A Highly Versatile Octasubstituted Phthalocyanine Scaffold for *ex post* Chemical Diversification

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This work is dedicated to Jenny Berthold on the occasion of her 60th birthday.

Abstract: The TBDPS protecting group was conveniently employed for the convergent synthesis of a highly soluble, fully protected octa-peripheral (*op*) substituted phthalocyanine (Pc). After facile deprotection, *ex post* modification of this full-fledged Pc scaffold by various linkers was successfully achieved. This strategy overcomes the downsides of widely established linear convergent approaches under harsh conditions, which are not only destructive to chemically sensitive substituents, but also detrimental to rapid diversification towards Pc libraries.

Key words: heterocycles, dendrimers, protecting groups, phthalocyanine, *ex post* diversification, divergent strategy

Since their discovery early in the last century, phthalocyanines (Pc) have been of great academic as well as industrial interest to chemists and physicists and have become one of the most studied classes of organic molecules. The plain core structure, due to its insolubility, was originally used in blue or green pigments.[1] Since then, manifold variations in substitution patterns have harnessed phthalocyanines for application in many important technical fields, such as nonlinear optics (including optical limitation), xerography (as photoconductors), optical data storage (as the laser absorption layer within recordable compact discs)[2] molecular electronics, solar energy conversion, catalysis, and as the active component of gas sensors.[3] The vast majority of these phthalocyanine derivatives have been synthesized via a convergent cyclotetramerization of their appropriately substituted *o*-phthalic precursors, thus conserving the initial substitution pattern. However, the utmost harsh conditions prevailing during the formation of the phthalocyanine ring system severely restrict synthetic scope, thus offering only relatively simple, robust structures with limited functionality. Obviously, phthalocyanines with sensitive substituents, e.g. peptides, carbohydrates etc., which are highly desirable for biomedical applications, are hard to access because they empirically do not survive the cyclotetramerization. An alternative divergent route via a straightforward *ex post* introduction of these ligands to a full-fledged phthalocyanine scaffold is obstructed by the lack of a suitable protective group and linker chemistry.[4] Curiously, broad scope protection/deprotection sequences and associated linker chemistry for the *ex post* modification of phthalocyanines have not been reported so far.

Herein, we introduce a fully protected, octa-peripheral (*op*) substituted phthalocyanine scaffold, which can be conveniently deprotected and subsequently *ex post* modified in a modular fashion under mild conditions. Starting from inexpensive pyromellitic dianhydride (PMDA), the TBDPS-protected phthalic anhydride **10** was obtained in a nine-step synthesis.[5] The TBDPS protecting group turned out to be most suitable[6] under the cyclotetramerization conditions according to the protocol of Uchida et al.[7] as well as for subsequent crystallization. H_2Pc **11** and ZnPc **12**, **13** were synthesized in good yields, providing structurally uniform products not contaminated with partially deprotected or decomposed specimens (Scheme 1).

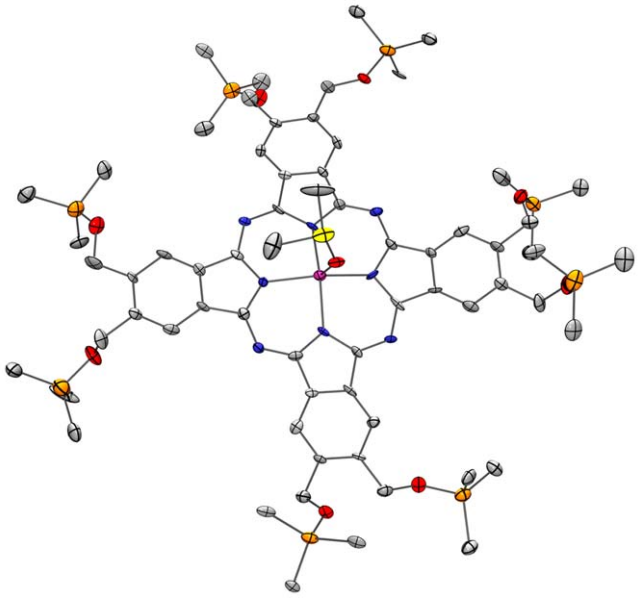

Figure 1 ORTEP Plot of the asymmetric unit of *a*-(DMSO)ZnPc-*op*-CH_2OTBDPS (**13**) recrystallized from CH_2Cl_2–PE with a small amount of DMSO; DMSO as fifth ligand.[8] View perpendicular to the Pc ring (for clarity, only the ipso C atoms of the phenyl rings and the central C atom of the *tert*-butyl groups are shown); carbon = gray, oxygen = red, nitrogen = blue, silicon = orange, sulfur = yellow, zinc = purple. (For full crystallographic details, see Supporting Information and CIF file.)

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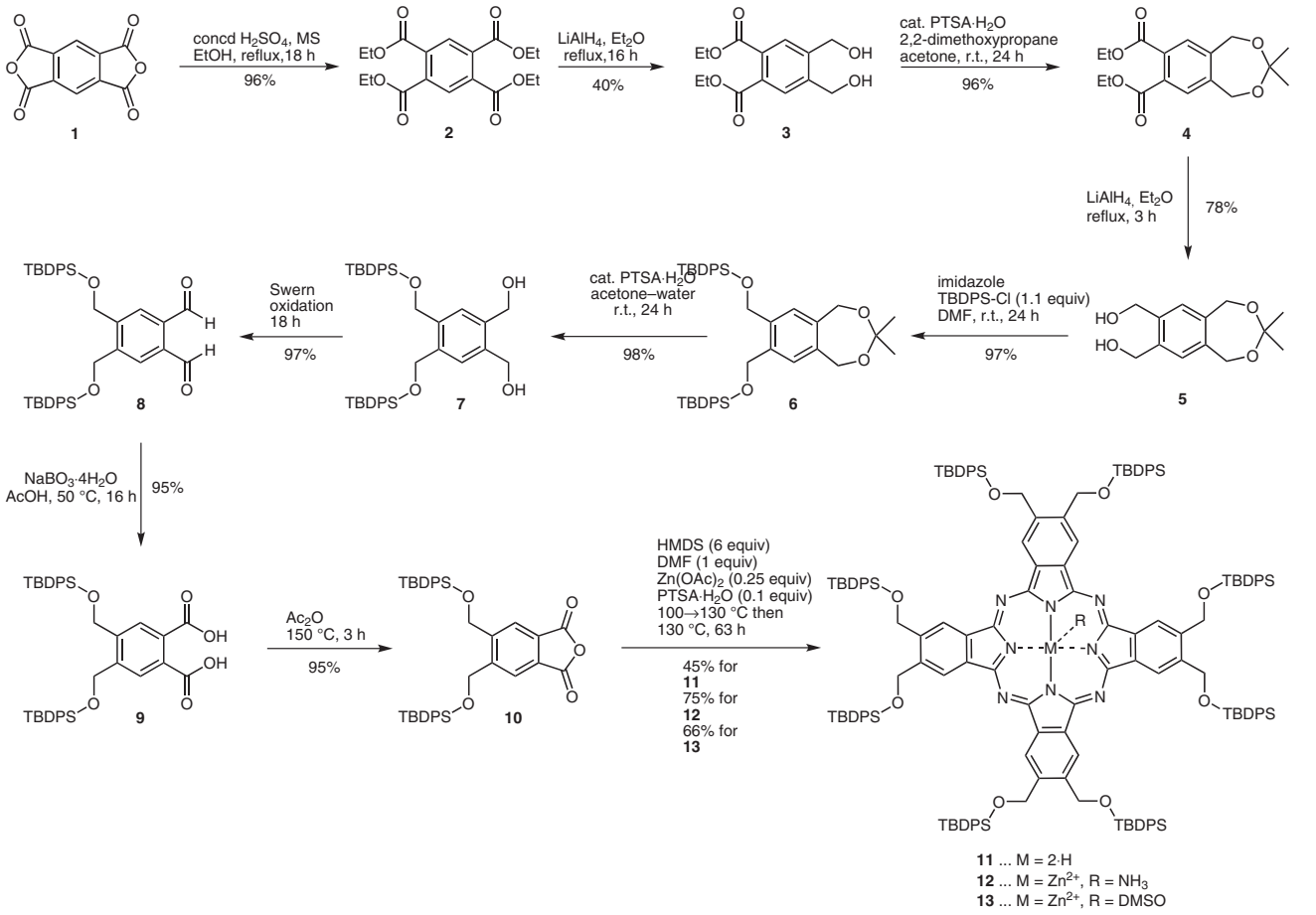


Scheme 1 Synthesis of H_2Pc **11** and ZnPc **12** and **13** starting from PMDA (**1**). For H_2Pc **11** the addition of $Zn(OAc)_2$ was omitted.

Depending on the workup and purification conditions two different ZnPc products were obtained. Precipitation from acetone afforded deep blue crystals of **12**. When using a solvent mixture (CH_2Cl_2–PE) containing a small amount of dimethyl sulfoxide for recrystallization, a crop of turquoise crystals of **13** was obtained (Figure 1). Both crystalline lots were subjected to X-ray crystal structure analysis. Interestingly, the crystal structures of these materials were not identical. Both lots showed the expected ZnPc structure, but differed with respect to the axial ligand coordinated to the central zinc atom. For **12**, this axial ligand was identified as ammonia (NH_3), which obviously originated from the *N*,*N*-dimethylformamide induced scission of hexamethyldisilazane.

The crystal structure of **13** showed evidence for dimethyl sulfoxide as the axial ligand, accountable to the recrystallization protocol (Figures 1 and 2), subsequently confirmed by elemental analysis. The axial coordination of dimethyl sulfoxide and methanol to ZnPcs, respectively, has precedence in the literature.[8]

For upscaling to multigram amounts, an optimized deprotection protocol was developed. Most conveniently, by choosing triethylamine trihydrofluoride in tetrahydrofuran for deprotection of **11** and **12**/**13**, all volatiles could be removed by evaporation after neutralization. The silylated cleavage products were separated by extractive workup with an organic biphasic system composed of dimethyl sulfoxide and petroleum ether. Aqueous workup of the dimethyl sulfoxide phase provided the deprotected H_2Pc-*op*-CH_2OH (**14**) or ZnPc-*op*-CH_2OH (**15**) in quantitative yields (Scheme 2). However, the metal-free H_2Pc-*op*-CH_2OH (**14**) displayed limited solubility due to rapid aggregation and, thus, was excluded from further experimentation. Albeit only soluble in a relatively small

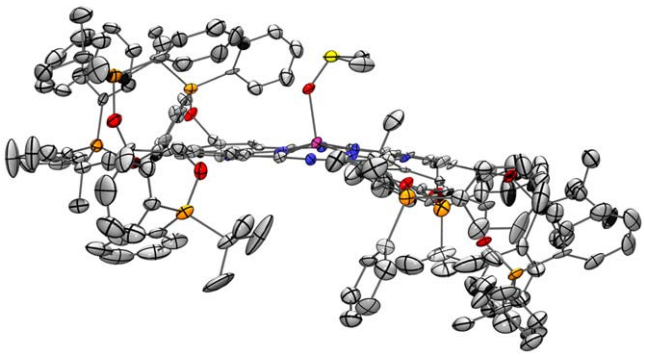
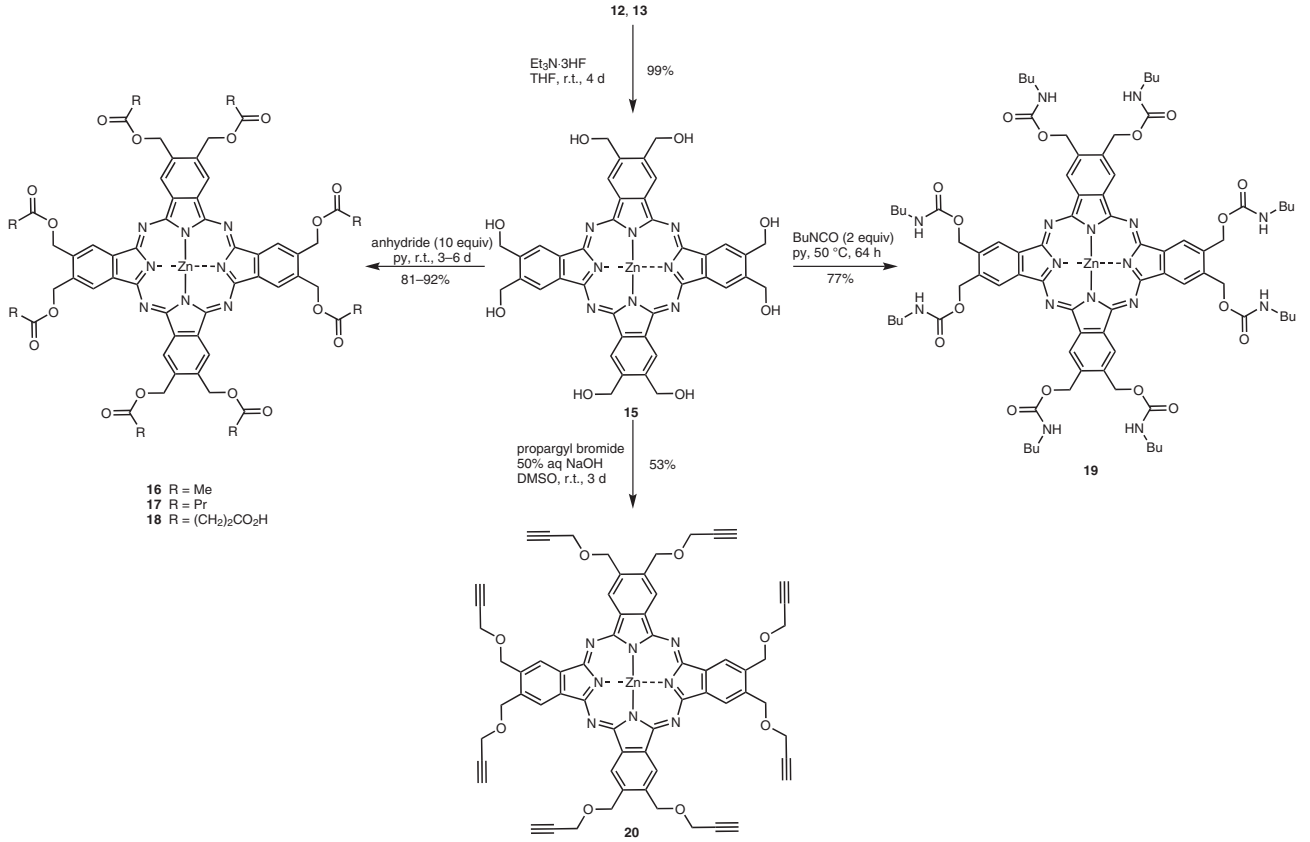


Figure 2 ORTEP Plot of the asymmetric unit of *a*-(DMSO)ZnPc-*op*-CH_2OTBDPS (**13**) recrystallized from CH_2Cl_2–PE with a small amount of DMSO; DMSO as fifth ligand.[8] View parallel to the Pc ring, showing that the zinc atom is positioned slightly above the Pc plane; carbon = gray, oxygen = red, nitrogen = blue, silicon = orange, sulfur = yellow, zinc = purple. (For full crystallographic details, see Supporting Information and CIF file.)



Scheme 2 Deprotection of **12** and **13** followed by divergent syntheses of ZnPcs by peripheral substitution of novel ZnPc-*op*-CH_2OH (**15**) with anhydrides, butyl isocyanate and propargyl bromide.

selection of solvents, mainly dimethyl sulfoxide and pyridine, the novel ZnPc-*op*-CH_2OH scaffold (**15**) holds high potential as progenitor for a vast range of new Pc-based molecules.[9] Nevertheless, the eightfold, dendrimer like functionality of this scaffold demands clean, complete, regio- and stereospecific reactions for all *ex post* derivatizations in order to avoid the formation of intractable isomeric mixtures. Firstly, as a model reaction, peracylation with carboxylic anhydrides in pyridine was chosen and smoothly executed for three examples **16**–**18**. Next, we reacted **15** with excess butyl isocyanate and conveniently isolated the corresponding octa-carbamate **19** uniformly in high yields. This linker chemistry will allow rapid diversification and optimization of Pc properties, e.g. in material sciences.

However, from a medicinal chemistry point of view, ester and carbamate linkages, aside from prodrug approaches, seem unfavorable due to their putative metabolic liabilities. Taking this into account, we elaborated an alkylation protocol along the lines of Wang et al.[10] by applying 50% aqueous sodium hydroxide–dimethyl sulfoxide as the reaction medium. A clean peralkylation of **15** with propargyl bromide afforded ZnPc **20** in good yields (Scheme 2). With the octa-propargyloxy derivative **20** in hand, access is gained to a plethora of cycloaddition reactions. In particular, the 1,3-dipolar cycloaddition of azides with alkynes, well-recognized as 'Sharpless click chemistry', is well-established as a mild, robust, and high-yielding method for the regio- and stereoselective functionalization of biologically interesting molecules.[11] The decoration of **20** with carbohydrate ligands by 'clicking' azido sugars will be reported in due course.

In summary, for the first time, we introduced a novel methodology for the protection/deprotection of a versatile Pc core. Linker chemistry of broad synthetic scope allows *ex post* modification of a full-fledged Pc scaffold. Thus, the synthetic limitations associated with the utmost harsh formation conditions during cyclotetramerization have been overcome. Pc scaffold **15** and, in particular, the octaalkynyl-substituted Pc **20** will serve as progenitors of highly complex Pcs. 'Click' chemistry has proven its viability for the synthesis of delicate molecules frequently occurring in the biomedical field.[12] Experimental protocols are convenient and suitable for the rapid generation of hitherto unknown Pc libraries of analytically pure substances in up to a multigram scale. The performance of the novel method will be demonstrated by 'clicking' azido sugars to **20** in due course.

Organic solvents used for reactions were of p.a. quality and used as purchased from Fisher Scientific, Merck, Acros, or SAF. Commercial available starting compounds and reagents were used directly without further purification from SAF, Lancaster, and Acros. Column chromatography was performed on Fluka silica gel 60 Å (40–63 μm). Bulk solvents used for chromatography and extraction were of technical grade. Analytic TLC was performed on aluminum sheets pre-coated with silica gel 60 Å with a fluorescent indicator

(Merck 60 F_{254}), and detection was effected by UV light at 254 and 366 nm and/or visualized with various spray reagents such as 10% H_2SO_4 in EtOH , acidic aq CAN soln, and ninhydrin in EtOH followed by heating or by a dipping bath of alkaline $KMnO_4$. ^1H and ^{13}C NMR spectra were recorded on Bruker AMX400, DRX500, or AV400 NMR spectrometer. ^1H and ^{13}C NMR, respectively, calibration of the spectra depending on the solvent was used [δ = 2.50/39.5 (DMSO-d_6), δ = 7.26/77.0 ($CDCl_3$), δ = 7.20/128.0 (C_6D_6), δ = 3.50/66.5 (1,4-dioxane-d_8), δ = 8.7/149.8 (pyridine-d_5), and δ = 2.7/30.1 (DMF-d_7)]; m_c = centered multiplet. 2D NMR techniques such as HH-COSY, TOCSY, NOESY, edited HSQC, and HMBC were used to assign the relative positions of protons and their carbons. ^{13}C NMR resonances are reported as the proton-decoupled chemical shifts, and in most cases the JMOD, PENDANT, or/and DEPT ^{13}C NMR technique was used to differentiate carbons. MS (FAB^+) spectra were obtained on a VG 70S mass spectrometer with a xenon FAB-gun and *m*-nitrobenzyl alcohol (3-NOBA) as matrix at 5000 resolution. MALDI-TOF mass spectrometric analysis were performed on a Bruker Biflex III, positive mode (matrix: anthracene-1,8,9-triol). 3D-Molecular structures from single crystals were obtained after X-ray diffraction (XRD) analysis that was performed on a Bruker SMART APEX 1 CCD irradiated with a diffraction ceramic tube KFF-Mo-2K-90 (MoKα radiation, λ = 71.073 pm) at 157 K (Oxford Cryosystem, 700 series Cryostream Cooler). The raw data were processed by Bruker AXS software package SMART APEX 5.0. UV-Vis spectra were recorded on a Perkin-Elmer dual-beam Bio50; log ε L/cm·mol. Melting points (uncorrected) were determined in an open capillary tube on an apotec – Otto Stein Inc. melting point apparatus.

Tetraethyl Benzene-1,2,4,5-tetracarboxylate (2)[5a]

PMDA (**1**, 50.0 g, 0.23 mol) was suspended in abs EtOH (500 mL) and refluxed until a soln was formed. Concd H_2SO_4 (30 mL, 1.1 mol) was added dropwise and the mixture was refluxed for 18 h. EtOH (350 mL) was distilled off from the reaction (atmospheric pressure). The remaining soln was actively cooled to r.t. and poured into cold (0 °C) 2 M NaOH (400 mL), while the internal temperature raised to 10 °C and a white precipitate was formed immediately. The aqueous phase was washed with MTBE (2 × 300 mL). To the acidic water phase 2 M NaOH was added (pH >9) and the mixture was washed with MTBE (100 mL). The combined organic phases were washed subsequently with H_2O and brine and dried (Na_2SO_4). Filtration and evaporation gave a slightly yellowish, highly viscous syrup; upon standing at r.t., white crystals formed; yield: 80.5 g, 0.22 mol (96%); mp 54 °C.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.06 (s, 2 H, H3), 4.33 (q, $^3J_{H6,H7} = {}^3J_{H10,H11}$ = 7.1 Hz, 8 H, H6/H10), 1.30 (t, $^3J_{H6,H7} = {}^3J_{H10,H11}$ = 7.1 Hz, 12 H, H7/H11).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.3 (C1/C5), 133.9 (C2/C4), 129.0 (C3), 62.0 (C6/C10), 13.8 (C7/C11).

HRMS (FAB^+, 3-NOBA): *m/z* [M – OCH_2CH_3]$^+$ calcd for $C_{16}H_{17}O_7$: 321.0969; found: 321.0982 (100%); *m/z* [M + H]$^+$ calcd for $C_{18}H_{23}O_8$: 367.1387; found: 367.1399 (30%).

Diethyl 4,5-Bis(hydroxymethyl)phthalate (3)[5a]

To a well-stirred soln of **2** (133 g, 362 mmol) in Et_2O (860 mL) was added a suspension of $LiAlH_4$ (16.5 g, 435 mmol) in Et_2O (600 mL) at a rate that maintained a steady reflux. After addition, the yellow mixture was refluxed 2.5 h. The progress of the reduction was monitored by LC-MS (**2**: t_R = 3.21 min; **3**: t_R = 2.25 min) after micro workup; the starting material was found to predominate, hence, a second portion of $LiAlH_4$ (5.70 g, 150 mmol) in Et_2O (200 mL) was added as before and reflux continued overnight. The yellow, heterogeneous mixture was cooled to r.t. and carefully quenched by addition to freshly prepared well-stirred sat. aq Na_2SO_4 soln. Salts were removed by filtration and washed with THF (500 mL). The organic phase was separated and the aqueous phase was washed with Et_2O (500 mL). The combined organic phases were evaporated to dryness, redissolved in $CHCl_3$ (500 mL), dried (Na_2SO_4), and concentrated to yield an orange oil (60 g). According to ^1H NMR, the oil consisted of the desired diethyl phthalate **3** (41 g, 40%) still containing the tetraethyl ester **2** (19 g). Column chromatography (silica gel, gradient PE → 80% EtOAc–PE) of sample of crude oil (3.6 g) gave analytically pure **3** (2.14 g, 7.58 mmol) as a pale yellow oil; R_f = 0.24 (PE–EtOAc, 60:40).

^1H NMR (400 MHz, DMSO-d_6): δ = 7.76 (s, 2 H, H3), 5.27 (br s, 2 H, OH), 4.58 (s, 4 H, H1), 4.28 (q, $^3J_{H6,H7}$ = 7.0–7.3 Hz, 4 H, H6), 1.28 (t, $^3J_{H6,H7}$ = 7.0–7.3 Hz, 6 H, H7).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.1 (C5), 142.7 (C2), 129.8 (C4), 126.0 (C3), 61.1 (C6), 59.2 (C1), 13.9 (C7).

HRMS (FAB^+, 3-NOBA): *m/z* [M – OCH_2CH_3]$^+$ calcd for $C_{12}H_{13}O_5$: 237.0757; found:237.0766 (100%); *m/z* [M + H]$^+$ calcd for $C_{14}H_{19}O_6$: 283.1176; found: 283.1184 (50%).

Diethyl 3,3-Dimethyl-1,5-dihydro-2,4-benzodioxepine-7,8-dicarboxylate (4)[5a]

The crude orange oil of **3** (34.6 g) was dissolved in THF (240 mL) and stirred with 2,2-dimethoxypropane (100 mL, 816 mmol) and PTSA·H_2O (1.0 g, 5.3 mmol) for 24 h. The reaction was quenched by addition of Et_3N (1.5 mL, 11 mmol). Volatiles were removed in vacuo and the resulting red-brown oil was dissolved in $CHCl_3$ (300 mL) and washed consecutively with H_2O (2 × 100 mL), sat. aq $NaHCO_3$ (2 × 200 mL), and brine, dried (Na_2SO_4), and concentrated to yield orange waxy crystals (41.4 g), which were used without further purification in the next reaction. ^1H NMR of the intermediate isolated reaction product still revealed contamination by tetraethyl ester **2** in a ratio identical to the starting mixture. Analytically pure **4** was obtained by reacting a sample of purified **3** (1.07 g, 3.80 mmol) in THF (12 mL, dried over MS) with 2,2-dimethoxypropane (3.0 mL, 25 mmol) and PTSA·H_2O (25 mg, 0.13 mmol) for 24 h. The reaction was quenched by addition of Et_3N (0.5 mL, 3.6 mmol). The clear soln was evaporated to dryness, dissolved in EtOAc, washed consecutively with aq 0.5 M NaOH, sat. aq $NaHCO_3$, and brine, dried (Na_2SO_4), and evaporated to yield **4** (1.16 g, 3.64 mmol, 96%) as pale yellow crystals; mp 85 °C; R_f = 0.66 (PE–EtOAc, 60:40).

^1H NMR (500 MHz, DMSO-d_6): δ = 7.50 (s, 2 H, H3), 4.87 (s, 4 H, H1), 4.26 (q, $^3J_{H6,H7}$ = 6.9–7.3 Hz, 4 H, H6), 1.42 (s, 6 H, H13), 1.27 (t, $^3J_{H6,H7}$ = 7.3 Hz, 6 H, H7).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 166.7 (C5), 142.0 (C2), 129.9 (C4), 126.6 (C3), 102.0 (C12), 63.3 (C1), 61.2 (C6), 23.4 (C13), 13.9 (C7).

HRMS (FAB^+, 3-NOBA): *m/z* [M + H]$^+$ calcd for $C_{17}H_{23}O_6$: 323.1489; found: 323.1503.

7,8-Bis(hydroxymethyl)-3,3-dimethyl-1,5-dihydro-2,4-benzodioxepine (5)[5a]

The crude orange, waxy crystals of the dioxepine dicarboxylate **4** (40.5 g) were dissolved in Et_2O (300 mL) and a suspension of $LiAlH_4$ (8.48 g, 223 mmol) in Et_2O (300 mL) was added at a rate that maintained a steady reflux. After addition, the yellow mixture was refluxed 3 h. Small samples were taken and worked up in order to monitor the progress of the reduction by LC-MS (**2**: t_R = 3.21 min; **4**: t_R = 3.06 min; **5**: t_R = 2.02 min). After completion of the reduction, the yellow, heterogeneous mixture was cooled to r.t. and carefully quenched by adding it to well-stirred sat. aq $NaHCO_3$. The organic phase was separated and the aqueous phase was washed with EtOAc (2 × 100 mL). The combined organic phases were concentrated and dried (Na_2SO_4). Evaporation of the solvent yielded an orange solid. Repeated recrystallization (MeOH) gave four crops of **5** (22.5 g, 94.3 mmol, 33% after 3 steps) as fine, white needles. An

analytical pure sample of **4** (2.03 g, 6.30 mmol) in Et_2O (50 mL) was subjected to the process described above using $LiAlH_4$ (0.50 g, 13 mmol) in Et_2O (30 mL). After workup, the remaining solid (1.29 g, 5.42 mmol, 86%) was suspended in Et_2O by means of ultrasound, chilled in a fridge, filtered, and washed with cold Et_2O to give **5** (1.16 g, 4.89 mmol, 78%) as fine, white needles; mp 137 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.11 (s, 2 H, H3), 5.02 (t, $^3J_{OH,H5}$ = 5.4 Hz, 2 H, OH), 4.76 (s, 4 H, H1), 4.48 (d, $^3J_{OH,H5}$ = 5.5 Hz, 4 H, H5), 1.41 (s, 6 H, H13).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 137.5 (C4), 136.3 (C2), 124.6 (C3), 101.5 (C12), 63.9 (C1), 60.0 (C5), 23.7 (C13).

7,8-Bis[(*tert*-butyldiphenylsilyloxy)methyl]-3,3-dimethyl-1,5-dihydro-2,4-benzodioxepine (6)[5b]

To a soln of **5** (20.4 g, 85.5 mmol) in anhyd DMF (150 mL) was added imidazole (35.1 g, 516 mmol) in portions. An endothermic enthalpy of solvation was observed. To the clear, colorless soln, TBDPSCl (53.0 mL, 207 mmol) was added dropwise with a syringe through a septum. A mild exothermic reaction occurred. After stirring at r.t. for 24 h, MTBE (500 mL) was added to the clear, yellow soln in order to precipitate imidazolium·HCl as a colorless solid. The organic layer was filtered and consecutively washed with H_2O (2 × 300 mL), 2 M HCl (2 × 200 mL), buffer (pH ~5, 100 mL), sat. aq $NaHCO_3$ (100 mL), and brine and dried (Na_2SO_4). Concentration yielded a clear, slightly yellow residue (67.9 g). The crude product was further purified by column chromatography (silica gel, gradient PE → 20% EtOAc–PE + 1 vol% Et_3N) to yield **6** (59.2 g, 82.7 mmol, 97%) as a clear, colorless, highly viscous oil; R_f = 0.76 (PE–EtOAc, 80:20).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.54 (dd, $^3J_{H7,H8}$ = 8.0 Hz, $^4J_{H7,H9}$ = 1.3–1.5 Hz, 8 H, H7), 7.43 (tt, $^3J_{H8,H9}$ = 7.4 Hz, $^4J_{H7,H9}$ = 1.3–2.3 Hz, 4 H, H9), 7.35 (dd, $^3J_{H7,H8}$ = 8.1 Hz, $^3J_{H8,H9}$ = 7.4 Hz, 8 H, H8), 7.10 (s, 2 H, H3), 4.77 (s, 4 H, H1), 4.70 (s, 4 H, H5), 1.42 (s, 6 H, H13), 0.91 (s, 18 H, H11).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 137.1 (C2), 135.8 (C4), 134.9 (C7), 132.6 (C6), 129.8 (C9), 127.8 (C8), 124.7 (C3), 101.6 (C12), 63.9 (C1), 63.0 (C5), 26.5 (C11), 23.6 (C13), 18.7 (C10).

HRMS (FAB$^+$, 3-NOBA): *m*/*z* [M – H]$^+$ calcd for $C_{45}H_{53}O_4Si_2$: 713.3477; found: 713.3510 (100%); *m*/*z* [M]$^+$ calcd for $C_{45}H_{54}O_4Si_2$: 714.3555; found: 714.3556 (65%); *m*/*z* [M + H]$^+$ calcd for $C_{45}H_{55}O_4Si_2$: 715.3633; found: 715.3549 (26%).

{4,5-Bis[(*tert*-butyldiphenylsilyloxy)methyl]-1,2-phenylene}dimethanol (7)

Dioxepine **6** (2.54 g, 3.55 mmol) was completely dissolved in acetone (134 mL). H_2O (ca. 37 mL) was added slowly in portions until opacity of the soln persisted. To this mixture, PTSA·H_2O (86 mg) was added at in one portion and the mixture was stirred at r.t. for 24 h. After 10 min the liquid already began to clarify. The reaction was terminated by addition of Et_3N until pH ~7–8. Evaporation to half of the volume (ca. 80 mL) caused turbidity again. The mixture was extracted with Et_2O (3 × 100 mL). The combined organic phases were washed consecutively with aq citric acid (0.5 wt%, pH ~3), sat. aq $NaHCO_3$, and brine, dried (Na_2SO_4), and concentrated to yield **7** (2.38 g, 3.47 mmol, 98%) as a colorless, highly viscous oil; R_f = 0.42 (PE–EtOAc, 60:40).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.57 (dd, $^3J_{H7,H8}$ = 8.0 Hz, $^4J_{H7,H9}$ = 1.3–1.5 Hz, 8 H, H7), 7.51 (s, 2 H, H3), 7.44 (tt, $^3J_{H8,H9}$ = 7.4–7.6 Hz, $^4J_{H7,H9}$ = 1.3–2.3 Hz, 4 H, H9), 7.35 (dd, $^3J_{H7,H8}$ = 8.1 Hz, $^3J_{H8,H9}$ = 7.4 Hz, 8 H, H8), 5.09 (t, $^3J_{OH,H1}$ = 5.3 Hz, 2 H, OH), 4.74 (s, 4 H, H5), 4.56 (d, $^3J_{OH,H1}$ = 4.6 Hz, 4 H, H1), 0.92 (s, 18 H, H11).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.2 (C2), 135.7 (C4), 134.9 (C6), 132.7 (C7), 129.8 (C9), 127.8 (C8), 125.8 (C3), 63.3 (C5), 60.3 (C1), 26.5 (C11), 18.7 (C10).

HRMS (FAB$^+$, 3-NOBA): *m*/*z* [M – H_2O – H]$^+$ calcd for $C_{42}H_{47}O_3Si_2$: 655.3058; found: 655.3078 (100%); *m*/*z* [M – H]$^+$ calcd for $C_{42}H_{49}O_4Si_2$: 673.3164; found: 673.3147 (50%); *m*/*z* [M]$^+$ calcd for , $C_{42}H_{50}O_4Si_2$: 674.3242; found: 674.3195 (22%).

4,5-Bis[(*tert*-butyldiphenylsilyloxy)methyl]phthalaldehyde (8)[5c]

According to the procedure of Farooq,[5c] oxalyl chloride (0.65 mL, 7.70 mmol) was dissolved in CH_2Cl_2 (6 mL) and cooled to –78 °C. A soln of DMSO (1.20 mL, 16.9 mmol) in CH_2Cl_2 (11.0 mL) was added dropwise. The soln was stirred for 20 min and **7** (2.03 g, 3.00 mmol) dissolved in CH_2Cl_2 (6 mL) was added dropwise. The mixture was stirred at –78 °C for 3 h and then Et_3N (5.0 mL, 35.9 mmol) was slowly added at –78 °C. The mixture was allowed to reach r.t. overnight and then the yellow, heterogeneous mixture was diluted with CH_2Cl_2 (200 mL), extracted with aq 2 M HCl, sat. aq $NaHCO_3$, and brine, and dried (Na_2SO_4). On evaporation gave **8** (1.95 g, 2.91 mmol, 97%) as a yellow, highly viscous oil. For analytical characterization, adsorption on silica gel and subsequent column chromatography (silica gel, gradient PE → 20% EtOAc–PE) yielded **8** (1.03 g, 1.53 mmol, 51%) as a colorless, highly viscous oil; R_f = 0.80 (PE–EtOAc, 80:20).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.5 (s, 2 H, H1), 8.07 (s, 2 H, H3), 7.54 (dd, $^3J_{H7,H8}$ = 8.0 Hz, $^4J_{H7,H9}$ = 1.3–1.5 Hz, 8 H, H7), 7.44 (tt, $^3J_{H8,H9}$ = 7.4 Hz, $^4J_{H7,H9}$ = 1.3–2.3 Hz, 4 H, H9), 7.35 (dd, $^3J_{H7,H8}$ = 8.1 Hz, $^3J_{H8,H9}$ = 7.4 Hz, 8 H, H8), 4.84 (s, 4 H, H5), 0.94 (s, 18 H, H11).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 192.5 (C1), 143.5 (C4), 135.2 (C2), 134.9 (C7), 132.2 (C6), 130.0 (C9), 127.9 (C8), 127.7 (C3), 62.6 (C5), 26.5 (C11), 18.7 (C10).

HRMS (FAB$^+$, 3-NOBA): *m*/*z* [M – O + H]$^+$ calcd for $C_{42}H_{47}O_3Si_2$: 655.3058; found:655.3119 (100%); *m*/*z* [M – O + 2 H]$^+$ calcd for $C_{42}H_{48}O_3Si_2$: 656.3136; found: 656.3141 (49%); *m*/*z* [M + H]$^+$ calcd for $C_{42}H_{47}O_4Si_2$: 671.3007; found: 671.3027 (48%).

4,5-Bis[(*tert*-butyldiphenylsilyloxy)methyl]phthalic Acid (9)[5d]

To a soln of **8** (21.8 g, 32.4 mmol) in AcOH (133 mL) was added $NaBO_3$·4 H_2O (14.0 g, 91.0 mmol) in 1 portion and stirred at 50 °C for 16 h. AcOH was removed by evaporation under reduced pressure. The remaining white, crystalline residue was first sonicated with EtOAc (3 × 100 mL) and decanted. The remaining insoluble mass was dissolved in aq citric acid (0.5 wt%, 200 mL, pH ~3) and extracted with EtOAc (100 mL). The combined organic phases were washed consecutively with aq citric acid (pH ~3) and brine, dried (Na_2SO_4), and concentrated to yield a white, crystalline solid (21.7 g, 95%). Recrystallization (EtOAc–PE, 60 °C then storage in a fridge) gave several crops of **9** (20.3 g, 28.9 mmol, 89%); mp 137 °C; R_f = 0.74 (*t*-BuOH–H_2O–AcOH, 60:20:20).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.1 (br s, 2 H, H1), 7.77 (s, 2 H, H3), 7.54 (dd, $^3J_{H7,H8}$ = 8.0 Hz, $^4J_{H7,H9}$ = 1.5 Hz, 8 H, H7), 7.44 (tt, $^3J_{H8,H9}$ = 7.3–7.5 Hz, $^4J_{H7,H9}$ = 1.3–2.3 Hz, 4 H, H9), 7.35 (dd, $^3J_{H7,H8}$ = 8.0 Hz, $^3J_{H8,H9}$ = 7.5 Hz, 8 H, H8), 4.77 (s, 4 H, H5), 0.93 (s, 18 H, H11).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.5 (C1), 140.2 (C4), 134.9 (C7), 132.3 (C6), 131.6 (C2), 129.9 (C9), 127.9 (C8), 126.5 (C3), 62.5 (C5), 26.4 (C11), 18.7 (C10).

HRMS (FAB$^+$, 3-NOBA): *m*/*z* [M + H]$^+$ calcd for $C_{42}H_{47}O_6Si_2$: 703.2906; found: 703.2913.

4,5-Bis[(*tert*-butyldiphenylsilyloxy)methyl]phthalic Anhydride (10)[5e]

A degassed and argon flushed suspension of **9** (15.5 g, 22.0 mmol) in Ac_2O (300 mL) was stirred at 145–150 °C (oil bath) for 3 h with exclusion of moisture. After cooling to 60 °C all volatiles were removed under reduced pressure. The amorphous residue (16.2 g) was washed (anhyd PE). Recrystallization (anhyd EtOAc, fridge) gave

10 (14.5 g, 21.1 mmol, 95%); as pale yellow crystals; mp 118 °C. These crystals were used for X-ray analysis.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.06 (s, 2 H, H3), 7.54 (dd, $^3J_{H7,H8}$ = 7.9 Hz, $^4J_{H7,H9}$ = 1.5 Hz, 8 H, H7), 7.45 (tt, $^3J_{H8,H9}$ = 7.3–7.6 Hz, $^4J_{H7,H9}$ = 1.2–2.1 Hz, 4 H, H9), 7.36 (dd, $^3J_{H7,H8}$ = 7.9 Hz, $^3J_{H8,H9}$ = 7.6 Hz, 8 H, H8), 4.89 (s, 4 H, H5), 0.94 (s, 18 H, H11).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.0 (C1), 146.6 (C4), 134.9 (C7), 132.0 (C6), 130.4 (C2), 130.0 (C9), 127.9 (C8), 122.4 (C3), 62.6 (C5), 26.4 (C11), 18.7 (C10).

HRMS (FAB$^+$, 3-NOBA): *m/z* [M + H]$^+$ calcd for $C_{42}H_{45}O_5Si_2$: 685.2800; found: 685.2817.

Crystal data for **10**: $C_{42}H_{44}O_5Si_2$, M_r = 684.95, T = 153(2) K, λ = 0.71073 Å, triclinic, $P\bar{1}$, a = 10.0725(10) Å, b = 12.3224(12) Å, c = 16.1951(16) Å, V = 1875.0(3) Å^3, Z = 2, D_x = 1.213 g cm^{-3}, F(000) = 728, m = 0.138 mm^{-1}, crystal size 0.40 × 0.25 × 0.05 mm^3, No. of unique data (Bruker AXS Smart APEX CCD area detector using MoKα radiation) = 8363, No. of parameters = 448, R (all data) = 0.0818, wR (all data) = 0.1030, r = 0.495 e Å^{-3}. $R1$ = 0.0521 [$I > 2\sigma(I)$, 5654 reflections]. CCDC deposition number = 748149.

2,3,9,10,16,17,23,24-Octakis[(*tert*-butyldiphenylsilyloxy)methyl]phthalocyanine (11)[7]

The reaction was conducted in two screw cap vials (each 50 mL) which were charged in the following order with **10** (7.31 g, 10.7 mmol), HMDS (14.5 mL, 67 mmol), and DMF (0.82 mL, 10.6 mmol. The amounts were equally divided and a vigorous stream of argon was bubbled through the stirred suspension for 5 min before PTSA·H_2O (0.11 g, 0.58 mmol) was added to each vial. The vials were sealed and placed in a pre-heated (100 °C) aluminum block when the temperature was increased to 130 °C. The mixtures were stirred at this temperature for 10 h. The pressurized, sealed vials were carefully opened after cooling to r.t. and the sticky, solid products were combined, dissolved in CH_2Cl_2 and subjected to flash chromatography (silica gel, CH_2Cl_2 then gradient PE–EtOAc, 60:40 → EtOAc → THF). Evaporation of the solvents and precipitation from acetone gave two crops of **11** (2.50 g, 0.94 mmol, 45%) as a blue powder; mp 263–264 °C. Note: In order to prevent light-induced decomposition of the substance, protection from light is strongly recommended!

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.51 (s, 8 H, H3), 7.80–7.78 (m, 32 H, H7), 7.36–7.31 (m, 48 H, H8/H9), 5.35 (s, 16 H, H5), 1.16 (s, 72 H, H11), –0.17 (br s, 2 H, NH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5 (C1), 141.3 (C4), 136.1 (C2), 135.7 (C7), 133.4 (C6), 129.8 (C9), 127.8 (C8), 122.1 (C3), 65.0 (C5), 27.0 (C11), 19.4 (C10); (C1 and C2 were derived from HMBC spectra).

MS (MALDI-TOF, anthracene-1,8,9-triol): *m/z* [M + H]$^+$ calcd for $C_{168}H_{179}N_8O_8Si_8$: 2660.1995; *m/z* (%) found: 2661.19 (100), 2662.18 (90), 2660.22 (87), 2663.14 (60), 2659.25 (50), 2664.12 (37), 2665.12 (23).

UV-Vis (THF): λ_{max} (log ε) = 700 (665) nm (1.5 × 10^5).

Anal. Calcd for $C_{168}H_{178}N_8O_8Si_8$: C, 75.80; H, 6.74; N, 4.21. Found: C, 75.68; H, 6.89; N, 4.18.

{2,3,9,10,16,17,23,24-Octakis[(*tert*-butyldiphenylsilyloxy)methyl]phthalocyaninato}zinc(II)–Ammonia Complex (12) or {2,3,9,10,16,17,23,24-Octakis[(*tert*-butyldiphenylsilyloxy)methyl]phthalocyaninato}zinc(II)–Dimethyl Sulfoxide Complex (13)[7]

The reaction was conducted in two screw cap vials (each 50 mL) which were charged in the following order with **10** (7.46 g, 10.88 mmol), $Zn(OAc)_2$ (0.51 g, 2.8 mmol), HMDS (13.4 mL, 65 mmol), and DMF (0.85 mL, 11 mmol). A vigorous stream of argon was bubbled through the stirred suspension for 5 min and then PTSA·H_2O (0.12 g, 0.60 mmol) was added to each vial. The vials were sealed and placed in a pre-heated (100 °C) aluminum block when the temperature was increased to 130 °C. The mixtures were stirred at this temperature for 36 h. The pressurized, sealed vials were carefully opened after cooling to r.t. and the sticky, solid products were combined (9.6 g), dissolved in CH_2Cl_2 and subjected to flash chromatography (silica gel, CH_2Cl_2 then gradient PE–EtOAc, 60:40 → 40:60) to give a crude crystalline product (5.3 g, 72%). Evaporation of the solvents and recrystallization [PE–CH_2Cl_2 (90:10) with a small amount of DMSO; fridge] gave two crops of **13** (3.66 g, 1.34 mmol, 49% and 1.29 g, 0.47 mmol, 17%) as turquoise shiny crystals.

In the course of resynthesis on the same scale and using the procedure as described above, **12** (75% yield) was isolated after heating at 130 °C for 48 h and purification by flash chromatography (silica gel) followed by precipitation from acetone. Fortunately, in the precipitate blue, opaque crystals were found appropriate for the X-ray analysis of **12**. Note: In order to prevent light-induced decomposition of the substance, protection from light is strongly recommended!

^{1}H NMR (400 MHz, acetone-d_6): δ = 9.60 (s, 8 H, H3), 7.87–7.85 (m, 32 H, H7), 7.41–7.40 (m, 48 H, H8/H9), 5.58 (s, 16 H, H5), 1.18 (s, 72 H, H11).

^{1}H NMR (400 MHz, DMSO-d_6–$CDCl_3$, 6:2): δ = 9.42 (s, 8 H, H3), 7.73–7.71 (m, 32 H, H7), 7.35–7.31 (m, 48 H, H8/H9), 5.34 (br s, 16 H, H5), 1.08 (s, 72 H, H11).

^{13}C NMR (100 MHz, DMSO-d_6–$CDCl_3$, 6:2): δ = 153.2 (C1), 139.9 (C4), 137.2 (C2), 134.9 (C7), 132.6 (C6), 129.6 (C9), 127.6 (C8), 120.8 (C3), 64.4 (C5), 26.5 (C11), 18.8 (C10).

MS (MALDI-TOF, anthracene-1,8,9-triol): *m/z* [M]$^+$ calcd for $C_{168}H_{176}N_8O_8Si_8Zn$: 2721.1051; *m/z* (%) found: 2722.12 (100), 2723.14 (93), 2721.20 (93), 2724.10 (82), 2720.25 (74), 2725.08 (63), 2719.27 (47).

UV-Vis (THF): λ_{max} (log ε) = 675 nm (2.6–4.3 × 10^5).

Zinc–Ammonia Complex 12

Mp 294–296 °C.

Anal. Calcd for $C_{168}H_{176}N_8O_8Si_8ZnH_2O$: C, 73.55; H, 6.54; N, 4.08. Found: C, 73.53; H, 6.72; N, 4.06.

Crystal data for **12**:[13] $C_{168}H_{179}N_9O_8Si_8Zn$·2.5 acetone·$H_2O$, M_r = 2904.50, T = 153(2) K, λ = 0.71073 Å, triclinic, $P\bar{1}$, a = 18.2775(18) Å, b = 19.700(2) Å, c = 24.290(2) Å, V = 8148.5(14) Å^3, Z = 2, D_x = 1.184 g cm^{-3}, F(000) = 3092, m = 0.271 mm^{-1}, No. of unique data (Bruker AXS Smart APEX CCD area detector using MoKα radiation) = 28579, No. of parameters = 1876, R (all data) = 0.1506, wR (all data) = 0.1186, r = 0.470 e Å^{-3}. $R1$ = 0.0582 [$I > 2\sigma(I)$, 11703 reflections]. CCDC deposition number = 748148.

Zinc–Dimethyl Sulfoxide Complex 13

Mp 239–241 °C.

Anal. Calcd for $C_{168}H_{176}N_8O_8Si_8Zn$·DMSO: C, 72.83; H, 6.59; N, 4.00; S, 1.14. Found: C, 72.54; H, 6.64; N, 4.10; S, 1.12.

Crystal data for **13**: $C_{170}H_{182}N_8O_9SSi_8Zn$, M_r = 2803.39, T = 153(2) K, λ = 0.71073 Å, monoclinic, $P2_1/c$, a = 22.4151(19) Å, b = 41.541(4) Å, c = 17.8269(16) Å, V = 15611(2) Å^3, Z = 4, D_x = 1.193 g cm^{-3}, F(000) = 5952, m = 0.292 mm^{-1}, crystal size 0.50 × 0.10 × 0.07 mm^3, No. of unique data (Bruker AXS Smart APEX CCD area detector using MoKα radiation) = 16078, No. of parameters = 1795, R (all data) = 0.1573, wR (all data) = 0.1151, r = 0.579 e Å^{-3}. $R1$ = 0.0703 [$I > 2\sigma(I)$, 7995 reflections]. CCDC deposition number = 748147.

2,3,9,10,16,17,23,24-Octakis(hydroxymethyl)phthalocyanine (14)

Deprotection of **11** (2.50 g, 0.94 mmol) was analogously performed as described for the synthesis of **15**. After lyophilization a deep blue solid (696 mg, 0.92 mmol, 98%) was isolated. Due to limited solubility and rapid aggregation, characterization in concentrated soln, as necessary for ^{13}C NMR, could not be performed; mp >360 °C.

^1H NMR (400 MHz, DMSO-d_6): δ = 9.00 (br s, 8 H, H3), 5.74 (br s, 8 H, OH), 5.07 (s, 16 H, H5).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 119.5 (C3), 60.7 (C5) via HSQC 2D-NMR technique.

MS (MALDI-TOF, anthracene-1,8,9-triol): *m*/*z* $[M]^+$ calcd for $C_{40}H_{34}N_8O_8$: 754.2494; *m*/*z* (%) found: 754.4 (100), 755.3 (90), 756.2 (41), 757.2 (12).

Anal. Calcd for $C_{40}H_{34}N_8O_8 \cdot 2\ H_2O$: C, 60.75; H, 4.84; N, 14.17. Found: C, 61.13; H, 4.88; N, 13.99.

[2,3,9,10,16,17,23,24-Octakis(hydroxymethyl)phthalocyaninato]zinc(II) (15); Typical Procedure

A PTFE vessel with a screw cap was charged with **12** or **13** (3.15 g, 1.16 mmol) and dissolved in THF (200 mL). An initial amount of $Et_3N \cdot 3$ HF (4.0 mL, 75 mmol) was added and the mixture was stirred for 3 h before a second portion of $Et_3N \cdot 3$ HF (4.0 mL, 75 mmol) was added and the mixture was stirred overnight. The reaction was monitored continuously by TLC, hence a final portion of $Et_3N \cdot 3$ HF (4.0 mL, 75 mmol) was added. According to TLC, deprotection was completed after 3 d. The mixture was carefully neutralized in portions by addition of a soln of NaOMe in MeOH. The solvent was removed under reduced pressure and the residue dissolved in DMSO (300 mL) and extracted with PE (8 × 100–150 mL) until no UV active spot could be detected on TLC. The DMSO phase was separated and reduced to a minimum. The remaining slurry was dropped into aq 2 M HCl and the precipitate thus formed was collected by centrifugation. The resulting sticky, deeply blue paste was repeatedly suspended in distilled H_2O by using ultrasound and centrifuged until the aqueous phase was neutral. Finally, the product was lyophilized to give **15** (0.97 g, 1.18 mmol, 99%) as free-flowing, fine flakes; mp >360 °C.

^1H NMR (500 MHz, DMSO-d_6): δ = 9.40 (s, 8 H, H3), 5.72 (t, $^3J_{OH,H5}$ = 5.4–5.7 Hz, 8 H, OH), 5.12 (d, $^3J_{OH,H5}$ = 5.4 Hz, 16 H, H5).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 153.0 (C1), 141.7 (C4), 136.6 (C2), 120.0 (C3), 60.9 (C5).

MS (MALDI-TOF, anthracene-1,8,9-triol): *m*/*z* $[M]^+$ calcd for $C_{40}H_{32}N_8O_8Zn$: 816.1629; *m*/*z* (%) found: 816.80 (100), 818.80 (60), 817.81 (56), 820.79 (46), 819.80 (38), 821.80 (18).

UV-Vis (DMSO): λ_{max} (log ε) = 681 nm (6.7×10^5).

Anal. Calcd for $C_{40}H_{32}N_8O_8Zn \cdot 3.5\ H_2O \cdot 0.5$ DMSO: C, 54.04; H, 4.54; N, 12.30; S, 1.76. Found: C, 53.43; H, 4.57; N, 12.28; S, 1.67.

[2,3,9,10,16,17,23,24-Octakis(acetoxymethyl)phthalocyaninato]zinc(II) (16)

Upon sonication, **15** (0.109 g, 0.133 mmol) was dissolved in anhyd pyridine (10.0 mL. 124 mmol), and Ac_2O (3.0 mL, 32 mmol) was added dropwise. The mixture was stirred in the dark at r.t. for 3 d. Evaporation of the solvent and column chromatography (silica gel, gradient PE–EtOAc, 40:60 → EtOAc → THF) followed by drying yielded **16** (0.125 g, 0.108 mmol, 81%). Alternatively, instead of column chromatography, purification was carried out by extraction with EtOAc. The organic phase was washed with citric acid (pH ~3) followed by sat. aq $NaHCO_3$ and brine and dried (Na_2SO_4). Evaporation yielded analytically pure **16**; mp >360 °C.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.77 (br s, 8 H, H3), 5.73 (br s, 16 H, H5), 2.33 (s, 24 H, H7).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.4 (C6), 151.2 (C1), 136.9 (C2), 135.5 (C4), 122.7 (C3), 63.9 (C5), 20.8 (C7).

MS (MALDI-TOF, anthracene-1,8,9-triol): *m*/*z* $[M + H]^+$ calcd for $C_{56}H_{49}N_8O_{16}Zn$: 1153.2553; *m*/*z* (%) found: 1153.09 (100), 1154.07 (99.7), 1155.06 (87), 1152.11 (82), 1156.05 (80), 1157.05 (61), 1158.04 (33), 1159.04 (17).

Anal. Calcd for $C_{56}H_{48}N_8O_{16}Zn \cdot 0.8\ H_2O$: C, 57.54; H, 4.28; N, 9.59. Found: C, 57.73; H, 4.58; N, 9.42.

[2,3,9,10,16,17,23,24-Octakis(butyryloxymethyl)phthalocyaninato]zinc(II) (17)

To a sonicated soln of **15** (0.11 g, 0.13 mmol) in anhyd pyridine (10.0 mL. 124 mmol) was added dropwise butyric anhydride (2.20 mL, 13.4 mmol) and the mixture was stirred in the dark at r.t. for 6 d. The solvent was evaporated, the remaining residue dissolved in the minimum of THF (3 mL) and precipitated by dropwise addition to PE (40 mL) then this was centrifuged. The supernatant was discarded and the precipitate was washed with MeOH and dried under vacuum to give **17** (0.16 g, 0.12 mmol, 92%); mp >360 °C.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.72 (br s, 8 H, H3), 5.74 (br s, 16 H, H5), 2.60 (t, $^3J_{H7,H8}$ = 7.0–7.3 Hz, 16 H, H7), 1.79 (sext, $^3J_{H7,H8} = {}^3J_{H8,H9}$ = 7.3–7.5 Hz, 16 H, H8), 1.07 (quint, $^3J_{H8,H9}$ = 6.3–7.5 Hz, 24 H, H9).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 172.7 (C6), 151.1 (C1), 136.8 (C2), 135.5 (C4), 122.4 (C3), 63.8 (C5), 35.5 (C7), 18.1 (C8), 13.5 (C9).

Anal. Calcd for $C_{72}H_{80}N_8O_{16}Zn$: C, 62.72; H, 5.85; N, 8.13. Found: C, 62.38; H, 6.03; N, 8.18.

{2,3,9,10,16,17,23,24-Octakis[(3-carboxypropanoyloxy)methyl]phthalocyaninato}zinc(II) (18)

Upon sonication, **15** (100 mg, 124 μmol) was dissolved in anhyd pyridine (10.0 mL, 124 mmol) and succinic anhydride (1.05 g, 10.5 mmol) was added and the mixture was stirred in the dark at r.t. for 6 d. After evaporation of the solvent, the remaining residue was washed with EtOAc and centrifuged to remove the excess of anhydride. The residue was dissolved in the minimum of DMSO (3 mL) and dropwise added to MeCN (40 mL). The precipitate thus obtained was dissolved again in DMSO (3 mL) and added dropwise to deionized H_2O (50 mL). The mixture was lyophilized and dried in an evacuated desiccator over P_4O_{10} for 5 d to yield **18** (170 mg, 105 mmol, 85%) as a blue, free-flowing powder; mp >360 °C.

^1H NMR (400 MHz, DMSO-d_6): δ = 12.3 (br s, 8 H, H9), 8.96 (br s, 8 H, H3), 5.76 (br s, 16 H, H5), 2.83 (t, $^3J_{H7,H8}$ = 6.0–6.8 Hz, 16 H, H7), 2.67 (t, $^3J_{H7,H8}$ = 6.3–6.8 Hz, 16 H, H8).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 173.4 (C9), 172.2 (C6), 151.7 (C1), 137.1 (C2), 135.8 (C4), 123.1 (C3), 64.1 (C5), 28.82 (C7), 28.77 (C8).

Anal. Calcd for $C_{72}H_{64}N_8O_{32}Zn \cdot 5\ H_2O$: C, 50.61; H, 4.36; N, 6.56. Found: C, 50.77; H, 4.31; N, 6.87.

{2,3,9,10,16,17,23,24-Octakis[(*N*-butylcarbamoyloxy)methyl]phthalocyaninato}zinc(II) (19)[14]

Compound **15** (0.10 g, 0.13 mmol) was dissolved in anhyd pyridine (10.0 mL, 124 mmol) by using ultrasound and then BuNCO (0.5 mL, 4.4 mmol) was added and the mixture was stirred in the dark at r.t. for 4 d. Additional amounts of BuNCO were added after 4 d (0.3 mL, 2.7 mmol), 7 d (0.2 mL, 1.8 mmol), and 8 d (0.2 mL, 1.8 mmol), and DMAP (0.1 g, 0.82 mmol, 1 equiv) was added after 5 d. According to TLC (THF), the conversion was still unsatisfactory, hence after 8 d the mixture was warmed to 50 °C for 3 d. Volatiles were removed by evaporation. The residue was dissolved in a minimum of pyridine (4 mL) by the means of ultrasound, precipitated

by dropwise addition to MeCN (40 mL) and centrifuged to yield **19** (0.15 g, 0.10 mmol, 77%) as deep blue crystals; mp >295 °C (dec.).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.20 (br s, 8 H, H3), 7.59 (t, $^3J_{NH,H7}$ = 5.1 Hz, 8 H, NH), 5.70 (br s, 16 H, H5), 3.19 (br d, $^3J_{NH,H7}$ = 5.6 Hz, 16 H, H7), 1.55 (quint, $^3J_{H7,H8}$ = $^3J_{H8,H9}$ = 6.9–7.1 Hz, 16 H, H8), 1.41 (sext, $^3J_{H8,H9}$ = 6.9 Hz, $^3J_{H9,H10}$ = 7.1–7.4 Hz, 16 H, H9), 0.92 (dd, $^3J_{H9,H10}$ = 7.1–7.4 Hz, 24 H, H10).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 156.2 (C1/C6, two overlapping signals), 137.1 (C2), 136.8 (C4), 122.2 (C3), 63.6 (C5), 40.3 (C7, overlap with DMSO-d_6; thus derived from HSQC), 31.6 (C8), 19.5 (C9), 13.6 (C10).

^{1}H NMR (400 MHz, pyridine-d_5): δ = 9.49 (br s, 8 H, H3), 8.09 (br s, 8 H, NH), 6.20 (br s, 16 H, H5), 3.54 (br s, 16 H, H7), 1.75 (br s, 16 H, H8), 1.49 (br d, $^3J_{H9,H10}$ = 6.8 Hz, 16 H, H9), 0.92 (t, $^3J_{H9,H10}$ = 6.8–7.1 Hz, 24 H, H10).

^{13}C NMR (100 MHz, pyridine-d_5): δ = 157.4 (C1/C6), 123.7 (C3), 65.3 (C5), 41.3 (C7), 32.5 (C8), 20.3 (C9), 13.9 (C10) (C2 and C4 overlapping with pyridine-d_5 signals).

Anal. Calcd for $C_{80}H_{104}N_{16}O_{16}Zn$: C, 59.64; H, 6.51; N, 13.91. Found: C, 59.37; H, 6.65; N, 13.83.

{2,3,9,10,16,17,23,24-Octakis[(prop-2-ynyloxy)methyl]phthalocyaninato}zinc(II) (20)

To a vigorously stirred soln of **15** (0.10 g, 0.12 mmol) in DMSO (9 mL) was added aq NaOH (50 wt%, 0.90 mL, 17 mmol) to form a gel-like suspension. Immediately, propargyl bromide (80 wt% in xylene, 1.7 mL, 16 mmol) was added dropwise, and the mixture was further stirred for 3 d in the dark. The resulting suspension was diluted with THF (25 mL) and EtOAc (75 mL), and poured into H_2O (100 mL). The organic phase was separated and consecutively washed with aq 1 M HCl, sat. aq $NaHCO_3$, and brine. The soln was dried (Na_2SO_4) and concentrated to give crude material (450 mg) that was purified by column chromatography (silica gel, PE–EtOAc, 60:40 → EtOAc → THF). Appropriate fractions were combined (180 mg) and evaporated. In order to remove still remaining impurities, the material was precipitated from THF in MeOH and isolated by centrifugation to yield **20** (72 mg, 64 μmol, 53%); mp >360 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.86 (br s, 8 H, H3), 5.18 (br s, 16 H, H5), 4.65 (d, $^4J_{H6,H8}$ = 2.3 Hz, 16 H, H6), 3.72 (t, $^4J_{H6,H8}$ = 2.3 Hz, 8 H, H8).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 151.4 (C1), 137.0 (C2), 136.7 (C4), 121.7 (C3), 80.5 (C7), 77.8 (C8), 69.3 (C5), 57.8 (C6).

MS (MALDI-TOF, anthracene-1,8,9-triol): *m/z* $[M]^+$ calcd for $C_{64}H_{48}N_8O_8Zn$: 1120.2881; *m/z* (%) found: 1120.47 (100), 1122.43 (96), 1121.46 (87), 1123.41 (74), 1124.39 (73), 1125.39 (51), 1126.37 (24).

Anal. Calcd for $C_{64}H_{48}N_8O_8Zn \cdot 2\,H_2O$: C, 66.35; H, 4.52; N, 9.67. Found: C, 66.13; H, 4.37; N, 9.36.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis. Included are NMR, MALDI-TOF, UV-Vis spectra and single-crystal ORTEP plots of selected compounds as well as drawings with assignment of protons and carbons.

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