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First Generation and Trapping of a Dehydrometallophthalocyanine Starting from Triazole-Functionalized Zinc Phthalocyanine

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Abstract: Direct 1*N*-amination of the triazole-fused zinc phthalocyanine **2** and oxidation of the formed amino derivative **3** resulted in the generation of the very reactive intermediate, the dehydrometallophthalocyanine **4**, which was not known previously. The latter was trapped in situ with different dienes, for example, furan, tetraphenylcyclopentadienone, and anthracene to form the corresponding Diels–Alder adducts. The products were characterized by ^{1}H and ^{13}C-dept135 NMR, and UV/Vis spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis, which are fully in agreement with their structure. The developed synthetic procedure opens a simple and versatile pathway towards unsymmetrical peripheral modification of phthalocyanines, which is readily applicable to the micromol scale and is important for the design of new interesting Pc-based systems.

Keywords: cycloaddition · dehydrometallophthalocyanine · phthalocyanines · spectroscopic properties · zinc

Introduction

Unsymmetrical peripheral derivatization of phthalocyanines and their metal complexes (Pcs and PcMs) has received much attention recently.[1] The design of new unsymmetrical Pcs and PcMs is driven by the potential applications of these systems in new fields of materials science.[1,2] Certain unsymmetrical derivatization of phthalocyanines is preferred, for example, for the preparation of self-assembled surface-supported monolayers with the desired mutual orientation of the molecules, for the enhancement of nonlinear optical properties of Pcs and PcMs, for the facilitation of inter- and intramolecular electron- and energy-transfer effects, for the photodynamic therapy in living cells, etc.[1,2] One of the successful synthetic strategies for peripheral derivatization is to find an unsymmetrical Pc synthon capable of being converted into a variety of systems based on phthalocyanines. Among phthalocyanines with AAAB structure,[3] iodo-substituted soluble PcMs were, for example, successfully converted into a variety of differently substituted phthalocyanines such as peripherally bridged binuclear and trinuclear Pc systems.[1] However, the development of new unsymmetrical Pc synthons is still of high importance.

Recently we suggested that a dehydrometallophthalocyanine could also be a versatile synthon for such reactions.[4] Indeed, if the chemical behavior of dehydrometallophthalocyanine is comparable with that of simple dehydroarenes and -hetarenes, the dehydrometallophthalocyanine should participate easily in a variety of reactions, for example, [2+2], [2+3], and Diels–Alder cycloadditions, leading to a plethora of unsymmetric Pc derivatives.[5] A dehydrometallophthalocyanine-related species has not been described so far except for our work on Pc analogues such as arylporphyrazines.[4] We have shown recently that magnesium (dehydrobenzo)porphyrazine can be generated from magnesium (*o*-dibromobenzo)porphyrazine by reaction with a Grignard reagent in the presence of metallic Mg, and a successful trapping of this species was achieved with furan.

Now we have developed a convenient alternative method to generate a dehydrometallophthalocyanine, namely the oxidative decomposition of a 1-amino-1,2,3-triazole-func-

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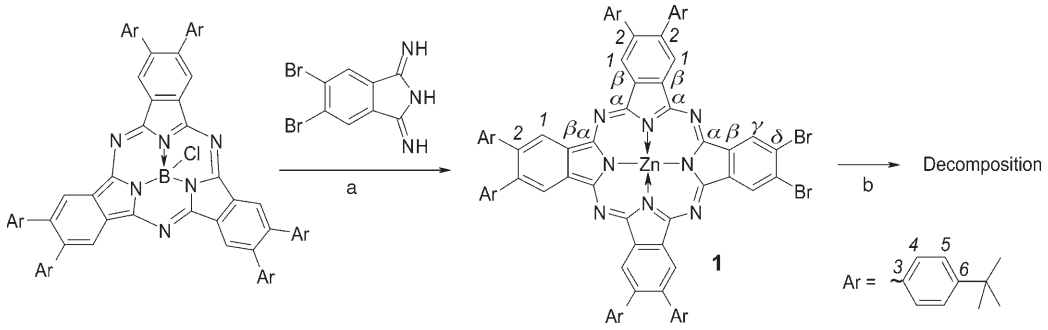
tionalized metal phthalocyanine, which proceeds by a route comparable to the oxidation of 1*N*-aminobenzotriazoles.[6] The dehydrometallophthalocyanine generated by this approach was successfully trapped with different dienes such as furan, tetraphenylcyclopentadienone (TPCD), and anthracene.

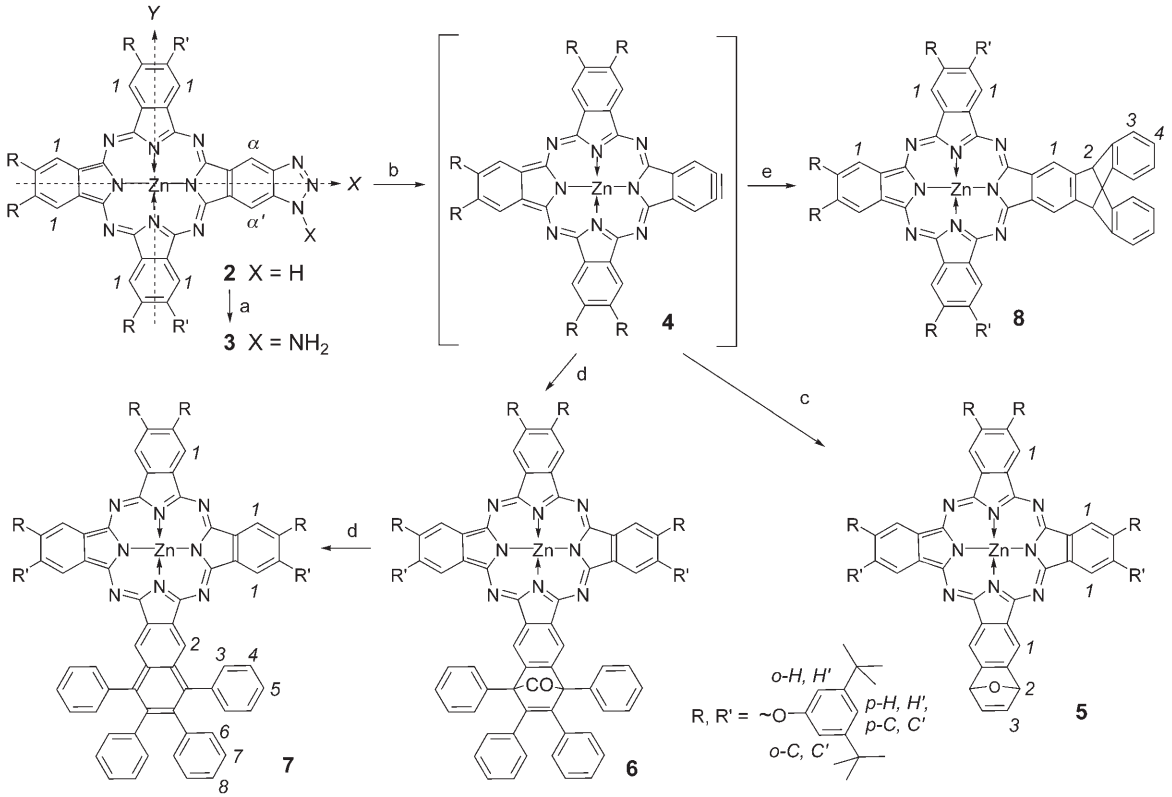
Results and Discussion

We have tried to apply the approach based on halogen–metal exchange on benzoporphyrazines[4] for the generation of a dehydrometallophthalocyanine, starting from functionalized PcMs of AAAB type, that is, containing one o-dibromobenzo moiety (B-part) and solubility-enhancing substituents (A-parts). For example, hexa-(*p-tert*-butylphenyl)dibromophthalocyaninatozinc (**1**) was prepared as shown in Scheme 1 (see also Experimental Section). The reaction of **1** with *n*BuLi or *t*BuMgCl in the presence of furan as described before for magnesium (o-dibromobenzo)porphyrazine[4] resulted, however, in a reduction of the Pc macrocycle, followed by its decomposition before metal–halogen interconversion took place. This is due to the fact that the reductive decomposition of Pcs occurs more easily than of arylporphyrazines.

In our recent work, we described the novel unsymmetrical triazole-fused PcZn **2** (Scheme 2), which displays good solubility in organic solvents.[7] This compound is a phthalocya-



Scheme 1. a) $ZnCl_2$, DMAE, 90 °C, 2–4 h; column chromatography, 56 % yield; b) *t*BuMgCl, Mg, THF/furan, 0–50 °C or *n*BuLi, THF/furan, −90 to −40 °C.



Scheme 2. a) excess DNAP and KOH in THF/H_2O, 45 °C, 20 min, 85 % yield; b) Et_2O + excess of corresponding diene, 1 equiv $Pb(OAc)_4$ in CH_3COOH, room temperature, without isolation; c) furan; column chromatography, 59 % yield; d) TPCD; column chromatography, 61 % yield; e) anthracene; column chromatography, 50 % yield.

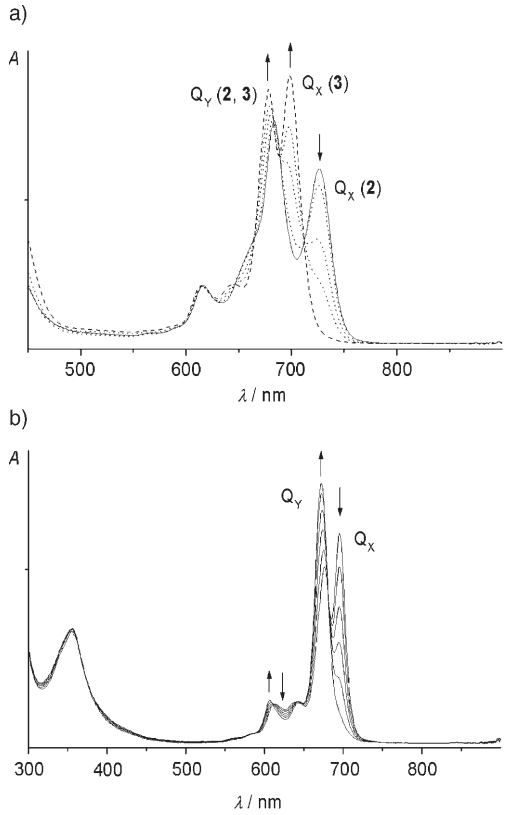


Figure 1. a) Reaction of **2** ($\sim 10^{-4}$ M) with excess DNAP in THF in the presence of a high excess of KOH and traces of water. Recorded in a 1-mm cuvette over a 1 h period at room temperature. b) Titration of **3** in Et_2O/furan solution ($\sim 10^{-5}$ M) by $Pb(OAc)_4$ dissolved in CH_3COOH (RT, 1-cm cuvette). Addition of the last portion resulted in a slight deviation from isobestic points due to oxidation of the Pc macrocycle.

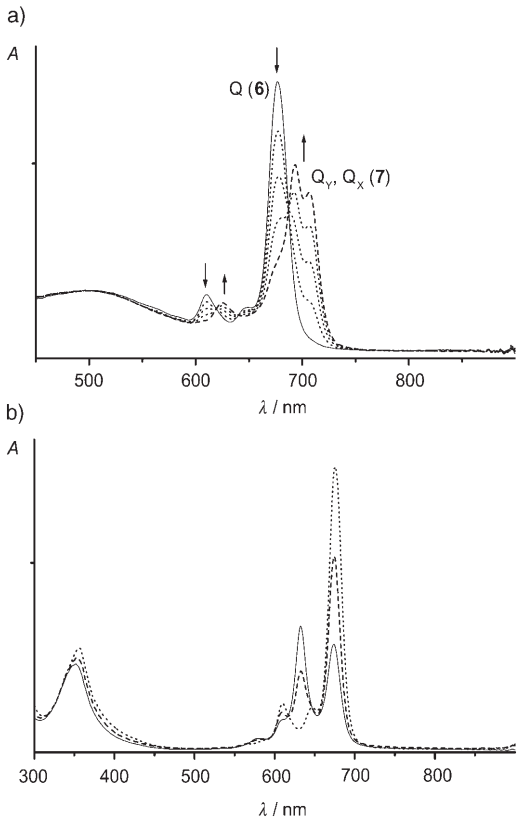


Figure 2. a) Conversion in situ of **6**, obtained by trapping **4** with excess TPCD in Et_2O (RT, 1-mm cuvette), into **7** over a ~1 h period. b) Normalized spectra of **8**: $\sim 1.5 \times 10^{-4}$ M in Et_2O (solid line), 1×10^{-5} M in Et_2O (dashed line), and 1×10^{-5} M in Et_2O/THF 1:1 (dotted line).

nine synthon for peripheral modifications, which should lead to various unsymmetrical Pc systems, taking into account the versatility of reactions known for benzotriazoles.[8] For example, introduction of the triflyl group into the 1-*N* position of the triazole ring in **2** activated the ring towards its opening and coupling with, for example, naphtholate to form an unsymmetrical PcZn conjugated with one azo dye moiety in quantitative yield.[9]

Benzotriazoles and other N-heterocycles can undergo direct *N*-amination with a variety of amino-group transfer reagents. Mainly *O*-hydroxylaminesulfonic acid was used for the amination of 1,2,3-benzotriazoles to yield 1*N*- and 2*N*-aminobenzotriazoles as mixtures or nearly as pure compounds depending on the reaction conditions.[6,10] Our attempts to apply *O*-hydroxylaminesulfonic acid to aminate **2** failed, in each case only the starting material was recovered. Therefore, another NH_2-group transfer reagent was used for the amination of **2**, namely 2,4-dinitro-*O*-aminophenol (DNAP).[10b,11] A test reaction of **2** (in a cuvette) with a large excess of DNAP and aqueous KOH in THF, which was monitored by UV/Vis spectroscopy, resulted in the conversion of **2** into the amino derivative **3** (see Figure 1a). Because of N–H dissociation in the triazole ring of **2** in the presence of strong bases, the Q_x band of **2** shows a notable red shift compared to the band in the spectrum in neutral solvents, whereas the Q_y band remains practically unaffected.[7] Introduction of a substituent such as $CH_3C(O)$-,[7] $CF_3S(O)_2$-,[9] or NH_2- into the triazole ring of **2** under basic conditions results in a hypsochromic shift of the Q_x-band maximum. A complete disappearance of the red-shifted Q_x band and the presence of isobestic points (see Figure 1a) in the course of the amination reveals the quantitative conversion of **2** into **3**. By applying this reaction on a preparative scale, it was found that the yield of **3** depends strongly on the reaction conditions, for example on the ratio of the reagents, temperature, and reaction time. The optimized synthesis is given in the Experimental Section.

Despite the similarity of the UV/Vis spectra of **2** and **3** in neutral solution, ^{1}H NMR, ^{13}C NMR, and MALDI-TOF spectra as well as elemental analysis of **3** prove unambiguously that it is a pure 1*N*-amino derivative. In addition, the chemical behavior of **3** and **2** differed considerably. Thus, when about one equivalent of $Pb(OAc)_4$ was added to a solution of **2** in diethyl ether/furan (~10:1) at room temperature, a simultaneous decrease of both the Q_x and Q_y absorption bands occurs because of a macrocycle oxidation, whereas in case of **3** the same procedure leads to the disappearance of the Q_x band and the growth of the Q_y band (see Figure 1b). This indicates that the reaction of **3** with $Pb(OAc)_4$

leads to an oxidation and the subsequent decomposition of the aminotriazole moiety with formation of an intermediate highly reactive dehydrometallophthalocyanine **4**, which undergoes trapping with furan (Scheme 2). When **4** is generated in the presence of an excess of other dienes, for example, tetraphenylcyclopentadienone (TPCD) or anthracene, the corresponding cycloaddition compounds **6** (**7**) and **8** are formed as the main products. The TPCD cycloadduct **6** is formed immediately upon addition of $Pb(OAc)_4$ to **3** in Et_2O at room temperature with a 20–30 fold excess of TPCD. Compound **6** undergoes aromatization of the 1,4-dihydro-1,4-methanonaphthalene-9-one fragment with the loss of CO in situ, resulting in the formation of **7**, which could be monitored by UV/Vis spectroscopy (see Figure 2a). On a preparative scale, **3** was converted into **5** or **7**, respectively, in about 60% yield and into **8** in 50% yield after purification by column chromatography.

The developed approach for the derivatization of a Pc, therefore, is versatile, simple, and allows one to work in micromol scale, which facilitates the empirical search for unsymmetrical Pc systems with the requested properties.

UV/Vis spectra of the compounds **5**, **6**, **7**, and **8** are rather typical and correspond to their structures from a theoretical point of view. Thus, **5**, **6**, and **8** dissolved in THF show an intense Q-band at approximately 680 nm, indicating no strong perturbation of the π-electron system of phthalocyanine despite the AAAB structure and lowered symmetry. In contrast, **7** shows a noticeable splitting and red shift of the Q-band because of the influence of the additional annulated benzene ring in the B-part of the macrocycle. Surprisingly, a second blue-shifted sharp Q-band with concentration-dependent intensity was observed for **8** in Et_2O (see Figure 2b), probably due to a preferential π–π dimerization rather than the formation of heavier aggregates in this solvent, which was not noticed for other derivatives described here. It was also observed that **8** undergoes a facile oxidation in halomethane solvents even in the absence of daylight. Further studies on **8** are in progress.

The structures of **5**, **7**, and **8** were unambiguously proven by ^1H and ^{13}C NMR, and MALDI-TOF spectra, as well as by elemental analysis (see Experimental Section). Thus, a comparison of the ^1H NMR patterns of compounds **2**, **3**, **5**, and **7** in the aromatic region (see Figure 3 and Scheme 2 for the designation) shows the characteristic differences of the patterns that correlate perfectly with the structures of compounds. It is especially noticeable for the protons of the Pc–macrocycle, for example H-1, H-α, and H-2. Furthermore,

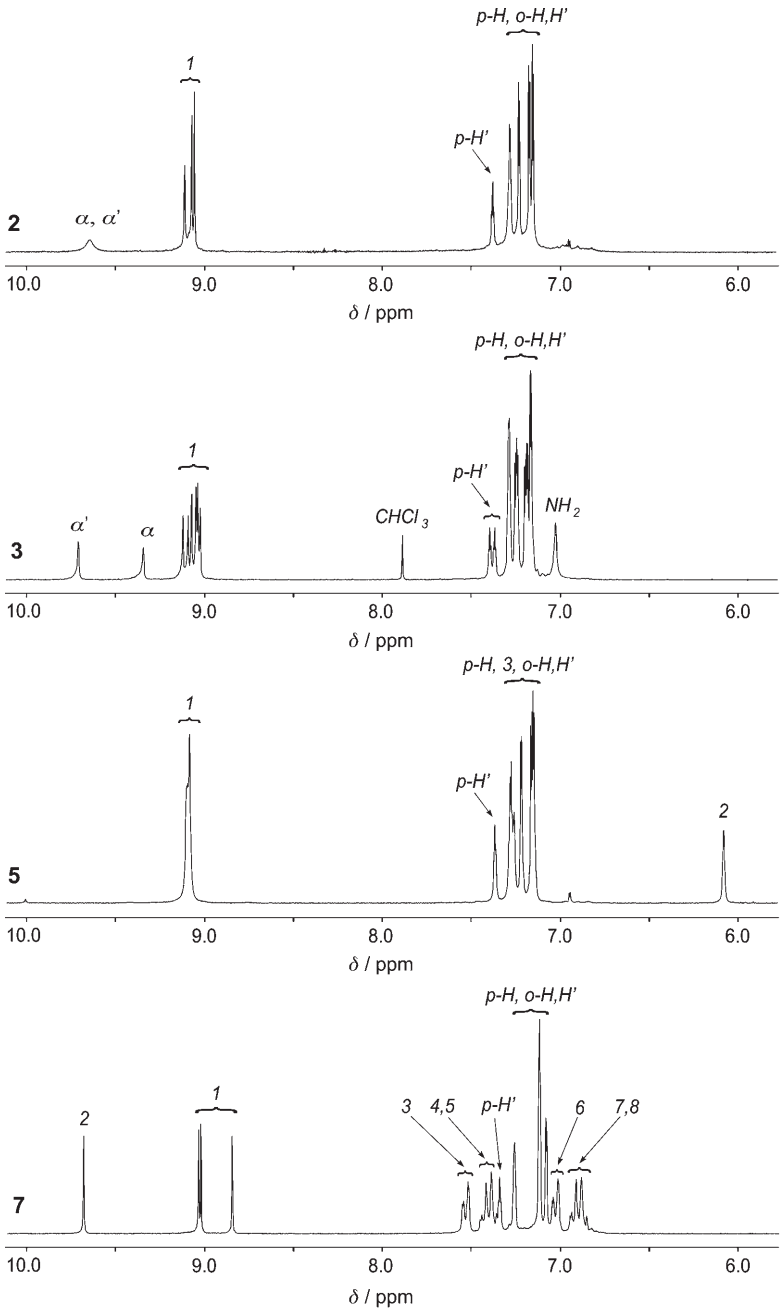


Figure 3. ^1H NMR spectra of **2**, **3**, **5**, and **7** in the aromatic region.

additional characteristic signals arise from the corresponding functional groups and new fragments of compounds **3**, **5**, **7**, and **8** both in ^{1}H and ^{13}C-dept135 NMR spectra (the dept135 pulse program does not show quaternary carbon atoms and was used for the simplicity). ^{1}H NMR spectra of **8** both in [D_8]THF and $CDCl_3$ were somewhat complicated due to broadening of the signals, probably, because of the observed unusual properties of this compound which were described above (see Experimental Section for the ^{1}H NMR data).

The following observations concerning the generation of the dehydrometallophthalocyanine **4** by the described approach have to be considered. Reaction of **3** with $Pb(OAc)_4$ also leads to an oxidation of the macrocycle as a side reaction, although the rate of this process depends strongly on the nature of solvent. In benzene or CH_2Cl_2, oxidation of the Pc macrocycle competes with the oxidation of aminotriazole moiety, whereas in Et_2O or THF nearly complete oxidation of the aminotriazole fragment occurs before the macrocycle undergoes a one-electron oxidation (see Figure 1 b). The latter oxidation is quasi-reversible, since one-electron oxidized Pc species slowly decompose in solution. These can be reduced back in situ if a reducing agent such as $NaBH_4$ or catechol is rapidly added. Thus, the cation radical species formed in the reaction of **3** with a slight excess of $Pb(OAc)_4$ in Et_2O/furan gave the typical absorption bands for Pc radicals, namely a broad low-intense absorption band at 850 nm and increased absorption in the 400–600 nm spectral window in the UV/Vis spectra of the reaction mixture, when recorded in CH_2Cl_2.[12] Disappearance of the band at 850 nm and growth of the Q-band is observed upon reduction of this solution. On TLC, the oxidized species or the product of its decomposition runs as a red spot with the highest R_f value, which is not observed after reduction.

In conclusion, we have shown that triazole-functionalized phthalocyanine is a synthon for the unsymmetrical modifications of the periphery of Pcs, including the generation of the previously unknown intermediate species, a dehydrometallophthalocyanine. The latter is shown to be a very active dienophile and an important synthon, as well. Further investigations on its reactivity are in progress, especially the study of dehydrometallophthalocyanine from a theoretical point of view as well as, if possible, its spectral characteristics.

Experimental Section

General: Hexakis(*p-tert*-butylphenyl)subphthalocyaninatoboron chloride,[13] 5,6-dibromo-1,3-diiminoisoindoline,[14] 2,4-dinitro-*O*-aminophenol,[11] and 9,10,16,17,23,24-hexakis-(3,5-bis-*tert*-butylphenoxy)-[1,2,3]triazole[4,5-*b*]phthalocyaninatozinc (**2**),[7] were prepared as described. Diethyl ether was purified by refluxing with maleic anhydride (10 g per 300 mL) for 24 h, followed by distillation. Other chemicals and solvents were purchased from commercial sources and were used without additional purification.

Instrumentation: UV/Vis: Shimadzu UV-365; ^{1}H and ^{13}C NMR: Bruker AC 250 (^{1}H: 250.131 MHz, ^{13}C: 62.902 MHz); MS (MALDI-TOF): Bruker Autoflex; elemental analysis: Euro EA 3000.

9,10,16,17,23,24-Hexakis(*p-tert*-butylphenyl)-2,3-dibromophthalocyaninatozinc (1): Hexakis(*p-tert*-butylphenyl)subphthalocyaninatoboron chloride (200 mg, 0.164 mmol), 5,6-dibromo-1,3-diiminoisoindoline (200 mg, 0.66 mmol), and anhydrous $ZnCl_2$ (100 mg, 0.74 mmol) were heated in *N*,*N*-dimethyl-2-aminoethanol (10 mL) at 90 °C for 2–4 h. After the mixture had been cooled, water (50 mL) was added. The precipitate was separated by centrifugation and washed thoroughly with methanol. After drying, the solid was chromatographed on silica (CH_2Cl_2 + 1–5 % THF) and the solvent was rotary evaporated to give **1** (140 mg; 56 %).

Elemental analysis calcd (%) for $C_{92}H_{86}N_8Br_2Zn\cdot 2H_2O$, M_r = 1529(+36): C 70.61, H 5.80, N 7.16; found C 70.74, H 5.92, N 6.34; ^{1}H NMR (250 MHz, [D_8]THF, 25 °C): δ = 1.43, 1.44 (2 s, 54 H; C(CH_3)$_3$); 7.44–7.58 (m, 24 H; H-4, H-5); 9.06 (s, 2 H; H-1, H-γ), 9.25 (s, 2 H; H-1, H-γ), 9.40 (s, 4H; H-1, H-γ) ppm; ^{13}C NMR (62.9 MHz, [D_8]THF, 25 °C): δ = 31.87, 31.90 (2 s; C(CH_3)$_3$); 35.24, 35.26 (2 s; *C*(CH_3)$_3$); 125.10, 125.24, 125.56 (3 s; C-1); 125.24 (s; C-δ); 125.70 (s; C-5); 127.88 (s; C-γ); 131.07, 131.12, 131.14 (3 s; C-4); 138.54, 138.59, 139.09, 139.10 (4 s, C-β); 140.45, 140.48 (s, C-3); 142.92, 143.05, 143.32 (3 s, C-2); 150.34, 150.39, 150.41 (3 s; C-6); 151.11, 154.24, 155.61, 156.08 (4 s; C-α) ppm; UV/Vis (THF): λ_{max} (rel. int.) = 688 (1.00), 619 (0.169), 362 (0.393); MALDI-TOF: *m*/*z* (%): 1528.5 (100) [M^+].

9,10,16,17,23,24-Hexakis(3,5-bis-*tert*-butylphenoxy)(1-amino[1,2,3]-triazole[4,5-*b*]phthalocyaninatozinc (3): Compound **2** (40 mg, 21.7 μmol) was dissolved in THF (3 mL), followed by addition of solid KOH (570 mg, 10.2 mmol) and H_2O (1 mL). The formed two-phase solution was warmed up to 45 °C with good stirring, and 2,4-dinitro-*O*-aminophenol (100 mg, 0.5 mmol) was added in one portion. The reaction mixture was stirred at 45 °C for 20 min, and ice–water (40 mL) was added. The formed dark brown solution was stirred in the open flask for another 20 min, the resulting precipitate was filtered off and washed thoroughly with 75 % aqueous acetonitrile until no UV absorption (up to 240 nm) was observed for the filtrate. The residue was dissolved in Et_2O and precipitated by addition of methanol and slow evaporation of Et_2O. The precipitate was decanted and dried in vacuo to give **3** (34 mg; 85 %) with the purity equivalent to that obtained after column chromatography, according to ^{1}H NMR spectroscopy. Chromatographic purification is also possible and can be carried out on silica gel with $CHCl_3$ or CH_2Cl_2 with gradual addition of Et_2O, but it may result in a lowered yield due to decomposition of **3** and its deamination during chromatography. The control of the conversion of **2** into **3** was carried out by TLC (CH_2Cl_2 + 1–5 % Et_2O, **3** has a higher R_f value than **2**) and by UV/Vis spectroscopy in THF in the presence of aqueous KOH (no red-shifted band or shoulder should be observed in the case of complete conversion, see Results and Discussion).

Elemental analysis calcd (%) for $C_{116}H_{136}N_{12}O_6Zn\cdot Et_2O$, M_r = 1860 (+74): C 74.53, H 7.61, N 8.69; found: C 74.68, H 7.69, N 8.61; ^{1}H NMR (250 MHz, [D_8]THF, 25 °C): δ = 1.12 (t, $^3J \approx 6.8$ Hz, ~6 H; (CH_3CH_2)$_2$O); 1.36, 1.42 (2 s, 108 H, C(CH_3)$_3$); 3.39 (q, $^3J \approx 6.8$ Hz, ~4 H; (CH_3CH_2)$_2$O); 7.03 (br. s, 2 H; NH_2); 7.17–7.30 (m, 16 H; *o*-H,H′; *p*-H); 7.38, 7.41 (2 t, $^4J \approx 1.6$ Hz, 2 H; *p*-H′); 9.03, 9.04, 9.05, 9.08, 9.10, 9.13 (6 s, 6 H; H-1); 9.35 (s, 1 H, H-α); 9.72 (s, 1 H, H-α′) ppm; ^{13}C NMR-dept135 (62.9 MHz, [D_8]THF, 25 °C): δ = 16.1 (s; (CH_3CH_2)$_2$O); 31.55 (s; C(*C*H_3)$_3$); 67.6 (s; (CH_3CH_2)$_2$O); 104.0 (s; C-α); 112.77, 112.93, 112.97, 113.01, 113.52, 113.80 (6 s; *o*-C,C′); 114.11, 114.47, 114.55, 114.66, 114.96 (5 s; C-1); C-α and one C-1 carbon signals are covered in the region 113.35–113.90 ppm; 117.40, 117.49 three overlapping singlets, 117.88, 118.10 (s; *p*-C,C′) ppm; UV/Vis (CH_2Cl_2 + 1 % Et_2O): λ_{max} (log(ε)) = 699 (5.29), 683 (5.23), 648 (shoulder), 619 (4.57), 353 (4.97), 291 (4.75); MALDI-TOF: m/z (%): 1859.7 (34) [M^+], 1831.7 (100) [$M^+ - N_2$], overlaps with [$M^+ - N_2$ + 2 H], see Figure 1 in the Supporting Information.

Generation of 9,10,16,17,23,24-hexakis(3,5-bis-*tert*-butylphenoxy)-2,3-dehydrophthalocyaninatozinc (4) and its trapping with dienes: general procedure: Compound **3** (17 mg, 8.8 μmol) and excess diene were dissolved in diethyl ether, purified as described above. A 54.6 mM solution of $Pb(OAc)_4$ in acetic acid was added, the reaction mixture was stirred for few minutes (the course of reaction can be monitored by TLC or UV/Vis spectroscopy), and a reducing agent was added (the red spot for the oxidized species on TLC should disappear). The solvent was removed by

rotary evaporation, the residue was dried in vacuo, and the product was separated by column chromatography (silica gel, CH_2Cl_2 with gradual addition of Et_2O) as a first large green or bluish-green fraction (excess of TPCD or anthracene were eluted with pure CH_2Cl_2). After rotary evaporation of the solvent, the residue was washed with methanol by decantation to give pure **5**, **7**, or **8**.

9,10,16,17,23,24-Hexakis(3,5-bis-*tert*-butylphenoxy)(1,4-dihydro-1,4-epoxybenzo)[2,3-*b*]phthalocyaninatozinc (5): Used for the synthesis: furan (0.4 mL), Et_2O (1 mL), $Pb(OAc)_4$ solution (0.17 mL, 9.3 μmol, added dropwise at 0 °C), and $NaBH_4$ (few small crystals). Yield 10 mg (59 %).

Elemental analysis calcd (%) for $C_{120}H_{138}N_8O_7Zn{\cdot}Et_2O$, $M_r = 1870$ (+74): C 76.61, H 7.67, N 5.76; found: C 76.26, H 7.55, N 5.65; ^{1}H NMR (250 MHz, [D$_8$]THF, 25 °C): $\delta = 1.11$ (t, $^3J \approx 6.8$ Hz, ~6H; $(CH_3CH_2)_2O$); 1.34, 1.40, (2s, 108H; $C(CH_3)_3$); 3.39 (q, $^3J \approx 6.8$ Hz, ~4H; $(CH_3CH_2)_2O$); 6.08 (s, 2H; H-2); 7.14–7.18 (m, 8H; *o*-H); 7.22 (d, $^4J \approx 1.6$ Hz, 4H; *o*-H′); 7.26 (br. s, 2H; H-3); 7.28–7.30 (m, 4H; *p*-H); 7.38 (t, $^4J \approx 1.6$ Hz, 2H; *p*-H′); 9.09–9.12 ppm (m, 8H; H-1); ^{13}C NMR-dept135 (62.9 MHz, [D$_8$]THF, 25 °C): $\delta = 16.1$ (s; $(CH_3CH_2)_2O$); 31.51 (s; $C(CH_3)_3$); 67.6 (s; $(CH_3CH_2)_2O$); 83.13 (s; C-2); 112.72, 113.01, 113.59 (3s; *o*-C,C′); 113.61, 114.54, 114.69, 115.09 (4s; C-1); 117.40, 117.57, 117.96 (3s; *p*-C,C′); 143.81 ppm (s; C-3); UV/Vis (CH_2Cl_2 + 1% Et_2O): λ_{max} (log(ε)) = 677 (5.38), 646 (shoulder), 610 (4.62), 354 (5.01), 288 (4.80); MALDI-TOF: *m*/*z* (%): 1871.3 (100) [*M*H$^+$].

9,10,16,17,23,24-Hexakis(3,5-bis-*tert*-butylphenoxy)(1,2,3,4-tetraphenylbenzo)[5,6-*b*]phthalocyaninatozinc (7): Used for the synthesis: tetraphenylcyclopentadienone (TPCD; 70 mg, 182 μmol), Et_2O (30 mL), $Pb(OAc)_4$ solution (0.16 mL, 8.7 μmol; added at once at room temperature), and $NaBH_4$ (one-two small crystals). Yield 12 mg (61 %).

Elemental analysis calcd (%) for $C_{144}H_{154}N_8O_6Zn{\cdot}Et_2O$, $M_r = 2158$ (+74): C 79.63, H 7.40, N 5.02; found: C 79.28, H 7.44, N 4.87; ^{1}H NMR (250 MHz, [D$_8$]THF, 25 °C): $\delta = 1.11$ (t, $^3J \approx 6.8$ Hz, ~6H, $(CH_3CH_2)_2O$); 1.32, 1.37 (2s, 108H, $C(CH_3)_3$); 3.38 (q, $^3J \approx 6.8$ Hz, ~4H;, $(CH_3CH_2)_2O$); 6.86–6.96 (m, 6H; H-7,8); 7.02–7.06 (m, 4H; H-6); 7.09, 7.13 (2s, 12H; *o*-H); 7.27 (br. s, 4H; *p*-H); 7.36 (t, $^4J \approx 1.5$ Hz, 2H; *p*-H′); 7.37–7.47 (m, 6H; H-4,5); 7.52–7.57 (m, 4H; H-3); 8.86, 9.03, 9.04 (3s, 6H; H-1); 9.69 ppm (s, 2H; H-2); ^{13}C NMR-dept135 (62.9 MHz, [D$_8$]THF, 25 °C): $\delta = 16.1$ (s; $(CH_3CH_2)_2O$); 31.49, 31.52 (2s; $C(CH_3)_3$); 67.6 (s; $(CH_3CH_2)_2O$); 112.71, 112.87, 113.02 (3s, *o*-C,C′); 114.48 (two overlapping singlets), 114.65 (3s, C-1); 117.46 (three overlapping singlets) (3s; *p*-C,C′); 122.20 (s; C-2); 125.94, 127.41 (2s; C-5, C-8); 127.12, 128.30, 131.99, 132.27 ppm (4s; C-3, C-4, C-6, C-7); UV/Vis (THF): λ_{max} (log(ε)) = 708 (shoulder), 697 (5.36), 629 (4.68), 354 (5.10); MALDI-TOF: *m*/*z* (%): 2158.7 (100) [*M*H$^+$], 2175.7 (14) [M^++H$_2$O].

9,10,16,17,23,24-Hexakis(3,5-bis-*tert*-butylphenoxy)-2,3-(9,10-dihydroanthracene-9,10-diyl)phthalocyaninatozinc (8): Used for the synthesis: anthracene (70 mg, 0.4 mmol), Et_2O (15 mL), $Pb(OAc)_4$ solution (0.16 mL, 8.7 μmol; added at once at room temperature), and 4-*tert*-butyl catechol as a reducing agent (few milligrams). Yield 9 mg (50 %). *Note*: **8** oxidizes apparently on TLC when eluted with CH_2Cl_2.

Elemental analysis calcd (%) for $C_{130}H_{144}N_8O_6Zn{\cdot}2\,CH_3OH$, $M_r = 1980$ (+64): C 77.56, H 7.50, N 5.48; found: C 77.28, H 7.69, N 5.31; ^{1}H NMR (250 MHz, [D$_8$]THF, 25 °C): $\delta = 1.34$, 1.35, 1.42 (3s, 108H, $C(CH_3)_3$); 3.25 (s, ~6H; CH_3OH); 5.98 (br. s, 2H; H-2); 7.03–7.07 (m with AA′BB′ pattern, 4H; H-4); 7.15–7.30 (m, 16H; *o*-H,H′, *p*-H); 7.39 (m, non-resolved, 2H; *p*-H′); 7.56–7.65 (m, non-resolved, 4H; H-3); 9.04–9.30 ppm (m, 8H; H-1); ^{1}H NMR in $CDCl_3$ + [D$_8$]THF (~5–10 %) shows the sharpening and increased resolution of peaks from H-2 and H-3 immediately after dissolving, followed by a decrease, broadening, and splitting of the macrocyclic proton signals with time. The origin of this effect is not clear yet and it will be studied in our subsequent work. UV/Vis (THF): λ_{max} (log(ε)) = 677 (5.46), 648 (4.61), 611 (4.66), 357 (5.05); MALDI-TOF: *m*/*z* (%): 1980.9 (100) [*M*H$^+$], 1998.9 (10) [*M*H$^+$ + H$_2$O].

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