# Metal Complexes with Tetrapyrrole Ligands, LXXV[‡]

# Osmium Complexes of the 5,10,15,20-Tetrakis(4-phosphonomethylphenyl)porphyrin Anion, A New Water-Soluble Tetraphenylporphyrinate System

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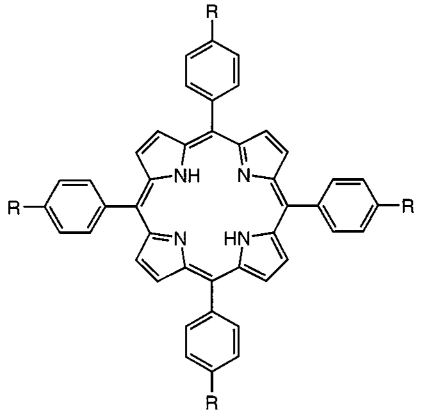
The synthesis of a new class of water-soluble osmium tetraphenylporphyrinates, complexes of the tetrakis(4-phosphonomethylphenyl)porphyrin anion $[H_2(tP_4O_8\{OH\}_4mpp)]^{4-}$ **(5)**, is described. Starting from OsCO(tmecpp)thf **(1a)** and $OsO_2$(tmecpp) **(1b)**, the new complexes **5a–c** were synthesized by a four-step reaction with $Os(t\{OH\}_4mpp)LL'$ **(2a–b)**, $Os(tBr_4mpp)LL'$ **(3a–b)**, and $Os(tP_4O_4\{OEt\}_8mpp)LL'$ **(4a–c)** as intermediates. The new complexes were characterized by UV/Vis, IR, $^1H$ NMR, and $^{31}P$ NMR spectroscopy, as well as by cyclic voltammetry and electrophoresis.

## Introduction

Only a few water-soluble porphyrin systems with anionic functional groups are known. Besides the tetrakis(4-sulfonatophenyl)porphyrin anion $[H_2(tpps_4)]^{4-}$ **(6)**, tetrakis(4-carboxyphenyl)porphyrin $H_2(tH_4cpp)$[2] **(7)**, and tetrakis(4-boronatophenyl)porphyrin **(8)**[3] are mentioned exclusively. Additionally, the tetrakis(4-phosphonophenyl)porphyrin is reported,[4] however, its synthesis is difficult. As compared with **6**, **7** and **8** are soluble only in alkaline media. All in all the tetrakis(4-sulfonatophenyl)porphyrin anion **6** is the only water-soluble porphyrin system that can be synthesized easily, and is soluble in aqueous media over the full pH range.

Anionic porphyrin systems are very interesting, due to their behaviour.[5−11] As the number of these porphyrins are limited, researchers look out for further possibilities of synthesizing new porphyrin systems with anionic functional groups. By a four-step reaction starting from $H_2$(tmecpp) **(1)**, Katzenmeier[12] was able to extend the number of anionic porphyrin systems. A new porphyrin, the tetra-sodium salt of 5,10,15,20-tetrakis(4-phosphonomethylphenyl)porphyrin anion $[H_2(tP_4O_8\{OH\}_4mpp)]^{4-}$ **(5)** was described. Like tetrakis(4-sulfonatophenyl)porphyrin anion **(6)**, compound **5** shows no reactions in alkaline or acidic media. The excellent solubility over almost the full pH-range must be noted.



| No. | R | Formula |
|---|---|---|
| **1** | COOMe | $H_2$(tmecpp) |
| **2** | $CH_2OH$ | $H_2(t\{OH\}_4mpp)$ |
| **3** | $CH_2Br$ | $H_2(tBr_4mpp)$ |
| **4** | $CH_2PO(OEt)_2$ | $H_2(tP_4O_4\{OEt\}_8mpp)$ |
| **5** | $CH_2PO_3H^-$ | $[H_2(tP_4O_8\{OH\}_4mpp)]^{4-}$ |
| **6** | $SO_3^-$ | $[H_2(tpps_4)]^{4-}$ |
| **7** | COOH | $H_2(tH_4cpp)$ |
| **8** | $B(OH)_2$ | $H_2(tB_4\{OH\}_4pp)$ |

With the exception of complexes with carbonic[13a,13b] or sulfonic[13] functional groups, no other water-soluble osmium porphyrin complexes are known. Attempts to synthesize cationic osmium porphyrin complexes have been described,[13b] although it was not possible to obtain the desirable products.

Water-soluble osmium(II) porphyrinates with sulfonate groups in the *para*-position of the phenyl rings can undergo reversible redox reactions,[13] and because of this behaviour are good cytochrome models. The aim of this work was to prove whether other hydrophilic osmium(II) porphyrinates show the same redox behaviour. Based on the results of Katzenmeier,[12] we were able to synthesize a new class of

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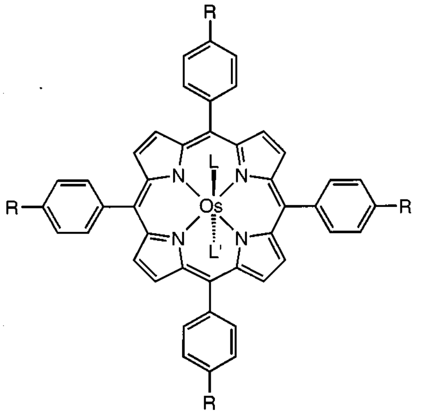
water-soluble osmium tetraphenylporphyrinates, the osmium complexes of the tetrakis(4-phosphonomethylphenyl)porphyrin anion $[Os(tP_4O_8\{OH\}_4mpp)LL']^{4-}$ **(5a−d)** and extend the number of water-soluble osmium porphyrin complexes. Synthesis and results are reported below.



| No. | R | Formula |
|---|---|---|
| **1a–b** | COOMe | Os(tmecpp)LL' |
| **2a–b** | $CH_2OH$ | $Os(t\{OH\}_4mpp)LL'$ |
| **3a–d** | $CH_2Br$ | $Os(tBr_4mpp)LL'$ |
| **4a–d** | $CH_2PO(OEt)_2$ | $Os(tP_4O_4\{OEt\}_8mpp)LL'$ |
| **5a–d** | $CH_2PO_3OH^-$ | $[Os(tP_4O_8\{OH\}_4mpp)LL']^{4-}$ |

## Synthesis

As shown previously,[13b] water-soluble osmium(II) porphyrin complexes cannot be synthesized directly by reaction of $K_2OsCl_6$ with the ionic porphyrin system: they must be synthesized by a four-step reaction with water-insoluble osmium porphyrin complexes as intermediates. Based on these results we decided to synthesize the osmium complexes of the tetrakis(4-phosphonomethylphenyl)porphyrin anion $[H_2(tP_4O_8\{OH\}_4mpp)]^{4-}$ **(5)** by metallation of $H_2(tP_4O_4\{OEt\}_8mpp)$ **(4)**, followed by saponification. Unfortunately, we were not able to obtain the product by the method described for metallation of $H_2$(tmecpp).[13] Indeed, complete metallation was confirmed by UV/Vis spectroscopy. However, some ester groups were saponified during the reaction. Also, several experiments in the presence of EtOH yielded only the diester $A_2[OsCO(tP_4O_6\{OEt\}_2\{OH\}_4mpp)thf]$ **(4d)**, as seen in the $^1H$ NMR spectra. Compound **4d** was saponified, for standardization. Neither saponification with $CH_3SiBr/KOH$,[12,14,15] nor KOH (4%)[13b,16] yielded the expected product, but instead a water-soluble residue was characterized as $K_2[OsCO(tP_4O_6\{OEt\}_2\{OH\}_4mpp)thf]$ **(5d)** by NMR spectroscopy and elemental analysis. Reaction of **5d** with 1-methylimidazole or MeOH, resulted in the axial ligand (thf) being substituted to yield $K_2[OsCO(tP_4O_6\{OEt\}_2\{OH\}_4mpp)MEOH]$ **(5e)** or $K_2[OsCO(tP_4O_6\{OEt\}_2\{OH\}_4mpp)(1\text{-}meim)]$ **(5f)**, respectively. The new axial ligands were established by IR spectroscopy.

In agreement with Künzel,[13b] it was not possible to synthesize the water-soluble osmochromes $K_4[Os(tP_4O_8\{OH\}_4mpp)LL']$ **(5h)** by oxidation of **5d** or by the reduction of the intermediate dioxo complex **5g**. As shown by the UV/Vis and IR spectra, either no reaction was observed, or **5g** was contaminated with decomposition compounds that could not be separated by chromatography or ultrafiltration. As a result, a different method of synthesis of **5h** was sought. The most important reference was given by the retro-synthetic work of Katzenmeier.[12] He was able to show that the tetrakis(4-phosphonomethylphenyl)porphyrin anion $[H_2(tP_4O_8\{OH\}_4mpp)]^{4-}$ **(5)** can be synthesized in a four-step reaction starting from the well-known tetrakis(4-methoxycarbonylphenyl)porphyrin $H_2$(tmecpp) **(1)**. Indeed, the corresponding osmium complexes are well-known too.[13b,16] We decided to synthesize the osmochromes $[Os(tP_4O_8\{OH\}_4mpp)LL']^{4-}$ **(5h)**, starting from **1a** and **1b**, by substitution in the porphyrin periphery.

Reduction of [OsCO(tmecpp)thf] **(1a)** or $[OsO_2(tmecpp)]$ **(1b)** with $LiAlH_4$ in anhydrous THF yielded the complexes **2a** and **2b**. During this procedure only the ester groups in the porphyrin periphery were reduced, and the osmium was not affected. This is shown by the characteristic Os=O oscillation of **2b** at 834 $cm^{-1}$. Partial reduction of the hydroxyl to the methyl groups was prevented by the thin layer chromatography control and hydrolysis of excess $LiAlH_4$.[17] Compound **2a** was transformed into $[OsCO(tBr_4mpp)thf]$ **(3a)** by nucleophilic substitution with $PBr_3$. The highest yields were obtained with $CH_2Cl_2$ as the solvent, whereas reactions in $CHCl_3$ mainly led to polymerization and decomposition products. Reaction of $[OsO_2(t\{OH\}_4mpp)]$ **(2b)** with $PBr_3$ did not yield the expected dioxo-complex $[OsO_2(tBr_4mpp)]$ **(3c)**, but the paramagnetic bis(bromo) complex $[Os(tBr_4mpp)Br_2]$ **(3b)**. Hitherto analogous bis(-bromo)osmium(IV)porphyrin complexes were synthesized exclusively by reaction of bis(ligand)osmium(II)porphyrin complexes with $CCl_4$.[18] Presumably, the osmium is reduced from the +6 to the +4 oxidation state by the $H_3PO_3$ formed from the reaction with $PBr_3$. Reaction of **3b** in the presence of 1-methylimidazole yielded the osmichrome $[Os(tBr_4mpp)(Br)(1\text{-}meim)]$ **(3c)**. During this procedure the substitution of $Br^-$ by 1-meim is followed by a reduction step with 1-methylimidazole as the reducing agent. Attempts to synthesize the analogous bis(1-methylimidazole) complex $[Os(tBr_4mpp)(1\text{-}meim)_2]$ **(3d)** by adding further amounts of $N_2H_4{\cdot}H_2O$ and 1-methylimidazole were not successful.

Following the Michaelis−Arbuzov-reaction,[19,20] compounds **3a** and **3b** were transformed into the tetrakis(4-diethylphosphonomethylphenyl)porphyrin complexes by adding $P(OEt)_3$. As shown by the NMR and IR spectra, the substitution in the porphyrin periphery occurred in conjunction with the substitution of the axial ligands. Reaction of **3a** with $P(OEt)_3$ yielded $[Os(tP_4O_4\{OEt\}_8mpp)\{P(OEt)_3\}_2]$ **(4a)**. Presumably, the weakly bound thf ligand is displaced by $P(OEt)_3$. Furthermore, back-bonding from the *trans*-CO ligand is weakened by this π-acceptor ligand and CO is finally displaced by $P(OEt)_3$. Satisfactory observations were made by Kokisch[21] for the osmium porphyrin complexes $[Os(oep)\{P(OMe)_3\}_2]$ and $[OsCO(oep)\{P(OMe)_3\}_2]$. As for **3b**, the ligand substitution is followed by reduction of osmium from the +4 to +3 oxidation state with $P(OEt)_3$ as the reducing agent,[22] to yield $[Os(tP_4O_4\{OEt\}_8mpp)\{P(OEt)_3\}Br]$ **(4b)**, which can be transformed into $[Os(tP_4O_4\{OEt\}_8mpp)\{P(OEt)_3\}(1\text{-}meim)]$ **(4c)** by reaction with 1-methylimidazole in the presence of $N_2H_4{\cdot}H_2O$. Compound **4c** can also be obtained by ligand substitution of **4a** with 1-methylimidazole.

The tetrakis(4-phosphonomethylphenyl)porphyrin complexes **5a−c** were synthesized as described for **5**,[12] by saponification of the complexes **4a−c** by silylation with $CH_3SiBr$ and subsequent addition of KOH (4%). The new water-soluble osmium porphyrin anions $[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}_2]^{4-}$ **(5a)**, $[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}Br]^{4-}$ **(5b)** and $[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}(1\text{-}meim)]^{4-}$ **(5c)** were obtained in good yields. Indeed, **5c** can be obtained by reaction of **5a** and **5b** with 1-methylimidazole in the presence of $N_2H_4{\cdot}H_2O$.

### Analytical Characterization

All compounds were identified by UV/Vis, IR, and $^1H$ NMR spectroscopy. The phosphorous containing complexes were also characterized by $^{31}P$ NMR spectroscopy (for individual data, see protocols 1−11). The new water-soluble complexes **5a−d** were also characterized by cyclic voltammetry and electrophoresis.

### UV/Vis Spectra

A special feature of the lipophilic osmochromes is their acid-induced autoxidation, which has been shown to proceed via superoxide formation.[21,23] Contrary to these results, compound **4c,** as well as the water-soluble complexes **5a** and **5c,** are oxidized to the osmichrome salts $[$**4c**, **5a**, **5c**$]^+$, also in the absence of acid (Equation 1, Figure 1, and Table 1). Indeed, the osmochromes can be restored by adding small amounts of $N_2H_4{\cdot}H_2O$ to the solution. As **4c**, **5a**, **5c** can perform this reversible redox reaction, these osmochromes are cytochrome models under these spectroscopic and functional aspects.[24]

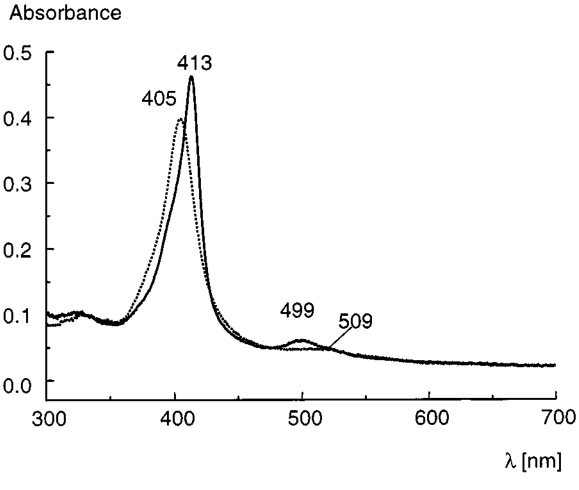


Figure 1. UV/Vis spectra of $[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}(1\text{-}meim)]^{4-}$ (**5c**$^-$) (full line) and $[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}(1\text{-}meim)]^{3-}$ (**5c**) (dotted line) in $H_2O$

Table 1. UV/Vis spectroscopic data ($\lambda_{max}$ [nm], lg ε in parentheses, at 25 °C in $H_2O$) of the osmochromes **5a** and **5c** ($n$ = +2) and the osmichromes ($n$ = +3) formed by autoxidation

| | $n$ | B (Soret) | Q and others |
|---|---|---|---|
| **5a** | +2 | 414 (5.19) | 322 (4.42), 499 (4.16) |
| | +3 | 403 (5.10) | 329 (4.41), 511 (4.00), 555 (3.82) |
| **5c** | +2 | 413 (5.07) | 326 (4.34), 499 (4.04) |
| | +3 | 405 (5.01) | 327 (4.34), 509 (3.94), 560 (3.75) |

$$[Os(tP_4O_8\{OH\}_4mpp)LL']^{4-} \xrightarrow{O_2} [Os(tP_4O_8\{OH\}_4mpp)LL']^{3-}$$

$L = P(OEt)_3$,
$L' = P(OEt)_3$, 1-meim

### Cyclic Voltammetry

In the voltage range from −1.5 to +1.5 V, osmochromes usually show two reversible oxidations ($E_1$ and $E_2$), both occurring at the metal centre and producing the osmium(III) and the osmium(IV) porphyrin complex, respectively.[13,21,22] Contrary to this result we observed only one quasi-reversible redox step ($E_1$) when studying the complexes **4a** and **4c** by cyclic voltammetry. In comparison with analogous complexes of the type Os(tmecpp)LL′,[25] the redox potentials of **4a** and **4c** are shifted to lower potentials, hence the $(tP_4O_4\{OEt\}_8mpp)$ system is characterized as a weaker π-acceptor ligand (Table 2).

Table 2. Comparison of the redox potentials of the complexes **4a**, **4c**, **5a**, and **5c** [**4a**, **4c**: $CH_2Cl_2$; **5a**, **5c**: DMF/$H_2O$ (9:1); 25 °C, $NBu_4PF_6$ as supporting electrolyte, potentials versus saturated calomel electrode (SCE)]

| Complex | No. | $E_1$ [V] | $E_2$ [V] |
|---|---|---|---|
| $Os(tP_4O_4\{OEt\}_8mpp)\{P(OEt)_3\}_2$ | **4a** | 0.147[a] | 1.123[b] |
| $Os(tP_4O_4\{OEt\}_8mpp)\{P(OEt)_3\}(1\text{-}meim)$ | **4c** | 0.027[a] | – |
| $[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}_2]^{3-}$ | **5a** | 0.078[a] | – |
| $[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}(1\text{-}meim)]^{3-}$ | **5c** | [c] | – |

[a] Quasireversible. − [b] Irreversible. − [c] Not analyzable.

Indeed, analysis of the complexes **5a** and **5c** by cyclic voltammetry was difficult. The complexes were completely insoluble in DMF and as a result the addition of small amounts of water to the suspension was necessary. To our disappointment, only broad quasi-reversible voltammograms ($E_1$) were seen under these conditions. Thus, a comparison with the redox potentials of water-soluble osmium porphyrin complexes published elsewhere[1,13,25] was neither sensible, nor possible.

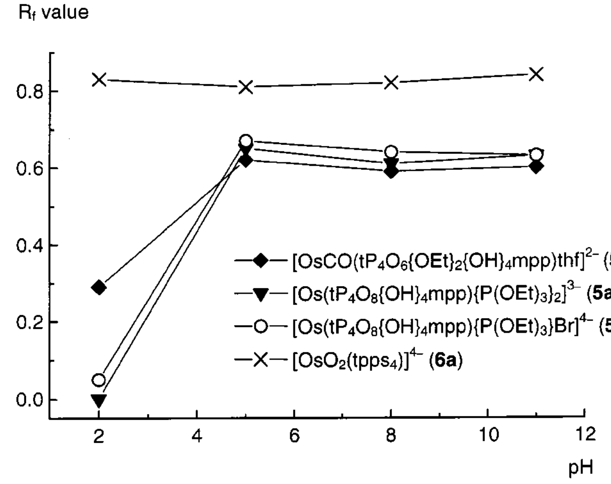


Figure 2. $R_f$ values of the osmium porphyrin complexes $[Os(tP_4O_8\{OH\}_4mpp)LL']^{n-}$ **5a**−**5d** and their pH dependence {agarose gel, $R_f$ values versus $K_4[InS_4]$ ($R_f$ = 1)}

### Electrophoresis

In accordance with the results of Katzenmeier,[12] **5a−d** showed no dependence on pH in the range from pH 3 to pH 11 (see Figure 2). Electrophoretic measurements at pH 12 could not be observed. This is due to the change of the total charge of the benzylphosphonate groups from −4 to −8.[12]

Compared with $[OsO_2(tpps_4)]^{4-}$ **(6a)** as an internal standard, we observed much smaller $R_f$ values for the osmichromes **5a** and **5c**. This effect can be explained by the formation of a so called "inner salt".[13b] In accordance with the complexes of the type $[Os(tpps_4)LL']^{3-}$, the positive charge of the osmium(III) ion is neutralized by one of the four anionic benzylphosphonate groups.

To our surprise, the $R_f$ values of **5a−d** were not influenced by a change in the effective charge $n$ of the osmium porphyrin complexes (Table 3). As demonstrated in Figure 2, compounds **5a−d** showed similar $R_f$ values in the pH range from 3 to 11, although the effective charges varied from $n = -4$ **(5b)** to $n = -2$ **(5d)**.

Table 3. $R_f$ Values of the osmium porphyrin complexes $[Os(tP_4O_8\{OH\}_4mpp)LL']^{n-}$ **5a**−**5d** and their pH dependence {agarose gel, $R_f$ values versus $K_4[InS_4]$ ($R_f$ = 1)}

| Ligands L | L′ | $n$ | No. | $R_f$ values pH 2 | pH 5 | pH 8 | pH 11 |
|---|---|---|---|---|---|---|---|
| CO | thf[a] | 2− | **5d** | 0.29 | 0.62 | 0.59 | 0.60 |
| $P(OEt)_3$ | $P(OEt)_3$ | 3− | **5a** | 0.00 | 0.65 | 0.61 | 0.63 |
| $P(OEt)_3$ | 1-meim | 3− | **5c** | 0.00 | 0.64 | 0.61 | 0.62 |
| $P(OEt)_3$ | $Br^-$ | 4− | **5b** | 0.05 | 0.67 | 0.64 | 0.63 |
| O | O[b] | 4− | **6a** | 0.83 | 0.81 | 0.82 | 0.84 |

[a] Diester $[OsCO(tP_4O_6\{OEt\}_2\{OH\}_4mpp)thf]^{2-}$. − [b] *trans*-Dioxoosmium(VI) porphyrin complex $[OsO_2(tpps_4)]^{4-}$ [13b,25] as internal standard.

At pH < 3 the benzylphosphonate groups are protonated, hence no electrophoretic measurements were obtained for **5a−c** at pH 2. A broad spot was observed for $[OsCO(tP_4O_6\{OEt\}_2\{OH\}_4mpp)thf]^{2-}$ **(4d)** at 0.29. Satisfactory observations were made by Katzenmeier[12] for $[H_2(tP_4O_8\{OH\}_4mpp)]^{4-}$ **(4)**.

## Experimental Section

**Methods and Materials:** UV/Vis: spectrometers Hewlett-Packard HP 8451A "Diode Array" and Bruins-Instruments Omega 10, programme SPECTRA CALC (Galactic Industries Corporation). − IR: Nicolet IMPACT 400 FT-IR-spectrometer, (KBr, 4000−400 $cm^{-1}$), programme Omnic (Nicolet Analytical Instruments). − NMR: spectrometers Bruker WM 300 and Bruker AM 200. − MS: Varian MAT 311 A, field desorption method. − Elemental analyses: Analytical Laboratories, P.O.B. 1106, D-51779 Lindlar. − Electrochemistry: Princeton Applied Research potentiostat M 173 controlled by an interface 175 with the software M 270/250; conditions: 25 °C, redox potentials versus SCE (Ingold), working electrode: platinum electrode (Beckman), reference electrode: platinum (Metrohm). − Ultrafiltration: Stirred cell 8400 and Diaflow ultrafiltration membranes YM1 from Amicon. − Electrophoresis: horizontal slab gel system type Desaphor HE 200 (Desaga), voltage multiplier Pherograph type 74 (Vetter KG). − Conductivity measurements: conductometer type CD 78 with cell CM 0.5/88 G from Tacussel, France. − $K_2OsCl_6$ was obtained from Degussa-Hüls; potassium indigo 5,5′,7,7′-tetrasulfonate ($K_4[InS_4]$) from Aldrich; Agarose, Tris, Glycin, DEGE, HCOOH 100%, $N_2H_4·H_2O$, DMF, DMSO, $LiAlH_4$, $PBr_3$, $P(OEt)_3$, KBr p.a., $CH_3SiBr$ from Fluka; DEGE from Acros; all other chemicals and solvents from Merck or Merck Schuchardt. − $Al_2O_3$ W 200 neutral (super I) was obtained from ICN Biomedicals, the lower activity grades were adjusted by adding adequate portions of water. − Analytical thin layer chromatography was performed on commercial aluminium sheets coated with silica gel 60 $F_{254}$, alumina 60 $F_{254}$ Typ E and alumina RP-18$F_{254s}$ (Merck). − 1,2,4-Trichlorobenzene (TCB) from Fluka was chromatographed on an alumina column (activity grade super I, basic, 40 × 3 cm) before use. All other solvents were distilled before use. − DMF for electrochemistry was prepared by a literature method.[26] 5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrin (**1**)[27], as well as **1a** and **1b**[13b,25] were prepared by literature methods.

**Protocol 1: General Procedure of Synthesis of Bis(ligand)-[5,10,15,20-tetrakis(4-hydroxymethylphenyl)porphyrinato]-osmium (2a, 2b):** $LiAlH_4$ (325 mg, 8563 μmol) was added in small portions to a solution of **1a** (299 mg, 263 μmol) or **1b** (233 mg, 218 μmol) in 200 mL of anhydrous THF, and the solutions were stirred for 30 min at 20 °C. Addition of 40 mL of hydrous THF destroyed the excess $LiAlH_4$ and the resulting slurry strained with silica gel. The silica gel containing residues of the product was put in an Twisselmannaufsatz and allowed to reflux in 70 mL of anhydrous THF for 2 h. After cooling the solvent of the combined filtrates was evaporated and the residue dried at 80 °C. The products $[OsCO(t\{OH\}_4mpp)thf]$ **(2a)**, and $[OsO_2(t\{OH\}_4mpp)]$ **(2b)** were isolated as blue-violet powders.

**Carbonyl(tetrahydrofuran)[5,10,15,20-tetrakis(4-hydroxymethylphenyl)porphyrinato]osmium(II) (2a):** 239 mg (89%). − UV/Vis (DMSO): $\lambda_{max}$ (lg ε) = 411 nm (5.34), 521 (4.06), 594 (3.71). − IR (KBr): ṽ = 1899 $cm^{-1}$ (CO), 1351, 1074 (thf), 1351, 1203, 1043 ($CH_2OH$). − $^1H$ NMR ([D6]DMSO): δ = 1.42 (m, 4 H, OH), 4.41 (m, 4 H, thf), 4.84 (m, 8 H, $CH_2R$), 5.53 (m, 4 H, thf), 7.71 (m, 8 H, phenyl-H), 7.98 (m, 4 H, phenyl-H), 8.14 (m, 4 H, phenyl-H), 8.46 (s, 8 H, pyrrole-H). − MS (FD); $m/z$ (%): 947 (100) [$M^+$ − thf, − 3 H].

***trans*-Dioxo[5,10,15,20-tetrakis(4-hydroxymethylphenyl)porphyrinato]osmium(VI) (2b):** 138 mg (66%). − UV/Vis (DMSO): $\lambda_{max}$ (lg ε) = 399 nm (4.80), 513 (3.91), 584 (3.67), 638 (3.45). − IR (KBr): $\tilde{\nu}$ = 834 $cm^{-1}$ (Os=O), 1205, 1131, 1051 ($CH_2OH$). − $^{1}H$ NMR ($[D_6]DMSO$): δ = 1.42 (m, 4 H, OH), 4.92 (s, 8 H, $CH_2R$), 7.85 (m, 8 H, *m*-phenyl-H), 8.30 (m, 8 H, *o*-phenyl-H), 9.17 (m, 8 H, pyrrole-H).

**Protocol 2: Carbonyl(tetrahydrofuran)[5,10,15,20-tetrakis(4-bromomethylphenyl)porphyrinato]osmium(II) (3a):** $PBr_3$ (1.2 mL, 12.72 mmol) was added dropwise to a suspension of $[OsCO(t\{OH\}_4mpp)thf]$ **(2a)** (361 mg, 352 μmol) in 700 mL of $CHCl_3$, and the suspension was refluxed for 1 h. After cooling and neutralization with saturated aqueous sodium carbonate solution the suspension was washed three times with 100 mL of water and dried by adding sodium sulfate. Evaporation of the solvent in vacuo and drying at 40 °C yielded 290 mg (65%) of **3a** as a blue-violet powder. − UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (lg ε) = 409 nm (5.11), 520 (4.11). − IR (KBr): $\tilde{\nu}$ = 1898 $cm^{-1}$ (CO), 1350, 1073 (thf), 608 ($CH_2Br$). − $^{1}H$ NMR ($CDCl_3$): δ = 4.10 (m, 4 H, thf), 4.80 (s, 8 H, $CH_2R$), 5.62 (m, 4 H, thf), 7.67 (m, 8 H, phenyl-H), 7.93 (m, 4 H, phenyl-H), 8.18 (m, 4 H, phenyl-H), 8.49 (m, 8 H, pyrrole-H).

**Protocol 3: Dibromo[5,10,15,20-tetrakis(4-bromomethylphenyl)porphyrinato]osmium(IV) (3b):** $PBr_3$ (0.9 mL, 9540 μmol) was added dropwise to a suspension of $[OsO_2(t\{OH\}_4mpp)]$ **(2b)** (250 mg, 261 μmol) in 400 mL of $CH_2Cl_2$, and the suspension was allowed to reflux for 1 h. After cooling and neutralization with saturated aqueous sodium carbonate solution the suspension was washed three times with 100 mL water and dried by adding sodium sulfate. Evaporation of the solvent in vacuo and drying at 40 °C in high vacuo yielded 143 mg (41%) of **3b** as a green-black powder. − UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (lg ε) = 332 nm (4.01), 407 (4.58), 453 (3.99), 514 (3.69), 605 (3.38). − IR (KBr): $\tilde{\nu}$ = 619 $cm^{-1}$, 600 ($CH_2Br$).

**Protocol 4: [5,10,15,20-Tetrakis(4-diethylphosphonomethylphenyl)porphyrinato]bis(triethyl phosphite)osmium(II) (4a):** A solution of $[OsCO(tBr_4mpp)thf]$ **(3a)** (242 mg, 189 μmol) in 30 mL of $P(OEt)_3$ was allowed to reflux for 6 h. After standing without stirring for 24 h, the solvent was removed in vacuo. 257 mg (78%) of **4a** was obtained as a blue-violet powder after chromatography on an alumina column (activity grade III, neutral, 10 × 2.5 cm, isolation of the first brown-red fraction) with $CH_2Cl_2$/EtOH (9:1). − UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (lg ε) = 328 nm (4.44), 421 (5.26), 509 (4.12). − IR (KBr): $\tilde{\nu}$ = 2978 $cm^{-1}$, 1528, 1028, 772, 727, 536 $\{P(OEt)_3\}$, 1260 (P=O), 1052 (P−O−R). − $^{1}H$ NMR ($CD_2Cl_2$): δ = 0.01 (m, 12 H, $P\{OCH_2CH_3\}_3$), 1.16 (m, 18 H, $P\{OCH_2CH_3\}_3$), 1.35 (m, 24 H, $CH_3$), 3.40 (m, 8 H, $CH_2P$), 4.14 (m, 16 H, $OCH_2$), 7.57−7.88 (m, 24 H, phenyl-H and pyrrole-H). − $^{31}P$ NMR ($CDCl_3$): δ = 25.44 (s), 27.56 (s). − MS (FD); *m/z* (%): 1734 (100) [$M^+$].

**Protocol 5: Bromo[5,10,15,20-tetrakis(4-diethylphosphonomethylphenyl)porphyrinato](triethyl phosphite)osmium(III) (4b):** A solution of $[Os(tBr_4mpp)Br_2]$ **(3b)** (124 mg, 92 μmol) in 25 mL of $P(OEt)_3$ was allowed to reflux for 7 h. After standing without stirring for 10 h, the solvent was removed in vacuo. The remaining oil was treated with 15 mL of THF and the product isolated by adding 60 mL of water. Drying at 60 °C in high vacuo yielded 51 mg (33%) of **4b** as a red-violet powder. − UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (lg ε) = 330 nm (4.29), 406 (5.03), 515 (3.88). − IR (KBr): $\tilde{\nu}$ = 2980 $cm^{-1}$, 1525, 1026, 771, 736, 556 $\{P(OEt)_3\}$, 1234 (P=O), 1051 (P−O−R). − $^{1}H$ NMR ($CD_2Cl_2$, + $N_2H_4 \cdot H_2O$): δ = −0.07 (m, 6 H, $P\{OCH_2CH_3\}_3$), 1.16 (m, 9 H, $P\{OCH_2CH_3\}_3$), 1.26 (m, 24 H, -$CH_3$), 3.41 (m, 8 H, -$CH_2P$), 4.19 (m, 16 H, $OCH_2$-), 7.58 (m, 8 H, *m*-phenyl-H), 7.94 (m, 8 H, *o*-phenyl-H), 8.06 (m, 8 H, pyrrole-H). − $^{31}P$ NMR ($CDCl_3$): δ = 25.25 (s), 27.24 (s).

**Protocol 6: (1-Methylimidazole)[5,10,15,20-tetrakis(4-diethylphosphonomethylphenyl)porphyrinato](triethyl phosphite)osmium(II) (4c): A) Reaction of 4a with 1-Methylimidazole:** A solution of $[Os(tP_4O_4\{OEt\}_8mpp)\{P(OEt)_3\}_2]$ **(4a)** (50 mg, 28 μmol) in 25 mL of $CH_2Cl_2$ and 1 mL of 1-methylimidazole were allowed to reflux under argon for 15 min. After standing without stirring for 12 h, the solvent was removed in high vacuo. The residue was treated with 10 mL of $CH_2Cl_2$ and chromatographed on an alumina column (activity grade III, neutral, 8 × 2.5 cm). Fractions were obtained as follows: with $CH_2Cl_2$ the red fraction of $[Os(tP_4O_4\{OEt\}_8mpp)\{P(OEt)_3\}(1\text{-}meim)]$ **(4c)** and with $CH_2Cl_2$/EtOH (2:1) the orange fraction of the oxidized complex $[Os(tP_4O_4\{OEt\}_8mpp)\{P(OEt)_3\}(1\text{-}meim)]^+$ **($4c^+$)**. $N_2H_4 \cdot H_2O$ (0.1 mL) was added to the combined fractions and the solution stirred for 15 min at 20 °C. Evaporation of the solvent and drying at 50 °C in high vacuo yielded 41 mg (85%) of **4c** as a blue-violet powder.

**B) Reaction of 4b with 1-Methylimidazole:** $N_2H_4 \cdot H_2O$ (0.1 mL) was added to a solution of $Os(tP_4O_4\{OEt\}_8mpp)\{P(OEt)_3\}Br$ **(4b)** (15 mg, 9 μmol) in 15 mL of $CH_2Cl_2$ and 1 mL of 1-methylimidazole, at 60 °C. After stirring for 4 h at 60 °C, the solution was cooled and the solvent removed in high vacuo. Drying at 50 °C in high vacuo yielded 9 mg (60%) of **4c** as a blue-violet powder. − UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (lg ε) = 328 nm (4.03), 416 (4.82), 501 (3.81). − IR (KBr): $\tilde{\nu}$ = 2963 $cm^{-1}$, 1529, 1024, 737 $\{P(OEt)_3\}$, 3124, 1529, 1399, 1095 (1-meim), 1261 (P=O), 1052 (P−O−R). − $^{1}H$ NMR ($CD_2Cl_2$ and $N_2H_4 \cdot H_2O$): δ = 0.06 (m, 6 H, $P\{OCH_2CH_3\}_3$), 1.27 (m, 9 H, $P\{OCH_2CH_3\}_3$), 1.36 (m, 24 H, $CH_3$), 1.91 (s, 1-meim), 2.32 (m, 1-meim), 3.45 (m, 8 H, $CH_2P$), 3.67 (s, 1-meim), 4.15 (m, 16 H, $OCH_2$), 7.58−8.05 (m, 24 H, phenyl-H and pyrrole-H). − $^{31}P$ NMR ($CDCl_3$): δ = 25.83 (s), 27.33 (s).

**Protocol 7: General Procedure of Saponification of Bis(ligand)-[5,10,15,20-tetrakis(4-diethylphosphonomethylphenyl)porphyrinato]osmium (4a,4b):** $CH_3SiBr$ (0.25 mL, 1950 μmol) was added to a solution of **4a** (50 mg, 28 μmol) or **4b** (28 mg, 16 μmol) in 25 mL of anhydrous $CH_2Cl_2$, and the mixture was stirred for 14 h at 20 °C. After neutralization with 25 mL of KOH (4%) the aqueous phase was washed twice with 40 mL of $CH_2Cl_2$, separated and cleaned via ultrafiltration. Evaporation of the solvent in vacuo and drying at 60 °C yielded the complexes $K_3[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}_2]$ **(5a-K)** and $K_4[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}Br]$ **(5b-K)** as blue-violet powders.

**Tripotassium [{5,10,15,20-Tetrakis(4-phosphonomethylphenyl)porphyrinato}bis(triethyl phosphite)osmate(III)], $K_3[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}_2]$ (5a-K):** 40 mg (86%). − UV/Vis ($H_2O$): $\lambda_{max}$ (lg ε) = 329 nm (4.41), 403 (5.10), 511 (4.00), 555 (3.82). − IR (KBr): $\tilde{\nu}$ = 2978 $cm^{-1}$, 1043, 776, 552 $\{P(OEt)_3\}$, 1181, 1164 (P=O). − $^{1}H$ NMR ($CD_3OD$, + $N_2H_4 \cdot H_2O$): δ = 0.01 (m, 12 H, $P\{OCH_2CH_3\}_3$), 1.24 (m, 18 H, $P\{OCH_2CH_3\}_3$), 3.92 (m, 8 H, $CH_2P$), 7.59 (m, 8 H, phenyl-H), 7.81 (m, 8 H, phenyl-H), 8.01 (m, 4 H, pyrrole-H), 8.08 (m, 4 H, pyrrole-H). − $^{31}P$ NMR ($CD_3OD$): δ = 16.98 (s), 18.17 (s).

**Tetrapotassium [(Bromo){5,10,15,20-tetrakis(4-phosphonomethylphenyl)porphyrinato}(triethyl phosphite)osmate(III)], $K_4[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}Br]$ (5b-K):** 22 mg (82%). − UV/Vis ($H_2O$): $\lambda_{max}$ (lg ε) = 329 nm (4.36), 403 (5.06), 511 (3.91), 557 (3.74). − IR (KBr): $\tilde{\nu}$ = 2978 $cm^{-1}$, 1522, 1048, 776, 553 $\{P(OEt)_3\}$, 1181, 1161 (P=O). − $^{1}H$ NMR ($CD_3OD$, + $N_2H_4 \cdot H_2O$): δ = 0.01 (m, 6 H, $P\{OCH_2CH_3\}_3$), 1.28 (m, 9 H, $P\{OCH_2CH_3\}_3$), 3.96 (m, 8 H, $CH_2P$), 7.68−8.11 (m, 24 H, phenyl-H and pyrrole-H). − $^{31}P$ NMR ($CD_3OD$): δ = 16.54 (s), 18.08 (s).

**Protocol 8: Tripotassium [(1-Methylimidazole){5,10,15,20-tetrakis(4-phosphonomethylphenyl)porphyrinato}(triethyl phosphite)osmate(III)] (5c-K): A) Saponification of 4c:** $CH_3SiBr$ (0.3 mL, 2340 µmol) was added to a solution of **4c** (30 mg, 18 µmol) in 25 mL of anhydrous $CH_2Cl_2$, and the mixture was stirred for 10 h at 20 °C. After neutralization with 25 mL of KOH (4%) the aqueous phase was washed twice with 40 mL of $CH_2Cl_2$, separated and cleaned by ultrafiltration. Evaporation of the solvent in vacuo and drying at 60 °C in high vacuo yielded 19 mg (68%) of $K_3[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}(1\text{-meim})]$ **(5c-K)** as a red-violet powder.

**B) Reaction of 5a-K with 1-Methylimidazole:** $N_2H_4{\cdot}H_2O$ (0.1 mL) was added to a solution of $K_3[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}_2]$ **(5a-K)** (19 mg, 11 µmol) in 15 mL of Glycin-buffer pH 11[12,24] and 1 mL of 1-methylimidazole, at 70 °C. The solution was stirred for 4 h at 70 °C. After cooling, the solution was cleaned via ultrafiltration. Evaporation of the solvent in vacuo and drying at 60 °C in high vacuo yielded 17 mg (94%) of **5c-K** as a red-violet powder.

**C) Reaction of 5b-K with 1-Methylimidazole:** A solution of $K_4[Os(tP_4O_8\{OH\}_4mpp)\{P(OEt)_3\}Br]$ **(5b-K)** (3 mg, 1.9 µmol) in 5 mL of $H_2O$ and 0.5 mL of 1-methylimidazole was stirred for 2 h at 60 °C. After cooling, the solvent was removed in vacuo. Drying at 120 °C in high vacuo yielded 2 mg (69%) of **5c-K** as a orange-red powder. − UV/Vis ($H_2O$): $\lambda_{max}$ (lg ε) = 327 nm (4.34), 405 (5.01), 509 (3.94), 560 (3.75). − IR (KBr): $\tilde{\nu}$ = 2973 cm$^{-1}$, 1048, 734, 552 {P(OEt)$_3$}, 3129, 1539, 1403, 1096 (1-meim), 1181, 1161 (P=O). − $^1H$ NMR ($CD_3OD$, + $N_2H_4{\cdot}H_2O$): δ = 0.05 (m, 6 H, $P\{OCH_2CH_3\}_3$), 1.25 (m, 9 H, $P\{OCH_2CH_3\}_3$), 1.90 (m, 1-meim), 3.70 (s, 1-meim), 3.96 (m, 8 H, $CH_2P$), 5.46 (m, 1-meim), 6.99−8.10 (m, 24 H, phenyl-H and pyrrole-H). − $^{31}P$ NMR ($CD_3OD$): δ = 17.17 (s), 18.28 (s).

**Protocol 9: Reaction of $K_2OsCl_6$ with 5,10,15,20-Tetrakis(4-diethylphosphonomethylphenyl)porphyrin (4):** A solution of $K_2OsCl_6$ (66 mg, 132 µmol) in 10 mL formic acid was allowed to reflux under argon for 4 h. After cooling, the solvent was removed in high vacuo. The remaining residue was dissolved in 8 mL of TCB and 30 mL of DEGE, $H_2(tP_4O_4\{OEt\}_8mpp)$ **(4)** (122 mg, 100 µmol) was added and the solution was refluxed under CO for 18 h. After cooling, the solvent was removed in high vacuo and the residue dried in vacuo for 2 h at 80 °C.

As shown by the analytical thin layer chromatography, the ester groups of the porphyrin were partially saponified during metallation. For standardization, the residue was dissolved in an anhydrous mixture of 30 mL of $CH_2Cl_2$/THF/EtOH (1:1:1). After adding $CH_3SiBr$ (0.7 mL, 5460 µmol), the solution was stirred for 15 h at 25 °C. A further 50 mL of KOH (4%) was added and the aqueous phase was washed twice with 70 mL of $CH_2Cl_2$. The aqueous phase was separated and cleaned via ultrafiltration. Evaporation of the solvent in vacuo and drying at 60 °C yielded 141 mg (97%) of $K_2[OsCO(tP_4O_6\{OEt\}_2\{OH\}_4mpp)thf]{\cdot}2\,H_2O$ **(5d-K)** as a blue-violet powder. − UV/Vis (0.01 N NaOH): $\lambda_{max}$ (lg ε) = 409 nm (5.18), 5.21 (4.01), 555 (3.74), 589 (3.55), 644 (3.38). − IR (KBr): $\tilde{\nu}$ = 1897 cm$^{-1}$ (CO), 1351, 1070 (thf), 1206, 1188 (P=O). − $^1H$ NMR ($CD_3OD$): δ = 1.40 (m, 6 H, -$CH_3$), 3.17 ( m, 4 H, thf), 3.56 (m, 8 H, -$CH_2P$), 4.10 (m, 4 H, thf), 4.21 (m, 4 H, $OCH_2$-), 7.78−8.88 (m, 24 H, phenyl-H and pyrrole-H). − $^{31}P$ NMR ($CD_3OD$): δ = 19.83 (m), 27.47 (m). − $C_{57}H_{54}K_2N_4O_{14}OsP_4$ (1411.36): calcd. C 48.60, H 4.93, N 4.08, P 8.86, K 5.72; found C 48.51, H 3.86, N 3.97, P 8.78, K 5.54.

**Protocol 10: Reaction of $K_2[OsCO(tP_4O_6\{OEt\}_2\{OH\}_4mpp)thf]$ (5d-K) with MeOH:** A solution of $K_2[OsCO(tP_4O_6\{OEt\}_2\{OH\}_4mpp)thf]$ **(8d-K)** (60 mg, 41 µmol) in 15 mL of MeOH was stirred for 2 h at 60 °C. Evaporation of the solvent in vacuo and drying at 60 °C yielded 50 mg (81%) of $K_2[OsCO(tP_4O_6\{OEt\}_2\{OH\}_4mpp)MeOH]$ **(5e-K)** as a blue-violet powder. The new axial ligand MeOH was confirmed by IR spectroscopy. − UV/Vis (0.01 N NaOH): $\lambda_{max}$ (lg ε) = 4.11 nm (5.06), 521 (3.96), 555 (3.67), 589 (3.46), 646 (3.32). − IR (KBr): $\tilde{\nu}$ = 1889 cm$^{-1}$ (CO), 1352 (MeOH), 1205, 1186 (P=O).

**Protocol 11: Reaction of $K_2[OsCO(tP_4O_6\{OEt\}_2\{OH\}_4mpp)thf]$ (5d-K) with 1-Methylimidazole:** A solution of $K_2[OsCO(tP_4O_6\{OEt\}_2\{OH\}_4mpp)thf]$ **(5d-K)** (86 mg, 59 µmol) in 10 mL $H_2O$ and 2 mL 1-methylimidazole were stirred for 2 h at 80 °C. Evaporation of the solvent in vacuo and drying at 120 °C in high vacuo yielded 63 mg (69%) $K_2[OsCO(tP_4O_6\{OEt\}_2\{OH\}_4mpp)(1\text{-meim})]$ **(5f-K)** as a blue-violet powder. The new axial ligand 1-methylimidazole was confirmed by IR spectroscopy. − UV/Vis (0.01 N NaOH): $\lambda_{max}$ (lg ε) = 411 nm (5.02), 5.22 (3.92), 555 (3.68), 588 (3.48), 646 (3.31). − IR (KBr): $\tilde{\nu}$ = 1899 cm$^{-1}$ (CO), 3127, 1527, 1401, 1097 (1-meim), 1239, 1211, 1186 (P=O).

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[1] Part LXXIII: J. W. Buchler, T. Dippell, *Eur. J. Inorg. Chem.* **1998**, 445−449.

[2] Abbreviations used: (oep)$^{2-}$, (tmecpp)$^{2-}$, (t{OH}$_4$mpp)$^{2-}$, (tBr$_4$mpp)$^{2-}$, (tP$_4$O$_4${OEt}$_8$mpp)$^{2-}$: dianions of 2,3,7,8,12,13,17,18-octaethylporphyrin, 5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin (**1**), 5,10,15,20-tetrakis(4-hydroxymethylphenyl)porphyrin (**2**), 5,10,15,20-tetrakis(4-bromomethylphenyl)porphyrin (**3**), 5,10,15,20-tetrakis(4-diethylphosphonomethylphenyl)porphyrin (**4**); (tP$_4$O$_8${OH}$_4$mpp)$^{6-}$, (tpps$_4$)$^{6-}$, (tcpp)$^{6-}$: hexaanions of 5,10,15,20-tetrakis(4-phosphonomethylphenyl)porphyrin (**5**), 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (**6**), 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (**7**); 1-meim, 1-methylimidazole; DEGE, diethyleneglycolmonomethylether; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; L, L′, axial ligands; SCE, saturated calomel electrode; TCB, trichlorobenzene; THF, thf, tetrahydrofuran.

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