# Electrochemical, Spectroelectrochemical and Structural Studies of Mono- and Diphosphorylated Zinc Porphyrins and Their Self-Assemblies 

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## 1. Spectral data for porphyrins 3a,d and 5a,d



Figure S1. ${ }^{1}$ H NMR spectrum of [5,15-bis(diethoxyphosphoryl)-10,20-bis(4'-methoxyphenyl)porphyrinato(2-)]zinc (3a) $\left(\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{OD}, 2: 1 \mathrm{v} / \mathrm{v}\right)$. Solvent satellite peaks are indicated with *. Solvent peaks are indicated with ** ( $\delta_{\mathrm{H}} 7.26 \mathrm{ppm}-$ $\mathrm{CHCl}_{3}, \delta_{\mathrm{H}} 5.13 \mathrm{ppm}-\mathrm{CH}_{2} \mathrm{Cl}_{2}, \delta_{\mathrm{H}} 4.20 \mathrm{ppm}-\mathrm{DOH}$ and $\mathrm{H}_{2} \mathrm{O}, \delta_{\mathrm{H}} 3.13 \mathrm{ppm}-\mathrm{CD}_{2} \mathrm{HOD}$ ). Impurities in the $\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{OD}$ mixture are indicated with $\Delta$.


Figure S2. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of [5,15-bis(diethoxyphosphoryl)-10,20-bis(4'-methoxyphenyl)porphyrina-to(2-)]zinc (3a) $\left(\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{OD}, 2: 1 \mathrm{v} / \mathrm{v}\right)$.


Figure S3. UV-vis spectrum of [5,15-bis(diethoxyphosphoryl)-10,20-bis(4'-methoxyphenyl)porphyrina-to(2-)]zinc (3a) $\left(\mathrm{CHCl}_{3}\right)$.


Figure S4. HR-ESI mass spectrum of complex 3a.


Figure S5. ${ }^{1}$ H NMR spectrum of [5,15-bis(diethoxyphosphoryl)-10,20-bis(4'-cyanophenyl)porphyrinato(2-)]zinc (3d) $\left(\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{OD}, 2: 1 \mathrm{v} / \mathrm{v}\right)$. Solvent satellite peaks are indicated with *. Solvent peaks are indicated with $* *\left(\delta_{\mathrm{H}} 7.26 \mathrm{ppm}-\right.$ $\mathrm{CHCl}_{3}, \delta_{\mathrm{H}} 5.13 \mathrm{ppm}-\mathrm{CH}_{2} \mathrm{Cl}_{2}, \delta_{\mathrm{H}} 4.20 \mathrm{ppm}-\mathrm{DOH}$ and $\mathrm{H}_{2} \mathrm{O}, \delta_{\mathrm{H}} 3.13 \mathrm{ppm}-\mathrm{CD}_{2} \mathrm{HOD}$ ). Impurities in the $\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{OD}$ mixture are indicated with $\Delta$.


Figure S6. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of [5,15-bis(diethoxyphosphoryl)-10,20-bis(4'-cyanophenyl)porphyrina-to(2-)]zinc (3d) $\left(\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{OD}, 2: 1 \mathrm{v} / \mathrm{v}\right)$.


Figure S7. UV-vis spectrum of [5,15-bis(diethoxyphosphoryl)-10,20-bis(4'-cyanophenyl)porphyrinato(2-)]zinc (3d) $\left(\mathrm{CHCl}_{3}\right)$.


Figure S8. HR-ESI mass spectrum of 3d.


Figure S9. ${ }^{1} \mathrm{H}$ NMR spectrum of [5,15-dibromo-10,20-bis(4'-methoxyphenyl)-porphyrinato(2-)]zinc (5a) $\left(\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{OD}, 2: 1 \mathrm{v} / \mathrm{v}\right)$.


Figure S10. MALDI TOF mass spectrum of [5,15-dibromo-10,20-bis(4'-methoxyphenyl)porphyrinato(2-)]zinc (5a).


Figure S11. UV-vis spectrum of [5,15-dibromo-10,20-bis(4'-methoxyphenyl)porphyrinato(2-)]zinc (5a) in $\mathrm{CHCl}_{3}$.


Figure S12. ${ }^{1} \mathrm{H}$ NMR spectrum of [5,15-dibromo-10,20-bis(4'-cyanophenyl)-porphyrinato(2-)]zinc (5d) (CDCl ${ }_{3}$ ). Solvent satellite peaks are indicated with *. Solvent peaks are indicated with $* *\left(\delta_{\mathrm{H}} 7.26 \mathrm{ppm}-\mathrm{CHCl}_{3}, \delta_{\mathrm{H}} 1.54 \mathrm{ppm}-\mathrm{DOH}\right.$ and $\mathrm{H}_{2} \mathrm{O}$ ). Impurities in the $\mathrm{CDCl}_{3} / \mathrm{CD}_{3} \mathrm{OD}$ mixture are indicated with $\Delta$.


Figure S13. MALDI TOF mass spectrum of [5,15-dibromo-10,20-bis(4'-cyanophenyl)porphyrinato(2-)]zinc (5d).


Figure S14. UV-vis spectrum of [5,15-dibromo-10,20-bis(4'-cyanophenyl)porphyrinato(2-)]zinc (5d) $\left(\mathrm{CHCl}_{3}\right)$.

## 2. Electrochemical studies of porphyrins 2a-d and 3a-d

Table S1. Half-wave and peak potentials (V vs. SCE) of reduction processes of investigated porphyrins 2a-d and 3a-d in pyridine containing 0.1 M TBAP

| R | Cpd | Reduction |  |  | Ref |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Por |  | Phl |  |
|  |  | 1st | 2nd | 3rd |  |
| OMe | 1 a | -1.49 | -1.97 | - | $t w$ |
|  | 2a | -1.27 | -1.83 | - | $t w$ |
|  | 3a | -1.01 | -1.57 | -1.99 | tw |
| Me | 1b | -1.46 | -1.98 | - | tw |
|  | 2b | -1.27 | -1.84 | - | $t w$ |
|  | 3b | -0.99 | -1.58 | - | $t w$ |
| H | 1c | -1.46 | -1.96 | - | $t w$ |
|  | 2 c | -1.27 | $-1.75{ }^{\text {a }}$ | -1.94 | $t w$ |
|  | 3c | -0.98 | -1.53 | -1.94 | tw |
| CN | 1d | -1.34 | -1.74 | - | tw |
|  | 2d | -1.18 | -1.68 | - | $t w$ |
|  | 3d | -0.92 | -1.45 | -1.72 | $t w$ |



Figure S15. Cyclic voltammograms of 1d, 2d and 3d in pyridine containing 0.1 M TBAP. Scan rate $=0.1 \mathrm{~V} / \mathrm{s}$.


Figure S16. Cyclic voltammograms of reduction processes of investigated mono-phosphorylated porphyrins in pyridine containing 0.1 M TBAP.


Figure S17. Correlation between redox potentials and Hammett substituent constants $\sigma$ on the meso-phenyl groups of the mono phosphorylated porphyrins 2a-2d in PhCN .


Figure S18. Cyclic voltammograms of 2d in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at different temperatures.

## 3. NMR studies of the self-assembly of diphosphorylporphyrin 3d



Figure S19. ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{3 d}$ in $\mathrm{CDCl}_{3}$ at $323 \mathrm{~K}\left(10^{-3} \mathrm{M}\right)$ before (a) and after a gradual addition of $10-$ $100 \mu \mathrm{~L}$ of $\mathrm{MeOH}-d 4$ : (b) $10 \mu \mathrm{~L}$; (c) $20 \mu \mathrm{~L}$; (d) $30 \mu \mathrm{~L}$; (e) $50 \mu \mathrm{~L}$; (f) $100 \mu \mathrm{~L}$. Proton labels: $\beta=\mathrm{H} 3, \mathrm{H} 7, \mathrm{H} 13$ and H17; $\beta^{\prime}=\mathrm{H} 2, \mathrm{H} 8, \mathrm{H} 12$ and H18. Stars label the signals of impurities.


Figure S20. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of complex 3d in $\mathrm{CDCl}_{3}$ at $323 \mathrm{~K}\left(1 \cdot 10^{-3} \mathrm{M}\right)$ before (a) and after a gradual addition of $10-100 \mu \mathrm{~L}$ of $\mathrm{MeOH}-d 4$.


Figure S21. ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY spectrum of compound $\mathbf{3 d}$ in $\mathrm{CDCl}_{3}$ at 223 K .


Figure S22. Selected regions of ${ }^{1} \mathrm{H}$ VT-NMR spectra of $\mathbf{3 d}$ in $\mathrm{CDCl}_{3} / \mathrm{MeOH}-d 4$ at $218-313 \mathrm{~K}$.

## DOSY experiments.

Diffusion coefficients were determined from the change in the intensity of the pyrrolic and aromatic signals (Figure S19). The average values are given in the Table S2.


Figure S23. DOSY spectrum of porphyrin 3d in $\mathrm{CDCl}_{3}$ (blue) and $\mathrm{CDCl}_{3} / \mathrm{MeOH}(10: 1 \mathrm{v} / \mathrm{v})($ red $)$ at 323 K .

Table S2. Diffusion ordered Spectroscopy (DOSY) data for solutions of 3d in $\mathrm{CDCl}_{3}$ and a $\mathrm{CDCl}_{3} / \mathrm{MeOD}$ mixture and solvents used in these experiments.

|  | $\mathrm{D},{ }^{\mathrm{a}} \mathrm{m}^{2} \mathrm{~s}^{-1}$ | $\mathrm{R} \mathrm{(d)}, \AA$ |
| :--- | :--- | :--- |
| $\mathrm{CDCl}_{3}$ | $3.509 \times 10^{-9}$ |  |
| $\mathrm{CDCl}_{3}+10 \mu \mathrm{~L} \mathrm{MeOH}-d 4$ | $3.508 \times 10^{-9}$ |  |
| $\mathrm{CDCl}_{3}+50 \mu \mathrm{~L} \mathrm{MeOH}-d 4$ | $3.55 \times 10^{-9}$ |  |
| 3d in $\mathrm{CDCl}_{3}$ | av. $6.51 \times 10^{-10}$ | $8.61(17.22)$ |
| 3d in $\mathrm{CDCl}_{3}+10 \mu \mathrm{~L} \mathrm{MeOH-} d 4$ | av. $7.59 \times 10^{-10}$ | $7.39(14.78)$ |
| 3d in $\mathrm{CDCl}_{3}+20 \mu \mathrm{~L} \mathrm{MeOH-} d 4$ | av. $7.93 \times 10^{-10}$ | $7.07(14.14)$ |
| 3d in $\mathrm{CDCl}_{3}+50 \mu \mathrm{~L} \mathrm{MeOH}-d 4$ | av. $8.20 \times 10^{-10}$ | $6.84(13.67)$ |

${ }^{\text {a }}$ Two diffusion coefficients were determined from the change in the intensity of the pyrrolic and aromatic signals. The average values are given in the table.

The blank measurements (pure $\mathrm{CDCl}_{3}$ and mixtures of $\mathrm{CDCl}_{3} / \mathrm{MeOH}-d 4$ have shown that the self-diffusion coefficient of $\mathrm{CDCl}_{3}$ remains virtually unchanged upon the addition of $10-40 \mu \mathrm{~L}$ of MeOD to the sample, testifying the negligible change of the solvent viscosity. Therefore, the viscosity value for $\mathrm{CDCl}_{3}$ at $323 \mathrm{~K} \eta=0.422 \times 10^{-3} \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}$ was used for calculating the effective hydrodynamic radius of $\mathbf{3 d}$ in solution by the Stokes-Einstein equation ( $D=k T /(6 \pi \eta R)$ ) using the spherical model.

Under identical conditions for two molecules diffusing with diffusion coefficients $D_{1}$ and $D_{2}$ and molecular weights $\mathrm{M}_{1}$ and $\mathrm{M}_{2}$, the following relation holds [4]:

$$
\frac{D_{1}}{D_{2}}=\sqrt[3]{\frac{M_{2}}{M_{1}}}
$$

This equation is strictly correct for spherical molecules and implies that the molecular weight doubling should lead to a decrease in the diffusion coefficient of about $26 \%$. Such an increase in the diffusion coefficient was actually observed when going from the solution of $\mathbf{3 d}$ in $\mathrm{CDCl}_{3}$ to the solution in $\mathrm{CDCl}_{3} / \mathrm{MeOD}(10: 1)$ (Table S2). The character of the NMR spectra of these solutions at 323 K allows us to assume that the former is dominated by the dimer $(\mathbf{3 d})_{2}$ involved in rapid exchange through the cleavage/formation of a $\mathrm{Zn}-\mathrm{OP}$ coordination bond (D2), while the latter contains mainly the monomer (D1). The ratio of the experimental diffusion coefficients is $D_{1} / D_{2}=8.20 / 6.51=1.26$. The cubic root of the ratio of the molecular weights for the dimer and monomer ( $\mathrm{M} 2=1690$ and $\mathrm{M} 1=$ 845 Da , respectively) is 1.26 . These data are consistent with the above assumption.


Figure S24. The structure of dimer (6) ${ }_{2}$.

## 4. Crystal data for compound $\left(\mathbf{3 d} \cdot \mathbf{0} \cdot \mathbf{5} \mathrm{CHCl}_{3}\right)_{\mathbf{n}}$

X-ray structure analysis of 3d Bruker AXS SMART 1000, CCD-detector $\lambda(\operatorname{MoK} a)=0.71073 \AA ́$, graphite monochromator, $\omega$-scanning, $2 \theta_{\max }=56^{\circ} . \mathrm{C}_{42.50} \mathrm{H}_{36.50} \mathrm{Cl}_{1.50} \mathrm{~N}_{6} \mathrm{O}_{6} \mathrm{P}_{2} \mathrm{Zn}, \mathrm{M}=907.76$, monoclinic, space group $\mathrm{P} 2(1) / \mathrm{c}, \mathrm{a}=16.455(10) \AA, \mathrm{b}=11.217(7) \AA, \mathrm{c}=12.398(7) \AA, \beta=103.994\left(9^{\circ}, \mathrm{V}=2220(2)\right.$ $\AA^{3}(150 K), Z=2, D_{\text {calc }}=1.358 \mathrm{~g} / \mathrm{cm}^{3}, 4821$ measured reflections, 2655 independent reflections with $\mathrm{F}^{2}>2 \sigma(\mathrm{I}), \mu=0.768 \mathrm{~mm}^{-1}, \mathrm{R}_{1}=0.0958, \mathrm{wR}_{2}=0.1635$. Corrections for absorption were made by SADABS [1]. The structure was solved by direct method and refined by full-matrix least squares method for $F^{2}$ with anisotropic parameters for all non-hydrogen atoms. All calculations were performed with the use of the SAINT [2] and SHELXTL-97 [3] program packages.


Figure S25. Independent part of polymer ( $\left.\mathbf{( d d} \cdot \mathbf{0} \mathbf{. 5} \mathbf{C H C l}_{\mathbf{3}}\right)_{\mathbf{n}}$. Thermal ellipsoids are drawn at $\mathbf{3 0 \%}$ probability. Hydrogen atoms are omitted for clarity.


Figure S26. Elemental fragment of polymer ( $\left.\mathbf{( d \bullet} \bullet \mathbf{0} \mathbf{5} \mathbf{C H C l}_{3}\right)_{\mathbf{n}}$. Hydrogen atoms and chloroform molecules are omitted for clarity.


Figure S27. Fragment of a paddle-wheel-like layer in the crystals of $\left(\mathbf{3 d} \cdot \mathbf{0} \mathbf{. 5} \mathbf{C H C l}_{\mathbf{3}}\right)_{\mathbf{n}}$. Hydrogen atoms and chloroform molecules are omitted for clarity.


Figure 28. Arrangement of layers in the crystals of $\left(\mathbf{3 d} \cdot \mathbf{0} . \mathbf{5} \mathbf{C H C l}_{3}\right)_{\mathbf{n}}$. Hydrogen atoms and chloroform molecules are omitted for clarity.

Table S3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for $\left(\mathbf{3 d} \cdot \mathbf{0} \cdot \mathbf{5} \mathbf{C H C l}_{\mathbf{3}}\right)_{\mathrm{n}}$.

| Zn1 N2 2.041(5) | Zn1 N2 2.041(5) |
| :---: | :---: |
| Zn1 N1 2.046(5) | Zn1 N1 2.046(5) |
| Zn1 O1 2.432(4) | Zn1 O1 2.432(4) |
| P1 O1 1.469(5) | P1 O2 1.565(5) |
| P1 O3 1.576(5) | P1 C5 1.811(6) |
| N1 C1 1.368(7) | N1 C4 1.365(8) |
| N2 C6 1.359(8) | N2 C9 1.367(7) |
| N3 C17 1.132(10) | O2 C20 1.454(8) |
| O3 C18 1.421(9) | C1 C10 1.412(8) |
| C1 C2 1.417(9) | C2 C3 1.353(9) |
| C3 C4 1.443(9) | C4 C5 1.414(8) |
| C5 C6 1.415(8) | C5 P1 1.811(6) |
| C6 C7 1.451(8) | C7 C8 1.339(9) |
| C8 C9 1.430(8) | C9 C10 1.414(8) |
| C10 C1 1.412(8) | C10 C11 1.492(7) |
| C11 C14 1.356(9) | C11 C12 1.398(9) |
| C12 C13 1.375(9) | C13 C16 1.381(10) |
| C14 C15 1.402(9) | C15 C16 1.368(10) |
| C16 C17 1.451(10) | C18 C19 1.518(12) |
| C20 C21 1.423(14) | C1S Cl3 1.7498(14) |
| C1S Cl1 1.7498(15) | C1S Cl2 1.7500(13) |
| C1S Cl2 1.86(3) | Cl1 Cl2 1.991(19) |
| $\mathrm{Cl} 2 \mathrm{Cl} 21.52(3)$ | C12 C1S 1.86(3) |
| Cl2 Cl1 1.991(19) |  |


| N2 Zn1 N2 180.0 | N2 Zn1 N1 88.27(19) |
| :---: | :---: |
| N2 Zn1 N1 91.73(19) | N2 Zn1 N1 91.73(19) |
| N2 Zn1 N1 88.27(19) | N1 Zn1 N1 180.00(9) |
| N2 Zn1 O1 92.57(18) | N2 Zn1 O1 87.43(18) |
| N1 Zn1 O1 86.92(17) | N1 Zn1 O1 93.08(17) |
| N2 Zn1 O1 87.43(18) | N2 Zn1 O1 92.57(18) |
| N1 Zn1 O1 93.08(17) | N1 Zn1 O1 86.92(17) |
| O1 Zn1 O1 180.0 | O1 P1 O2 114.9(3) |
| O1 P1 O3 112.5(3) | O2 P1 O3 101.9(3) |
| O1 P1 C5 117.5(3) | O2 P1 C5 102.4(3) |
| O3 P1 C5 105.9(3) | C1 N1 C4 106.2(5) |
| C1 N1 Zn1 125.5(4) | C4 N1 Zn1 128.4(4) |
| C6 N2 C9 105.5(5) | C6 N2 Zn1 129.0(4) |
| C9 N2 Zn1 125.3(4) | P1 O1 Zn1 158.4(3) |
| C20 O2 P1 121.3(5) | C18 O3 P1 119.7(5) |
| N1 C1 C10 125.4(6) | N1 C1 C2 109.9(5) |
| C10 C1 C2 124.7(5) | C3 C2 C1 108.0(5) |
| C2 C3 C4 105.8(6) | N1 C4 C5 125.0(6) |
| N1 C4 C3 110.1(5) | C5 C4 C3 124.9(6) |
| C6 C5 C4 124.7(6) | C6 C5 P1 119.5(4) |
| C4 C5 P1 115.8(4) | N2 C6 C5 124.7(5) |
| N2 C6 C7 110.1(5) | C5 C6 C7 125.2(6) |
| C8 C7 C6 106.8(6) | C7 C8 C9 106.7(5) |
| N2 C9 C10 125.7(5) | N2 C9 C8 111.0(5) |
| C10 C9 C8 123.3(5) | C1 C10 C9 126.2(5) |
| C1 C10 C11 116.8(5) | C9 C10 C11 117.0(5) |
| C14 C11 C12 119.2(6) | C14 C11 C10 121.1(6) |
| C12 C11 C10 119.7(6) | C13 C12 C11 120.4(6) |
| C12 C13 C16 119.8(7) | C11 C14 C15 120.9(7) |
| C16 C15 C14 119.4(7) | C15 C16 C13 120.4(6) |
| C15 C16 C17 119.3(7) | C13 C16 C17 120.3(7) |
| N3 C17 C16 179.2(11) | O3 C18 C19 107.1(8) |
| C21 C20 O2 112.0(8) | Cl3 C1S Cl1 104.9(11) |
| C13 C1S Cl2 120.5(12) | C11 C1S Cl2 111.8(11) |
| C13 C1S Cl2 114.5(13) | C11 C1S Cl2 66.8(9) |
| C12 C1S Cl2 49.7(10) | C1S Cl1 Cl2 59.3(11) |
| C12 Cl2 C1S 69.0(14) | C12 Cl2 C1S 61.3(11) |
| C1S C12 C1S 130.3(10) | C12 Cl2 Cl1 110.5(13) |
| C1S Cl2 Cl1 158.8(12) | C1S Cl2 Cl1 53.9(6) |

## 5. References

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