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Symmetrical tetra-β″-sulfoleno-*meso*-aryl-porphyrins — synthesis, spectroscopy and structural characterization

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Dedicated to Professor Aslan Tsivadze on the occasion of his 70th birthday

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ABSTRACT: We report here the preparation (in "one-pot") of a tetra-β″-sulfoleno-*meso*-aryl-porphyrin in about 80% yield by using an optimized modification of Lindsey's variant of the Adler–Longo approach. The Zn(II)-, Cu(II)- and Ni(II)-complexes of the symmetrical porphyrin were prepared and characterized spectroscopically. Crystal structures of the fluorescent Zn(II)- and of the non-fluorescent Ni(II)-tetra-β″-sulfoleno-*meso*-aryl-porphyrinates showed the highly substituted porphyrin ligands to be nearly perfectly planar. The Zn(II)-complex of this porphyrin has been used as a thermal precursor of a reactive diene, and — formally — of lateral and diagonal bis-dienes, of a tris-diene and of a tetra-diene, which all underwent [4+2]-cycloaddition reactions *in situ* with a range of dienophiles. Thus, the tetra-β″-sulfoleno-*meso*-aryl-porphyrin and its metal complexes represent reactive building blocks, "programmed" for the syntheses of symmetrical and highly functionalized porphyrins.

KEYWORDS: crystal structure, metalloporphyrins, nickel, salt effect, synthesis, zinc.

INTRODUCTION

Synthetic porphyrins are fascinating heterocyclic compounds, inspired by the ubiquitous "pigments of life" [1]. The characteristic and extensively π-conjugated chromophore of the porphyrins, their capacity for coordination of the transition metal ions, and their rigid molecular structures give these macrocyclic tetrapyrroles a unique capacity for unusual photochemistry, for redox-processes for catalysis and for being building-blocks in supramolecular structures having a wealth of interesting chemical properties [2–4].

The tetra-β″-sulfoleno-*meso*-aryl-porphyrin **1** and its metal complexes **1-M** were designed as masked dienes, which were expected to undergo efficient [4+2]-cycloaddition reactions [5]. Towards this goal, the β″-sulfoleno-pyrrole **2** [6–10] was used as pyrrol moiety, which reacted with 3,5-di-*tert*-butyl-benzaldehyde (**7**) to furnish, after oxidation, the tetra-β″-sulfoleno-*meso*-aryl-porphyrin **1** in 44% yield [5]. Incorporation of a Zn(II)-ion occurred readily and nearly quantitatively to provide the Zn(II)-tetra-β″-sulfoleno-*meso*-aryl-porphyrinate **1-Zn** [5]. The potential diene-reactivity of the Zn-complex **1-Zn** could easily be set free by heating at 140 °C and by (four fold) thermal extrusion of sulfur dioxide [5, 11]. To date, the symmetrical complex **1-Zn** was used for the preparation of mono-and bisfullereno-Zn(II)-porphyrins [5], of tris- and tetra-fullereno-Zn(II)-porphyrins [11], of blackened Zn(II)-porphyrins [12], of an unsymmetrical porphyrin-chlorin spiro-dimer [13] and of a hexafullereno-diporphyrin [14] (see Fig. 1). Thus, the Zn-porphyrin **1-Zn** was applied as a versatile reactive building block, allowing the construction of more complex covalent assemblies by porphyrin-LEGO® [14]. In a related approach, tris-*meso*-aryl-tetra-β″-sulfoleno-corroles were

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[◊] SPP full member in good standing

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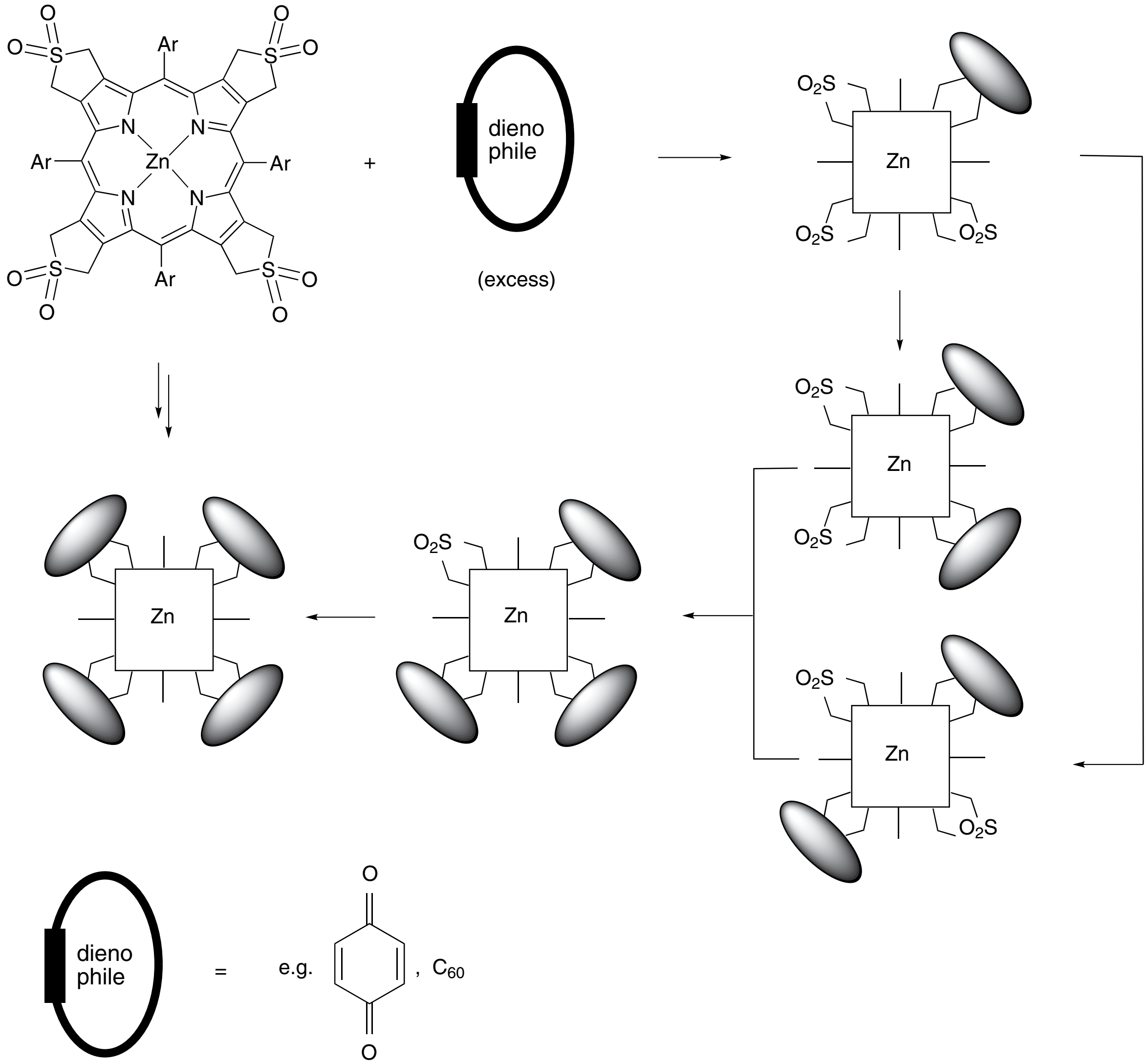


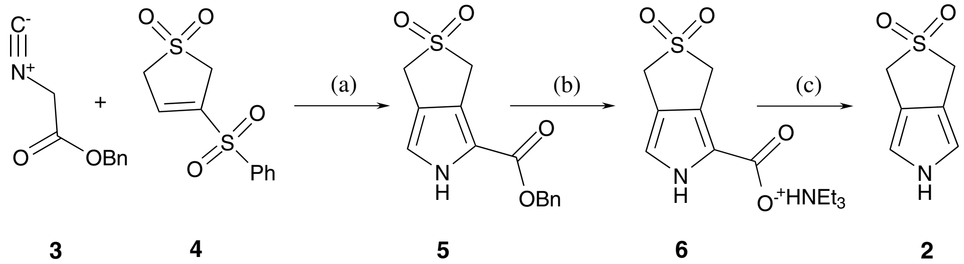
Fig. 1. Tetra-β″-sulfoleno-*meso*-aryl-porphyrin is a symmetrical, reactive building-block. The zinc(II)-complex **1-Zn** was used in (multiple) model [4+2]-cycloaddition reactions with dienophiles, *e.g.* with C_{60}-fullerene and with 1,4-benzoquinone, to furnish a range of mono-, bis-, tris- and tetra-cycloadducts

prepared and used to synthesize a difullereno-corrole with excellent regioselectivity [15]. In view of the relevance of the pyrrole **2** and the porphyrin **1** as the main building blocks in porphyrin-LEGO® approaches [14], it was our interest to improve the yields for their preparation, as well as to explore transition metal complexes closely related to the Zn-complex **1-Zn**, as is reported here.

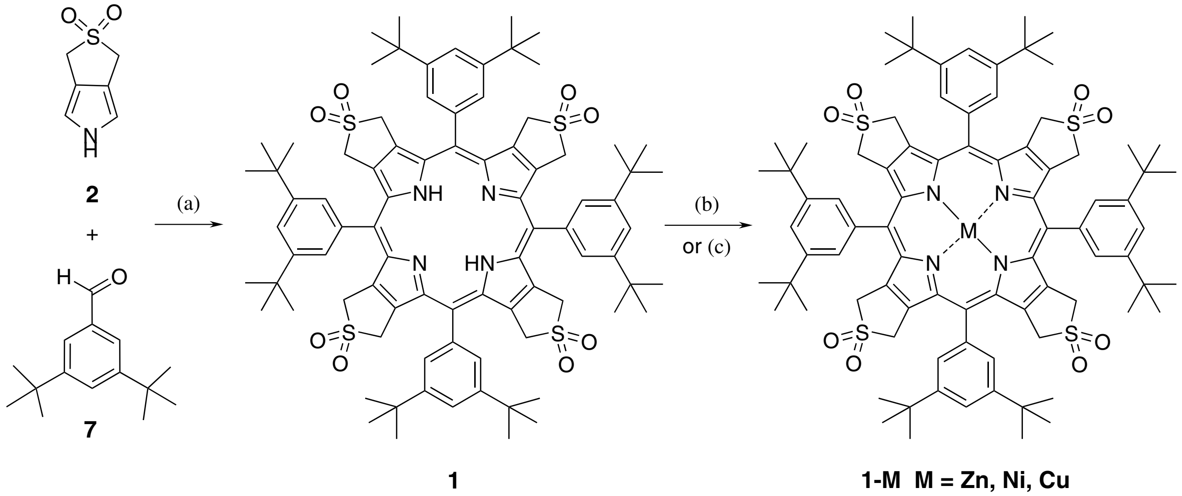
RESULTS AND DISCUSSION

β″-Sulfoleno-pyrrole (**2**) was synthesized in a multi-step sequence *via* benzyl-β″-sulfoleno-pyrrole 2-carboxylate **5** [9] from benzyl-2-isocyanoacetate (**3**) and the α,β-unsaturated bissulfone **4**, based on the so called "(3+2)-pyrrole approach" and using an established protocol [7–9] (Scheme 1): The benzyl group of the substituted pyrrole **5** was removed efficiently by hydrogenolysis, which was carried out in the presence of triethylamine, and providing the white crystalline triethyl ammonium salt **6** in 92% yield. Acid mediated decarboxylation of the pyrrole 2-carboxylic acid **6** in a thoroughly degassed mixture of acetic acid-trifluoro acetic acid (5:1, v/v) at 100 °C (4.5 h heating to reflux under argon) followed by work-up and chromatographic purification gave the β″-sulfoleno-pyrrole **2** [7] in 71% yield (Scheme 1, see Experimental section). The sulfoleno-pyrrole **2** could be recrystallized from solutions in MeOH. Good quality crystals were obtained this way, suitable for X-ray structure analysis [10].

Having in hand an improved method for the preparation of the pyrrole **2**, the stage was now set for the condensation of **2** and 3,5-di-*tert*-butylbenzaldehyde (**7**), followed by oxidation to give the porphyrin **1**. Originally,



Scheme 1. Synthesis of sulfoleno pyrrole: (a) KO^{t}Bu, THF, -20 °C, 17 h, 67%. (b) H_2 (1 atm.), 10% Pd/C, MeOH, NEt_3 at rt/36 h, 92%; (c) CF_3COOH, CH_3COOH (1:5), 100 °C, 4.5 h, 71%



Scheme 2. Synthesis of tetrasulfolenoporphyrin **1** and of the complexes **1-Zn**, **1-Cu** and **1-Ni**. (a) 0.25 equiv. $(C_{16}H_{33})(CH_3)_3N^+Cl^-$, CH_2Cl_2, $CH_3CH(OEt)_3$, $BF_3{\cdot}OEt_2$, 24 h, rt (79%); (b) $Zn(OAc)_2{\cdot}2H_2O$, DMF 40 min, 100 °C (90%) or $Ni(OAc)_2{\cdot}4H_2O$, DMF, 2.5 h, 100 °C (91%); (c) $Cu(OAc)_2{\cdot}H_2O$, CH_2Cl_2/MeOH (10:1), 2 h reflux (99%)

the tetrasulfoleno-porphyrin **1** was prepared (in 44% yield) in a $BF_3{\cdot}OEt_2$ catalyzed tetramerization of pyrrole **2** and aldehyde **7**, followed by *in-situ* chloranil oxidation [5] (Scheme 2). The Adler–Longo type porphyrin synthesis reaction proceeds *via* the reversible condensation of aryl aldehyde and pyrrole to provide a porphyrinogen, as investigated by Lindsey and coworkers [16]. This group also reported a beneficial effect of specific salt additives, resulting in an improvement of the yield of the acid catalyzed condensation for the peparation of tetraaryl porphyrins [17]. In their preparations, organic-soluble $R_4N^+Cl^-$ and $R_4P^+X^-$ salts (X = Cl, BPh_4, R = alkyl, aryl and mixed) were used to obtain up to 2-fold increase of yields. Although influencing factors remained less clear, optimization with $Bu_3BzlNCl$ and with a variety of aldehydes was reported. Thus, in our work, attention concentrated on hexadecyl trimethyl ammonium chloride. Indeed, addition of $C_{16}H_{33}(CH_3)_3NCl$ improved the yield best (Table 1, entry 5), and this effect was then explored further to find improved reaction conditions. Keeping the $C_{16}H_{33}(CH_3)_3NCl$ concentration constant at 0.2 eq., increasing amounts of $BF_3{\cdot}OEt_2$ from 0.8 eq. to 6 eq. lead to gradually improved yields (Table 1, entries 5 to 8). Further optimization indicated that 6 eq. of $BF_3{\cdot}OEt_2$ with 0.25 eq. of $[C_{16}H_{33}(CH_3)_3NCl]$, in 10 mM concentration (in each reactant), condensation for 24 h and chloranil oxidation gave the porphyrin in yields of around 80–90% (Table 1, entries 8 and 9). Under the same conditions, but without the addition of the quaternary ammonium salt, the reaction gave 51% of porphyrin (Table 1, entry 10). To get good yields of the porphyrin **1**, sulfoleno-pyrrole **2** and 3,5-di-*tert*-butyl-benzaldehyde (**7**) were recrystallized from MeOH and EtOH respectively, and dried on high vacuum, before their use in the tetramerization reaction.

Crystalline sulfoleno-pyrrole **2** (50.4 mg, 0.321 mmol), recrystallized 3,5-di-(*tert*-butyl) benzaldehyde (**7**, 1.2 eq.) and $C_{16}H_{33}(CH_3)_3NCl$ (0.25 eq.) were dissolved in abs. CH_2Cl_2 (conc. = *ca* 10 mM), and triethyl orthoacetate (1.7 eq.) was added. $BF_3{\cdot}OEt_2$ (6 eq.) was added to the mixture, which was stirred for 24 h at room temperature under argon and under protection from light. Then chloranil (1.4 eq.) was added and the mixture was heated to reflux for 1.5 h. Work up gave crude porphyrin **1** in up to 90% yield (see Experimental section). Pure porphyrin **1** was obtained by silica gel chromatography and precipitation in CH_2Cl_2-MeOH. The precipitate was washed with diethyl ether and

Table 1. Optimization experiments for the synthesis of the tetra-β″-sulfoleno porphyrin **1**[a]

Entry	Salt (eq. *vs.* **2**)	$BF_3 \cdot OEt_2$; time	Yield, %[b]
1	None	0.8; 24 h	47
2	Bu_4NBr; 0.2	0.8; 11 h	39.4
3	$C_{19}H_{42}NCl$; 0.2	0.8; 12 h	50
4	$C_{19}H_{42}NCl$; 1.0	0.8; 12 h	33.3
5[c]	$C_{19}H_{42}NCl$; 0.2	0.8; 24 h	50
6	$C_{19}H_{42}NCl$; 0.2	1.6; 24 h	37
7	$C_{19}H_{42}NCl$; 0.2	3; 24 h	58
8	$C_{19}H_{42}NCl$; 0.2	6; 24 h	82
9	$C_{19}H_{42}NCl$; 0.25	6; 24 h	90
10	None	6; 24 h	51

[a] Standard initial concentrations of pyrrole **2** and aldehyde: 10 mM; [b] calculated from UV-vis-spectra with ε_{420nm} = 380200 $M^{-1}.cm^{-1}$; [c] initial concentrations of pyrrole **2** and aldehyde: 1.6 mM.

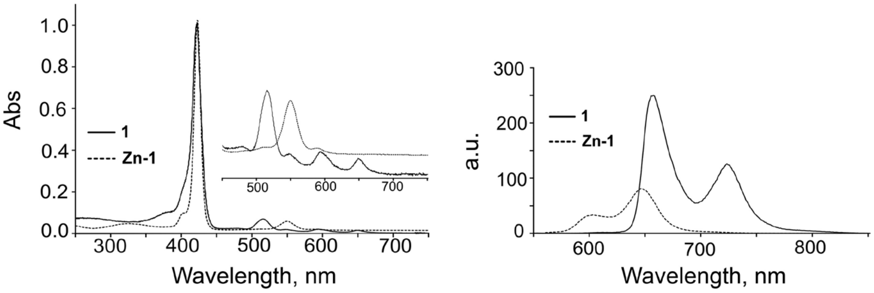


Fig. 2. UV-vis- and fluorescence spectra of **1** and the zinc-complex **1-Zn**. Left. Overlay of UV-vis-spectra normalized to a common intensity maximum of the "Soret" band; right. Fluorescence spectra of solutions of **1** (excitation at 516 nm) and of **1-Zn** (excitation at 554 nm) in CH_2Cl_2 and recorded at room temperature

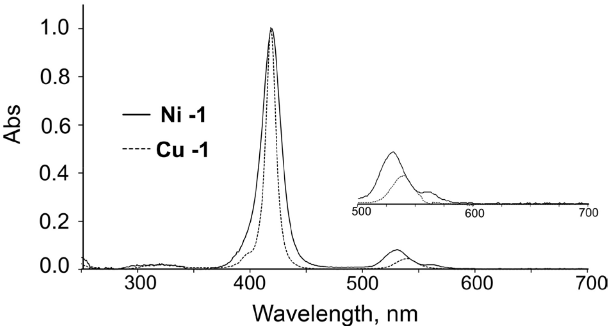


Fig. 3. UV-vis-spectra of non-fluorescent **1-Cu** and of **1-Ni** (in CH_2Cl_2, room temperature; overlay of the two spectra normalized to a common intensity maximum of the "Soret" band)

dried under HV at 50 °C for 15 h to give a sample of 89.8 mg (78.7% yield) of the porphyrin **1** as a microcrystalline sample. The strongly fluorescent porphyrin **1** was identified by its UV-vis-, mass- and ^1H NMR-spectra [5]. In addition, **1** was further characterized by fluorescence-spectroscopy (see Fig. 2), as well as $^1H,^1H$-homo- and $^1H,^{13}C$-hetero-nuclear NMR-spectra (^{13}C NMR: see Supporting information).

Having the porphyrin **1** in hand, Cu(II)-, Zn(II)- and Ni(II)- ions were inserted by using Cu(II)-acetate in CH_2Cl_2-MeOH solution (by heating at reflux) or, with Zn(II)- and Ni(II)-acetates, in DMF at 100 °C. The reaction progress was followed with UV-vis-spectroscopy and by TLC. UV-vis spectra of metalloporphyrins **1-Ni**, **1-Cu**, **1-Zn** had characteristic strong Soret and weak Q-band absorption bands (see Figs 2 and 3, and Experimental section).

The Zn(II)-porphyrin **1-Zn** has been prepared and characterized earlier [5]. X-ray diffraction quality crystals of **1-Zn** were obtained here by diffusing hexane into a solution of CH_2Cl_2. The crystal structure of **1-Zn** (Fig. 4) showed a practically planar porphyrin core, and *meso*-aryl groups that were nearly perpendicular (87° dihedral angle) to the porphyrin plane. The lengths of the equatorial bonds (*e.g.* Zn-N = 2.08 Å) were in standard range of Zn-N distances in porphyrins (2.05–2.08 Å) [18]. The C_α–C_β bonds were 1.345 Å long, indicating partial double bond character of an aromatic nature, and were shortened, compared to the sulfoleno-pyrrol (1.421 Å). The methylene-SO_2 groups were slightly bent from the porphyrin plane. The zinc-ion was penta-coordinate due to axial coordination of one water molecule, with a Zn–O bond distance of 2.09 Å. The Zn atom was situated at 0.303 Å above the porphyrine core, increasing the four N–Zn–O angles to 98.7°. Two of the N–Zn–N angles amounted to 162.5°, and four to 88.7°, respectively.

The copper complex **1-Cu** was prepared by heating **1** with Cu(II)-acetate in 10:1 of CH_2Cl_2-MeOH at 60 °C for 2 h and isolation (in 99% yield) by precipitation in CH_2Cl_2-MeOH. The UV-vis-spectrum of the non-fluorescent Cu(II)porphyrin **1** showed Soret and Q-bands at 418 and 539.5 nm, respectively. A ^1H NMR characterization was not performed for the paramagnetic Cu^{II} porphyrin **1-Cu**. However mass spectrometry confirmed the stoichiometric metal incorporation. The pseudo-molecular ion $[M + H]^+$ occurred at *m/z* = 1484.7, corresponding to the molecular formula $C_{84}H_{100}N_4O_8S_4Cu$ (*m/z* calcd. = 1483.6). The base-peak at *m/z* = 1227.9 indiacted efficient loss of 4 SO_2 groups. Fragments due to loss of a Cu-ion were not found in the spectrum of **1-Cu** (some loss of the Cu-ion in a FAB-mass spectrometric study of metallo-prophyrins has been reported) [19]. Crystals, grown by diffusing *n*-heptane

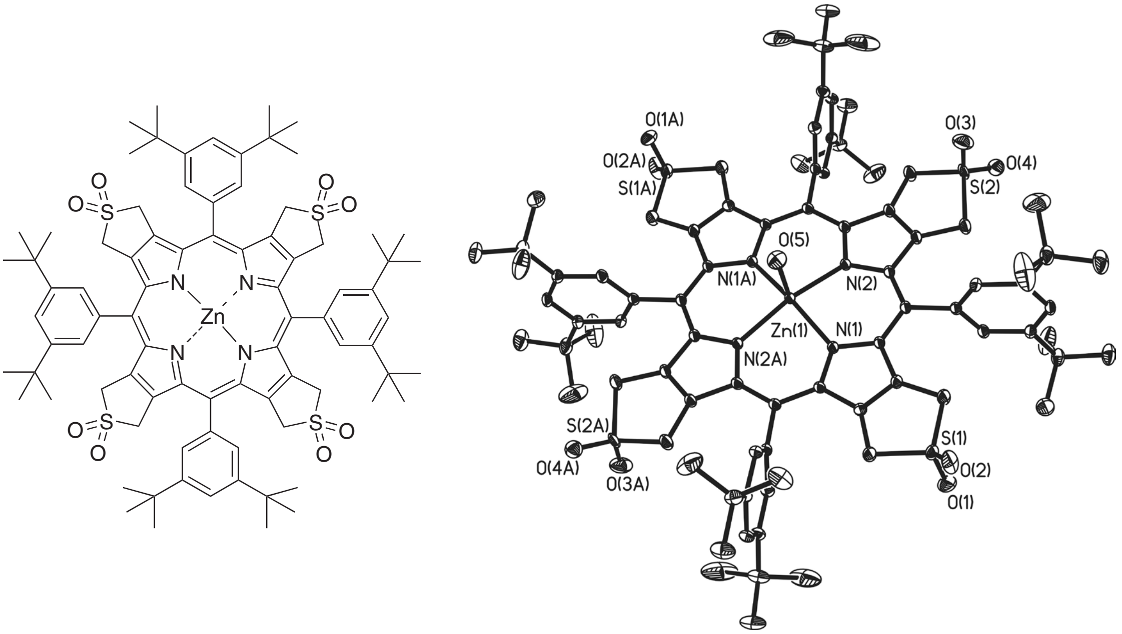


Fig. 4. Structural formula and crystal structure of **1-Zn** (which crystallized as a mono-aqua-complex)

into a CH_2Cl_2 solution of **1-Cu**, did not have the quality needed for an X-ray structure determination.

The Ni(II)-insertion was completed in 2.5 h when $Ni(OAc)_2$ and **1** were heated in DMF at 100 °C. The Ni(II)-tetrasulfoleno-porphyrinate **1-Ni** was obtained in 91% yield, after recrystallization. The UV-vis-absorption spectrum of the Ni(II)poprhyrin **1-Ni** showed a strong Soret band at 418 nm, and a Q-band at 530 nm, as is typical of Ni(II)-porphyrins [20]. A solution of **1-Ni** in CH_2Cl_2 was non-fluorescent, as expected. Its MS-spectrum indicated a pseudomolecular ion $[M + H]^+$ at *m/z* = 1479.4, and a base-peak at *m/z* = 1223.6 ($[M - 4SO_2 + H]^+$). The ^1H NMR-spectrum of the diamagnetic complex **1-Ni** showed the spectrum of a D_{4h} symmetric compound, with signal positions and shapes similar to that of **1-Zn**. The small shift differences may be due largely to the smaller ionic radii of Ni(II)- than Zn(II)-ions and correspondingly shorter equatorial bond lengths in **1-Ni** (see below).

The **1-Ni** porphyrin was crystallized by slow diffusion of n-hexane into CH_2Cl_2 solution, and X-ray quality crystals were obtained. X-ray structure showed (Fig. 5) a planar porphyrin core, with an ideal square planar coordination of the Ni atom (four N–Ni–N angles of 90° and two of 180°). The Ni–N bonds were 1.975 Å long, *i.e.* in the range of standard Ni–N bond lengths in nickel porphyrins (1.942–2.002 Å) [18]. The C_α–C_β bond lengths were 1.343 Å, *i.e.* similar to those in **1-Zn**. The *meso*-aryl groups were nearly perpendicular to the porphyrin plane (dihedral angles of 87° and 89°). The CH_2–SO_2·groups were tilted by 14.3° from the porphyrin plane. These latter structural properties were similar to those of the Zn(II)-porphyrin **1-Zn**.

EXPERIMENTAL

General

3-Sulfolene, potassium *tert*-butanolate (KOtBu) were from Fluka and were used as received. Dichloromethane (CH_2Cl_2), ethyl acetate (EtOAc), petrol ether 40–60 (PE), methanol (MeOH), tetrahydrofurane (THF), acetic acid (HOAc), trifluoroacetic acid (TFA) were from ACROS and were distilled before use. For synthesis, solvents were dried (CH_2Cl_2 over P_2O_5, THF over Na). Glassware for all reactions was oven dried at 110 °C and cooled under HV, and purged with nitrogen flow prior to use. Column chromatography (CC): Fluka silica gel 60 (230–400 mesh). High vacuum (HV): *ca.* 0.05 mbar.

Spectroscopy: UV-vis: Hitachi U-3000, λ_{max} (log ε) in nm. Fluorescence: Varian Cary Eclipse, λ_{Ex} and λ_{Em} in nm. ^1H and ^{13}C NMR: *Brucker 300,* Varian 500 unity (300 K); chemical shifts (δ) in ppm, with $\delta(C\mathit{H}Cl_3)$ = 7.26 ppm, $\delta(^{13}CHCl_3)$ = 76.3 ppm, $\delta(C\mathit{HD}_2OD)$ = 3.31 ppm, $\delta(^{13}CD_3OD)$ = 49.0 ppm. FAB-MS: *Finnigan MAT-95*, positive ion mode, glycerine matrix; *m/z* (rel. intensity %).

Synthesis

Triethylammonium sulfolenopyrrole-2-carboxylate 6. A two neck round bottomed flask equipped with magnetic stirring bar and a three way adapter, was charged 10 g of benzyl pyrrole-2-carboxylate (**5**) (34.33 mmol, 1 equiv.) and 250 mL of MeOH. A suspension of **5** was obtained, which was purged with argon, whereupon 4.75 mL (34.3 mmol, 1 equiv.) triethylamine were added

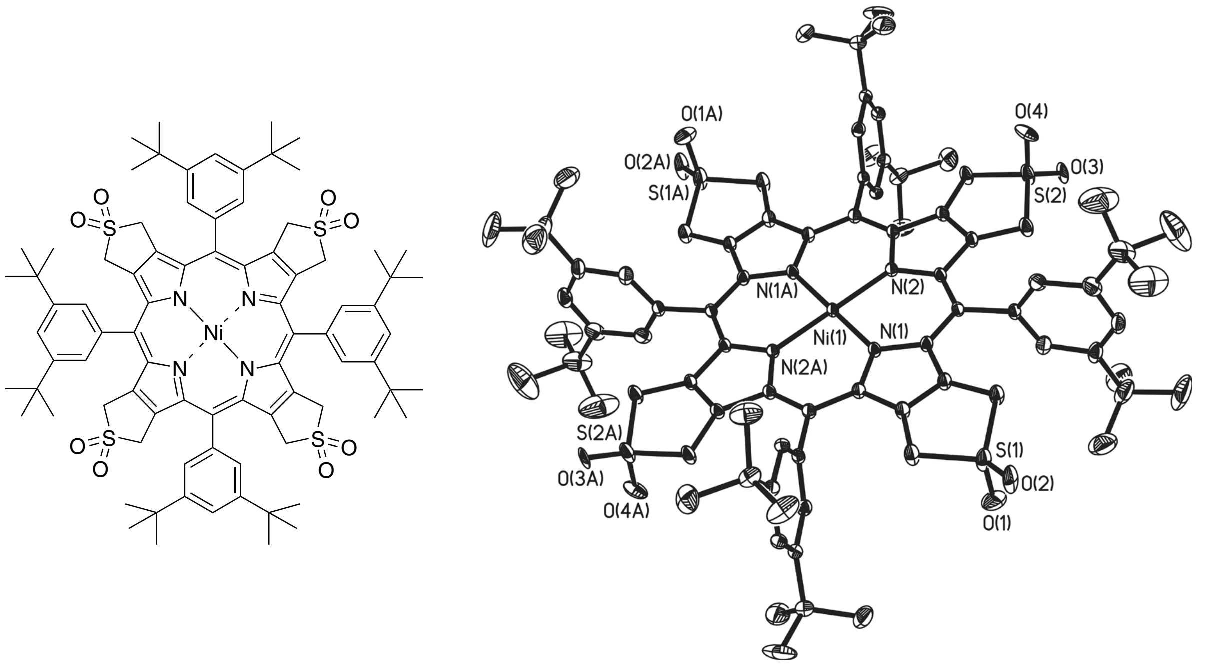


Fig. 5. Structural formula and crystal structure of **1-Ni**

under argon. Then 1 g of 10% Pd/C (0.94 mmol, 0.27 equiv.) was added under argon. The mixture was vented with argon, followed by bubbling-in hydrogen for 3 min. The reaction was stirred at room temperature first under one atmosphere of hydrogen (15 h), followed by further reaction under a balloon filled with hydrogen (for 33 h additional). Then the reaction was stopped, the mixture was diluted with 250 mL of MeOH, filtered through cellite and washed with 100 mL of acetone. The solvents were removed under reduced pressure and a yellow powder was obtained. The dry powder was then dissolved in 300 mL of CH_2Cl_2 and 5 mL of triethylamine, the solution was filtered, to remove insoluble material. Solvents were removed under reduced pressure and the residual yellow powder was first washed with diethyl ether, and dried on HV overnight to give 9.5 g (91.6%) of microcrystalline colorless pyrrole **6**. 300 MHz ^{1}H NMR ($CDCl_3$): δ, ppm 1.28 (t, $J = 7.4$ Hz, 9H, N–CH_2–CH_3), 3.04 (q, $J = 7.4$ Hz, 6H, N–CH_2–CH_3), 4.16 (s, 2H, CH_2–SO_2), 4.40 (s, 2H, CH_2–SO_2), 6.67 (br s, 1H, C*H*py), 9.71 (br s, 1H, **N***H*).

β″-Sulfoleno-pyrrole 2. An oven dry argon-flushed 1 L round-bottomed flask, equipped with an intense cooler, was charged under argon with 2 g of triethylammonium sulfolenopyrrole-2-carboxylate (**6**, 6.62 mmol), 240 mL of HOAc and 50 mL of trifluoro acetic acid (0.74 mol, 200 eq.). The solution was degassed by sonication and venting with argon for 5 min, and the flask was kept under argon filled balloon. The reaction flask was immersed in a pre-heated oil bath at 100 °C and heated to reflux for 4.5 h, where upon it turned red. The flask was removed from the oil bath and the hot solution was poured into a 2 L beaker containing 1 kg of ice kept in an ice-bath. Then 485 mL of 10 M NaOH were added in small amounts and with intense stirring to the ice-cooled reaction mixture, followed by Na_2CO_3 powder (in small amounts) until the pH reached *ca.* 9. The mixture was extracted with EtOAc (5 × 200 mL), and the collected organic extracts were washed with water (200 mL), and brine (100 mL). The pooled solution was dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure to obtain brown mixture which was purified by column chromatography (15 × 2.5 cm). The product **2** was eluted with 3–5% of EtOAc in CH_2Cl_2. The collected product fractions were evaporated to dryness under reduced pressure to obtain a light yellow powder. This was washed with 2–3 mL of ether and the coloured solution was removed and discarded. The white crystalline product **2** was transferred to a small vial, dried on HV at 50 °C for overnight to give 720.1 mg (70%). For crystallization, a saturated methanolic solution of **2** was left to evaporate slowly at room temperature. TLC: EtOAc/CH_2Cl_2, 1:9; $R_f = 0.4$, mp 220 °C (dec., Lit. 235 °C dec. [6]). 300 MHz ^{1}H NMR (CD_3OD): δ, ppm 4.18 (s, 4H, $H_2C(3^1)$), 6.75 (br s, 2H, HC(2)).

Tetra-β″-sulfoleno-porphyrin 1. An oven dry argon-flushed round-bottomed flask was charged with 50.4 mg (0.321 mmol) of sulfoleno pyrrole (**2**), 81.1 mg (0.371 mmol, 1.18 equiv.) of 3,5-di-*tert*-butyl-benzaldehyde and 25 mg (0.0784 mmol, 0.25 equiv.) of hexadecyl trimethyl ammonium chloride. The mixture was dried under HV for 3 h at 25 °C, and under argon 35 mL of abs CH_2Cl_2 were added (concentration in each reactant is *ca.* 10 mM). The obtained colorless solution was flushed with argon for 5 min, and, while stirring, 100 μL (88.9 mg, 0.548 mmol, 1.7 equiv.) of triethyl orthoacetate were added, followed by stirring for 10 min at 25 °C. To the solution 500 μL of $BF_3{\cdot}OEt_2$ (48% solution in Et_2O, 287.9 mg, 1.99 mmol, 6 equiv.) was added through the septum and continued to stir at room temperature for 24 h under protection from light. To the obtained dark rose coloured solution, 110 mg of chloranil (0.441 mmol, 1.4 equiv.) was added under argon and the reaction mixture was heated to reflux for 1.5 h. The cold solution was poured in sat.$NaHCO_3$ (50 mL) and the products were extracted with CH_2Cl_2 (5 × 50 mL). The collected brown organic phases were washed with sat. NaCl solution (60 mL) and filtered through a plug of dried cotton. The product was purified by column chromatography (20 × 2.5 cm) with a CH_2Cl_2-PE gradient. The product eluted with 3:2 CH_2Cl_2/PE (v/v). The reddish product containing fractions were combined and the solvents were removed under reduced pressure. The dry residue was re-dissolved in CH_2Cl_2 (*ca.* 10 mL) and precipitated with excess of PE (*ca.* 40 mL). The microcrystalline precipitate was washed with diethyl ether and dried under HV at 50 °C for 15 h to give 89.8 mg (78.7%) of the porphyrin **1**. TLC: (red fluorescent spot under 365 nm UV light) CH_2Cl_2/PE, 8:2; $R_f = 0.35$, mp 132–135 °C (dec.). UV-vis (CH_2Cl_2, c = 3.93×10^{-5} M): λ_{max}, nm (log ε) 648.0 (3.68), 592.0 (3.80), 547 (3.71), 514.5 (4.37), 480.5 (3.66), 420 (5.58), 380 sh (4.54), 270 (4.40). Fluorescence (in CH_2Cl_2, c = 7.58×10^{-6} M): λ_{Ex}, nm 516 (O.D. = 0.2); λ_{Em}, nm (a.u) 656.8 (250.1), 722 (126.1). 300 MHz ^{1}H NMR ($CDCl_3$): δ, ppm -3.08 (br s, 2H), 1.51 (s, 72H), 4.15 (br s, 16H), 7.83 (d, *J* = 1.7 Hz, 8H), 7.96 (t, *J* = 1.7 Hz, 4H). 75 MHz ^{13}C NMR ($CDCl_3$): see Table S1, Supporting information. FAB-MS (positive ion, $C_{84}H_{102}N_4O_8S_4$: calcd. 1422.66): *m/z* (%) 1425.6 (10), 1424.6 (20), 1423.6 (36, $[M + H]^+$), 1422.6 (12, M^+), 1360.7 (10), 1359.7 (12, $[M - SO_2 + H]^+$), 1296.8 (8), 1295.8 (6, $[M - 2SO_2 + H]^+$), 1232.8 (5), 1231.8 (5, $[M - 3SO_2 + H]^+$), 1169.8 (18), 1168.8 (52), 1167.8 (90, $[M - 4SO_2 + H]^+$), 1166.8 (100, $[M - 4SO_2]^+$), 1165.8 (70).

Zn(II)-tetra-β″-sulfoleno-porphyrinate (1-Zn). A dry argon flushed flask equipped with reflux condenser was charged with 50 mg (35.11 μmol) of tetrasulfoleno porphyrin **1**, 160 mg (728.93 μmol, 20.76 equiv.) of $Zn(OAc)_2{\cdot}2H_2O$ and 25 mL of DMF. The resulting brown solution was flushed with argon and stirred at 100 °C under argon, reaction progress was followed with TLC (17:3 CH_2Cl_2/PE) and UV-vis-spectra. After 40 min no starting material was left and the flask was removed from the oil bath. The cooled reaction mixture was washed with water (100 mL), extracted the product with EtOAc (4 × 40 mL). The collective organic extractions were filtered through a plug of dried cotton and solvents were removed under reduced pressure. The dry crude product was re-dissolved in minimum amount of CH_2Cl_2, and the porphyrin **1-Zn** was precipitated with excess of PE (~1:5 v/v). The precipitate was dried under HV at 50 °C for 15 h to yield 47 mg (90%) of Zn(II)-tetra-β″-sulfoleno-porphyrinate (**1-Zn**). TLC: (CH_2Cl_2/MeOH, 10/0.05) $R_f = 0.2$. UV-vis (CH_2Cl_2, c = 3.83×10^{-5} M): λ_{max}, nm (log ε) 590 (3.92), 549.5 (4.41), 424 (5.85), 402 (4.73), 326 br (4.25). Fluorescence (CH_2Cl_2, c = 1.104×10^{-5} M): λ_{Ex}, nm 554 (O.D. = 0.25); λ_{Em}, nm (a.u.) 650 (129), 601 (70.6). 300 MHz ^{1}H NMR ($CDCl_3$): δ, ppm 1.50 (s, 72H, $^{t\text{-}}Bu^{531}$), 4.18 (s, 16H, H_2C^{21}), 7.81 (d, *J* = 1.8 Hz, 8H, HC^{52}), 7.96 (t, *J* = 1.8 Hz, 4H, HC^{54}). FAB-MS (pos. ion, $C_{84}H_{100}N_4O_8S_4Zn$, calcd. 1484.57): *m/z* (%) 1491.3 (5), 1490.3 (10), 1489.3 (16), 1488.3 (21), 1487.3 (24), 1486.3 (24), 1485.3 (22, $[M + H]^+$), 1484.3 (19, $[M]^+$), 1424.4 (4), 1423.4 (5), 1422.4 (5), 1421.4 (4, $[M - SO_2 + H]^+$), 1296.5 (6), 1295.5 (9), 1294.5 (10), 1293.5 (11, $[M - 3SO_2 + H]^+$), 1292.5 (10, $[M - 3SO_2]^+$), 1291.4 (9), 1246.5 (17), 1245.5 (20), 1244.5 (21), 1243.5 (15), 1242.5 (16), 1233.5 (41), 1232.5 (62), 1231.5 (69), 1230.5 (95), 1229.5 (100, $[M - 4SO_2 + H]^+$), 1228.5 (94, $[M - 4SO_2]^+$), 1227.5 (37), 1226.5 (30), 1217.5 (16), 1216.5 (21), 1215.5 (24), 1214.5 (26), 1213.5 (25), 1212.5 (20).

X-ray structure analysis, crystal data and structure refinement: for crystallization, a layer of *n*-hexane was added on top of a solution of *ca.* 2 mg of **1-Zn** in CH_2Cl_2 (3 mL), and the sample was stored at room temperature over few days (for crystallography, see Supporting information).

Cu(II)-tetra-β″-sulfoleno-porphyrinate (1-Cu). A dry and argon flushed round-bottomed flask charged with 24.7 mg (17.3 μmol) of sulfoleno porphyrin **1** and 35 mg (171 μmol, 10 equiv.) of $Cu(OAc)_2{\cdot}H_2O$. The mixture was evacuated under HV for 1 h and under argon 15 mL of abs CH_2Cl_2 and 1.5 mL of abs MeOH (10:1, v/v) were added. The resulting brown solution was heated to reflux in a pre-heated oil bath at 60 °C under argon. The reaction progress was followed by TLC, (17:3 CH_2Cl_2/PE; red non-fluorescent product spot slightly ahead of the spot of **1-2H**) and UV-vis spectra. After 2 h, **1-2H** was completely consumed and the flask was removed from the oil bath and allowed to cool down. The mixture was washed with water (30 mL) and extracted in CH_2Cl_2 (4 × 25 mL). The collected organic extracts were dried over Na_2SO_4, filtered and the solvents were evaporated under reduced pressure. The dry residue was re-dissolved in CH_2Cl_2 (4–5 mL) and precipitated with excess of PE (20 mL). The precipitate was dried under HV at 50 °C for 15 h to give 26.1 mg (99%) of the Cu(II)-tetrasulfoleno-porphyrinate **1-Cu**. TLC: CH_2Cl_2/PE, 8.5:1.5; $R_f = 0.45$. UV-vis (CH_2Cl_2, c = 1.764×10^{-5} M): λ_{max}, nm (log ε) 539.5 (4.44), 418 (5.76), 397 sh (4.61), 323 br (4.16). FAB-MS (pos. ion, $C_{84}H_{100}N_4O_8S_4Cu$, calcd. 1483.57): *m/z* (%) 1486.7 (29), 1485.7 (33), 1484.7 (34, $[M + H]^+$), 1422.8 (6), 1421.6 (8), 1420.7 (10, $[M - SO_2 + H]^+$), 1419.7 (6), 1260.8 (28), 1259.8 (33), 1258.8 (38), 1257.8 (33), 1244.9 (25), 1243.9 (28), 1241.8 (28), 1231.8 (30), 1230.7 (56), 1229.8 (61), 1228.9 (86, $[M - 4\ SO_2 + H]^+$), 1227.9 (100, $[M - 4\ SO_2]^+$), 1226.8 (43), 1225.9 (38).

Tetrasulfoleno Ni(II) porphyrin (1-Ni). A dry and argon flushed round-bottomed flask charged with 55 mg (38.6 μmol) of sulfoleno porphyrin **1**, 205 mg of (824 µmol, 21 equiv.) $Ni(OAc)_2 \cdot 4H_2O$ and 16 mL of dimethyl formamide (DMF). The resulting solution was purged with argon, stirred in a pre-heated oil bath at 100 °C under argon. The reaction progress was followed with TLC, and UV-vis spectra. After 2.5 h, complete conversion of **1** was observed, and the flask was removed from the oil bath. The cold reaction mixture was washed with water (100 mL) and the porphyrin was extracted into EtOAc (4 × 40 mL). The collected organic phases dried on Na_2SO_4, filtered and the solvent was removed under reduced pressure. The red dry product was re-dissolved in CH_2Cl_2 (6 mL), added PE 40–60 (35 mL) and placed in 4 °C refrigerator to give micro-crystals overnight, which were dried under HV at 50 °C for 15 h. In this way, 52.2 mg (91.3%) of tetrasulfoleno Ni(II)-porphyrin (**1-Ni**) were obtained. TLC: CH_2Cl_2/PE, 8.5:1.5; $R_f = 0.3$. UV-vis (CH_2Cl_2, $c = 4.255 \times 10^{-5}$ M): λ_{max}, nm (log ε) 562 (3.45), 530 (4.30), 418 (5.42), 300 br (4.17), 240 (4.40). ^1H NMR (300 MHz, $CDCl_3$): δ, ppm 1.47 (s, 72H), 4.06 (br s, 16H), 7.67 (d, $J = 1.7$ Hz, 8H), 7.89 (t, $J = 1.8$ Hz, 4H). 75 MHz ^{13}C NMR ($CDCl_3$): see Table S2, Supporting information. FAB-MS (pos. ion, $C_{84}H_{100}N_4O_8S_4Ni$, calcd. 1478.58): *m/z* (%) 1483.5 (12), 1482.5 (18), 1481.5 (32), 1480.4 (26), 1479.4 (22, $[M + H]^+$), 1478.4 (20, $[M]^+$), 1419.5 (8), 1418.5 (14), 1417.5 (18), 1416.5 (19), 1415.5 (29, $[M - SO_2 + H]^+$), 1227.6 (20), 1226.6 (42), 1225.6 (68), 1224.6 (92), 1223.6 (100, $[M - 4SO_2 + H]^+$), 1222.6 (94), 1221.6 (60), 1220.6 (50).

X-ray structure analysis, crystal data and structure refinement: for crystallization, *n*-hexane was added as a layer on top of a solution of *ca.* 2 mg of **1-Ni** in CH_2Cl_2 (3 mL), and the sample was stored at room temperature over few days (for crystallography, see Supporting information).

CONCLUSION

The here reported improved synthesis of the β″-tetrasulfolenopyrrol **1** made use of the beneficial effect of added detergent salts on the pyrrole tetramerization to porphyrinogens [16]. The versatile porphyrinoid building block **1** was obtained in a remarkable yield of up to 80–90%, paving the way to further studies of the chemistry of this type of reactive porphyrins. The synthesis of several transition metal complexes of **1** is described here. The functionalizable tetrasulfoleno porphyrins, obtained from **1**, are valuable basic units in up to four sequential cycloaddition reactions, as investigated in recent studies with the Zn(II)-complex **1-Zn** [5, 11, 12, 14].

Supporting information

Supplementary material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

Crystallographic data for structures **1-Ni** and **1-Zn** (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under numbers CCDC-950012 and 950013. Copies can be obtained on request, free of charge, *via* www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

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