triplets), and 32 methylene proton signals (quadruplets) for two isomers is neither seen for the cerium nor for the zirconium complex (Figure 2). Due to the movement of the ethyl groups both the methyl proton signals as well as the methylene proton signals of the M(oemep)$_2$ sandwich complexes are broad and not helpful for the determination of the isomers. Separate signals of methyl protons or methylene protons belonging to different isomers cannot be distinguished.

Scheme 1. **A**: vicinal, **B**: transversal isomer of M(oemep)$_2$ (M = Ce, Zr). $C_2$ in **A** or **B** indicates the twofold symmetry axes

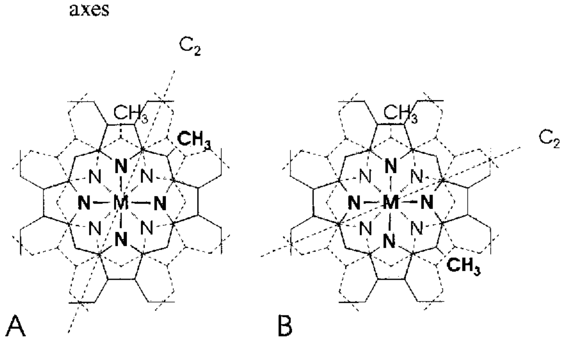
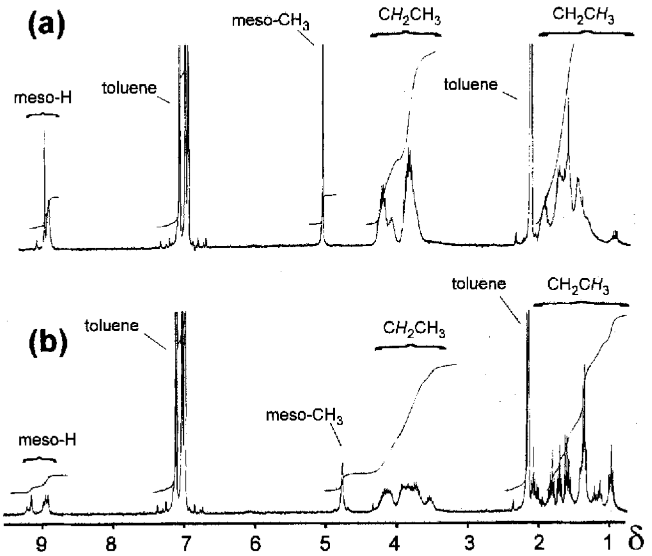


Figure 2. $^1$H-NMR spectra of Ce(oemep)$_2$ (**a**) and Zr(oemep)$_2$ (**b**) ([D$_8$]toluene, δ scale, int. TMS, 300 MHz, 303 K)



The *meso*-methyl signals of Ce(oemep)$_2$ and Zr(oemep)$_2$ appear each as one singlet. This can be explained by accidental isochronism which leads to a superposition of the signals of the vicinal and transversal isomers. The chemical shifts of the *meso*-methyl protons increase in the series H$_2$(oemep) < Zr(oemep)$_2$ < Ce(oemep)$_2$, amounting to 4.61, 4.73, and 5.06 ppm, respectively. The reason for this behavior is not clear. This may indicate that on more closely compressing the two porphyrin rings these protons move into a more deshielding region of the anisotropy cone. In contrast, the methyne protons may move to a more shielding region since their resonances are slightly shifted to higher field (δ = 9.83/10.03, 8.94....9.11, and 8.9....9.2, respectively).

Finally, the pattern of the *meso*-methyne proton signals of both Ce(oemep)$_2$ and Zr(oemep)$_2$ shows the presence of isomers. Both the vicinal and the transversal isomers have three non-equivalent methyne protons. This should give rise to a maximum of three singlets with equal intensity for each isomer if there is no accidental isochronism of the methyne protons. In the case of free rotation of the porphyrin ligands with respect to each other two singlets in the ratio 2:1 should be observed as found for the free porphyrin. The patterns of signals appearing in the methylene region of Ce(oemep)$_2$ and Zr(oemep)$_2$ in any case is more complex and demonstrates the presence of different isomers.

Therefore, it is proposed that Ce(oemep)$_2$ and Zr(oemep)$_2$ both consist of a mixture of vicinal and transversal isomers (Scheme 1). The methyne signal patterns can be explained as unsymmetrical superpositions of *meso*-methyne signals of the two geometrical isomers. The somewhat different shapes of the signal patterns of Ce(oemep)$_2$ and Zr(oemep)$_2$ reflect the varying ligand-ligand distance which is shorter for Zr(oemep)$_2$ and causes stronger ring-current effects in the latter.

$^1$H-NMR spectra of both complexes were recorded in [D$_8$]toluene between 203 and 373 K to investigate the rotational rigidity of the double-decker system. To simplify the interpretation of the spectra only the signals of the *meso*-methyne protons are considered (Figure 3). Between 203 and 373 K, neither for the cerium nor for the zirconium complex the *meso*-methyne proton signals appear as two singlets in the ratio 2:1. Thus, free rotation of the porphyrin ligands with respect to each other does not occur up to 373 K. While the pattern of the *meso*-methyne signals of the zirconium complex is almost unchanged over the whole range of temperatures, the signals of the cerium complex merge to three sharp singlets in the ratio 1:2:3. This could indicate an increased movement of the two porphyrin macrocycles with respect to each other in the case of the cerium complex but by no means free rotation of the ligands.

### Electrochemical Characterization of the Double-Deckers

The cyclic voltammograms of the new sandwich complexes Ce(oemep)$_2$ and Zr(oemep)$_2$ as well as of the free porphyrin H$_2$(oemep) were measured in CH$_2$Cl$_2$ and compared with the electrochemical data of their oep analogs Ce(oep)$_2$[7a], Zr(oep)$_2$[5a], and H$_2$(oep)[18], respectively. The porphyrins H$_2$(oep) and H$_2$(oemep) show two reversible oxidations and one reversible reduction in their cyclic voltammograms. Due to the electron-donating methyl group, H$_2$(oemep) is easier to oxidize than H$_2$(oep), i. e. both the first ($E_2$) and the second ($E_1$) oxidation potential is smaller than for H$_2$(oep) (Table 2). Reduction of H$_2$(oemep), on the other hand, occurs at a more negative potential ($E_3$).

The complexes Ce(oemep)$_2$ and Zr(oemep)$_2$ both show two reversible oxidation steps as found for Ce(oep)$_2$ and Zr(oep)$_2$. Due to the methyl groups of the porphyrin system in Ce(oemep)$_2$ and Zr(oemep)$_2$, both oxidation steps are

Figure 3. $^1H$ resonance signals of the *meso*-methyne protons of $Ce(oemep)_2$ (a) and $Zr(oemep)_2$ (b) ([$D_8$]toluene, δ scale, int. TMS, 300 MHz, 303 K)

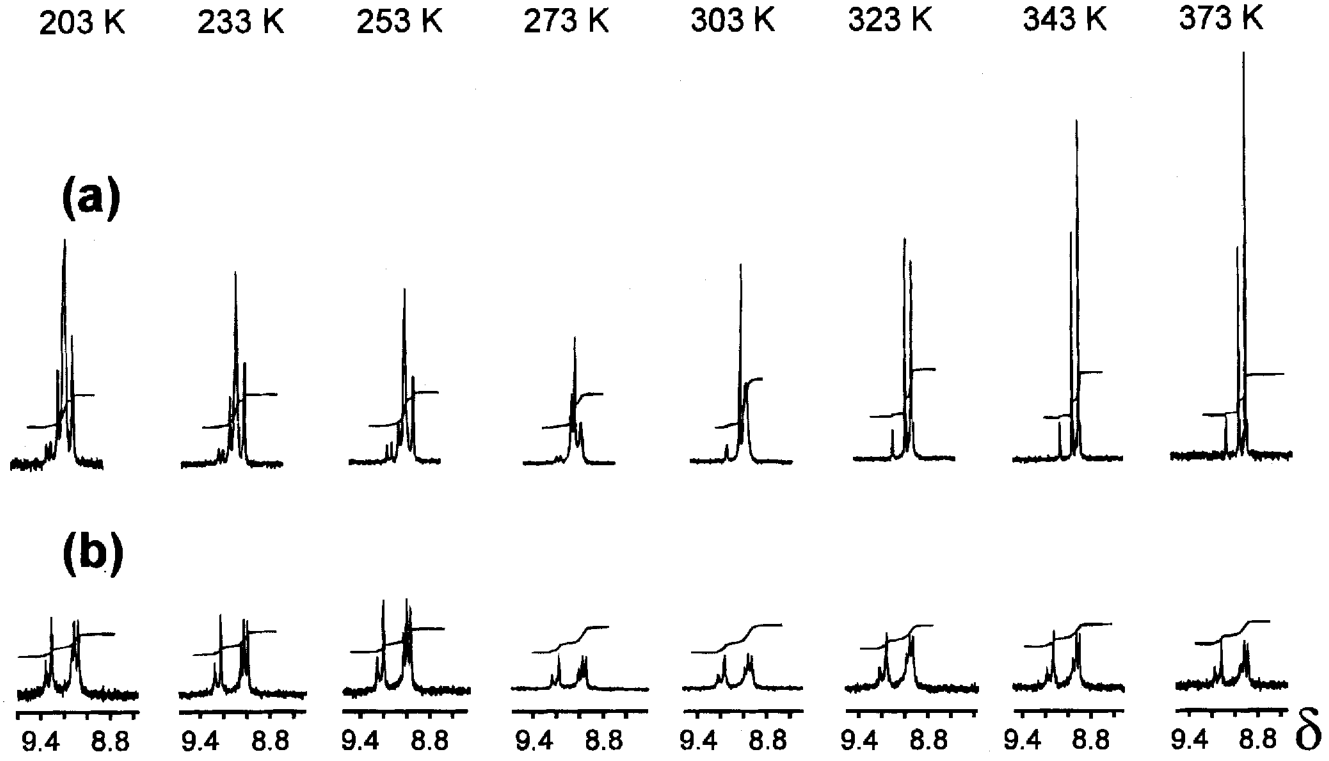


Table 2. Comparison of the redox potentials of (oep) and (oemep) derivatives ($CH_2Cl_2$, $NBu_4PF_6$ as supporting electrolyte, calomel electrode)

| Compound | $E_1$ | $E_2$ | $E_3$ |
|---|---|---|---|
| $H_2$(oep) | 1.300 | 0.810 | -1.460 |
| $H_2$(oemep) | 1.109 | 0.727 | -1.520 |
| Ce(oep)$_2$ | 0.745 | 0.170 | -0.58[a)] |
| Ce(oemep)$_2$ | 0.675 | 0.130 | -0.614[a)] |
| Zr(oep)$_2$ | 0.576 | -0.026 | -1.663 |
| Zr(oemep)$_2$ | 0.556 | -0.038 | -1.116[b)] |

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

facilitated as compared with $Ce(oep)_2$ and $Zr(oep)_2$ (Table 2, redox steps are labeled according to eq. 3). The oxidation potentials of the zirconium complexes $E_1$ and $E_2$ reflect the effect of the smaller ionic radius of this ion as compared with cerium: both oxidations are facilitated[5a].

$$\begin{array}{ccccccc} & E_1 & & E_2 & & E_3 & \\ [M(p)_2]^{2+} & \rightleftharpoons & [M(p)_2]^+ & \rightleftharpoons & [M(p)_2] & \rightleftharpoons & [M(p)_2]^- \\ [H_2(p)] & & [H_2(p)] & & [H_2(p)] & & [H_2(p)] \end{array} \qquad (3)$$

As found in the case of $Ce(oep)_2$, the quasireversible reduction of $Ce(oemep)_2$ ($E_3$) is the reduction of the cerium ion and not of the porphyrin rings. While for $Zr(oep)_2$ a reversible reduction at −1.663 V was observed, the reduction of $Zr(oemep)_2$ occured irreversibly at −1.116 V. The instability of the $[Zr(oemep)_2]^-$ anion could be explained by a more rapid protonation (by water impurities in the solvent) and disproportionation of the radical anions as compared with $Zr(oep)_2$.

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## Experimental

Spectrometers, sources of analytical data, and chemicals used were specified in a previous paper of this series[13]. – 2,3,7,8,12,13,17,18-Octaethyl-5-methylporphyrin[15] (**1**) was prepared from 2,3,7,8,12,13,17,18-Octaethylporphyrin[19] according to literature procedures. UV/Vis of **1**: $\lambda_{max}$ (lg ε): 406.4 nm (5.22), 506.9 (4.12), 541.1 (3.76), 577.0 (3.73), 630.5 (3.17).

*Bis(2,3,7,8,12,13,17,18-octaethyl-5-methylporphyrinato)-cerium(IV)* [Ce(meoep)$_2$]: A solution of 0.8 mmol of *n*BuLi in 0.5 ml of hexane was added to a solution of 200 mg (0.36 mmol) of $H_2$(oemep) in 60 ml of TCB under nitrogen. The solution was stirred for 10 min at room temp. After addition of 738 mg (1.62 mmol) of $Ce(acac)_3 \cdot H_2O$ the solution was heated at reflux for 4 h. After cooling and removal of the TCB in vacuo the residue was treated with 15 ml of toluene and filtered. The filtrate was chromatographed on an alumina column (I, basic, 7 × 2.5 cm). The first brown fraction was eluted with toluene and contained Ce(oemep)$_2$. The second violet fraction contained unreacted $H_2$(oemep). Evaporation of the solvent of the first fraction and recrystallization of the residue from $CH_2Cl_2$/MeOH (1:1) yielded 124 mg (56%) of the product as blue-violet crystals. – MS, *m/z* (%): 1232 (100) [$M^+$]. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (lg ε) = 388.9 nm (5.22), 482.6 (4.01), 540.2 (3.87), 581.9 (4.04), 647.0 (3.44). – IR (KBr), seven most intense bands: $\tilde{\nu}$ = 2965 $cm^{-1}$, 2930, 2870, 1460, 1058, 1014, 933. – $^1H$ NMR ($[D_8]$Toluene): $\delta$ = 0.8–2.0 (m, 48H, $CH_2CH_3$), 3.95–4.15 and 4.15–4.30 (m, 20H and m, 12H; respectively; $CH_2CH_3$), 5.06 (s, 6H, *meso*-$CH_3$), 8.94–9.11 (m, 6H, *meso*-H). – CV ($CH_2Cl_2/NBu_4PF_6$): 0.675 V, 0.130, −0.614. – $C_{74}H_{92}CeN_8$ (1233.7): calcd. C 72.04, H 7.52, N 9.08; found C 71.91, H 7.45, N 9.14.

*Bis(2,3,7,8,12,13,17,18-octaethyl-5-methylporphyrinato)-zirconium(IV)* [Zr(meoep)$_2$]: A solution of 1.44 mmol of *n*BuLi in 0.9 ml of hexane was added to a solution of 200 mg (0.36 mmol) of $H_2$(ocmep) in 50 ml TCB under nitrogen. After stirring at room temp. for 15 min, 210 mg (0.72 mmol) of Zr(cp)$_2$Cl$_2$ was added and the solution heated at reflux for 2 h. After removal of TCB in vacuo the residue was treated with 20 ml of cyclohexane and filtered to remove insoluble unreacted $H_2$(oemep) and an unidentified zirconium monoporphyrinate. The cyclohexane solution was chromatographed on alumina (II, basic, 3.5 · 10 cm). Fractions were obtained as follows: with cyclohexane/toluene (1:1) an orange forerun of unknown composition, with toluene a blue-green fraction 1 containing Zr(oemep)$_2$, with $CH_2Cl_2$ a reddish-brown fraction 2 of unreacted $H_2$(oemep), with $CH_2Cl_2$/MeOH (9:1) fraction 3 which contained again Zr(oemep)$_2$, and then a brown fraction 4 with an unknown decomposition compound. The solvent of the combined fractions 1 and 3 were evaporated in vacuo, and the residue was crystallized from 5 ml of $CH_2Cl_2$/MeOH (1:1) to afford 48 mg (22%) of Zr(oemep)$_2$ as blue microcrystals. – MS, *m/z* (%): 1182 (100) [$M^+$]. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$) = 391.2 nm (5.05), 501.9 (4.02), 546.7 (3.72), 597.6 (3.94), 609.9 (3.91), 719.6 (3.17). – IR (KBr), six most intense bands: $\tilde{\nu}$ = 2965 $cm^{-1}$, 2930, 2870, 1460, 1058, 952. – $^1H$ NMR ($[D_8]$Toluene): $\delta$ = 0.8–2.05 (m, 48H, $CH_2CH_3$), 3.38–3.53 (m, 4H, $CH_2CH_3$), 3.53–3.95 (m, 18H, $CH_2CH_3$), and 3.95–4.25 (m, 10H, $CH_2CH_3$), 4.73 (s, 6H, *meso*-$CH_3$), 8.90–8.96 and 9.14–9.20 (m, 6H, *meso*-H). – CV ($CH_2Cl_2/NBu_4PF_6$): 0.556 V, −0.038, −1.16. – $C_{74}H_{92}N_8Zr$ (1184.8): calcd. C 75.02, H 7.83, N 9.46; found C 74.20, H 7.04, N 8.44.

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[1] Abbreviations used: $(p)^{2-}$, $(oep)^{2-}$, $(ttp)^{2-}$, $(oemep)^{2-}$, dianions of a general porphyrin, 2,3,7,8,12,13,17,18-octaethylporphyrin, tetrakis(4-methylphenyl)porphyrin, 2,3,7,8,12,13,17,18-octaethyl-5-methylporphyrin, respectively; H(acac), acetylacetone; H(cp), cyclopentadiene; TCB, 1,2,4-trichlorobenzene.

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