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Mono- and dizinc complexes of diporphyrins with flexible spacers of variable length

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Abstract

The di- and mono-zinc(II) complexes of diporphyrins (D) were synthesized, in which two porphyrin halves were covalently linked through a variable length hydrocarbon spacer ($-CH_2)_n-$, where $n = 2$–4, D2–D4, respectively) attached via the *ortho* oxygen atom of the *meso*-phenyl ring. Three *p*-tolyl substituents were attached to other *meso* positions of both porphyrins. The zinc(II) complexes were studied by 1-D and 2-D COSY and NOESY ^{1}H NMR spectroscopy. The stability constants of dizincdiporphyrins with azaaromatic ligands: pyridine (py), pyrazine (pyr), and 4,4′-bipyridyl (bipy) were determined by spectrophotometric titration. The discriminating factor for stability of dinuclear complexes with diazaaromatic ligands was the length of the diporphyrin spacer. The formation constant for ZnTTP with pyr and bipy were very close to that for py, whereas they were about 1.3 orders of magnitude larger for **D2Zn$_2$**-pyr, **D3Zn$_2$**-bipy, and **D4Zn$_2$**-bipy complexes which was attributed to the formation of nitrogen base bridged species. The monozincdiporphyrin complexes were demonstrated to be a convenient starting material for synthesis of heterodimetallodiporphyrins. The Zn(II)/Cu(II)diporphyrin complex was synthesized and characterized by EPR spectroscopy.

Keywords: Diporphyrins; Zinc(II) complexes; Nitrogen base ligation; Stability constants

1. Introduction

Diporphyrins are suitable ligands that are able to coordinate two metal ions. This feature renders them good candidates for synthesis of dinuclear complexes, which can be applied as bifunctional catalysts, especially in the case when two different catalytic metal ions are incorporated. The diporphyrins linked with rigid spacers attached to *meso* positions were studied in detail [1–7]. The most explored were those with *ortho*-, *meta*- or *para*-phenylene [1,2] and pillard diporphyrins, in which biphenylene, anthracene, xanthene and 1,10-phenanthroline were attached to *meso* positions of the porphyrin subunits [3–7]. Some heterodimetallodiporphyrins containing for example Mn(III)/Cu(II) and Al(III)/Co(II) metal ion pairs were characterized structurally [3,7]. Synthesis of heterodimetallodiporphyrins requires the insertion of the metal ion under stoichiometric control. In this paper, we have described the synthetic route for obtaining the di- and monozinc complexes of the diporphyrins with flexible spacers. Two porphyrin halves are linked via *meso* positions at which phenyl substituents are connected by variable length hydrocarbons attached to the *ortho* oxygen. The monozincdiporphyrins are useful starting materials for synthesis of heterodimetallodiporphyrins, which was exemplified by the mixed-metal Zn(II)/Cu(II)diporphyrin complex, characterized by EPR spectroscopy.

2. Experimental

2.1. Syntheses

2.1.1. General syntheses

The 5-(*ortho*-hydroxyphenyl)-10,15,20-tris(*p*-tolyl)-porphyrin (**H$_2$TTP-*o*-OH**) and diporphyrins with variable-length hydrocarbon spacers **S** attached to the peripheral oxygen of two porphyrin macrocycles:

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(H_2TTP-*o*-OCH_2)$_2$(CH_2)$_n$: **D2H$_4$** ($n = 0$, **S** = 2), **D3H$_4$** ($n = 1$, **S** = 3) and **D4H$_4$** ($n = 2$, **S** = 4) were synthesized as described previously [8–12]. The 5,10,15,20-tetra(*p*-tolyl)porphyrin (**TTPH$_2$**) was obtained as a side-product and its zinc(II) complex (**TTPZn**) was used for comparative purposes.

*2.1.2. Mono- and bis-zinc(II)diporphyrin complexes (DSH$_2$Zn, DSZn$_2$, **S** = 2, 3 and 4)*

The insertion of the zinc(II) ion into diporhyrins **DSH$_4$** was performed on the 30–75 μmol scale (50–100 mg of diporphyrins were used) by stepwise addition of ca. 0.1 M zinc(II) chloride in methanol into a refluxing solution of **DSH$_4$** in chloroform containing potassium carbonate (about 1 g). The progress of reaction was monitored by TLC on silicagel using 65/35 v/v% dichloromethane/hexane eluent The chromatographic mobility decreased in order: **DSH$_4$** > **DSZnH$_2$** > **DSZn$_2$** in every case. The insertion procedure was continued until the near disappearance of starting **DSH$_4$** was noticed. Separation of **DSZnH$_2$** and **DSZn$_2$** was achieved by column chromatography on silicagel using dichloromethane/hexane eluent; traces of **DSH$_4$** were eluted with 30% CH_2Cl_2, while fractions eluted with 35% and 45% CH_2Cl_2 contained almost pure of **DSZnH$_2$** and **DSZn$_2$**, respectively. The second fractions were re-chromatographed using the same conditions in order to obtain high-purity **DSZnH$_2$**. Total yields of the products of insertion were close to 100% (45% and 50% for **DSZnH$_2$** and **DSZn$_2$**, respectively). The free ligands **DSH$_4$** were recoverable by the demetallation procedure based on the extraction of a chloroform solution of **DSZnH$_2$** and/or **DSZn$_2$** with 2 M HCl 1:1 H_2O: CH_3OH within 1 h with about 20% loss of diporhyrin, which in those conditions gave starting ***o*-HOTTPH$_2$** and other products, which were easy to separate from **DSH$_4$** due to their chromatographic immobility under standard conditions. The complexes have been identified on the basis of their ^{1}H NMR spectra. Resonances were assigned using standard ^{1}H COSY and NOSEY experiments. The numbering scheme of the ligands is presented in Fig. 1.

2.1.3. Synthesis of D2ZnCu

To the solution of **D2ZnH$_2$** (35 mg, 2.4×10^{-2} mmol) in chloroform (50 cm^3) containing 1 g K_2CO_3 under reflux, 1.8-fold molar excess of $CuCl_2$ was added dropwise as a 0.058 M methanolic solution. The color of the mixture changed from pink-purple to orange-red. The products of reaction were separated chromatographically on silicagel. The first compound eluted with 35% CH_2Cl_2/hexane (v/v) was $D2Cu_2$ (15 mg, 1.0×10^{-2} mmol, 42%), identified by comparison with an authentic sample of the complex obtained in a separate synthesis, while **D2ZnCu** was eluted with CH_2Cl_2 (yield 18 mg, 1.2×10^{-2} mmol, 50%).

D2ZnCu was demetallated by stirring of a chloroform solution (20 cm^3) of the complex with 2 M HCl H_2O/CH_3OH (20 cm^3) for 2 h, followed by chromatographic separation of **D2H$_4$**, which was identified easily by its ^{1}H NMR spectrum.

2.2. Analytical data

2.2.1. D4H$_4$

^{1}H NMR ($CDCl_3$, 298 K); chemical shift (ppm) (intensity, multiplicity, assignment, coupling constant): −2.85 (4H, s, NH), −0.23 (4H, t, CH_2(2)), 2.56 (4H, t, CH_2(1)), 2.65 (12H, s, 2x(*p*-CH_3(1))), 2.68 (6H, s, CH_3 (*p*-CH_3(2))), 6.02 (2H, d, m_6-H, $J(m_6\text{-}p) = 7.4$ Hz), 6.84 (2H, ddd, *p*-H, $J(p\text{-}m_5) = 8.0$ Hz, $J(p\text{-}o_5) = 1.9$ Hz), 6.97 (2H, dd, m_5-H, $J(m_5\text{-}o_5) = 7.5$ Hz), 7.40–7.56 (12H, m, m_1-m_4-H), 7.73 (2H, dd, o_5-H), 7.92–8.11 (12H, m, o_1-o_4-H), 8.40 and 8.65 (4H and 4H, d and d, 2(8)-H, 3(7)-H, $J(2,3) = 4.7$ Hz), 8.82 (8H, s, 12,13,17,18-H).

RF = 0.60.

2.2.2. D4Zn$_2$

^{1}H NMR ($CDCl_3$, 298 K); chemical shift (ppm) (intensity, multiplicity, assignment, coupling constant):

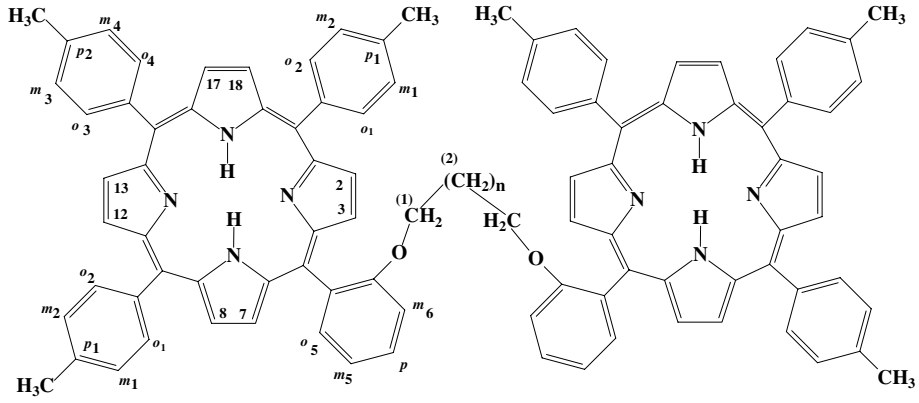

Fig. 1. The numbering scheme in diporphyrin. The variable length spacers **S** = 2 ($n = 0$), **S** = 3 ($n = 1$) and **S** = 4 ($n = 2$).

−0.29 (4H, t, CH_2(2)), 2.59 (4H, t, CH_2(1)), 2.65 (12H, s, 2x(*p*-CH_3(1))), 2.69 (6H, s, *p*-CH_3(2)), 6.00 (2H, d, m_6-H, $J(m_6\text{-}p) = 7.5$ Hz), 6.66 (2H, ddd, *p*-H, $J(p\text{-}m_5) = 8.1$ Hz, $J(p\text{-}o_5) = 1.9$ Hz), 6.77 (2H, dd, m_5-H, $J(m_5\text{-}o_5) = 7.1$ Hz), 7.37–7.57 (12H, m, m_1-m_4-H), 7.63 (2H, dd, o_5-H), 7.88–8.12 (12H, m, o_1-o_4-H), 8.38 and 8.75 (4H and 4H, d + d, 2(8)-H, 3(7)-H, $J(2,3) = 4.7$ Hz), 8.91 (8H, AB spectrum, $\delta_A = 8.89$, $\delta_B = 8.91$, 12(18)-H, 3(17)-H, $J(12,13) = 4.7$ Hz).

RF = 0.44.

UV–Vis: 422 (4.6×10^5, Soret band), 510 (5.2×10^3), 550 (2.7×10^4), 592 (4.9×10^3).

2.2.3. $D4ZnH_2$

^{1}H NMR ($CDCl_3$, 298 K); chemical shift (ppm) (intensity, multiplicity, assignment, coupling constant): −2.88 (2H, s, NH), −0.24 (4H, m, CH_2(2,2′)), 2.48 (4H, m, CH_2(1,1′)), 2.65 (12H, s, 2x(*p*-CH_3(1,1′))), 2.68 and 2.69 (3H and 3H, s and s, *p*-CH_3(2) and *p*-CH_3(2′)), 5.79 (2H, d, m_6-H, $J(m_6\text{-}p) = 8.1$ Hz), 6.18 (2H, d, $m_{6'}$-H, $J(m_{6'}\text{-}p') = 8.1$ Hz), 6.44 (2H, ddd, *p*-H, $J(p\text{-}m_5) = 8.1$ Hz, $J(p\text{-}o_5) = 1.9$ Hz), 6.64 (2H, dd, m_5-H, $J(m_5\text{-}o_5) = 7.5$ Hz), 6.96 (2H, ddd, *p*′-H, $J(p\text{-}m_5) = 8.1$ Hz, $J(p'\text{-}o_{5'}) = 1.9$ Hz), 7.02 (2H, dd, $m_{5'}$-H, $J(m_{5'}\text{-}o_{5'}) = 7.1$ Hz), 7.48–7.57 (12H, m, m_1-m_4-H + $m_{1'}$-$m_{4'}$-H), 7.68 (2H, dd, o_5-H), 7.78 (2H, dd, $o_{5'}$-H), 7.88.- 8.12 (12H, m, o_1-o_4-H + $o_{1'}$-$o_{4'}$-H), 8.17, 8.61 (2H + 2H, d + d, 2(8)-H, 3(7)-H, $J(2,3) = 4.7$ Hz), 8.55, 8.77 (2H + 2H, d + d, 2′(8′)-H, 3′(7′)-H, $J(2',3') = 4.7$ Hz), 8.79 (4H, AB spectrum, $\delta_A = 8.78$, $\delta_B = 8.80$, 12(18)-H, 3(17)-H, $J(12,13) = 4.7$ Hz), 8.91 (4H, AB spectrum, $\delta_A = 8.89$, $\delta_B = 8.93$, 12′(18′)-H, 3′(17′)-H, $J(12',13') = 4.7$ Hz).

RF = 0.56.

UV–Vis: 421 (4.3×10^5, Soret band), 510 (4.3×10^3), 550 (2.5×10^4), 592 (4.3×10^3).

2.2.4. $D3H_4$

^{1}H NMR ($CDCl_3$, 298 K); chemical shift (ppm) (intensity, multiplicity, assignment, coupling constant): −2.76 (4H, s, NH), 0.60 (2H, q, CH_2(2)), 2.71 (12H, s, 2x(*p*-CH_3(1))), 2.72 (6H, s, CH_3 (*p*-CH_3(2))), 2.77 (4H, t, 2xCH_2(1)), 5.82 (2H, d, m_6-H, $J(m_6\text{-}p) = 8.0$ Hz), 6.58 (2H, ddd, *p*-H, $J(p\text{-}m_5) = 8.0$ Hz, $J(p\text{-}o_5) = 1.5$ Hz), 6.96 (2H, dd, m_5-H, $J(m_5\text{-}o_5) = 8.4$ Hz), 7.51–7.57 (12H, m, m_1-m_4-H), 7.77 (2H, dd, o_5-H), 8.03–8.14 (12H, m, o_1-do_4-H), 8.56 and 8.73 (4H + 4H, d and d, 2(8)-H, 3(7)-H, $J(2,3) = 4.8$ Hz), 8.86 (8H, s, 12,13,17,18-H).

RF = 0.73.

2.2.5. $D3Zn_2$

^{1}H NMR ($CDCl_3$, 298 K); chemical shift (ppm) (intensity, multiplicity, assignment, coupling constant): 0.61 (2H, q, CH_2(2)), 2.71 (18H, s, 2x(*p*-CH_3(1) + *p*-CH_3(2))), 2.76 (4H, t, 2xCH_2(1)), 5.76 (2H, d, m_6-H, $J(m_6\text{-}p) = 8.1$ Hz), 6.41 (2H, dd, *p*-H, $J(p\text{-}m_5) = 8.1$ Hz), 6.82 (2H, dd, m_5-H, $J(m_5\text{-}o_5) = 8.0$ Hz), 7.50–7.58 (12H, m, m_1-m_4-H), 7.73 (2H, d, o_5-H), 8.03–8.16 (12H, m, o_1-o_4-H), 8.53 and 8.82 (4H + 4H, d and d, 2(8)-H, 3(7)-H, $J(2,3) = 4.4$ Hz), 8.96 (8H, s, 12,13,17,18-H).

RF = 0.63.

UV–Vis: 420 (4.2×10^5, Soret band), 520 (4.0×10^3), 561(2.3×10^4), 601(3.9×10^3).

2.2.6. $D3ZnH_2$

^{1}H NMR ($CDCl_3$, 298 K); chemical shift (ppm) (intensity, multiplicity, assignment, coupling constant): −2.79 (2H, s, NH), 0.59 (2H, m, CH_2(2)), 2.69 (2H, m, CH_2(1)), 2.71 (18H, s, 2x(*p*-CH_3(1) + *p*-CH_3(2))), 2.83 (2H, t, CH_2(1′)), 5.59 + 5.95 (1H + 1H, d + d, m_6-H + $m_{6'}$-H, $J(m_6\text{-}p) = 8.0$ Hz, $J(m_{6'}\text{-}p') = 8.0$ Hz), 6.30 + 6.65 (1H + 1H, dd + dd, *p*-H + *p*′-H, $J(p\text{-}m_5) = 8.0$ Hz, $J(p'\text{-}m_{5'}) = 8.1$ Hz), 6.75 + 6.98 (1H + 1H, dd + dd, m_5-H + $m_{5'}$-H, $J(m_5\text{-}o_5) = 8.0$ Hz, $J(m_{5'}\text{-}o_{5'}) = 8.0$ Hz), 7.49-7.59 (12H, m, m_1-m_4-H + $m_{1'}$-$m_{4'}$-H), 7.65 + 7.86 (1H + 1H, d + d, o_5-H + $o_{5'}$-H), 8.02–8.16 (12H, m, o_1-o_4-H + $o_{1'}$-$o_{4'}$-H), 8.39, 8.71 (4H, d + d, AB spectrum, 2(8)-H, 3(7)-H), 8.69, 8.86 (4H, d + d, AB spectrum, 2′(8′)-H, 3′(7′)-H), 8.85 and 8.98 (4H and 4H, s and s, 12,13,17,18-H and 12′,13′,17′,18′-H).

RF = 0.68.

UV–Vis: 421 (4.0×10^5, Soret band), 519 (4.0×10^3), 561 (2.0×10^4), 595 (3.7×10^3).

2.2.7. $D2H_4$

^{1}H NMR ($CDCl_3$, 298 K); chemical shift (ppm) (intensity, multiplicity, assignment, coupling constant): −2.73 (4H, s, NH), 2.68 (12H, s, 2x(*p*-CH_3(1))), 2.71 (6H, s, CH_3 (*p*-CH_3(2))), 3.34 (4H, s, 2xCH_2), 5.82 (2H, dd, *p*-H, $J(p\text{-}m_5) = 8.1$ Hz, $J(p\text{-}m_6) = 8.1$ Hz), 5.88 (2H, d, m_6-H), 6.43 (2H, dd, m_5-H, $J(m_5\text{-}o_5) = 8.0$ Hz), 7.46–7.59 (12H, m, m_1-m_4-H), 7.61 (2H, d, o_5-H), 8.00–8.15 (12H, m, o_1-o_4-H), 8.50 and 8.73 (4H and 4H, d and d, AB spectrum, 2(8)-H, 3(7)-H, $J(2,3) = 4.7$ Hz), 8.86 (8H, s, 12,13,17,18-H).

RF = 0.63.

2.2.8. $D2Zn_2$

^{1}H NMR ($CDCl_3$, 298 K); chemical shift (ppm) (intensity, multiplicity, assignment, coupling constant): 2.66 (6H, s, CH_3 (*p*-CH_3(2))), 3.34 (4H, s, 2xCH_2), 2.69 (12H, s, 2x(*p*-CH_3(1))), 5.91 (2H, dd, *p*-H, $J(p\text{-}m_5) = 8.0$ Hz, $J(p\text{-}m_6) = 8.0$ Hz), 5.93 (2H, d, m_6-H), 6.43 (2H, dd, m_5-H, $J(m_5\text{-}o_5) = 8.0$ Hz), 7.45 (2H, d, o_5-H), 7.46-7.59 (12H, m, m_1-m_4-H), 7.98–8.14 (12H, m, o_1-o_4-H), 8.50 and 8.81 (4H and 4H, d and d, AB spectrum, 2(8)-H, 3(7)-H, $J(2,3) = 4.7$ Hz), 8.93 (8H, AB spectrum, $\delta_A = 8.92$, $\delta_B = 8.94$, 12(18), 13(17) – H, $J(12,13) = 4.7$ Hz).

RF = 0.45.

UV–Vis: 420 (4.3×10^5, Soret band), 510 (3.6×10^3), 548 (2.5×10^4), 586 (6.3×10^3).

2.2.9. D2ZnH$_2$

^{1}H NMR ($CDCl_3$, 298 K); chemical shift (ppm) (intensity, multiplicity, assignment, coupling constant): −2.76 (2H, s, NH), 2.66 (12H, s, 2x(p-CH_3(1)) + 2x(p-CH_3(1′))), 2.69 (6H, s, CH_3 (p-CH_3(2)) + CH_3(p-CH_3(2′))), 3.29 and 3.31 (2H and 2H,s and s, CH_2(1) + CH_2(1′)), 5.86–6.06 (4H, m, p-H + m_6-H + p'-H + $m_{6'}$-H, $J(p\text{-}m_5) = 8.0$ Hz, $J(p\text{-}m_6) = 8.0$ Hz, $J(p'\text{-}m_5) = 8.0$ Hz, $J(p'\text{-}m_{6'}) = 8.0$ Hz), 6.26–6.51 (4H, m, m_5-H + $m_{5'}$-H), 7.40–7.60 (12H, m, m_1-m_4-H, o_5-H, and $o_{5'}$-H), 7.98–8.13 (12H, m, o_1- o_4-H), 8.37 and 8.69 (2H and 2H, d and d, AB spectrum, 2(8)-H, 3(7)-H, $J(2,3) =$ 4.7 Hz), 8.59 and 8.82 (2H and 2H, d and d, AB spectrum, 2′(8′)-H, 3′(7′)-H, $J(2',3') = 4.7$ Hz), 8.83 (4H, s, 12,13,17,18-H), 8.92 (4H, s, 12′,13′,17′,18′-H).

RF = 0.50.

UV–Vis: 420 (3.6×10^5, Soret band), 516 (7.5×10^3), 549 (1.5×10^4), 589 (4.0×10^3), 646 (1.4×10^3).

2.2.10. D2ZnCu

MS (ESI): m/e: (**1**$^+$) 1496 (40%); (**1**-Zn + 3H) 1434 (100%).

2.3. Spectrophotometric titration of DSZn$_2$ with nitrogen bases

Formation constants of PZnL (where P is the porphyrin subunit in **DSZn$_2$** or TTP, and L = pyridine (py), pyrazine (pyr) or 4,4′-bipyridyl (bipy)) have been obtained by spectrophotometric titration of **DSZn$_2$** (concentration 3.00×10^{-5} mol/dm^3) with L (concentration varied in the 3.00×10^{-5}–0.1 mol/dm^3 range) with the assumption that no other species are present in the equilibrium except those defined by reaction scheme

$$\mathrm{PZn} + \mathrm{L} \Longleftrightarrow \mathrm{PZnL}$$

Stability constants were calculated from the general formula

$$K = \frac{(\varepsilon_1 C_{\mathrm{Zn}} - A)(\varepsilon_1 - \varepsilon_2)}{(A - \varepsilon_2 C_{\mathrm{Zn}})[C_{\mathrm{L}}^0(\varepsilon_1 - \varepsilon_2) - \varepsilon_1 C_{\mathrm{Zn}} - A]},$$

derived from initial equations:

$$C_1 + C_2 = C_{\mathrm{Zn}},$$

$$C_{\mathrm{L}}^0 = C_{\mathrm{L}} + C_2,$$

$$K = \frac{C_2}{C_1 C_{\mathrm{L}}},$$

$$A = \varepsilon_1 C_1 + \varepsilon_1 C_2,$$

where C_1 and C_2 are concentrations of PZn starting complex and PZnL adduct, respectively, C_{L}^0 is total concentration of L, C_{L} is concentration of free L, ε_1 and ε_1 are extinction coefficients of PZn and PZnL, respectively, A is the value of absorbance at the monitoring wavelength, and K is the formation constant. The monitoring wavelength corresponding to Q-bands was chosen for every case.

2.4. Methods and instruments

^{1}H NMR spectra were obtained with a Bruker AMX300 spectrometer operating in the quadrature mode at 300 MHz. The residual peaks of deuterated solvents were used as internal standards. ^{1}H COSY and NOESY spectra were obtained using standard pulse sequences as described before [10]. UV–Vis spectra were recorded on Beckman DU 640 instrument. EPR spectra were obtained with a Bruker ESP300E at X band for frozen solutions (77 K) in CH_2Cl_2/toluene 1/3 v/v. The mass spectrum was obtained on a Finnigan MAT TSQ 700 spectrometer by the ESI method at 4.5 kV ionization potential and 250 °C capillary temperature in chloroform.

3. Results and discussion

3.1. ^{1}H NMR studies of DSH$_4$, DSZn$_2$ and DSZnH$_2$

It has been demonstrated previously that the ring current effect imposed by a porphyrin macrocycle caused an upfield shift of the adjacent second porphyrin in diporhyrins [10,12]. It is especially pronounced in the case of a peripheral *meso*-phenyl substituent to which the spacer is attached (Table 1). A simple comparison of the chemical shifts of m_6-H, p-H, m_5-H and o_5-H in the diporphyrins studied here with those for the mono-porphyrin reference compound (Table 1) shows that: (i) the upfield shift decreases in order $m_6 > p > m_5 > o_5$ for **S** = 3 and 4, and $p > m_6 > m_5 > o_5$ for **S** = 2, (ii) the upfield shift of m_6-H decreases with increasing spacer length, i.e., in order of **S**; $2 \cong 3 > 4$, (iii) the same relationship holds for **DSZn$_2$** complexes as well as for **DSZnH$_2$** and (iv) introducing one zinc(II) ion into the porphyrin subunit induces considerable differentiation of the chemical shifts of the two porphyrin subunits, which can be exemplified by Δ (where Δ is the chemical shift difference between the corresponding resonances of linking 5-phenyl and pyrrole β-H protons in PH_2 and PZn porphyrin halves (see Fig. 2)). In the case of **D3ZnH$_2$** and **D4ZnH$_2$** Δ decreases in the order:

D3ZnH$_2$: $m_6(0.36) > p(0.35) > m_5 = \beta_{2,3}$ $(0.23) > o_5(0.21) > \beta_{12,13}(0.18)$.

D4ZnH$_2$: $p(0.52) > m_6(0.39) > m_5(0.28) > \beta_{2,3}(0.13) o_5$ $(0.10) > \beta_{12,13}(0.09)$.

The largest values of Δ for **D4ZnH$_2$** indicate that the ring current effect is most pronounced in this case. On the other hand the Δ values for **D2ZnH$_2$** are very small

Table 1
Relevant ^{1}H NMR data of **DSH$_4$**, **DSZnH$_2$** and **DSZn$_2$**

Entry	Compound	Chemical shift (ppm) (chemical shift difference related to reference[a])			
		m_6	p	m_5	o_5
1	**TTP-*o*-PrBr**[a]	7.32	7.76	7.37	8.04
2	**D2H$_4$**	5.88 (−1.44)	5.82 (−1.84)	6.43 (−0.94)	7.61 (−0.43)
3	**D2Zn$_2$**	5.93 (−1.39)	5.91 (−1.85)	6.43 (−0.94)	7.45 (−0.59)
4	**D3H$_4$**	5.82 (−1.50)	6.58 (−1.18)	6.96 (−0.41)	7.77 (−0.27)
5	**D3Zn$_2$**	5.76 (−1.56)	6.41 (−1.35)	6.82 (−0.55)	7.73 (−0.31)
6	**D3ZnH$_2$**	5.95 (−1.37)	6.65 (−1.11)	6.98 (−0.39)	7.86 (−0.18)
		5.59 (−1.73)	6.30 (−1.46)	6.75 (−0.62)	7.65 (−0.39)
7	**D4H$_4$**	6.02 (−1.30)	6.84 (−0.92)	6.97 (−0.40)	7.73 (−0.31)
8	**D4Zn$_2$**	6.00 (−1.32)	6.66 (−1.10)	6.77 (−0.60)	7.63 (−0.41)
9	**D4ZnH$_2$**	5.79 (−1.53)	6.44 (−1.32)	6.64 (−0.73)	7.68 (−0.36)
		6.18 (−1.14)	6.96 (−0.80)	7.02 (−0.35)	7.78 (−0.26)

[a] The chemical shifts were related to reference compound of C_{2v} effective symmetry; 5-(*ortho*-(3-bromopropoxy)phenyl)-10,15,20-tris(*para*-methylphenyl)porphyrin (entry 1, **TTP-*o*-PrBr**).

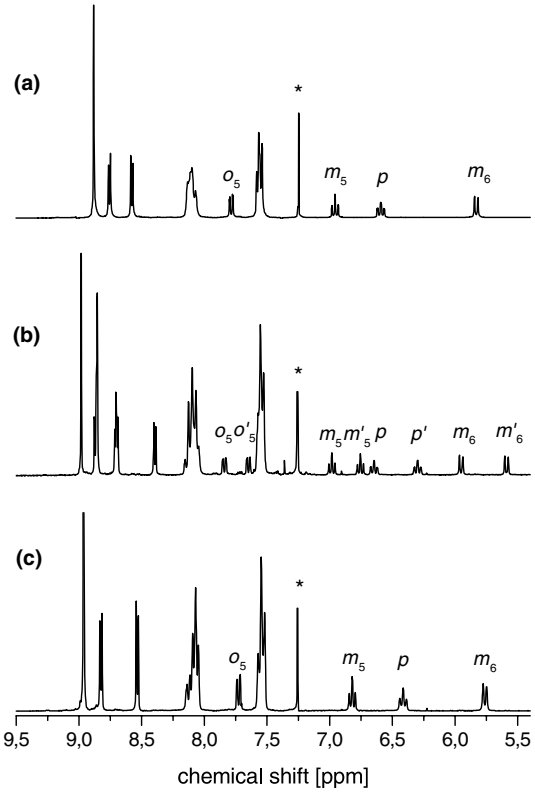

Fig. 2. Relevant fragments of the ^{1}H NMR spectra of **D3H$_4$** (a); **D3ZnH$_2$** (b) and **D3Zn$_2$** (c). The residual $CHCl_3$ resonance is labelled with an asterisk. The resonances labelled with $\prime$ at trace B were tentatively attributed to the PZn part of **D3ZnH$_2$**.

and the corresponding resonances of 5-*meso*-phenyl substituents almost overlap. These features suggest that in all **DSZnH$_2$** the two porphyrin subunits are in face-to-face conformation, however, in the case of $\mathbf{S} = 2$ the average conformation is slightly different from those for $\mathbf{S} = 3$ and 4.

3.2. Coordination of nitrogen aromatic ligands into dizincdiporphyrins

Coordination of pyridine-type bases into PZn causes red shift of the Soret band and a 14 nm red shift of the Q-band centered at about 550–560 nm. The titration of PZn indicated well-resolved isosbestic points for all studied systems at the concentration of L up to 10^{-2} M (Fig. 3). Above that concentration of L a further red shift (1–2 nm) of the Q-band could be detected, typical for formation of PML_2 (P – porphyrin or phthalocyanine) [13] with a very small change of extinction at the analytical wavelength. In order to avoid overlapping equilibrium related to the formation of bis-ligand $PZnL_2$ complexes only the points for base concentration below 10^{-3} M were used for the calculation of formation constants. The values of ε_1 and ε_2 were taken from

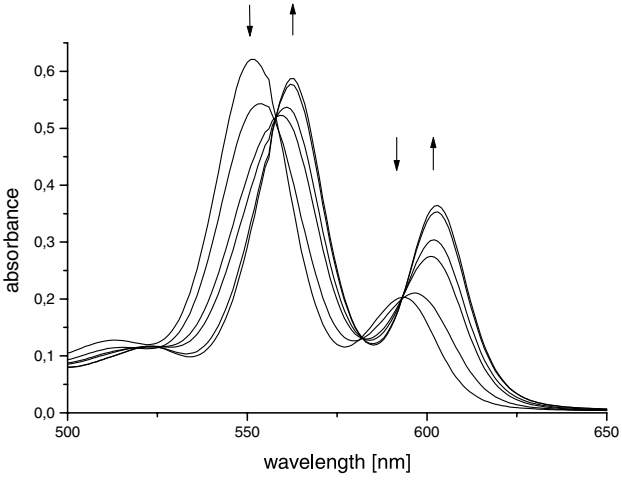

Fig. 3. The Q-band regions of UV–Vis spectra of the solutions containing **D4Zn$_2$** ($c = 2.2 \times 10^{-5}$ mol dm^{-3}) and pyr in CH_2Cl_2. Vertical arrows indicate absorbance changes upon addition of pyr, whose concentrations are (from top to bottom at 550 nm): 0; 3.0×10^{-5}; 6.0×10^{-5}; 2.5×10^{-4}; 5.0×10^{-3} and 0.10 mol $\times$ dm^{-3}.

Table 2
Formation constants of PZnL complexes (where L = py, pyr and bipy) determined by spectrophotometric titration of PZn in methylene dichloride at 298 K

Entry	Starting complex	log K (K – formation constant in mol/dm^3) (EM (mol dm^{-3}))		
		py	pyr	bipy
1	**TTPZn**	3.61 (3.68)[a]	3.90	3.20
2	**D2Zn$_2$**	3.35	4.61 (0.00065)	3.22
3	**D3Zn$_2$**	3.63	4.90 (0.0012)	4.63 (0.017)
4	**D4Zn$_2$**	3.65	3.83	5.19 (0.062)
5	**D4ZnH$_2$**	3.03	3.10	3.12

[a] Determined in benzene solution [14].

experimental data at an analytical wavelength chosen at the maximum of two Q-bands of PZnL. The calculated data on K are collected in Table 2. The formation constants of PZnL, where L = py are in every case close to that of TTPZnL. Pyrazine and bipyridyl form in some cases considerably stronger complexes, which was attributed to an entropic factor due to the bridging mode of coordination of the ligands. Thus, the best fit between size of heteroaromatic base and length of spacer was obtained for bipy and **D4Zn$_2$**, while for pyr the best fit was in the case of **D3Zn$_2$** and **D2Zn$_2$**. The complementarity between host (dizincdiporphyrin) and bidentate ligand (here pyr or bipy) can be rationalized using the concept of effective molarity [15] expressed as

$$\mathrm{EM} = K/K_i^2,$$

where K_i is the microscopic equilibrium constant for binding of monodentate ligand into metal ion.

This approach was successfully applied for quantification of oligopyridyl ligands to butadiyne-linked porphyrin dimers, trimers and tetramers [16]. The best host–guest complementarity was found in the case of a relatively rigid cyclic diporphyrin with bipy, resulting in EM as large as 76 mol dm^{-3}, while in the case of the corresponding linear diporphyrin the EM was merely 0.5 mol dm^{-3}.

Here the EMs were calculated using experimental K_i obtained as the formation constant for binding bidentate ligand into TTPZn (entry 1 in Table 2). The values of EM are listed in Table 2. Obtained EM are much lower in comparison with those found for well-fitted host–guest pairs based on rigid cyclic oligoporphyrins [16], which seems reasonable considering the flexibility of the diporhyrins studied here. Nevertheless, the best complementarity within the **D4Zn$_2$**/bipy and **D3Zn$_2$**/pyr pairs is clearly seen.

3.3. Synthetic route to heterodimetallodiporphyrin D2ZnCu

The insertion of Cu(II) ion into **D2ZnH$_2$** was accompanied by partial replacement of Zn(II) with Cu(II) resulting in the formation of two species: **D2ZnCu** and **D2Cu$_2$**. The complexes were identified by their EPR spectra (Fig. 4). The **D2Cu$_2$** complex was obtained in an independent synthesis by insertion of Cu(II) into **D2H$_4$**. The mixed-metal **D2ZnCu** was identified by MS measurement. Moreover, the complexes were demetallated and the identity of **D2H$_4$** was verified by its ^{1}H NMR spectrum. The EPR spectrum of **D2Cu$_2$** is composed of broad lines, probably due to weak interaction between the two copper(II) centers and does not show superhyperfine coupling with nitrogen donors [17]. The characteristic feature of **D2ZnCu** is the presence of 18 lines of superhyperfine structure related to two distinct $g_\perp$, typical for monomeric copperporphyrins [17].

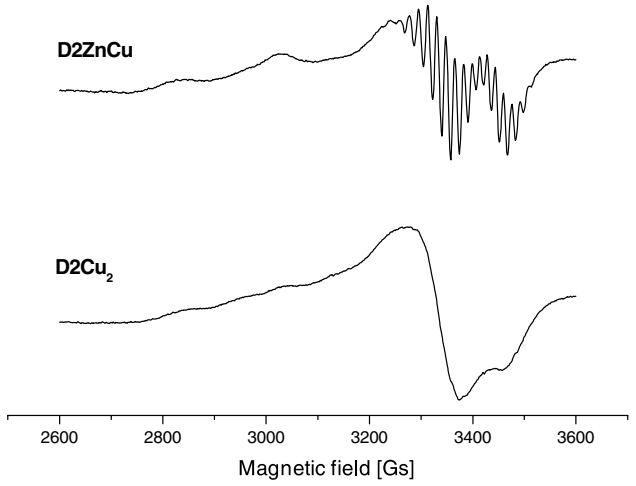

Fig. 4. EPR spectra of **D2ZnCu** and **D2Cu$_2$** in CH_2Cl_2/toluene glass in 77 K.

4. Conclusion

We have presented the successful method of synthesis and separation of mono-zinc diporphyrin complexes, which are useful starting materials for the synthesis of heterodimetallodiporphyrins. Heterometallodiporphyrins with flexible spacers of tunable length and geometry may be used as catalysts in many reactions, depending on the metal ions incorporated. The most promising is the application of diiron(II)diporphyrins in activation of dioxygen and oxygen atom

transfer from diferryldiporphyrins into dienes. Especially interesting seems to study the influence of different metal ions in Fe(II)/M(II)diporphyrin complexes on the chemoselectivity of such catalytic reaction.

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