Synthesis and Properties of an Unsymmetrical Triazole-Functionalized (Phthalocyaninato)zinc Complex

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Keywords: Phthalocyanines / Metal complexes / Unsymmetrical derivatization / Triazole / Spectroscopic properties / Zinc

The synthesis of 5,6-dicyano-1*H*-1,2,3-benzotriazole (**2**) was significantly simplified and its overall yield was increased. This opens up the possibility for an extended use of **2** as a precursor for triazole-functionalized phthalocyanines. One of them, the unsymmetrical {9,10,16,17,23,24-hexakis(3,5-di-*tert*-butylphenoxy)[1,2,3]triazolo[4,5-*b*]phthalocyaninato}-zinc (**5**) was prepared in a statistical condensation of **2** and 4,5-bis(3,5-di-*tert*-butylphenoxy)phthalonitrile (**3**) with subsequent separation by column chromatography. The triazole-functionalized (phthalocyanine)zinc complex **5** shows interesting spectral properties in solutions depending on the chemical medium because of the reactions which are typical for the triazole fragment. These are acid ionization of NH, coordination to metal ions, *N*-alkylation and *N*-acylation, among others. Compound **5** was characterized in detail using UV/Vis, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry (MALDI-TOF), and elemental analysis.

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Introduction

Phthalocyanines and their metal complexes (Pc's and PcM's), as well as their analogues, e.g. porphyrazines, naphthalocyanines, etc., have been studied for many years, and they are still the subject of intense investigation. The high level of interest in this type of compounds is due to their potential application in materials science. Phthalocyanines are used as dyes and catalysts for different processes, as liquid crystals and semiconductors, gas sensors and photosensitizers, as active materials in nonlinear optical and electrochromic devices and recordable optical information carriers, among other uses.[1] The reasons for the applicability of phthalocyanines and related compounds to that extended area of materials science are the peculiarities of their molecular and electronic structure.[1]

Among phthalocyanines, those with an unsymmetrical substitution pattern on the periphery of the macrocycle are of high interest due to their special chemical, physical, and optical properties.[2] Unsymmetrical substitution in Pc's and PcM's results in specific redistribution of their electron density, leading to a change in the general dipole moment and appearance of push-pull effects, changing the redox properties, causing intramolecular and intermolecular electron and energy transfers, etc.[2] Unsymmetrical phthalocyanines are required for the generation of second-order nonlinear optical effects and are expected to give a higher third-order nonlinear optical response in comparison to the symmetrical Pc's.[3] The latter property promotes a new application of phthalocyanines, namely optical limiting.[3,4] Certain unsymmetrical functionalization of the Pc's periphery is often preferable for the formation of highly organized phthalocyanine thin films, polymer-grafted materials or metal-supported phthalocyanine monolayers and other self-organized systems based on phthalocyanines and their complexes.[2,5] Unsymmetrical phthalocyanines possessing certain hydrophilic and lipophilic groups at the same time have a potential as biologically active materials, and are intensively studied for example, for their use in cancer therapy.[6]

A plethora of symmetrical and unsymmetrical phthalocyanines functionalized with different substituents have been prepared to date.[2,7] Among them, the phthalocyanines containing additional heteroatoms in the macrocycle, e.g. N and S, or fused heterocyclic rings, have received special attention, since such structures very often enable different interesting properties of these macrocycles. Thus, various pyrazine-, phenanthroline-, *N*-substituted imidazole-, thia- and selenadiazole- and other heterocycle-annulated phthalocyanines and porphyrazines were prepared and intensively investigated.[8,9] 1,2,3-Triazole-functionalized phthalocyanines, which are especially interesting, have not been reported yet, besides a poorly characterized [tetra(triazolo)phthalocyaninato]cobalt compound.[10] The only reported property of the latter is its solubility in water/alkali solution. Additionally, its UV/Vis spectra in DMF,

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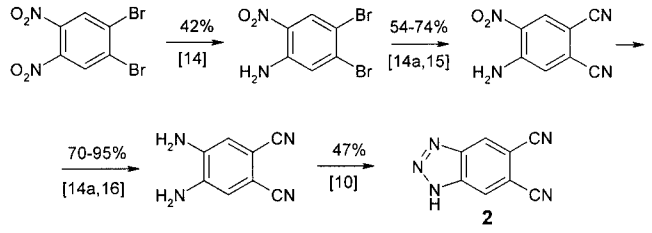
concentrated H_2SO_4, and aqueous NaOH were tabulated.[10] It is known, that imidazolo- or triazolo-porphyrazine derivatives, both symmetrical and unsymmetrical, with free NH function of the fused heterocycle rings were not formed in a cyclotetramerization reaction of the corresponding dinitriles.[8a,9c] Therefore, it is of interest whether the unsymmetrical triazole-annulated phthalocyanine with a free triazole NH group can be obtained in a statistical cross-condensation from the suitable phthalodinitriles. The lack of information on 1,2,3-triazole-fused phthalocyanines is mostly due to the difficult synthesis of the corresponding starting material, the dicyanobenzotriazole **2** (see Scheme 1). Triazole-fused phthalocyanines, e.g. **5** in Scheme 3, require more attention, because this type of functionalization can give unique properties to a phthalocyanine both from the synthetic (further peripheral functionalization) and the spectroscopic point of view. Benzotriazoles are amphoteric compounds, which can form different complexes with metal ions and can give different derivatives by substitution of the N–*H* atom.[11] The known substituents at the triazole ring are alkyl, acyl, sulfonyl, amino, and other groups, the introduction of which can activate the triazole for further reactions. Thus, *N*-aminobenzotriazole can be easily oxidized with formation of benzyne.[12] We expect that an *N*-aminotriazole-fused phthalocyanine can be a precursor for the generation of the unknown dehydrophthalocyanine.[13a] The analogous dehydrobenzoporphyrazine was generated recently by us by a different approach and trapped with furan,[13b] showing that, in general, this type of intermediate can exist.



Scheme 1.

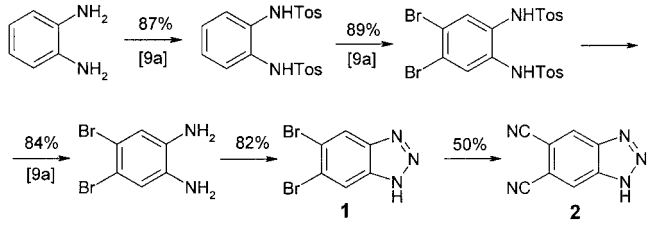
In the following we report on the synthesis and properties of a mono(triazole)-annulated phthalocyanine complex, soluble in many common organic solvents for example $CHCl_3$, THF or DMF, namely {9,10,16,17,23,24-hexakis(3,5-bis-*tert*-butylphenoxy)[1,2,3]triazolo[4,5-*b*]phthalocyaninato}zinc (**5**). Additionally, the improved synthesis of 5,6-dicyano-1*H*-1,2,3-benzotriazole (**2**) is reported.

Results and Discussion

Synthesis

As mentioned above, the precursor for a triazole-annulated phthalocyanine, the dicyanobenzotriazole **2** (see Schemes 1, 2 and 3), is relatively difficult to obtain. The synthesis described in the literature includes several steps, some of which proceed with low yields, as shown in Scheme 1.[10,14–16] Additionally, the starting material 1,2-dibromo-4,5-dinitrobenzene is not commercially available and needs to be prepared as well.[14b]

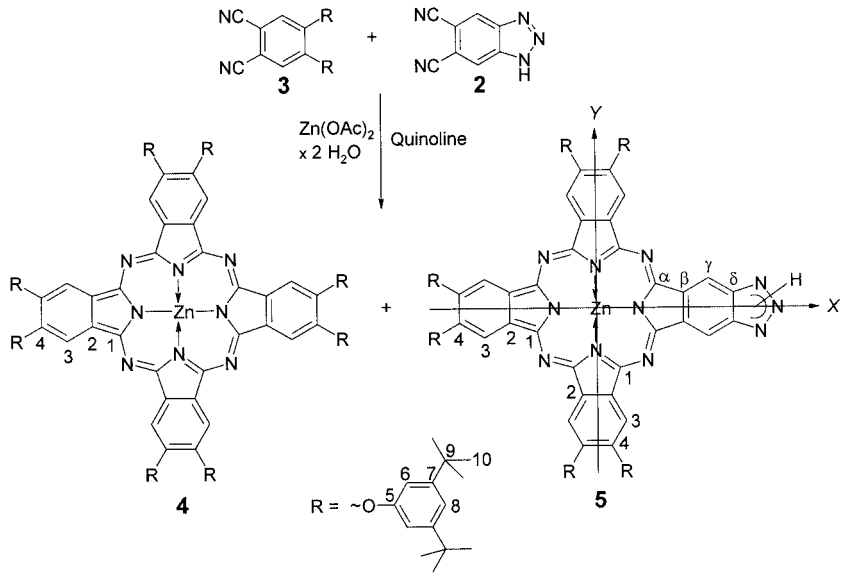
Therefore, we have developed an alternative route, which also is a multi-step synthesis, but with good yields except for the last step to yield **2**, which, however, is acceptable for this type of reaction (see Scheme 2 and below). The starting material *o*-phenylenediamine is cheap and commercially available. The only difficult step in this route is the last one, in which 5,6-dibromo-1*H*-benzotriazole **1** is treated with excess Cu^ICN (Rosenmund–von-Braun reaction). The usual conditions for the Rosenmund–von-Braun reaction (heating of the mixture of dibromobenzenes with CuCN in hot DMF) were not applicable in the case of **1**, since dibromobenzotriazole **1** forms strong complexes with copper(I) cyanide, similar to other benzotriazoles and metal salts.[17]



Scheme 2.

These complexes are practically insoluble in DMF, and the substitution of bromine in **1** by the cyano group does not occur under reflux in DMF even with a high excess of CuCN. However, pyridine is known to solubilize these types of complexes.[17] Therefore, we have performed the Rosenmund–von-Braun reaction in a mixture of Py/DMF (approx. 40:60) with excess CuCN under reflux for 24 h. Usage of a rather high excess of CuCN is necessary for a complete substitution of both bromine atoms in **1**. If the reaction time or the amount of CuCN were lowered, a noticeable amount of monobromo-monocyano product was obtained. The additional important step is the workup of the product, since after the reaction is completed, **2** remains as a stable copper complex (coordination through the triazole functionality). The only possibility found for destroying this complex was its treatment with concentrated nitric acid, as described in the Exp. Sect. The final purification of dinitrile **2** was achieved by crystallization from an ethanol/water mixture with charcoal.

It is known that a statistical cross-condensation of substituted phthalonitriles always results in a mixture of phthalocyanines, however, this method is commonly used for the preparation of different unsymmetrical Pc's.[8a,18] The template cross-condensation of dinitrile **2** with a threefold excess of 4,5-bis(3,5-di-*tert*-butylphenoxy)phthalonitrile (**3**) in the presence of an equimolar amount of $Zn(OAc)_2{\cdot}2H_2O$ in quinoline gave a mixture of compounds consisting mainly of symmetrical [octakis(3,5-di-*tert*-butylphenoxy)phthalocyaninato]zinc complex **4** and the desired 3-to-1 (A_3B) cyclization product **5** (see Scheme 3). Compound **3** was chosen for the cross-condensation with **2** because of two reasons. First, di-*tert*-butylphenoxy substituents in **3** lead to a high



Scheme 3.

solubility of the desired phthalocyanine **5** in common organic solvents. Second, these types of substituents give simple ^1H and ^{13}C NMR spectra, thus facilitating the structural characterization of the cross-condensation products. It was found to be important not to use an excess of $Zn(OAc)_2$ for this synthesis because of the strong tendency of triazole-functionalized phthalocyanines to form Zn complexes through the triazole ring, which could not be demetallated to give **5** and which disturb the purification of the desired product and lower its yield.

The separation of **4** and **5** was achieved by column chromatography using pure dichloromethane or CH_2Cl_2 with small amounts of THF to elute PcZn **4**. Phthalocyanine complex **5** is eluted upon addition of higher amounts of THF or traces of pyridine. The separation was monitored continuously by UV/Vis, since **4** and **5** have UV/Vis spectra, which are distinct enough to draw a conclusion about the composition of eluted fractions, considering the relative intensity of absorption bands (see below). A complete purification of **5** was achieved with a second chromatographic step. However, one has to take into account the unusual behavior of **5** during chromatography: it was observed that a part of **5** was eluted very quickly upon addition of small amounts of THF to CH_2Cl_2, whereas the other part of **5** stays on the column and moves down only upon addition of higher amounts of THF or Py. Both fractions are, nevertheless, the same compound according to UV/Vis and MALDI-TOF analysis. Additionally, they show the same behavior when checked by TLC (silica gel, CH_2Cl_2/THF mixtures), moving with equal R_f values as tailing spots. The explanation for this behavior lies in the ability of the phthalocyanine complex **5** to form relatively stable coordination complexes and intermolecular hydrogen bonds through the triazole functionality, depending on the solvent {compare for example with [tri(benzo)(pyridino)porphyrazinato]-zinc[18b]}. The tendency towards dimerization of **5** was also observed in its MALDI-TOF spectrum (see below).

When higher amounts of pyridine were added to the eluent, other colored compounds were eluted from the column as a complex mixture according to the analysis using the MADLI-TOF technique. Among other peaks in the MALDI-TOF spectrum of this mixture, the signal of the A_2B_2 (m/z = 1477) product, also expected from the statistical condensation, was observed.

UV/Vis Spectra

The UV/Vis absorption of **5** is unique in comparison, for example with the symmetrical PcZn **4**. The Q band is split into two components (Q_x and Q_y bands) due to the lowered symmetry of **5** (see Figure 1). The Q_x band of **5** in comparison to **4** shifts noticeably to the red because of the conjugation effect with the triazole ring, whereas the Q_y band remains practically at the same position as the Q band in **4**. This is in agreement with the four-orbital theory of electronic spectra of phthalocyanines and more recent calculations.[19] The positions of the absorption maxima in **4** or **5** depend on the solvent, which is also a common feature of phthalocyanines. Additionally, the ratio of the intensities of the Q_x and Q_y bands in **5** was found to be sensitive to the nature of the solvent, which might be due to the tendency of **5** to dimerization in nonaromatic solvents with low polarity through the triazole ring. The UV/Vis spectrum of **4** freshly dissolved in hexane shows practically no interaction between the phthalocyanine molecules in solution at least at low concentrations ($<10^{-5}$ M), which is not the case for **5** (see Figure 1). The strong decrease in absorption of the Q_x band indicates some kind of interaction between molecules of **5** involving the fused triazole ring. Indeed, according to theory,[19] it is expected that the changes in electronic structure of the triazole ring annulated to a phthalocyanine system should affect mostly the transition polarized along the x axis (see Scheme 3), namely the Q_x band.

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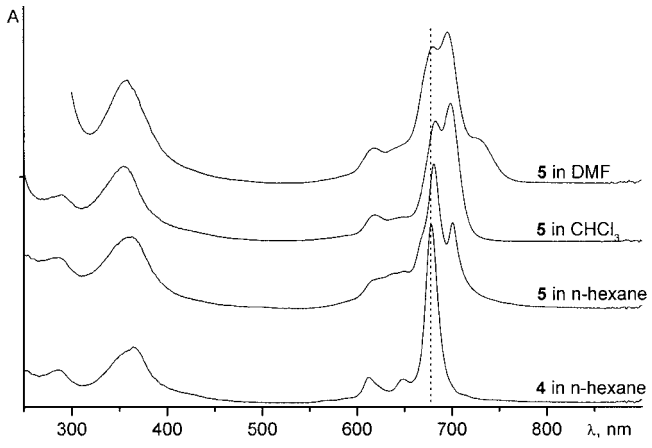

Figure 1. UV/Vis spectra of **4** and **5** in different solvents.

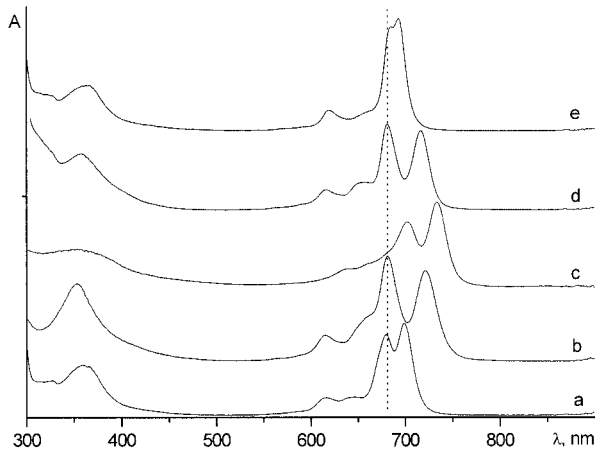

Figure 2. Spectra of **5** in (a) THF + 20% Py; (b) THF over solid NaOH; (c) $CHCl_3$/approx. 5×10^{-3} M CF_3COOH; (d) THF + 20% Py over solid $Ni(OAc)_2 \cdot 4H_2O$; (e) THF + 20% Py after addition of a small amount of acetic anhydride.

Polar solvents like methanol or acetonitrile do not solubilize **4** or **5**, but **5** is relatively soluble in DMF, in contrast to **4**, which is practically insoluble in DMF.

Benzotriazoles are weak acids and can dissolve in aqueous alkali,[11] which is also the case for the tetra(triazole)-substituted (phthalocyaninato)cobalt complex.[10] We have studied the UV/Vis spectra of **5** in the presence of bases. The UV/Vis spectrum of **5** in THF, $CHCl_3$ or pyridine corresponds to a "neutral monomeric form" of the triazole-annulated phthalocyanine complex **5** [see Figures 1 and 2 and Table 1; for log(ε) values in $CHCl_3$/0.1% Py see Exp. Sect.]. Addition of 1 drop of tetrabutylammonium hydroxide in MeOH (1 M) into a cuvette with a solution of **5** in THF resulted in a 27 nm bathochromic shift of the Q_x band due to ionization of the N–H bond of the triazole ring. This is because the formed anionic triazole fragment is a stronger electron donor towards the Pc macrocycle in comparison with the nonionized triazole ring.

The same spectral changes occur slowly when solid NaOH is added to a solution of **5** in THF. They are completely reversible, since upon neutralization of the basic solution with CF_3COOH the UV/Vis spectrum of the starting material **5** reappears. The excess of acid first leads to the protonation of the macrocycle on the *meso*-nitrogen atom, but not on the triazole ring, although the latter one is amphoteric.[11] This can be seen from the spectral changes taking place upon titration of **5** with CF_3COOH in $CHCl_3$. If protonation of the triazole ring would occur, the Q_x band should have shifted hypsochromically because of the electron-withdrawing effect of the positively charged triazole fragment. In contrast, both Q_x and Q_y bands shift to the red upon the first protonation, which indicates protonation of the *meso*-nitrogen atom of the macrocycle.[20] The expectation of a blue-shift of the Q_x band upon protonation of the triazole ring was also supported with the following experiment: acetic anhydride (2 drops) was added into the cuvette containing the solution of **5** (2 mL, approx. 10^{-5} M) in a THF/Py mixture (4:1) and the UV/Vis spectra were recorded, showing the complete change of the spectrum of **5** within 3 min. The resulting UV/Vis spectrum belongs to a derivative of **5** with acetylated triazole ring, and the Q_x band shifted slightly to the blue because of the electron-withdrawing effect of the acetyl group and showing the increase of the intensity of the Q bands (see Figure 2).

Table 1. UV/Vis data of compounds **4** and **5**.

Compound	Solvent	Additive	Absorption bands, λ_{max} [nm] (rel. intens.)				
			B	Q_x	Q_y	Satellites	
4	*n*-hexane	–	364 (0.331)	679 (1.00)		648 (0.154)	612 (0.165)
5	*n*-hexane	–	361 (0.519)	701 (0.613)	681 (1.00)	650 (0.291)	620 (shoulder)
5	$CHCl_3$	–	354 (0.558)	699 (1.00)	683 (0.875)	649 (shoulder)	619 (0.217)
5	THF	–	355 (0.574)	696 (1.00)	677 (0.864)	643 (0.196)	614 (0.191)
5	THF + 20%Py	–	360 (0.559)	699 (1.00)	680 (0.887)	647 (0.217)	616 (0.210)
5	THF	NaOH	353 (0.745)	722 (0.864)	682 (1.00)	660 (shoulder)	616 (0.265)
5	THF	$Bu_4N^+OH^-$ (traces)	–	723 (0.947)	682 (1.00)	662 (shoulder)	616 (0.280)
5	THF + 20%Py	$Zn(OAc)_2 \cdot 2H_2O$	359 (0.643)	711 (0.977)	679 (1.00)	651 (0.302)	615 (0.233)
5	THF + 20%Py	$Ni(OAc)_2 \cdot 4H_2O$	358 (0.666)	717 (0.925)	681 (1.00)	657 (0.345)	616 (0.259)
5	THF + 20%Py	$ZnCl_2$	358 (0.646)	710 (1.00)	679 (0.995)	651 (0.295)	615 (0.238)
5	THF + 20%Py	$NiCl_2$	357 (0.655)	717 (0.795)	684 (1.00)	658 (shoulder)	618 (0.241)
5	THF + 20%Py	$CoCl_2$	358 (0.607)	712 (0.878)	682 (1.00)	[a]	
5	$CHCl_3$	CF_3COOH (traces)	353 (0.469)	734 (1.00)	703 (0.778)		640 (shoulder)
5	THF + 20%Py	$(CH_3CO)_2O$	363 (0.421)	693 (1.00)	685 (0.928)		620 (0.200)

[a] Bands are overlapping with absorption of cobalt salt.

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Addition of several solid metal salts, e.g. Zn, Ni, Co chlorides and acetates, to the solution of **5** in THF/Py resulted in a red shift of the Q_x band, similarly to the above-described acid ionization of the triazole NH group, but with lower shift values, depending on the nature of the metal. The shift of the Q_x band maximum in these cases is due to the removal of the NH proton of the triazole ring and coordination of the latter to the metal ion. The presence of pyridine as the base is necessary, since we did not observe the described spectral changes upon addition of metal salts to **5** in pure THF. All UV/Vis data are summarized in Table 1.

^{1}H and ^{13}C NMR Spectra

The NMR spectra of compounds **4** and **5** are completely in agreement with their structures. The symmetrical PcZn **4** gave very simple ^{1}H and ^{13}C NMR spectra in $CDCl_3$/10% [D_8]THF (see Exp. Sect. and Scheme 3) with good resolution of the carbon signals of the aryloxy substituents, although the carbon signals of the phthalocyanine macrocycle were poorly resolved with the C-1 signals not resolved at all. 3-, 6-, and 8-H in **4** appear as singlets with a relative broadening for the 3-H signal. In contrast, the spectra of **5** in [D_8]THF are more complicated because of the loss of the symmetry, but they are better resolved. In general, the deuterated THF was found from our experience to be one of the best solvents for obtaining well-resolved ^{1}H and ^{13}C NMR spectra of aryl- and aryloxy-substituted phthalocyanines.[21,13b] Less polar or noncoordinating solvents often lead to a noticeable aggregation of phthalocyanines at the concentrations required for NMR measurements.

Each of the types of protons and carbons of **5** in [D_8]-THF (see Scheme 3) gives groups of signals consisting mainly of three. Thus, in the ^{1}H NMR spectrum of **5**, protons 6-H give three doublets, protons 8-H give one triplet and one multiplet, and protons 3-H appear as three sharp singlets, whereas the γ-protons appear as a broadened signal (see Figure 3). The protons of the *tert*-butyl groups also gave three singlets, two of them close to each other and the third noticeably down-field-shifted. The same difference in the shifts can be noticed for all other types of protons. Probably, the stronger down-field-shifted signals in the mentioned groups belong to the protons of the substituents closest to the triazole fragment. The signal of the NH proton of the triazole ring was not found at all, probably because of the tautomerism occurring with a rate close to the relaxation time of the proton under the conditions of the measurements (20 °C, [D_8]THF) or due to the masking by the intense signals of aromatic protons in the region δ = 7.0–7.5 ppm. An additional reason could be the deuterio exchange in the case where some D_2O is present in [D_8]-THF, since the concentration of **5** in [D_8]THF was relatively low. However, for a concentrated solution of compound **1** in [D_6]DMSO we also did not observe the NH signal (see Exp. Sect.).

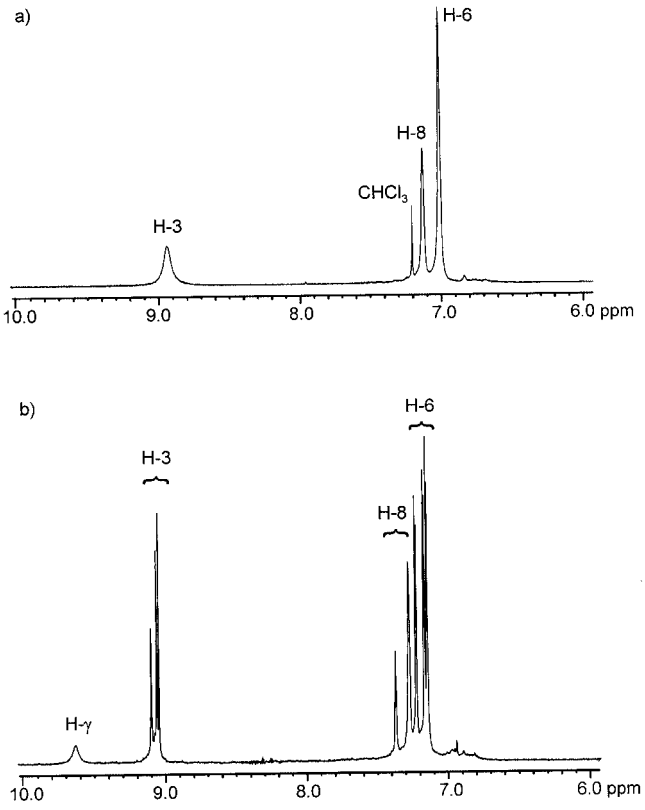

Figure 3. ^{1}H NMR (aromatic region) of compounds **4** in $CDCl_3$/[D_8]THF (a) and **5** in [D_8]THF (b).

The NH tautomerism of the triazole ring in **5** can be a reason for the broadening of the γ-H signal as well. ^{1}H NMR measurements on **5** in less polar solvents or at lower temperatures could decrease the rates of tautomer interconversion, thus leading to a split γ-H signal and, probably, to the appearance of two NH proton signals. However, it also would cause broadening, shifting, and splitting of other signals of phthalocyanine protons due to aggregation and other effects, resulting, in general, in poorly resolved spectra. On the other hand, **5** is not soluble enough in solvents which are noticeably more polar than THF. Nevertheless, we found the information obtained from the ^{1}H NMR spectrum of **5** in [D_8]THF at 20 °C to be sufficient for proving the structure of the compound.

Despite good resolution of all other carbon signals in **5**, signals C-α, -β, -δ, and even -γ were not found in the ^{13}C NMR spectrum of **5**, probably, due to masking by other strong signals or due to a substantial broadening. The signal of C-γ, which should be the most intense of the latter four, would be expected in the range δ = 110–120 ppm, where many other intense carbon signals appear (see Exp. Sect.).

MS (MALDI-TOF) Spectra

The data on MALDI-TOF spectra of compounds **4** and **5** fully support their structures. Phthalocyanine complex **4** gives the only cluster peak corresponding to its molecular

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ion [M^+] without any fragmentation (*m*/*z* = 2212) and with a good fit to the calculated isotopic distribution (when measured with internal standard). This indicates that under applied conditions the phthalocyanine charging proceeds through electron removal and not through protonation. Compound **5** gives a weak cluster peak at *m*/*z* = 3688, which was attributed to a dimeric species (dimerization through the triazole functionality), and two cluster peaks at *m*/*z* = 1844 and approx. 1816 (see Figure 4). The ratio of their intensities depends on the laser energy, but the peak at *m*/*z* = 1844 is always the most intense. Calculation of the isotopic distribution for the molecular ion of **5** [M^+] fits with the cluster peak at *m*/*z* = 1844 (when measured with internal standard). The cluster peak at *m*/*z* = 1816 corresponds to a fragmentation of **5** with the loss of dinitrogen, which is a common type of fragmentation for benzotriazoles (see Figure 4).[22] However, the isotopic distribution of this peak shows that it is probably due to several species, such as [$M^+ - N_2$] and [$MH^+ - N_2$]. Additional measurements using the PSD (Post-Source-Decay) technique were also carried out (*m*/*z* = 1831–1865 window was taken), showing that molecular ions of **5** fragment to give a poorly resolved peak at *m*/*z* = 1816–1820. Other heaviest fragments appeared at approx. *m*/*z* = 1418, 1404, 1312, 1152, 751, 697, 684, 633, 608, 554, 542, 488, 477, 455, and 424, when a wider *m*/*z* window was taken. Therefore, the loss of peripheral aryl groups without fragmentation of the macrocycle was not observed in this case. Surprisingly, the heaviest fragments in the PSD spectrum of **4** correspond to the loss of N or CH_2 [$M^+ - 14$], one *tert*-butyl group [$M^+ - 57$] (weak signal), and of the fragment with *m*/*z* = 171, giving the peak at *m*/*z* = 2042, which we find difficult to assign. The next intense peaks in the PSD spectrum of **4** are observed at *m*/*z* = 1706, 1694, 1206, 1193, 1147, 642, 630, 554, 542, 473, and some others, indicating the rupture of the macrocycle without the loss of peripheral substituents as well. The comparison of the fragmentation patterns of **4** and **5** reveals some similarity in the region of lower masses, and shows that the rupture of both macrocycles starts with the loss of the fragments related to bis(3,5-di-*tert*-butylphenoxy)isoindoline. MALDI-TOF measurements on compound **5** in the negative mode using the same matrix gave cluster peaks which correspond to a molecular ion [$M^- - H$] (formed upon NH group dissociation) and to a fragment without N_2. The difference between the values of the first isotopic peak of the molecular ion formed upon ionization of **5** in positive and negative modes was exactly one mass unit.

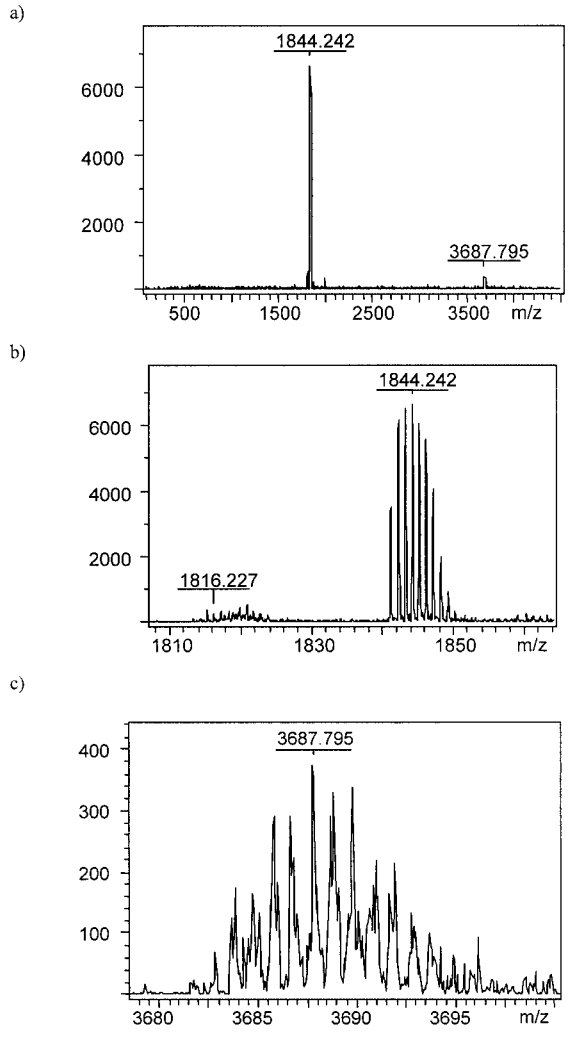

Figure 4. MALDI-TOF spectrum of compound **5** (a) and its zoomed view (b, c), measured without internal standard.

IR Spectra

The IR spectra of **4** and **5** are practically identical, since the main absorption bands in the region 650–1650 cm^{-1} are due to the peripheral aryloxy substituents, which are present in high number in both compounds. For this reason it is understandable that many other vibrations in the mentioned wavenumber region, which are due to the phthalocyanine core, are partially or completely masked, and the change of the core symmetry from **4** to **5** or addition of the triazole ring does not lead therefore to a change of the whole IR spectrum. The NH functionality of the triazole ring in **5**, which is expected to give vibration bands at 3100–3400 cm^{-1}, is also not observed, probably, because of the very low intensity of the corresponding bands in comparison with other bands in the spectrum and because of the covering by the broad absorption band of water in KBr.

Conclusions

We have shown the applicability of the statistical synthesis for the preparation of the unsymmetrical phthalocyanine complex **5** containing a triazole functionality on the periphery. Compound **5** is highly soluble in common organic solvents with medium polarity. Phthalocyanine complex **5** was found to possess unique spectral properties depending on the chemical medium due to the reactivity of the triazole fragment. Many reactions which are characteristic for benzotriazole, for example *N*-alkylation, *N*-acylation and

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others, are expected to be also typical for this phthalocyanine. Thus, the activity of **5** towards acetic anhydride under acylation conditions was observed in preliminary experiments using UV/Vis spectrophotometry. These types of reactions could be useful, for example, for binding the phthalocyanine to different surfaces, polymers, and biologically active molecules, which is of high interest for many applications in materials science. Additionally, the triazole fragment is an excellent precursor group for further unsymmetrical chemical modifications of the phthalocyanine macrocycle. The work on these topics is continuing within our research group.

Experimental Section

General: 4,5-Bis(3,5-di-*tert*-butylphenoxy)phthalonitrile (**3**) was prepared according to a procedure previously described.[23] Other chemicals and solvents were purchased from commercial sources and were used without additional purification, unless mentioned. 4,5-Dibromo-*o*-phenylenediamine was prepared according to the route described in ref.[9a]

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 (EI, MALDI-TOF): Finnigan TSQ 70 MAT, Bruker Autoflex. Elemental analysis: Euro EA 3000. FT-IR: Bruker Tensor 27.

5,6-Dibromo-1*H*-benzotriazole (1): 4,5-Dibromo-*o*-phenylenediamine (20 g, 0.075 mol)[9a] was dissolved in CH_3COOH (125 mL) and H_2O (20 mL), and the solution was cooled to 0 °C. $NaNO_2$ (5.6 g, 0.081 mol), dissolved in H_2O (10 mL), was added dropwise to this solution with good stirring, maintaining a temperature of 0 °C or below. The formed voluminous precipitate was filtered off, washed with a small portion of water, dried and crystallized from aqueous ethanol, giving slightly orange needles. Yield 17 g (82%) after drying. Crystallization with charcoal gave practically colorless crystals. $C_6H_3Br_2N_3$ (276.9): calcd. C 26.02, H 1.09, N 15.17; found C 25.96, H 1.06, N 14.87. EI MS: *m*/*z* (%) = 276.9 (100) [M^+], 248.9 (92) [$M^+ - N_2$]. ^{1}H NMR ([D$_6$]DMSO, numbering according to the nomenclature): δ = 8.27 (s, 2 H, 4,7-H) ppm. ^{13}C NMR ([D$_6$]DMSO, numbering according to the nomenclature): δ = 119.9 (s, broadened, C-4,7), 120.9 (s, C-5,6), 139.3 (s, broad, C-8,9) ppm.

5,6-Dicyano-1*H*-benzotriazole (2): Compound **1** (9 g, 32.5 mmol) was dissolved in DMF (60 mL, dried with molecular sieves) and CuCN (12 g, 134 mmol) was added to the solution, resulting in the formation of a yellowish precipitate. The suspension was heated with good stirring up to 140–145 °C, and pyridine (30–40 mL) was added portion-wise until the main part of the precipitate was dissolved. The reaction mixture was heated for 24 h during which two extra portions of CuCN (3 g, 33.5 mmol each portion) were added (approx. after 8 and 16 h). Then the hot mixture was poured on ice/water (approx. 0.5 L) with stirring, the formed precipitate was ground, filtered off, washed and dried. Then, 25–30% HNO_3 was added to it in small portions with good mixing, until no more evolution of NO_2 was observed upon addition of the acid (***Caution:*** Only in good ventilated hood!). The slightly greenish residue was filtered off, dried and dissolved in 65% HNO_3 (approx. 10–15 mL per 3 g) with heating. The formed solution was poured hot into ice/water (100 mL per 10 mL of acid) and placed into the refrigerator (0 °C) overnight. The formed precipitate was filtered off, washed with water, dried and recrystallized from water/ethanol (approx. 1:1) with charcoal. Yield 3.1 g (50%) of yellowish crystals (as hydrate). ^{1}H NMR ([D$_6$]DMSO, numbering according to the nomenclature): δ = 6.14 (s, broad, approx. 4 H, NH, H_2O); 8.80 (s, 2 H, 4,7-H) ppm. ^{13}C NMR ([D$_6$]DMSO, numbering according to the nomenclature): δ = 110.2 (s, C-5,6), 116.5 (s, C≡N), 124.5 (s, C-4,7), 139.8 (s, C-8,9) ppm. EI MS: *m*/*z* (%) = 169.1 (100) [M^+], 141.1 (68) [$M^+ - N_2$], 114.1 (18) [$M^+ - N_2 - HCN$], 87.2 (19), 63.2 (16). $C_8H_3N_5 \cdot 1.25H_2O$ (169.2 + 22.5): calcd. C 50.13, H 2.89, N 36.54; found C 50.00, H 2.59, N 36.42. Some part of **2** was purified by column chromatography ($CHCl_3$/THF) and obtained as a water-free compound. FT-IR spectra of the hydrate and water-free **2** (w/f **2**) show some difference. FT-IR of the hydrate (KBr): $\tilde{\nu}$ = 3586 (s) (absent for w/f **2**), 3363 (m), broad (absent for w/f **2**), 3275 (vw) shoulder (appears as sharp medium intensity band for w/f **2**), 3106 (m), 3036 (m), 2238 (s), 1623 (m), 1494 (w), 1405 (w), 1385 (vw) (appears as medium intensity band for w/f **2**) 1369 (w), 1312 (m), 1275 (m), 1218 (s), 1163 (m), 1075 (m), 990 (s) (splits into two at 1009 and 981 for w/f **2**), 919 (m), 888 (m), 826 (vw) (medium for w/f **2**), 775 (m), (very weak for w/f **2**), 655 (vw), (more intense for w/f **2**), 530 (s), 475 (m), broad (absent in w/f **2**) cm^{-1}.

[2,3,9,10,16,17,23,24-Octakis(3,5-bis-*tert*-butylphenoxy)phthalocyaninato]zinc (4) and {9,10,16,17,23,24-hexakis(3,5-di-*tert*-butylphenoxy)[1,2,3]triazolo[4,5-*b*]phthalocyaninato}zinc (5): Dinitriles **2** (0.34 g, 2 mmol) and **3** (3.2 g, 6 mmol) were mixed with $Zn(OAc)_2 \cdot 2H_2O$ (0.44 g, 2 mmol) and quinoline (3 mL), first passed through the column with basic alumina. The mixture was heated up to 200 °C and was allowed to react for 1.5 h. After cooling, the solidified mass was washed thoroughly with aqueous methanol, dried and subjected to column chromatography on silica gel. Using dichloromethane allowed the elution of the main part of **4**. Gradual addition of THF (starting from 0.2%) to CH_2Cl_2 resulted in elution of an additional part of **4**, followed by **5**. Addition of traces of pyridine helped to complete elution of **5**. The course of chromatography was continuously monitored by UV/Vis spectroscopy. Additionally, TLC control (silica gel) using CH_2Cl_2 with traces of THF can be applied to verify the separation of compounds: **4** has a higher R_f value than **5** and also moves rather quickly with pure CH_2Cl_2 ($R_f \approx 0.6$–0.8) in contrast to **5**. All collected fractions with phthalocyanine complex **5** were purified additionally by a second chromatography, the solvent was completely evaporated and the residue was washed several times with methanol with decantation.

4: 1.15 g (35%). UV/Vis ($CHCl_3$): λ (rel. intens.) = 289 (0.185), 357 (0.350), 615 (0.180), 653 (0.165), 683 (1.00) nm. FT-IR (KBr): $\tilde{\nu}$ = 2964 (vs), 2868 (w), 1609 (m), 1587 (s), 1450 (s), 1422 (s), 1401 (vs), 1363 (w), 1298 (s), 1270 (m), 1246 (w), 1198 (m), 1141 (w), 1090 (m), 1036 (m), 962 (m), 903 (w), 876 (w), 749 (w), 707 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$/10% [D$_8$]THF): δ = 1.25 (s, 144 H, 10-H); 7.05 (s, 16 H, 6-H); 7.17 (s, 8 H, 8-H); 8.95 (s, broadened, 8 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$/10% [D$_8$]THF): δ = 31.3 (s, C-10), 34.9 (s, C-9), 112.6 (s, C-6), 113.8 (s, poorly resolved, C-3), 117.3 (s, C-8), 134.3 (s, poorly resolved, C-2), 150.4 (s, poorly resolved, C-4), 152.4 (s, C-7), 156.9 (s, C-5) ppm. MS (MALDI-TOF, α-cyano-3-hydroxycinnamic acid as matrix): *m*/*z* = 2212 [M^+]. $C_{144}H_{176}N_8O_8Zn$ (2212.4): calcd. C 78.18, H 8.02, N 5.06; found C 78.15, H 7.97, N 4.84.

5: 0.36 g (10%). UV/Vis ($CHCl_3$ + 0.1% Py): λ (log ε) = 362 (4.95), 620 (4.53), 651 (4.51), 684 (5.19), 701 (5.25) nm. FT-IR (KBr): $\tilde{\nu}$ = 2964 (vs), 2869 (w), 1607 (m), 1587 (s), 1454 (s), 1422 (s), 1402 (vs), 1364 (w), 1297 (s), 1271 (m), 1197 (m), 1141 (w), 1119 (w), 1094 (m), 1035 (m), 961 (m), 902 (w), 864 (w), 746 (w), 707 (w) cm^{-1}. ^{1}H NMR ([D$_8$]THF): δ = 1.35 (s), 1.36 (s), 1.42 (s) (108 H, 10-H); 7.16 (d, $^4J \approx 1.5$ Hz), 7.18 (d, $^4J \approx 1.7$ Hz), 7.24 (d, $^4J \approx 1.7$ Hz) (12 H, 6-H); 7.29 (m), 7.39 (t, $^4J \approx 1.6$ Hz) (6 H, 8-H); 9.06 (s),

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9.08 (s), 9.12 (s) (6 H, 3-H); 9.65 (s, broadened,2 H, γ-H) ppm. ^{13}C NMR ([D_8]THF): δ = 31.88 (s) (C-10); 35.7 (s), 35.8 (s) (C-9); 113.1 (s), 113.3 (s), 113.9 (s) (C-6); 114.1 (s), 114.9 (s), 115.2 (s) (C-3); 117.78 (s), 117.83 (s), 118.3 (s) (C-8); 135.5 (s), 135.6 (s) (C-2); 150.8 (s), 151.1 (s), 151.7 (s) (C-4); 153.0 (s), 154.3 (s), 155.2 (s) (C-1); 153.3 (s), 153.6 (s) (C-7); 158.1 (s), 158.58 (s), 158.65 (s) (C-5) ppm:. MS (MALDI-TOF, α-cyano-3-hydroxycinnamic acid as matrix): *m/z* (%) = 3688 [2 M^+], 1844 (100) [M^+], 1816–1820 (poorly resolved) [$M^+ - N_2$] [$MH^+ - N_2$]. $C_{116}H_{135}N_{11}O_6Zn \cdot 0.5H_2O$ (1844.8 + 9): C 75.16, H 7.39, N 8.31; found C 74.99, H 7.31, N 8.36.

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