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Reactivity of Dehydrometallophthalocyanines and -porphyrazines

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Abstract: The zinc dehydrophthalocyanine **2** and zinc dehydrobenzoporhyrazine **8a** were generated from the 1*N*-aminobenzotriazole-annulated zinc phtalocyanine **1** and zinc benzoporhyrazine **8**, respectively, by oxidation with $Pb(OAc)_4$ in different solvents, for example, diethyl ether, tetrahydrofuran, acetic acid, and benzene. The reactivity of **2** and **8a** was studied in detail. These species not only easily undergo Diels–Alder additions with dienes, but also the used solvents can be added. Among the addition products with solvents ethoxy-, acetoxy-, acetoxybutyloxy-substituted and barrelen-fused phthalocyanines and benzoporpyrazines were isolated. No products resulting from the dimerization of two dehydro species were observed either for **2** or **8a**. Analysis of the reaction products in comparison with those obtained by oxidation of 1-aminobenzotriazole **15** under similar conditions proves a higher reactivity (electrophilicity) of the dehydro-PcZn **2** and dehydro-PzZn **8a** in comparison with unsubstituted benzyne towards the solvents used, such as diethyl ether and benzene.

Keywords: benzyne · dehydrobenzoporphyrazines · dehydrophthalocyanines · phthalocyanines · zinc

Introduction

We have shown recently that both a metal dehydrobenzoporphyrazine[1] as well as a metal dehydrophthalocyanine[2] can be generated as short-lived intermediates and used as synthons for the preparation of different unsymmetrically substituted phthalocyanines, for example.

Different methods were tried to generate these intermediates, one of which involved the formation of macrocyclic dehydro-species from *ortho*-dihaloderivatives by using particular metal–organic compounds.[1] Superposition of the macrocycle reactivity with the desired metal–halogen interconversion has to be taken into account in this case. For example, if 2,3-dibromobenzo-anulated magnesium porphyrazine is reacted with butyllithium, mainly the porphyrazine macrocycle reacts with it to form corresponding tetraazachlorine and other reduction products. Use of *tert*-butylmagnesium chloride in the presence of metallic magnesium instead of BuLi leads on the other hand to the formation of a dehydrobenzoporphyrazine analogous to **8a**, which was trapped with furan.[1] We also tried to apply the same approach for the generation of a metal dehydrophthalocyanine, starting from functionalized metal phthalocyanines (PcM's) of AAAB-type, that is, containing one *o*-dibromobenzo moiety (B part) and three solubility enhancing substituents (A parts). However, the reaction of such compounds with *n*BuLi or *t*BuMgCl in the presence of furan resulted only in a reduction of the Pc macrocycle, followed by its decomposition before metal–halogen interconversion took place.[2] The reductive decomposition of Pc's thereby occurs more easily than of benzoporphyrazines.

Therefore we applied an alternative method to generate metal dehydrophthalocyanines, namely the oxidative decomposition of a 1-amino-1,2,3-triazole-functionalized metal phthalocyanine, which proceeds by a route comparable to the oxidation of 1*N*-aminobenzotriazole.[2] The zinc dehydrophthalocyanine (**2**) generated by this approach (see

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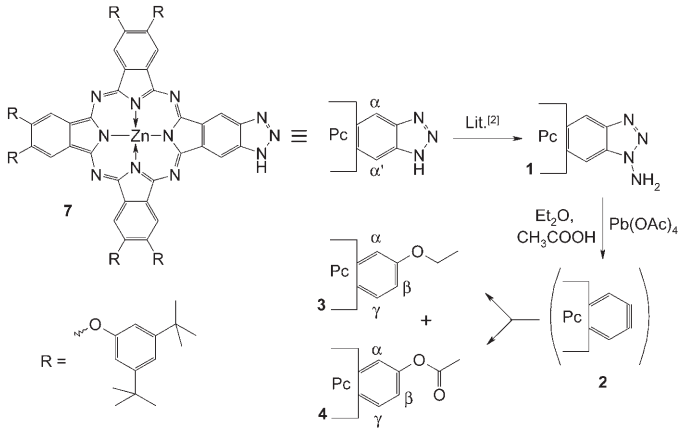
Scheme 1) was successfully trapped with different dienes, such as furan, tetraphenylcyclopentadinone, antracene, and so forth. By using diethyl ether as a solvent and excess of the mentioned dienes, the corresponding Diels–Alder cycloaddition products of dehydro-PcZn **2** were formed in 50–60% yield.[2]



Scheme 1.

In the following we report about more detailed investigations concerning the reactivity of zinc dehydrophthalocyanine **2** and zinc dehydrobenzoporphyrazine **8a**, generated from the corresponding 1*N*-aminotriazole-annulated macrocycles **1** (see Scheme 1) and **8**, respectively (see Scheme 2, later) upon oxidation with $Pb(OAc)_4$ under different conditions.

Results and Discussion

More detailed studies for the generation of dehydro-PcZn **2** form **1** exhibited clearly that the conditions of this reaction have to be quite specific. Thus, in Et_2O the amount of $Pb(OAc)_4$ cannot exceed one equivalent, otherwise in addition to the oxidation of the aminotriazole moiety in **1**, an oxidation of the macrocycle takes place. Moreover, if weakly or non-coordinating solvents, such as halomethanes, toluene, benzene, and so forth, are used, oxidation of the macrocycle competes noticeably with the desired aminotriazole oxidation. Coordinating solvents of N-basic nature, for example, pyridine and amines, could also not be applied, because they either drastically decrease the oxidizing potential of $Pb(OAc)_4$ or undergo a reaction with this oxidant, so that no generation of dehydro-PcZn **2** from PcZn **1** was observed even in the presence of excess $Pb(OAc)_4$.

We also investigated whether a [2+2] addition of two molecules of **2** can occur in absence of trapping reagents, as known, for example, for dehydrobenzene yielding biphenylene.[3] The corresponding dimer formed from **2** is expected to exhibit interesting optical and electronic properties.[4]

If **2** is generated in diethyl ether in the same manner as described in our previous work (a saturated solution of $Pb(OAc)_4$ in acetic acid was utilized to oxidize **1**),[2] but in absence of dienes, only a mixture of ethyloxy- (**3**) and the acetoxy- (**4**) derivatives (see Scheme 1) is formed in good yield. Although **3** and **4** could not be separated by column chromatography, both were clearly identified using MALDI-TOF and ^1H and ^{13}C NMR spectroscopy (see Supporting Information).

Formation of **3** and **4** results from the addition of the weak nucleophiles such as diethyl ether acid acetic and, respectively, to the triple bond of the generated zinc dehydrophthalocyanine **2**. The addition of carboxylic acids to benzyne has been known for a long time.[5a,b] Reaction of diethyl ether with differently substituted benzynes via the formation of a betaine and its subsequent cleavage leads to phenetole derivatives.[3] Though the cleavage of diethyl ether by unsubstituted benzyne is not reported, the more electrophilic tetrahalobenzynes give tetrahalophenetoles upon reaction with diethyl ether.[3,5c] Ethers of higher nucleophilicity, however, can react also with the unsubstituted benzyne. For example, the betaine formed by addition of 1,2-dimethoxyethane to benzyne was trapped and isolated.[3] Additional examples of insertion of arynes into σ-bonds are summarized in reference [5d].

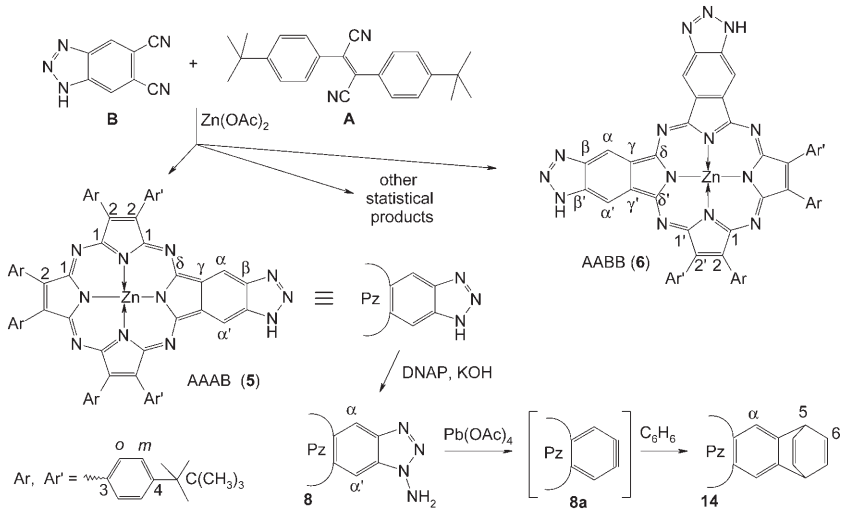
Therefore neither ethers nor carboxylic acids should be applied as solvents if dimerization of **2** is attempted. The conditions for the formation of biphenylene by dimerization of benzyne generated from 1-amino-benzotriazole were described by Campbell and Rees.[6] Thus, mixing solutions of $Pb(OAc)_4$ and 1-amino-benzotriazole in benzene or CH_2Cl_2 at room temperature gave excellent yields (up to 82%) of biphenylene; no adducts with solvents were mentioned.[6] As described above, **1** cannot be oxidized in either solvent, since a noticeable oxidation of Pc macrocycle occurs under these conditions. Up to now a Pc dimer comparable to biphenylene therefore could not be obtained.

An increase of the oxidation potential of the macrocycle in **1** by altering its structure, the peripheral substituents, or the central metal could stabilize the macrocycle against oxidation by $Pb(OAc)_4$ in solvents other than ethers.

We have observed earlier that for example, aryl-substituted porphyrazines possess higher photostability in solutions in comparison with soluble phthalocyanines,[7] and they have higher oxidation resistance.

This prompted us to synthesize aryl-porphyrazines bearing an annulated benzotriazole moiety by applying cross-condensation of bis(4-*tert*-butylphenyl)fumaronitrile (**A**) and 5,6-dicyano-1*H*-benzotriazole (**B**) in the presence of zinc acetate as described in the Experimental Section (see also Scheme 2). This reaction gave all possible statistical cross-condensation products, which were observed by UV/Vis spectroscopy during their chromatographic separation.

Due to the low yield and low solubility of some of the statistical products, we confined ourselves to the isolation and characterization of only two of them, namely the AAAB (**5**) and AABB[8] (**6**) species (the B part contains the triazole ring), shown in Scheme 2.



Scheme 2.

AAAB porphyrazine **5** is structurally related to monotriazole-annulated zinc phthalocyanine **7** (Scheme 1).[9] Investigation of its spectral properties (UV/Vis, ^{1}H and ^{13}C NMR) revealed many similarities between **5** and **7**.

In the UV/Vis spectra, the Q-band is split into two components (Q_x and Q_y) for **5** and **7**, and the Q_x component undergoes a red shift under strong basic conditions in both cases. It was therefore not surprising, that the method for amination of triazole ring of **7**, described earlier,[2] was also suitable for the introduction of the amino group into the triazole ring of **5**, leading to the NMR-pure 1*N*-amino compound **8**.

No oxidation of the macrocycle occurs when **8** is treated with $Pb(OAc)_4$ in diethyl ether or benzene, even in the presence of excess oxidizing agent (see results of spectrophotometric titrations in the Supporting Information), which was not the case for complex **1**. This confirms the expected increase of macrocycle oxidation stability when passing from phthalocyanine to monobenzoporphyrazine. However, immediate decomposition of **8** was observed when the oxidation was carried out in CH_2Cl_2 or 1,2-dichloroethane; this decomposition is due to the easy formation of free radicals in these solvents under action of $Pb(OAc)_4$, which usually causes fast decomposition of Pc-like macrocycles.[10] An alternative or additional reason could be the much higher oxidizing potential of lead(IV) in non-coordinating or poorly solvating media. A distinct stabilization of zinc porphyrazine **8** upon different solvation effects must also be considered.

In spite of the insolubility of $Pb(OAc)_4$ in hexane or cyclohexane and very poor solubility of **8** in these solvents, oxidation of **8** was observed as a heterogeneous process taking place on the surface of lead tetraacetate crystals. Also in these systems oxidation of both the aminotriazole moiety and the macrocycle took place as parallel processes.

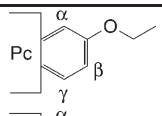
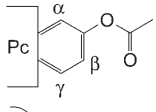
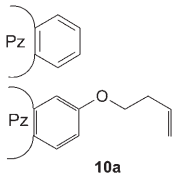
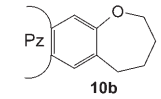
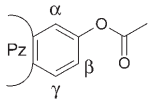
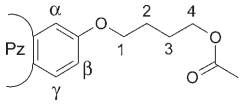
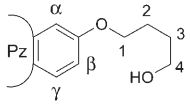
Among common solvents, tetrahydrofuran was found to dissolve **8** reaching the highest concentrations without noticeable aggregation, as seen by ^{1}H and ^{13}C NMR spectroscopy, which is preferable for conducting the [2+2] dimerization of this macrocycle via dehydrobenzoporphyrazine **8a**. However, THF is a cyclic ether and should react with **8a** similarly to the reaction of zinc dehydrophthalocyanine **2** with diethyl ether. To verify the reaction pathways of **8a** in THF, the oxidation of **8** was carried out in this solvent.

At least six products were found by TLC for this reaction. They were analyzed by MALDI-TOF and ^{1}H and ^{13}C NMR spectroscopy, when possible, to determine their structures taking into account the known literature data on the reaction of THF with benzyne and tetrahalobenzynes.[11,12] The least polar fraction contained mainly three compounds with $m/z = 1220$, 1291, and 2540 among other minor peaks in MALDI-TOF spectra, which could not be separated and unambiguously ascribed on the basis of ^{1}H NMR spectroscopy. The first two peaks in MALDI correspond to structures **9** (no substituents in the benzo ring) and **10** (1-buten-4-yloxy-substituted **10a** or its cyclic isomer **10b** or their mixture), respectively (see Table 1), whereas the peak at $m/z = 2540$ should belong to a dimeric porphyrazine, which is heavier than a biphenylene-bridged species ($m/z = 2438$).

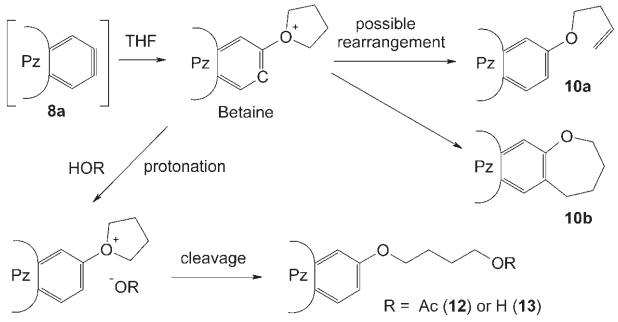
The more polar fraction contained mainly **11**, ($m/z = 1279$, acetoxy-substituted derivative formed from the addition of acetate to **8a**) and **12**, ($m/z = 1352$, 4-acetoxybutyloxy-substituted derivative). The next fraction was mainly the 4-hydroxybutyloxy derivative **13** ($m/z = 1309$, 70–75% pure as estimated by integration of its ^{1}H NMR spectrum), contaminated mainly with unreacted **8**. Zinc porphyrazine **5**, which formed as a result of deamination of **8**, was also eluted as the most polar zinc porphyrazine fraction. Only product **12** could be isolated in satisfactorily pure state from this reaction. However, the isolated and estimated yields of compounds, given in Table 1 and in Experimental Section, are lowered because of the losses during chromatographic separation and purification. These results clearly indicate no [2+2] dimerization of **8a** occurs, and that the addition of THF to **8a** occurs via an intermediate betaine compound as the main reaction route.[3,11,12] Presence of **10**, **12**, and **13** in the reaction products indicated at least two paths for the betaine conversion, both an intramolecular rearrangement and trapping upon attack by nucleophiles (see Scheme 3). These results also prove the activity of dehydrobenzoporphyrazine **8a** for the addition of nucleophiles as in case of **2**. The mechanism of formation of product **9** is not clear.

Oxidation of **8** in benzene also gave no trace of a dimeric biphenylene-bridged zinc porphyrazine. However, two other compounds were isolated, namely the acetic acid derivative of dehydro-PzZn **8a** (zinc acetoxybenzoporphyrazine **11**)

Table 1. Structures, observed characteristics, and yields of products from reaction of **1** with $Pb(OAc)_4$ in Et_2O/CH_3COOH and of **8** with $Pb(OAc)_4$ in THF.

	Structure and observed characteristics	Yield
3[a]	 MALDI: *m*/*z* calcd: 1845.0; found: 1844.9[c] ^{1}H NMR: $\delta =$ 1.65 (t, $^3J \approx 7$ Hz, -CH_3), 4.53 (q, $^3J \approx 7$ Hz, -O-CH_2-), 7.65 (d, $^3J \approx 8$ Hz, β-H), 8.78 ppm (s, α-H)	≈40 %[d]
4[a]	 MALDI: *m*/*z* calcd: 1859.0; found: 1858.8[c] ^{1}H NMR: $\delta = 2.48$ (s, -CH_3), 7.83 (d, $^3J \approx 8$ Hz, β-H), 9.01 (s, α-*H*), 9.27 ppm (d, $^3J \approx 8$ Hz, γ-*H*)	≈30 %[d]
9[b]	 MALDI: *m*/*z* calcd: 1218.6; found: 1219.9[e]	not estimated, very low
10a,**b**[b]	or  MALDI: *m*/*z* calcd: 1288.6; found: 1289.7[e]	not estimated, very low
11[b]	 MALDI: *m*/*z* calcd: 1276.6; found: 1277.8[e] see also Experimental Section, oxidation in benzene.	not estimated, very low
12[b]	 see Experimental Section	≈13 %
13[b]	 MALDI: *m*/*z* calcd: 1306.6; found: 1307.9[e] ^{1}H NMR: $\delta = 1.84$–1.96, 2.06–2.18 (2m, 2-, 3-*H*), 3.81 (t, $^3J \approx 6.3$ Hz, 4-*H*), 4.46 (t, $^3J \approx 6.4$ Hz, 1-*H*), 7.63 (dd, $^3J \approx 8.4$ Hz, $^4J \approx 2.2$ Hz, β-*H*), 8.70 (d, $^4J \approx 2.0$ Hz, α-*H*), 9.11 ppm (d, $^3J \approx 8.4$ Hz, β-*H*); ^{13}C-dept NMR: $\delta = 26.5$ (s, 2-*C*), 29.9 (s, 3-*C*), 61.8 (s, 4-C), 69.0 (s, 1-C), 107.7, 118.5, 124.7 ppm (3s, α-, β-, γ-C)	≈7 %[d]

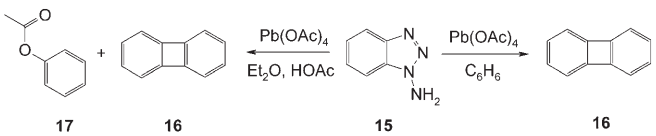
[a] Reaction of **1** with $Pb(OAc)_4$ in Et_2O/CH_3COOH. [b] Reaction of **8** with $Pb(OAc)_4$ in THF. [c] THF was used as a solvent for the measurement, resulting in $[M]^+$ peak. [d] Calculated from ^{1}H NMR without isolation as a single compound. [e] Dichloromethane was used as a solvent for the measurement, resulting in $[M+H]^+$ peak.



Scheme 3.

and the benzene derivative, in which benzene acts as a diene (zinc barreleno-fused benzoporphyrazine **14**). An explanation for this could be given as follows: a nearly saturated solution of **8** in benzene has a one order of magnitude lower concentration than the one applied by Campbell and Rees in their experiments with 1*N*-amino-benzotriazole.[6] A tenfold decrease of the concentration of **8** would reduce the dimerization rate by 100 in case if the dimerization of dehydrobenzene follows the second order rate, which would allow the competitive reactions to dominate.

To verify this, 1-aminobenzotriazole **15** was oxidized at low concentration in benzene. When the concentration of **15** was equal to that of **8** (approx. 8 mM), 65 % of biphenylene **16** was isolated (see Scheme 4). No traces of benzobarellene were found, indicating no influence of the tenfold dilution on the course of reaction described by Campbell and Rees. Therefore a pronounced difference in reactivity of the dehydrobenzoporhyrazine **8a** (and probably also steric factors) in comparison with unsubstituted benzyne must be responsible for the reaction pathway observed in our experiments. If the formed dehydrobenzoporphyrazine **8a** is more reactive than unsubstituted benzyne, the reaction of **8a** with solvents



Scheme 4.

should occur more easily, as observed, for example, when the reactivity of benzyne and tetrahalobenzynes towards aromatic compounds or ethers is compared.[5c,13] Adducts of simple arynes with benzene are known and are formed, for example, in case of thermal decomposition of *ortho*-diazonium carboxylates,[14a] especially if the electrophilicity of substituted benzynes is high.[13a]

Similar reactivity of dehydro-PcZn **2** and dehydro-PzZn **8a** towards nucleophiles can be expected due to the resemblance in their structures. Complex **2** easily cleaved diethyl ether, which indicates its increased reactivity in comparison with unsubstituted benzyne. This was proven by the oxidation of 1-aminobenzotriazole **15** carried out under the same conditions as in the experiment with **1** (see above), namely using the same concentration of the benzyne precursor and the same ratio of diethyl ether to acetic acid. In contrast to the reaction of **1**, from which the acetoxy and ethyloxy derivatives were isolated as main products, oxidation of **15** gave biphenylene **16** (≈32%) and phenylacetate **17** (≈14%) as the two main products. No traces of phenetole were found in this reaction. Therefore, it can be concluded that the observed selectivity of unsubstituted benzyne towards weak nucleophiles such as acetic acid and diethyl ether under the applied conditions is due to its weaker electrophility in comparison with **2**. The increased electrophilicity of dehydrophthalocyanine **2** and dehydroporphyrazine **8a** must be explained in terms of the inductive (−)*I* effect of the porphyrazine macrocycle towards the annulated dehydrobenzene ring.

Bulky substituents in the periphery of **1** or **8** could also hinder the dimerization of **2** or **8a**, respectively, thus leaving the only possibility for these species to react with the solvent, although it is known, for example, that a sterically hindered aryne, such as tetraphenylbenzyne, can dimerize to give octaphenylbiphenylene.[14b]

Conclusion

In conclusion, we have continued our investigations on the generation of dehydrophthalocyanines **2** and analogous dehydroporphyrazines **8a** and studied their reactivity in different solvents, such as diethyl ether, THF, benzene, and acetic acid. It was shown that the route for their generation through the oxidation of a fused aminotriazole functionality is applicable for both the porphyrazine and phthalocyanine type of macrocycle and is more effective than that described in our previous work for magnesium dehydrobenzoporphyrazine.[1] The studied dehydrobenzo macrocyclic derivatives **2** and **8a** both undergo easy Diels–Alder addition with dienes, but also addition of rather weak nucleophiles, such as carboxylic acids and aliphatic ethers, which has to be taken into account when using the latter as solvents for generation the dehydrobenzo macrocyclic species. Intermediate **8a** also reacts with benzene to give the barrelene-derivative **14**. In contrast to benzyne, neither **2** nor **8a** reacted with formation of any dimerization products. The obtained results point to a higher reactivity (electrophilicity) of both dehydro-PcZn **2** and dehydro-PzZn **8a** in comparison with benzyne.

Experimental Section

Instrumentation: FTIR spectroscopy: Bruker Tensor 27. UV/Vis spectroscopy: Shimadzu UV-365. ^{1}H and ^{13}C NMR spectroscopy: Bruker AC 250 (^{1}H: 250.131 MHz, ^{13}C: 62.902 MHz). MS (MALDI-TOF): Bruker Autoflex, the spectra were measured with α-cyano-*m*-hydroxycinnamic acid as matrix. Elemental analysis: Euro EA 3000.

General: 9,10,16,17,23,24-Hexakis-(3,5-bis-*tert*-butylphenoxy)(1-amino-[1,2,3]triazole[4,5-*b*])-phthalocyaninatozinc (**1**),[2] bis(4-*tert*-butylphenyl)fumaronitrile (**A**),[15] 5,6-dicyano-1*H*-benzotriazole (**B**),[9] and 1-aminobenzotriazole (**15**)[6] were prepared as described earlier. Other chemicals and solvents were purchased from commercial sources and were used without additional purification, unless mentioned.

Oxidation of 1 in Et_2O/CH_3COOH: Compound **1** (20 mg, 10.35 μmol) was dissolved in dry Et_2O (0.7 mL, 99.9%, inhibitor-free, Aldrich) in a flask closed with a septum stopper, and a solution of $Pb(OAc)_4$ in CH_3COOH (53.3 mM, 0.195 mL, prepared from 95%-pure salt, Acros Organics) was added by syringe into the flask in one portion at room temperature with good stirring. After 20 min, 4-*tert*-butyl catechol (a few milligrams) was added to reduce partially oxidized phthalocyanine products, and the solvent was allowed to evaporate without heating. The residue was subjected to chromatography on silica with $CHCl_3$ and the first green-blue fraction was collected, dried and washed with CH_3OH by decantation to give 14 mg of a mixture consisting of 9,10,16,17,23,24-hexakis-(3,5-bis-*tert*-butylphenoxy)-2-ethyloxyphthalocyaninatozinc (**3**) ($C_{118}H_{140}N_8O_7Zn$, 1847.9 g mol^{-1}, ≈40% yield calculated from ^{1}H NMR) and 9,10,16,17,23,24-hexakis-(3,5-bis-*tert*-butylphenoxy)-2-acetoxyphthalocyaninatozinc (**4**) ($C_{118}H_{138}N_8O_8Zn$, 1861.8 g mol^{-1}, ≈30% yield calculated from ^{1}H NMR). MALDI-TOF (THF, first isotopic peaks): *m*/*z*: 1844.9 $[M]^+$ (**3**), 1858.8 $[M]^+$ (**4**) (see Supporting Information for the spectrum). See also Results and Discussion, Table 1 and the Supporting Information for ^{1}H and ^{13}C NMR data.

Synthesis of 2,3,7,8,12,13-hexakis-(4-*tert*-butylphenyl)-1*H*-1,2,3-benzotriazole[5,6-*q*]porphyrazinatozinc (5) and 2,3,7,8-tetrakis-(4-*tert*-butylphenyl)-di(1*H*-1,2,3-benzotriazole[5,6-*l*;5,6-*q*])porphyrazinatozinc (6): Bis(4-*tert*-butylphenyl)fumaronitrile (**A**; 2 g, 5.8 mmol), $Zn(OAc)_2 \times 2H_2O$ (0.44 g, 2 mmol) and quinoline (3 mL) were first passed through a column with basic alumina and then were heated with stirring at 210 °C for ≈45 min until the mixture started turning green. Then, 5,6-dicyano-1*H*-benzotriazole (**B**; 0.36 g, 2.1 mmol), preliminary dried at 90 °C in vacuo, was added and the heating was continued for 3 h. After cooling, the reaction mixture was washed several times by centrifugation, by using aqueous MeOH with addition of little amounts of HCl, but no HCl was added for the last washing. The obtained precipitate was dried and dissolved in pyridine (≈200 mL), followed by addition of methanol (200 mL) and KOH (≈1 g). The mixture was placed in the refrigerator overnight, and the formed precipitate was filtered off, giving symmetrical octa(*p*-*tert*-butylphenyl)porphyrazinatozinc (≈350 mg). The filtrate was partially rotary evaporated in vacuo and water (≈400 mL) with HCl was added until slightly acidic pH and nearly colorless solution. The formed precipitate was filtered off, washed thoroughly with water, dried, and subjected to column chromatography on silica with $CHCl_3$ under UV/Vis spectroscopic control. The first fraction contained mainly unreacted **A** and little amount of symmetrical zinc porphyrazine (a sharp single Q-band was observed in the UV/Vis spectrum), followed by the fraction of **5** (Q-band was split into two). Elution of **5** was completed by addition of ≈0.5% THF. After that, a small amount of corresponding ABAB product[16] with some admixtures was eluted, and the content of THF was increased to several percents. This allowed the elution of **6** as a compound with an unsplit Q-band in UV/Vis spectrum. The complex corresponding to AB_3 structure was found upon elution with nearly pure THF, but it was not collected quantitatively because of its low solubility, and thus, in-

applicability for further chemical modification. Collected compounds **5** and **6** were purified by means of additional chromatography followed by washing with ≈90% aqueous MeOH and drying. Yields: 130 mg (5.3%) of **5** and 50 mg (4.4%) of **6**.

Data for ***5***: ^{1}H NMR (250 MHz, $CDCl_3$ + ≈1% *t*BuNH$_2$): δ = 0.90 (s, ≈75H; *tBu*NH$_2$), 1.50, 1.51 (2s, 54H; C(C*H*$_3$)$_3$), 1.96 (brs, ≈16H; *t*BuN*H*$_2$), 3.41 (s, ≈1.5H; C*H*$_3$OH), 7.54–7.59 (m, 8H; m-*H*), 7.68 (d, ^3J ≈8.4 Hz, 4H; m′-*H*), 8.26–8.40 (m, 12H; o-, o′-*H*), 9.56 ppm (s, 2H; α-*H*) (see the Supporting Information); ^{13}C NMR (62.9 MHz, $CDCl_3$ + ≈1% *t*BuNH$_2$): δ = 31.59, 31.61 (2s, C(*C*H$_3$)$_3$), 32.3 (s, *tBu*NH$_2$), 34.73, 34.76, 34.84 (3s, *C*(CH$_3$)$_3$), 47.4 (s, *tBu*NH$_2$), 50.2 (s, *C*H$_3$OH), 110.0 (brs, α-*C*), 124.92, 124.98 (2s, m-*C*), 125.17 (s, m′-*C*), 131.4, 131.6, 131.8 (3s, 3-*C*), 132.5 (s, o-, o′-*C*), 137.3 (br), 139.8, 140.5, 141.9, 142.3 (br) (5s, β-, γ-, 2-*C*), 150.0, 150.36, 150.43 (3s, 4-*C*), 155.2, 155.8, 157.9, 158.9 ppm (4s, δ-, 1-*C*); FTIR (KBr): $\tilde{\nu}$ = 3080 (vw), 3037 (vw), 2962 (vs), 2904 (m), 2868 (m), 1625 (w), 1610 (w), 1520 (w), 1474 (m), 1450 (w), 1383 (w), 1364 (m), 1327 (vw), 1269 (m), 1199 (w), 1159 (w), 1132 (w), 1103 (m), 1018 (vw), 993 (m), 979 (s), 893 (w), 882 (w), 839 (m), 808 (vw), 797 (vw), 759 (w), 745 (w), 667 (vw), 646 (vw) 629 (vw), 685 (vw), 567 (w), 534 cm^{-1} (vw); UV/Vis (CH_2Cl_2/1% THF): λ_{max}(log(ε)) = 364 (4.90), 580 (4.28), 629 (4.83), 680 nm (4.96); MS MALDI-TOF (CH_2Cl_2): *m*/*z* calcd for [*M*+H]$^+$: 1260.6; found: *m*/*z* (%): 1261.0 (100) [*M*+H]$^+$; elemental analysis calcd (%) for $C_{80}H_{81}N_{11}Zn \times 0.5\,CH_3OH$ (1262 + 16 g mol^{-1}): C 75.66, H 6.55, N 12.06; found: C 75.69, H 6.67, N 11.87.

Data for ***6***: ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 1.61, 1.63 (2s, 36H; C-(C*H*$_3$)$_3$), 7.53, 7.72 (2d, ^3J ≈8.0 Hz, 8H; m′-,m-*H*), 8.18, 8.29 (2d, ^3J ≈8.0 Hz, 8H; o′-, o-*H*), 8.84, 9.25 (2brs, 4H; α, α′-*H*), 15.01 ppm (very brs, <2H; N*H*) (see Supporting Information); ^{13}C NMR (250 MHz, [D$_8$]THF): δ = 32.1, 32.2 (2s, C(*C*H$_3$)$_3$), 35.5 (s, *C*(CH$_3$)$_3$), 125.4, 125.5 (2s, m-, m′-*C*), 132.8, 133.3 (2s, 3-, 3′-*C*), 133.54, 133.59 (2s, o-, o′-*C*), 138.7, 141.0 (br) (2s, 2-, 2′-*C*), 150.50, 150.54 (2s, 4-, 4′-*C*), 152.6, 154.7 (br), 155.8 (br), 158.9 ppm (br) (4s, 1-, 1′-, δ-, δ′-*C*); signals of other carbon atoms, close to the triazole moieties of **6**, were not observed because of the tautomeric conversions in triazole rings; FTIR (KBr): $\tilde{\nu}$ = 2962 (vs), 2905 (s), 2867 (m), 1625 (m), 1525 (w), 1481 (m), 1449 (m), 1370 (s), 1339 (vw), 1269 (m), 1200 (m), 1188 (m), 1153 (w), 1138 (m), 1104 (m), 1055 (vw), 1018 (vw), 987 (vs), 890 (m), 869 (w), 840 (m), 802 (w), 773 (vw), 755 (m), 739 (w), 678 (vw), 657 (w), 626 (w), 565 (m), 524 cm^{-1} (w); UV/Vis (CH_2Cl_2/1% THF): λ_{max}(log(ε) = 363 (4.94), 604 (4.55), 670 nm (5.22); MS MALDI-TOF (CH_2Cl_2): *m*/*z* calcd for [*M*+H]$^+$ 1087.4; found: *m*/*z* (%): 1087.8 (100) [*M*+H]$^+$; elemental analysis calcd (%) for $C_{64}H_{58}N_{14}Zn \times CH_3OH$ (1089 + 32 g mol^{-1}): C 69.66, H 5.58, N 17.50; found: C 69.83, H 5.58, N 17.04.

2,3,7,8,12,13-Hexakis-(4-*tert*-butylphenyl)(1-amino-1,2,3-benzotriazole-[5,6-*q*])porphyrazinatozinc (8): Compound **8** was prepared similarly to our earlier described procedure,[2] by using **5** (55 mg, 43 μmol), 2,4-dinitro-*O*-aminophenol (DNAP) (200 mg, 1.48 mmol), KOH (1.14 g, 20.4 mmol), THF (6 mL) and H_2O (2 mL). In the course of purification, 65–70% aqueous acetonitrile was used for washing **8** on the filter, THF/CH_2Cl_2 was applied to wash it down from the filter, followed by evaporation to dryness. Aqueous methanol (80–85%) was used for decantation. Yield 53 mg (95%); ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 1.52, 1.54, 1.58, 1.60 (4s, 54H; C(C*H*$_3$)$_3$), 7.00 (s, 2H; N*H*$_2$), 7.55–7.63 (m, 8H; m-*H*), 7.73, 7.78 (2d, ^3J = ≈8.4 Hz, 4H; m′-*H*), 8.26–8.40 (m, 12H; o-, o′-*H*), 9.23 (s, 1H; α-*H*), 9.56 ppm (s, 1H; α′-*H*); ^{13}C NMR (62.9 MHz, [D$_8$]THF): δ = 32.03, 32.06, 32.11 (3s, C(*C*H$_3$)$_3$), 35.46, 35.48, 35.52, 35.55 (4s, *C*(CH$_3$)$_3$), 105.2 (s, α′-*C*), 115.1 (s, α-*C*), 125.60, 125.63, 125.68, 125.82 (4s, m-, m′-*C*), 132.52, 132.60, 132.85, 132.96, 132.98 (5s, 3-*C*), 133.51, 133.57 (2s, o-, o′-*C*), 135.5, 137.1, 140.0, 140.7, 141.0, 141.3, 141.5, 142.6, 142.8, 147.1 (10s, β-, γ-, 2-C), 150.7, 151.0, 151.1, 151.3 (4s, 4-*C*), 155.5, 155.7, 155.9, 156.5, 157.4, 158.1, 159.0, 159.5 ppm (8s, δ-, 1-*C*); FTIR (KBr): $\tilde{\nu}$ = 3080 (vw), 3036 (vw), 2961 (vs), 2904 (s), 2867 (m), 1633 (m), 1612 (m), 1521 (w), 1475 (s), 1450 (w), 1364 (s), 1328 (vw), 1269 (m), 1199 (w), 1161 (w), 1131 (w), 1103 (s), 1017 (vw), 993 (s), 978 (vs), 893 (w), 881 (w), 838 (s), 810 (vw), 799 (vw), 773 (vw), 759 (m), 746 (m), 671 (vw), 585 (vw), 567 cm^{-1} (m); UV/Vis (CH_2Cl_2/1% THF): λ_{max}(rel. int.) = 365 (0.891), 377 (0.851), 581 (0.229), 630 (0.776), 681 nm (1.00); MS MALDI-TOF (THF): *m*/*z* calcd for [*M*]$^+$: 1274.6; found: *m*/*z* (%): 1274.9 (100) [*M*]$^+$, 1246.9 (80) [*M*−N$_2$]$^+$ (overlaps with [*M*−24]$^+$); MALDI-TOF (CH_2Cl_2): *m*/*z* calcd for [*M*+H]$^+$: 1275.6; found: *m*/*z* (%): 1276.0 (100) [*M*+H]$^+$, 1248.0 (80) [*M*−N$_2$]$^+$ (overlaps with [*M*−24]$^+$); elemental analysis calcd (%) for $C_{80}H_{82}N_{12}Zn \times 1.5\,H_2O$ (1277 + 27 g mol^{-1}): C 73.69, H 6.57, N 12.89'; found: C 73.58, H 6.69, N 12.80.

Oxidation of 8 in THF: Pb(OAc)$_4$ (95%, 13 mg, 28 μmol) was added to a solution of **8** (30 mg, 23 μmol) in not absolutized THF (0.75 mL) with good stirring at room temperature. Immediate evolution of gas was observed and the reaction mixture was stirred at room temperature for additional 15 min. Then, 4-*tert*-butyl catechol (a few milligrams) was added and the solvent was evaporated by air-blowing. The residue was subjected to column chromatography on silica, by using pure CH_2Cl_2 first, followed by addition of small amounts THF (0.3–1%). Several fractions consisting of mixtures of zinc porphyrazines were collected (see Results and Discussion). The largest fraction, collected as the last by using pure CH_2Cl_2, gave 4 mg of acceptably pure compound **12** {2,3,7,8,12,13-hexakis-(4-*tert*-butylphenyl)(2-(4-acetoxybutyloxy)benzo[5,6-*q*])porphyrazinatozinc} after washing with MeOH and drying (13% yield). ^{1}H NMR (250 MHz, $CDCl_3$ + ≈1% *t*BuNH$_2$): δ = 1.02, 1.09 (2s, *tBu*NH$_2$), 1.487, 1.494, 1.524 (3s, 54H; C(C*H*$_3$)$_3$), 1.96–2.14 (m, 4H; 2-, 3-*H*), 2.08 (s, 3H; OC(O)C*H*$_3$), 4.25 (t, ^3J ≈6.3 Hz, 2H; 4-*H*), 4.45 (t, ^3J ≈6.1 Hz, 2H; 1-*H*), 7.55–7.60 (m, 8H; m-*H*), 7.63 (dd, ^3J ≈8.2 Hz, ^4J ≈2.3 Hz, 1H; β-*H*), 7.70 (d, ^3J ≈8.4 Hz, 4H; m′-*H*), 8.30–8.40 (m, 12H; o-, o′-*H*), 8.69 (d, ^4J ≈2.2 Hz, 1H; α-*H*), 9.11 ppm (d, ^3J ≈8.3 Hz, 1H; γ-H) (see Supporting Information); ^{13}C-dept NMR (62.9 MHz, $CDCl_3$ + ≈1% *t*BuNH$_2$): δ = 21.4 (s, OC(O)*C*H$_3$), 25.9, 26.5 (2s, 2-, 3-*C*), 32.00, 32.03 (2s, C(*C*H$_3$)$_3$), 32.8 (s, *tBu*NH$_2$), 64.5 (s, 4-*C*), 68.6 (s, 1-*C*), 107.7, 118.6, 124.8 (3s, α-, β-, γ-*C*), 125.37, 125.4, 125.5, 125.6 (4s, m-, m′-*C*), 132.96, 133.02 ppm (2s, o-, o′-*C*); UV/Vis (CH_2Cl_2): λ_{max}(rel. int.) = 368 (0.957), 581 sh. (0.237), 630 (0.918), 671 nm (1.00). MALDI-TOF (CH_2Cl_2): *m*/*z* calcd for [*M*+H]$^+$ 1349.7; found: *m*/*z* (%): 1349.9 (100) [*M*+H]$^+$; elemental analysis calcd (%) for $C_{86}H_{86}N_8Zn \times 2\,C_4H_9NH_2$ (from NMR solvent) (1297 + 146 g mol^{-1}): C 75.40, H 7.67, N 9.35; found: C 75.63, H 7.46, N 9.89.

Oxidation of 8 in benzene: Compound **8** (15 mg, 11.5 μmol) was dissolved in benzene (1.4 mL), preliminarily dried over sodium. Pb(OAc)$_4$ (6.5 mg, 14 μmol) was added with good stirring to this solution at room temperature. Immediate evolution of gas could be observed during few seconds. After 1 h, 4-*tert*-butyl catechol (a few milligrams) was added, and the reaction mixture was transferred to a chromatographic column. Elution with CH_2Cl_2 allowed the collection of two well-separable fractions. First fraction gave 6 mg (≈40%) of compound **14**, the second fraction contained 2 mg (≈14%) **11**. Addition of THF to the eluent allowed the elution nearly all colored material as a third fraction, consisting mainly of deaminated starting material, namely compound **5**.

Data for ***14***: ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 1.50, 1.51, 1.59 (3s, 54H; *tBu*), 5.49 (m, 2H; 5-*H*), 7.12 (m, 4H; 6-*H*), 7.54–7.62 (m, 8H; m-*H*), 7.78 (d, ^3J ≈8.1 Hz, 4H; m′-*H*), 8.29–8.42 (m, 12H; o-, o′-*H*), 8.96 ppm (s, 2H; α-*H*); ^{13}C-dept NMR (62.9 MHz, [D$_8$]THF): δ = 31.43, 31.47 (2s, C-(*C*H$_3$)$_3$), 50.5 (s, 5-*C*), 116.8 (s, α-*C*), 125.06, 125.17 (2s, m-, m′-*C*), 132.94, 132.99 (2s, o-, o′-*C*), 140.0 ppm (s, 6-*C*); UV/Vis (CH_2Cl_2): λ_{max}(rel. int.) = 364 (1.00), 581 sh. (0.252), 630 (0.938), 665 nm (0.983); MS MALDI-TOF (THF): *m*/*z* calcd for [*M*]$^+$: 1294.6; found: *m*/*z* (%): 1294.8 (100) [*M*]$^+$; elemental analysis calcd (%) for $C_{86}H_{86}N_8Zn \times H_2O$ (1297 + 18 g mol^{-1}): C 78.55, H 6.74, N 8.52; found: C 78.27, H 6.74, N 9.22.

Data for ***11***: ^{1}H NMR (250 MHz, $CDCl_3$ + ≈1% *t*BuNH$_2$): δ = 1.05, 1.15 (2s, *tBu*NH$_2$), 1.48, 1.52 (2s, 54H; C(C*H*$_3$)$_3$), 2.52 (s, 3H; OC(O)C*H*$_3$), 7.54–7.60 (m, 8H; m-*H*), 7.70 (d, ^3J ≈8.0 Hz, 4H; m′-*H*), 7.81 (dd, ^3J ≈8.0 Hz, ^4J ≈2.0 Hz, 1H; β-*H*), 8.27–8.39 (m, 12H; o-, o′-*H*), 8.91 (d, ^4J ≈2.0 Hz, 1H; α-*H*), 9.24 ppm (d, ^3J ≈8.0 Hz, 1H; γ-*H*); ^{13}C-dept NMR (62.9 MHz, $CDCl_3$ + ≈1% *t*BuNH$_2$): δ = 21.8 (s, OC(O)*C*H$_3$), 32.0 (s, C-(*C*H$_3$)$_3$), 32.8 (s, *tBu*NH$_2$), 116.6 (s, α-*C*), 124.0, 124.5 (2s, β-, γ-*C*), 125.4, 125.62, 125.66 (3s, m-, m′-*C*), 132.90, 132.98, 133.01 ppm (3s, o-, o′-*C*); MS MALDI-TOF (THF): *m*/*z* calcd for [*M*]$^+$: 1276.6; found: *m*/*z* (%): 1276.8 (100) [*M*]$^+$.

Oxidation of 1-aminobenzotriazole (15) in benzene: Compound **15** (72 mg, 0.54 mmol) was dissolved in dry benzene (70 mL) and Pb(OAc)$_4$ (260 mg, 0.56 mmol) was added in one portion with stirring. After ≈1 h the solution was filtered and the solvent was removed under reduced

pressure. The residue was subjected to chromatography on silica with hexane as eluent to give 27 mg (65%) of biphenylene **16** practically as the only aromatic hydrocarbon among the reaction products. The ^{1}H and ^{13}C NMR spectra were identical to those previously described.[17]

Oxidation of 1-aminobenzotriazole (15) in Et_2O: Compound **15** (100 mg, 0.75 mmol) was dissolved in diethyl ether (50 mL, 99.9%-pure, inhibitor-free), and $Pb(OAc)_4$ (350 mg, 0.75 mmol) in acetic acid (14 mL) was added in one portion to the solution. The reaction mixture was stirred for 1 h, filtered and neutralized with a saturated solution of sodium carbonate. The organic phase was separated and the aqueous phase extracted with Et_2O ($\approx$25 mL). The organic phases were combined and were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was subjected to chromatography (silica gel, hexane) to give biphenylene **16** (18 mg, 32%, colorless crystals) and phenyl acetate **17** (14 mg, 14%, yellowish oil) as the two main products. ^{1}H and ^{13}C NMR spectra of products were identical to those previously described.[17,18]

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