New Unsymmetrical Zinc-Phthalocyanine Conjugated with One Azo-Dye Moiety: Synthesis via Opening the Fused Triazole Ring and Spectral Properties

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A new method for the preparation of compounds containing an azo-dye moiety via opening the activated triazole ring upon coupling with nucleophiles was successfully applied to a mono-triazole-fused phthalocyaninato zinc complex **1**. The prepared unsymmetrical zinc-phthalocyanine **3** conjugated with a 2-hydroxy-1-naphthylazo moiety in the periphery was characterized by means of UV/Vis-, FTIR-, ^{1}H and ^{13}C NMR spectroscopy, MALDI-TOF spectrometry, and elemental analysis, and the data support its structure. The assignment of signals in the ^{1}H and ^{13}C NMR spectra of compound **3** was based on the data from 2-D CH-COSY and HC-HMBC measurements (C–H coupling across one bond and long-range H–C coupling). The compound exhibits interesting spectroscopic properties, indicating high acidity of the hydroxy group. This phthalocyanine behaves as a strongly solvatochromic compound and can exist in different forms depending on the concentration and nature of solvent. Additionally, photodecomposition of **3** in chloroform and tetrahydrofuran was found to proceed via different pathways.

Introduction

Phthalocyanines (Pc's) and their metal complexes (PcM's), as well as their analogues, e.g. porphyrazines (Pz's) and naphthalocyanines (Nc's), attract much attention because of their electronic structure features, giving rise to a plethora of applications in materials science.[1] The properties of phthalocyanines can be widely modulated via changes in their chemical structure, introducing different coordinated elements into the cavity of the macrocycle or in the periphery when appropriate substituents are present, varying axial and peripheral ligands and substituents, changing the symmetry of the macrocycle, etc.

Unsymmetrical phthalocyanines, despite the comparatively complicated preparation methods, are gaining more consideration recently because of their high potential for modern applications,[2a,2b] e.g. in molecular electronics, mostly as self-assembled, highly-ordered thin films.[2c–2e] For these reasons, macrocyclic synthons useful for various unsymmetrical functionalizations of phthalocyanines are of special interest. Among others, iodo-substituted Pc's with other peripheral substituents for increasing their solubility are especially often utilized for the construction of different phthalocyanine-based systems.[3] These unsymmetrical Pc synthons have been used for the preparation of ethynyl-substituted phthalocyanines, ethynyl- and diethynylethene-bridged bis(phthalocyanines), binuclear and trinuclear phthalocyanine-containing phosphonium salts, as well as for the synthesis of other important Pc synthons containing vinyl or aldehyde functionalities.[3] Recently, we reported the preparation of a new unsymmetrical, soluble zinc-phthalocyanine with one fused 1,2,3-triazole ring in the periphery (compound **1** in Scheme 1).[4] First investigations on the properties of **1** have shown that it is another useful synthon for various unsymmetrical modifications of phthalocyanines. Due to the reactivity of the NH-function of the triazole moiety in **1**, it can presumably be bound to different surfaces, polymers and biologically active molecules using proper spacers. Here we demonstrate that triazole-functionalized phthalocyanine **1** can serve as an excellent precursor for the formation of the system having an azo-dye fragment conjugated with the Pc macrocycle. Peripheral functionalization of the phthalocyanine with one conjugated azo-dye moiety imparts peculiar optical properties to the Pc molecule, which will be discussed below. This synthesis is based on the recent findings that 1*H*-benzotriazole can be activated towards coupling with nucleophiles such as phenol-

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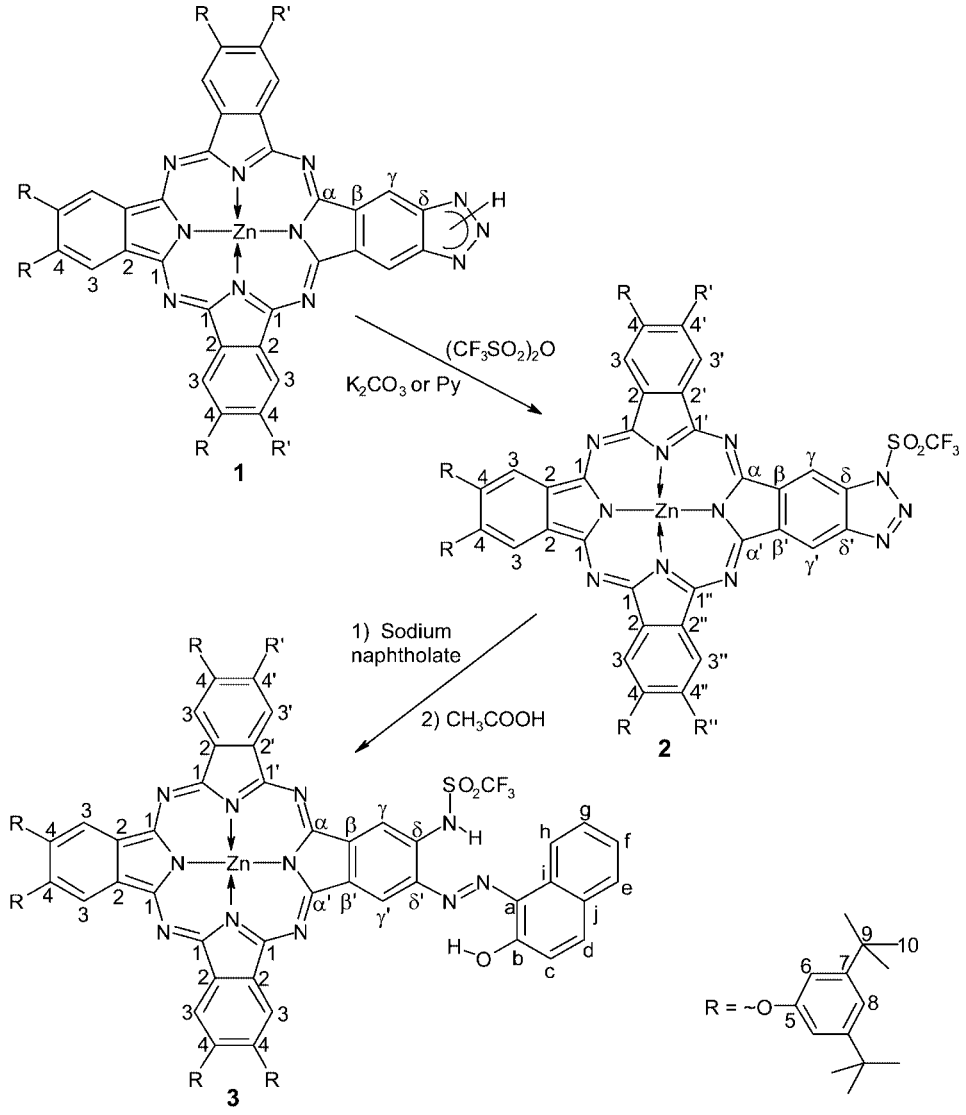


Scheme 1. Synthesis of compounds **2** and **3** and designation of the atoms used for ^{1}H and ^{13}C NMR spectroscopy.

ates, naphtholates and some others, leading to the opening of the triazole ring and formation of an azo moiety in high yields.[5,6] The activation of benzotriazole is achieved by introduction of strong electron-withdrawing groups such as nonaflyl[5] or triflyl[6] onto the triazole ring at the 1N-position.

To the best of our knowledge, only one report on the synthesis of a phthalocyanine substituted with azo groups has been published till now, namely the template tetramerization of 4-[4-(diethylamino)phenylazo]phthalonitrile to yield the corresponding phthalocyanine and its copper complex as mixtures of four positional isomers.[7] UV/Vis absorption spectra of these compounds in neutral THF and as thin films on TiO_2 were recorded, showing several new broad bands in the region 370–570 nm. These bands are unusual for the unsubstituted and for most substituted Pc's. However, no other properties of these new phthalocyanines were reported.

Results and Discussion

Synthesis

As we showed earlier,[4] triazole-fused phthalocyanine **1** easily undergoes acetylation of the triazole moiety with acetic anhydride in presence of pyridine. Similarly, addition of a trifluoromethanesulfonyl (triflyl) group to this phthalocyanine results in 93% yield of only the 1N-isomer, **2** (see Scheme 1), the structure of which was proved entirely by spectroscopic techniques (see Exp. Section). One must take into account the relative instability of this compound due to the reactivity of the triflated triazole moiety, reactivity observed also for simple benzotriazoles,[5,6] especially under daylight exposure. Therefore, **2** was protected from light during the workup and its purification by column chromatography. Introduction of the triflyl group is usually promoted by equimolar (or higher) amounts of base, which

was pyridine or anhydrous potassium carbonate in our case. The use of pyridine results, however, in its coordination to the phthalocyaninatozinc **2**. The coordinated pyridine is rather difficult to remove upon mild heating in vacuo, but strong heating can also destroy the triflated triazole ring. For example, under the mild conditions of MALDI-TOF measurement on this product, fragmentation of the triazole ring is observed. The spectrum shows a weak peak corresponding to a bis-pyridine adduct of **2** (*m*/*z* = 1977 + 158 + 1), but no molecular peak (*m*/*z* = 1977) without the coordinated pyridine. The most intense signal corresponds to the loss of N_2 from **2** (*m*/*z* = 1977–28 + 1), in contrast to the spectrum of precursor **1**,[4] where the main peak corresponded to a molecular ion, and only little fragmentation with the loss of N_2 was observed. Other signals in the spectrum of the bis-pyridine adduct of **2** fit with the loss of CF_3 and N_2 (*m*/*z* = 1879), SO_2CF_3 (*m*/*z* = 1843), SO_2CF_3 and N_2 (*m*/*z* = 1817), and $SOCF_3$ and N_2 (*m*/*z* = 1833). However, no rupture of the phthalocyanine macrocycle is observed. On the other hand, when potassium carbonate is used as a base, the yield of **2** is nearly the same, but, according to the brownish color of the reaction mixture, the removal of trifluoromethanesulfonic acid by this base is not very effective due to the heterogeneity of the reaction, resulting in partial protonation of the phthalocyanine macrocycle **2**. However, deprotonation of the macrocycle takes place in the course of column chromatography without any addition of external base, yielding the pure compound **2**. The MALDI-TOF spectrum of pure **2** shows nearly the same fragmentation pattern as its pyridine adduct.

The triflyl group on the triazole ring activates its opening in presence of strong nucleophiles, such as phenolate or naphtholate anions, in such a way that formation of the azo-dye takes place, similar to azo-coupling.[5,6] In the case of triflated, triazole-fused phthalocyanine **2**, this process is complete in a few minutes after addition of **2** to sodium naphtholate in toluene, resulting in an "ink-blue" solution. The workup of the reaction mixture with acetic acid and purification of the compound as described in the Exp. Section gives 2-hydroxynaphthylazo-substituted phthalocyanine **3** in 86% yield. In the MALDI-TOF spectrum, **3** gives only two main cluster peaks, one corresponding to the molecular ion (*m*/*z* = 2121) and another to a fragment which results from the loss of 1-imino-2-naphthalenone (*m*/*z* = 1964), additionally supporting the structure shown in Scheme 1.

The elemental analysis of both **2** and **3** shows satisfactory agreement of C, H and N compositions with calculated values−always within the limits of allowed error. It was surprising, therefore, to find 0% sulfur for both compounds, whereas 1.62% and 1.51% were calculated for **2** and **3** respectively. This is due to the formation of stable, nonvolatile inorganic zinc-sulfur compounds (for example, sulfate) under the conditions of combustion of zinc phthalocyanines **2** and **3** in the analyzer.

Spectroscopic Properties

^1H and ^{13}C NMR spectra of compounds **2** and **3** prove their structures unambiguously. As we pointed out earlier,[4] the γ-protons in the starting material **1** appear in the ^1H NMR spectrum in [D_8]THF as one broadened singlet due to the tautomerization of the NH bond of the fused triazole ring (see Scheme 1), and protons H-3 give three well defined singlets due to the lowered symmetry of **1**. Introduction of the triflyl group onto the triazole ring (compound **2**) results in the strong splitting of the signals from protons γ and γ′ into two sharpened singlets (see Figure 1, b). This splitting indicates a complete substitution of the triazole proton by the triflyl group at the 1-N position without any noticeable formation of the 2-N isomer, as is typical for simple benzotriazoles.[8] We expect that the most downfield-shifted signal in the ^1H NMR spectrum of **2** should belong to a proton in the vicinity of the SO_2CF_3 group (γ-proton, see Scheme 1) due to the electron-withdrawing, and consequently deshielding, effect of the latter. Similar to compound **1**, the protons H-3 in **2** give three singlets, but less separated and shifted to higher field. Protons H-8′ and H-8′′ in **2** are the most deshielded among the protons of group H-8, giving two separated triplets, whereas in **1** they are equivalent and give one downfield-shifted triplet, 8′, according to the integration (see Figure 1, part a). The other aromatic protons of the peripheral substituents, R, R′ and R′′, in **2** give rise to a multiplet in the region 7.18–7.31 ppm. The protons of the *tert*-butyl substituents give four singlets. In the ^{13}C NMR spectrum of **2**, each group of carbon atoms gives five or six singlets, except the *tert*-butyl substituents (C-9 and C-10, see Scheme 1 and Exp. Section). The groups of signals could be easily distinguished from each other, whereas the assignment of each signal within a group to a specific carbon atom is practically impossible. The assignment of the groups of signals is given in the Experimental part and was based on data obtained when different pulse-programs were applied, such as SGPG and DEPT-135 for one-dimensional ^{13}C NMR spectra, and HSQC and HMBC for two-dimensional HC-coupling spectra. Additionally, the correlation of the γ-proton with the γ-carbon (δ =115.8 ppm) and of the γ′-proton with the γ′-carbon (δ =104.9 ppm) was clearly seen in the measurement of C–H coupling across one bond. However, long range coupling measurements did not reveal any correlation between H-γ and C-δ, C-β, or C-α, nor between H-γ′ and C-δ′, C-β′, or C-α′ due to the low intensity of the signals. The signals of the latter carbon atoms were found in the ^{13}C NMR spectrum of **2** after all other signals were assigned.

The same procedures were undertaken for the assignment of H- and C-signals in the NMR spectra of compound **3**. HSQC measurements of **3** in [D_8]THF + Et_3N show a clear correlation between H-γ and C-γ (δ =109.7 ppm). The signal from C-γ′, which couples with H-γ′, appears at δ = 118.1 ppm and is overlapped with a signal from one of the C-8 atoms. A downfield shift of C-γ′ and an upfield shift of C-γ signals are observed when **3** is compared with **2**. HMBC measurements of **3** show the coupling of H-γ with C-δ, C-β and also C-α, whereas a clear coupling with H-γ′ could be observed only for C-δ′ and C-β′. All the protons of the naphthalene moiety give clear couplings to carbon atoms across one bond (HSQC measurements) and across

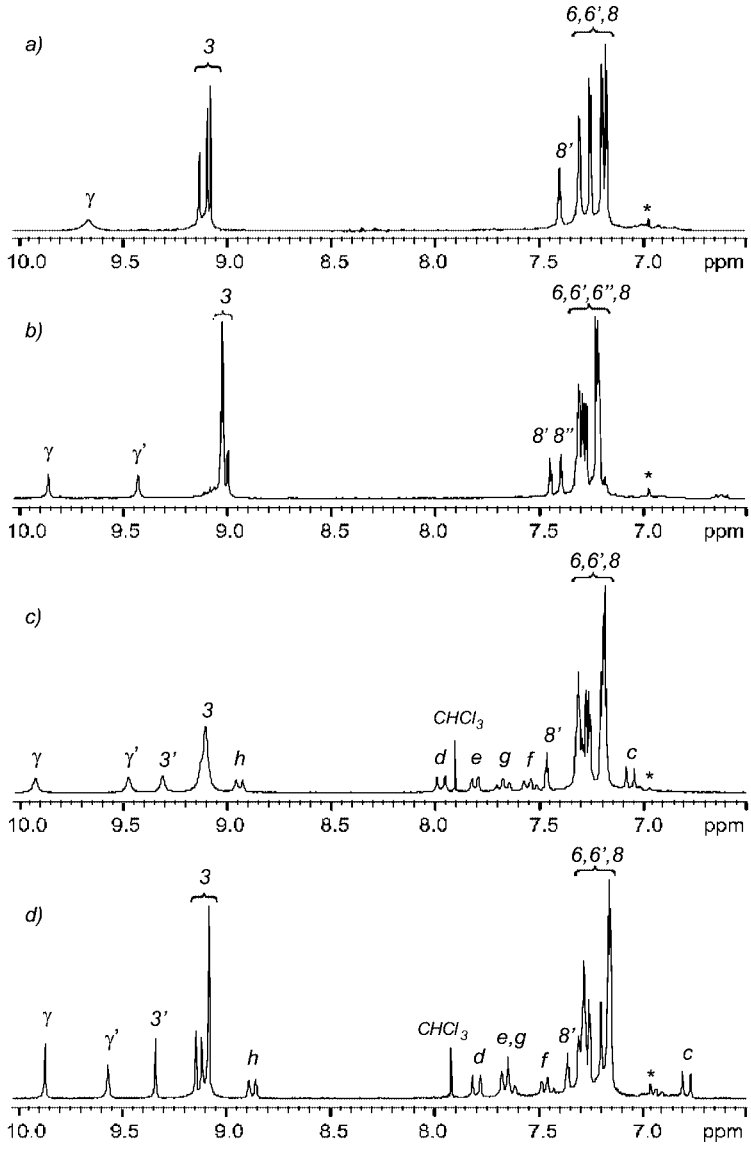


Figure 1. Fragments of ^{1}H NMR spectra of compounds: a) **1** in [D_8]THF; b) **2** in [D_8]THF; c) **3** in pure [D_8]THF; d) **3** in [D_8]THF with addition of triethylamine.

two bonds (HMBC measurements). Additionally, the previous results from the NMR spectra of [2-(2-hydroxy-1-naphthylazo)-*N*-phenyl]trifluoromethylsulfonamide were taken into account when the signals of the naphthalene fragment in **3** were assigned.[6]

Compound **3**, as expected from its structure, gives ^{1}H and ^{13}C NMR spectra which depend on the basicity of the solvent. Previous studies on the analogous azo-dyes derived from benzotriazole show relatively strong acidity of the hydroxy group in the naphthalene moiety.[5,6] The OH proton in these compounds appears in the range of 15–16 ppm as a broadened signal, and can be easily removed by mild bases. Even higher chemical shift value and strong broadening of the signal were observed for the OH proton in case of **3**. Acid ionization of the OH group should lead to a change in the NMR spectra of compound **3** in comparison with the neutral form. Thus, aromatic protons H-γ, H-γ′, H-3′, and H-3 of the phthalocyanine macrocycle in **3** appear as broadened peaks in pure [D_8]THF (see Figure 1, c). Addition of triethylamine to this solution results in a noticeable sharpening of signals from H-γ, H-γ′, H-3′ and H-3 with enhanced resolution of the group of protons H-3. Furthermore, signals from protons H-e, H-d and H-c of the naphthalene fragment experience a noticeable upfield shift upon addition of triethylamine (see Figure 1, d). The difference in the ^{13}C NMR spectra of **3** in pure [D_8]THF and with addition of Et_3N is even more drastic. Many C-signals were not resolved, were broadened or were shifted when pure [D_8]THF was used as a solvent. This can be due to the reason explained below. According to the mechanism of coupling between activated benzotriazole and phenolate or naphtholate,[5] only the trans isomer of **3** can be formed. The latter one can form several conformers stabilized via hydrogen bonding. For example, nonafluoro-{*N*-[(*E*)-2-(2-hydroxyphenyl)diazenyl]phenyl}-1-butanesulfonamide[9] exists in crystalline state as a conformer forming two six-

membered rings via hydrogen-bonding of the OH and the NH of the sulfonamido group with the N-atoms of the azo-bridge, similar to what is shown in Scheme 1 for compound **3**. In solution, the energy barriers for rotation along the C-δ′–N and C-a–N bonds are not high enough to stabilize different conformations that would cause the broadening of the signals of protons and carbon atoms; at least, line-broadening was not observed in the case of simpler azo-dyes derived from benzotriazole.[6] In case of phthalocyanine **3**, the presence of additional basic centers, such as the *meso*-N atoms of the macrocycle, can allow partial intramolecular or intermolecular proton transfer from the highly acidic OH group to the nearest *meso*-nitrogen with the formation of the acid associate, H-associate, ion-ionic associate or fully ionized form, depending on the "depth of protonation".[10] This proton transfer would result in a perturbation of the electron density in the Pc molecule and originate the equilibria of several forms of **3** in neutral solution due to self-protonation, which might be a reasonable explanation for the broadening of the C and H signals in the NMR spectra of **3** in pure [D_8]THF, and for their sharpening upon removal of the OH proton with a strong external base such as triethylamine. The effect of triethylamine on the ^{13}C NMR spectrum of **3** was especially noticeable for the signals of the internal carbon atoms of the pthalocyanine macrocycle and of the C-b atom of the naphthalene fragment, which should be the most influenced by the proton transfer from the OH to a *meso*-N atom. For example, the C-b atom appears at δ = 169.4 ppm in pure [D_8]THF as a very broad signal, and as a sharp peak at δ = 178.7 ppm when Et_3N is added.

The putative self-protonation in **3** is strongly supported by our observations of its UV/Vis spectra. The electron absorption spectra of **3** depend on the nature and purity of solvent, on the concentration of the compound, and are very sensitive to the presence of acids or bases. In solvents which can not solvate the proton of the OH group, such as dry CH_2Cl_2 or $CHCl_3$, the B and especially Q bands (split into Q_x and Q_y due to the lowered symmetry of **3**) are substantially broadened, and the Q_x band is shifted bathochromically in comparison with those of phthalocyanine **2** (see Figure 2, a). The addition of traces of triethylamine results in the sharpening and increased intensity of the Q bands, and a new band appears in the region 540–560 nm due to the absorption with a charge transfer (CT) in the 2-hydroxynaphthyl-azo moiety, indicating the acid ionization of OH group. The position and extinction coefficient of the CT band in **3** are practically the same as was found in simple azo-dyes derived from benzotriazole,[6] indicating no strong influence of the phthalocyanine macrocycle. The spectral changes which take place during titration of this solution with CF_3COOH are shown in Figure 3. Neutralization of Et_3N resulted in a lowered intensity of the CT band at 550 nm, and shoulders grown in on the red and blue sides of the Q band, leading to a UV/Vis spectrum close to the one of **3** in pure CH_2Cl_2 (compare curve 2 in Figure 3, with the spectrum in Figure 2, a, solid line). Further addition of acid leads to an increase of the red shoulder of the Q band because of the protonation of one *meso*-N atom[10] and to a decrease of the CT band to a minimum, due to a completely suppressed dissociation of the OH group (see curves 3, 4 and 5 in Figure 3). This means that in neutral chloroform or dichloromethane the OH group of compound **3** at low concentrations is partially dissociated and the macrocycle is partially protonated on the *meso*-nitrogen. In pure dry THF, which is able to solvate the proton, the UV/Vis spectrum of a 2.7×10^{-6} M solution of **3** reveals the complete dissociation of the hydroxynaphthyl group without protonation of the macrocycle. However, in a 5.4×10^{-5} M solution of **3** in THF, the broadening and lowering of the Q band is observed, and the CT band at 550 nm decreases noticeably (see Figure 2, b). This decrease indicates the suppression of OH dissociation at higher concentrations of **3**, while the protonation of the macrocycle at this concentration is still not observed clearly. The obvious decrease in the intensity of the Q-band can originate either from intramolecular or intermolecular interactions of compound **3** at high concentrations, appearing only when the OH group is not completely dissociated (compare the spectra in Figure 2, b). An additional reason for a complete dissociation of the OH group in a very diluted (2.7×10^{-6} M) solution of **3** in dry THF is, despite the usual procedure for drying THF, the traces of water in the solvent, which help to solvate the proton.

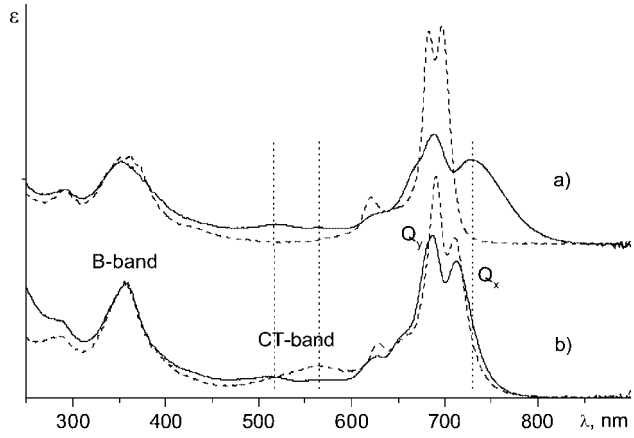


Figure 2. Normalized UV/Vis spectra of compounds: a) **2** in CH_2Cl_2 (dashed line) and **3** in CH_2Cl_2 (solid line) at a concentration of 5.8×10^{-6} M; b) **3** in THF at concentrations of 2.7×10^{-6} M (dashed line) and 5.4×10^{-5} M (solid line).

We also studied the UV/Vis spectra of **3** in chloroform at different concentrations in order to shed light on the nature of self-protonation of **3** in this solvent. Surprisingly, a very complicated dependence of UV/Vis absorption upon the concentration of **3** was found. For example, three normalized spectra at different concentrations of **3** are shown in Figure 4. At concentrations higher than 10^{-5} M a new, relatively sharp band at 789 nm appears. The origin of this band is not clear, although according to its shape and position it could belong to a phthalocyanine **3** doubly protonated on the *meso*-N atoms of the macrocycle rather than to a J-aggregate. Indeed, the absorption of phthalocyanine J-aggregates is red-shifted but very broadened and has low

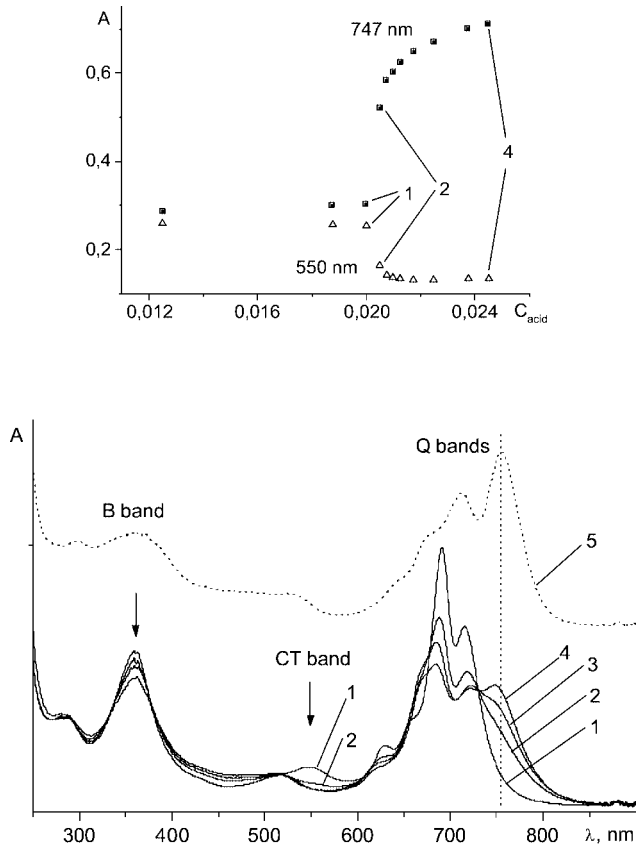


Figure 3. Titration (top) of a solution of triethylamine (ca. 2×10^{-2} M) in $CHCl_3$ with trifluoroacetic acid in the presence of compound **3** (ca. 10^{-5} M). The spectra shown (bottom) are for the following concentrations of added acid: 1: 2×10^{-2} M; 2: 2.05×10^{-2} M; 3: 2.1×10^{-2} M; 4: 2.45×10^{-2} M; 5: 5.7×10^{-2} M. Spectrum 5 (dotted line) is shifted up the scale to make the picture more clear.

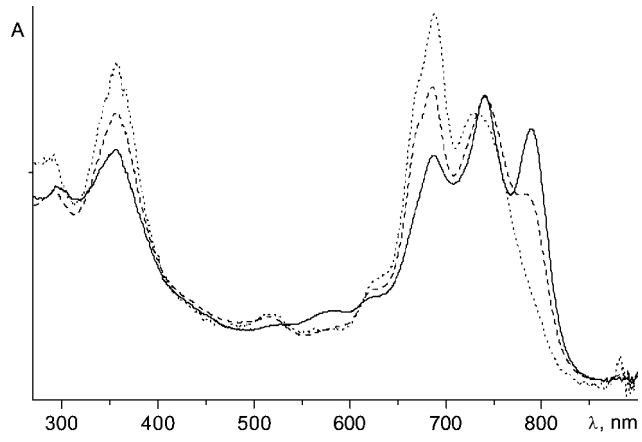
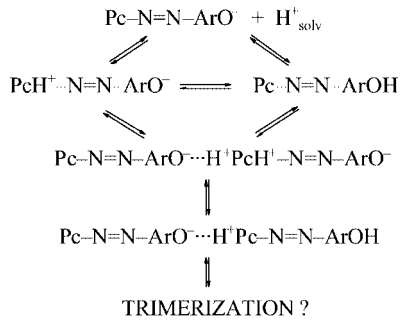


Figure 4. Normalized spectra of **3** in $CHCl_3$ at 1.23×10^{-4} M (solid line), 1.23×10^{-5} M (dashed line) and 3.08×10^{-6} M (dotted line).



Scheme 2. Possible equilibria of **3** in solution. The phthalocyaninatozinc core is indicated as "Pc" and the azo-dye moiety as "–N=N–ArOH".

intensity.[11] The absorption in the region of the CT-band also has complicated concentration dependence. There is a maximum of absorption at approximately 580 nm at high concentrations which decreases its intensity upon dilution, while a new maximum at 517 nm appears at low concentrations. We believe that formation of a doubly-protonated species can be explained in terms of H-association between two molecules of **3**, one of which has undergone intramolecular protonation. This would also explain the dependence of the intensity of the band at 789 nm on the concentration of compound **3**. Addition of triethylamine to the solutions with different concentrations of **3** gives the CT-band with a pronounced maximum at 550 nm and the Q bands identical to what is shown in Figure 3, curve 1. This can also be observed as a change of the color of solutions from dirty-green to violet-blue. The equilibria which can take place in the neutral solution of **3** are depicted in Scheme 2. The ratio of different forms shown in this Scheme depends on the concentration of **3** and the nature of solvent.

Keeping the solution of **3** in chloroform with excess triethylamine for several hours in daylight resulted in the change of the violet-blue color to pink. The UV/Vis spectrum of the pink solution shows a broadened absorption band at 535 nm, typical for the salts of 2-hydroxy-naphthylazo-dyes,[6] but no absorption due to the phthalocyanine macrocycle was observed, indicating its complete photodecomposition. It is known, that many tetrapyrrolic macrocycles and their metal complexes can undergo photobleaching in solution or in thin films,[12,13] and the extension of the π-conjugated system or the introduction of electron-donor substituents into these macrocycles decreases their photostability.[13a,13b] In many cases, the mechanisms of their photodegradation involve participation of singlet oxygen,[13b,13c] and the decomposition rates of the selfsame compound can vary with the nature of the solvent and additives.[12] We have observed that not only the rate, but also the route of photodecomposition of compound **3** depends on the nature of solvent. Thus, samples with equal concentrations of **3** in pure $CHCl_3$, pure THF, $CHCl_3$ with addition of Et_3N and THF with addition of Et_3N were exposed to daylight simultaneously. In a few hours, the sample in $CHCl_3$ + Et_3N turned pink, showing no absorption related to the phthalocyanine macrocycle in the UV/Vis spectrum (Figure 5, solid line, a), whereas the probe in pure $CHCl_3$ showed approx. 50% decomposition of the macrocycle (Figure 5, solid line, b), turning grey-brown. The sample in THF + Et_3N showed practically no decomposition of compound **3** for the same time period, and only little degradation after several days of irradiation, which could

be seen as a slight decrease of the Q_x-band intensity (see Figure 5, dotted line). For the sample in pure THF, after one day under daylight exposure, the intensity of the Q_y band increased and it underwent a slight broadening, whereas the intensity of the Q_x-band noticeably decreased. Keeping the pure THF solution of **3** for a longer period under day-light resulted in the loss of the azo-dye moiety, since in its absorption spectrum the CT-band in the region 500–550 nm disappeared and the Q band became sharp and unsplit with the maximum at 676 nm, similar to the symmetrical PcM's (see Figure 5, dashed line). Further irradiation of this solution resulted in a slow degradation of the macrocycle, observed as a decrease of the 676 nm band intensity. However, no substantial decomposition of **3** in THF or $CHCl_3$ solutions was observed when keeping them protected from light for over one week.

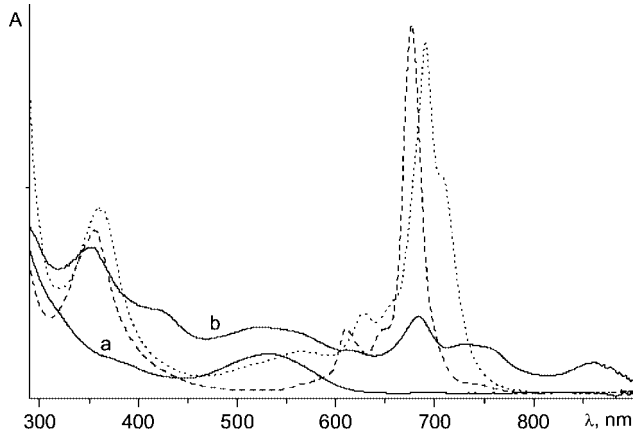


Figure 5. Spectra of **3** after light-exposure: less than one day in $CHCl_3$ + Et_3N (a: solid line, in pure $CHCl_3$ (b: solid line, several days in pure THF (dashed line) and in THF + Et_3N (dotted line).

In general, many different substituted phthalocyanines and their metal complexes decompose relatively quickly when dissolved in chloroform or other solvents and exposed to light.[14] According to our results, it can be supposed that the decomposition of **3** in $CHCl_3$ proceeds via a photocatalytic generation of trichloromethyl, dichloromethyl and other highly reactive radicals, as well as dichlorocarbene, upon irradiation.[15a,15b] The reductive formation of halomethane radicals is caused by PcZn **3** upon excitation, as suggested, for example, in the photooxidation of unsubstituted zinc-phthalocyanine in a CH_2Cl_2/CBr_4 system.[15c] The presence of electron-donor substituents in **3** can decrease its oxidation potential in the excited state, facilitating its photooxidation. Although PcZn in CH_2Cl_2/CBr_4 forms a stable cation-radical,[15c] this is not the case for **3** in $CHCl_3$. According to the UV/Vis measurements, decomposition of the macrocycle takes place for **3** in $CHCl_3$ with time, since a decrease of absorption without any isosbestic points was observed in the spectra. The reason for the decomposition of **3** and other substituted phthalocyanines in chloroform might be their reaction with the radicals generated from solvent. This reaction is centered at the phthalocyanine macrocycle since, in the case of PcZn **3**, the azo-dye chromophore survives the photodecomposition. The addition of triethylamine seems to accelerate these processes for several reasons: it can facilitate basic generation of dichlorocarbene by removal of HCl from chloroform, or it can participate as an additional donor of electrons in the photosensitized reductive generation of radicals from chloroform via formation of an $Et_3N{\cdot}CHCl_3$ complex.[15d] The photoreductive mechanism is also known to be realized during the formation of radicals from chloroform in the presence of aromatic amines.[15e] In contrast, addition of a radical quencher, such as 4-*tert*-butylcatechol, to $CHCl_3$ was found to stabilize **3** in solution, decreasing its rate of decomposition in comparison with that in pure $CHCl_3$ solution. Furthermore, the spectral changes which take place upon decomposition of **3** in pure $CHCl_3$ or with addition of catechol are different. The broadened band at approximately 860 nm, which can be attributed to a relatively long-living phthalocyanine-radical species,[16] appears upon photodecomposition of **3** in pure chloroform, whereas no band at this wavelength was observed in presence of 4-*tert*-butylcatechol.

An additional decomposition route can be due to generation of singlet oxygen upon irradiation, which can also attack PcZn **3**.[12] In pure THF, the singlet oxygen sensitized by zinc phthalocyanine **3** can be consumed by the solvent, probably with intermediate formation of THF peroxides,[17] or it can attack the electron-rich azo-bridge at the periphery of the phthalocyanine **3**, possibly with formation of *N*-oxides, leading to the rupture of the azo-bridge with no decomposition of the macrocycle at this stage. A rupture of the azo-bridge could also occur upon attack of THF peroxide, but only in presence of light, because when H_2O_2 was added to a THF solution of **3** protected from light, no decomposition of **3** was observed.

Triethylamine in THF can cause physical and chemical quenching of singlet oxygen.[18] It also can quench THF peroxides with formation of *N*-oxides, similar to the reaction with hydrogen peroxide,[19] thus noticeably stabilizing compound **3**. Therefore, the conversion of **3** into a phthalocyanine species without an azo-bridge takes much longer in THF + Et_3N than in pure THF. When K_2CO_3 was used as a base to ionize **3** in THF solution, faster decomposition of **3** was observed, similar to that in pure THF. However, as stated previously, the azo-dye chromophore survives under irradiation in $CHCl_3$ + Et_3N practically without decomposition, whereas the phthalocyanine macrocycle is destroyed completely. Also, in pure chloroform the azo-dye chromophore survives while the macrocycle of PcZn **3** decomposes. This could be seen from a change from the red-brownish color of decomposed solution to pink upon addition of Et_3N. Therefore, there is a clear indication that the nature of active species causing photodecomposition of **3** in $CHCl_3$ and THF is different.

Phthalocyanine **3** in solution is sensitive to the presence of water in the solvents. If a relatively dilute solution of **3** in THF or $CHCl_3$ is kept in a cuvette in the dark not tightly closed, a change of color to violet-blue can be observed due to the appearance of the CT-band at 550 nm, which is a sign of ionization of the OH group in the 2-hydroxynaph-

thylazo moiety. This also happens when a drop of water is added to a THF solution of **3** (approx. 2 mL), resulting in a change of spectrum similar to what is shown in Figure 2, part b (from a solid line spectrum to a dashed line one). This observation also indicates the high acidity of the OH group in **3**.

One could explain the self-protonation of **3** in neutral solvents as an effect of residual acetic acid, used in the chromatographic purification of **3**. However, vacuum drying and washing of solid **3** with methanol by decantation allowed complete removal of the acid, as could be seen from the ^1H and ^{13}C NMR spectra, as well as from the FTIR spectrum of **3**. The intense vibration of the carboxy group at approximately 1700 cm^{-1} would be seen in the IR spectrum of **3** if acetic acid were present in the sample. In contrast, no absorption band was observed in this region of spectrum of **3**. However, the comparison of the FTIR spectra of **1**, **2** and **3** reveals some differences in the region 500–1550 cm^{-1} (see Figure 6). Thus, the introduction of the trifluoromethylsulfonyl group in **2** and **3** is expected to bring the new bands into their vibrational spectra in comparison with **1** due to the intense stretching vibrations of the $–CF_3$ group and different vibrations of the $–SO_2–$ group. The usual intense symmetrical and asymmetrical stretching vibrations of the $–SO_2–$ group could not be seen in the spectra of **2** and **3**, probably because they were masked by the vibrations of the phthalocyanine macrocycle. However, the $–SO_2–$ group on the triazole ring (compound **2**) gives two new intense bands at 619 and 582 cm^{-1} due to combinatorial vibrations, which degenerate into one band at 597 cm^{-1} with lowered intensity when the triazole ring is opened (compound **3**). We believe also that one of the stretching vibrations of the $–CF_3$ group appears at 1226 and 1229 cm^{-1} in compounds **2** and **3**, respectively, whereas compound **1** has a minimum in the IR spectrum in this region.

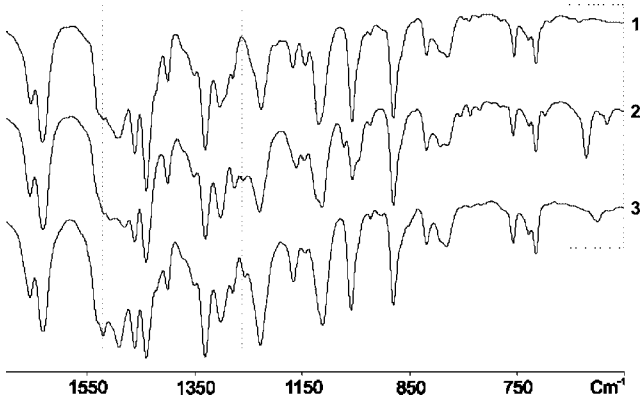


Figure 6. FTIR spectra of compounds **1**, **2** and **3** in the range 550–1700 cm^{-1}.

Conclusions

It was found that the reaction of triflated benzotriazoles with phenolate or naphtholate to yield azo-dyes in good yields is also applicable to a triazole-functionalized zinc phthalocyanine, **1**, using the same synthetic pathway and conditions. Thus, the corresponding triflated triazole-fused zinc phthalocyanine **2** and the phthalocyanine conjugated with a 2-hydroxynaphthylazo moiety (**3**) were formed in nearly quantitative yields (see Scheme 1). Introduction of a 2-hydroxynaphthylazo group on the periphery of a zinc phthalocyanine strongly affects the spectroscopic properties of the phthalocyanine. Thus, the Q band in the UV/Vis spectrum of **3** is split into Q_x and Q_y components due to the unsymmetrical conjugation with the azo-dye moiety, and the shapes and positions of the maxima depend strongly on the nature of solvent and the concentration. Additionally, the new CT-band at approximately 550 nm appears in the spectrum of **3** due to absorption with charge transfer in the azo-dye fragment if the hydroxy group is ionized. The acidity of the hydroxy group in **3** is high enough to lead to a partial self-protonation of **3** on the *meso*-nitrogens in CH_2Cl_2 or $CHCl_3$, which could be observed in the UV/Vis measurements as a broadening of the Q-bands and an appearance of a red shoulder on the Q_x-band at low concentrations of **3**. It is possible that both inter- and intramolecular interactions between *meso*-N atoms and OH protons take place, depending on the concentration of **3**. The intermolecular proton transfer, however, can stop at the stage of H-associates, resulting in the dimerization or oligomerization of Pc molecules via hydrogen bonding. This oligomerization could be a reasonable explanation for the observed dependence of the UV/Vis spectra of **3** on the concentration of the compound in chloroform.

Compound **3** was found to be light-sensitive in solution and its photodecomposition in $CHCl_3$ and THF appeared to proceed via different pathways, involving different active species. It is likely that in chloroform the phthalocyanine is attacked by free radicals generated from the solvent, leading to the rupture of the macrocycle without affecting the azo-dye moiety. In THF, singlet oxygen sensitized by PcZn **3** is possibly the main active species, which causes decomposition of the azo-dye chromophore.

Experimental Section

General: 9,10,16,17,23,24-Hexakis(3,5-di-*tert*-butylphenoxy)[1,2,3]triazolo[4,5-*b*]phthalocyaninato zinc (**1**) was prepared as described previously.[4] Dichloromethane, THF, and toluene for use in reactions and UV/Vis measurements were dried with CaH_2 or Na, respectively, followed by distillation.

Instrumentation: FTIR: Bruker Tensor 27. UV/Vis: Shimadzu UV-365. ^1H and ^{13}C NMR: Bruker AC 250 (^1H: 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.

Phthalocyaninatozinc Complex 2. Method A: To a stirred solution of **1** (100 mg, 54 μmol) in anhydrous dichloromethane (3 mL) was added pyridine (20 μL, 240 μmol). The reaction mixture was cooled to 0 °C. After 15 min, trifluoromethanesulfonyl anhydride (20 μL, 240 μmol) was added dropwise. The reaction mixture was stirred

at room temperature for ca. 2 h, and the progress of the reaction was monitored by TLC. After removal of the solvent, the crude product was purified by chromatography on silica gel under protection from light [eluent: chloroform] to give **2** + 2Py (102 mg, 88%).

Method B: To a stirred solution of **1** (50 mg, 27 μmol) in anhydrous dichloromethane (2 mL) was added potassium carbonate (41 mg, 30 μmol). The reaction mixture was cooled to 0 °C. After 15 min, trifluoromethanesulfonyl anhydride (20 μL, 240 μmol) was added dropwise. The reaction mixture was stirred at room temperature for ca. 2 h, and the progress of the reaction was monitored by TLC. After removal of the solvent, the crude product was purified by chromatography on silica gel under protection from light [eluent: chloroform] to give **2** (50 mg, 93%).

2: FTIR (KBr), $\tilde{\nu}$ = 539 vw, 580 w, 617 m, 691 vw, 707 m, 720 w, 748 m, 807 vw, 824 vw, 842 vw, 878 m, 902 m, 961 s, 1003 w, 1035 m, 1049 w, 1088 s, 1120 m, 1134 m, 1200 s, 1229 m, 1244 m, 1269 s, 1297 vs, 1317 m, 1364 m, 1402 vs, 1422 vs, 1440 s, 1586 vs, 1608 m, 2360 vw, 2869 m, 2906 m, 2964 vs, 3072 w cm^{-1}. UV/Vis (CH_2Cl_2, $c = 4.77 \times 10^{-6}$ M): λ (logε) = 291 (4.68), 352 (4.88), 620 (4.57), 683 (5.23), 697 (5.23) nm. ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 1.36 s, 1.37 s (72 H, H-10), 1.41 (s, 18 H, H-10′′), 1.44 (s, 18 H, H-10′), 7.18–7.31 (m, 16 H, H-6, 6′, 6′′, 8), 7.39 (t, J = 1.85 Hz, 1 H, H-8′′), 7.44 (t, J = 1.83 Hz, 1 H, H-8′), 9.00 s, 9.02 s, 9.03 s (6 H, H-3), 9.43 (s, 1 H, H-γ′), 9.86 (s, 1 H, H-γ) (ppm). ^{13}C NMR (250 MHz, [D$_8$]THF): δ = 31.92 [C-10], 35.77, 35.83 [C-9], 104.93 (C-γ′), 113.09, 113.22, 113.41, 113.96, 114.44 [C-6], 114.17, 114.25, 115.28, 115.34, 115.50 [C-3], 115.84 (C-γ), 117.72, 117.82, 117.95, 118.35, 118.69 [C-8], 123.16 (C-δ′), 124.59 (C-py), 133.07 (C-β′), 134.90, 135.21, 135.68, 135.75, 135.76, 135.80 [C-2], 137.62 (C-py), 138.01 (C-β), 141.40 (C-α′), 147.35 (C-α), 147.60 (C-py), 150.48 (C-δ), 150.33, 150.88, 151.47, 151.53, 152.06, 152.29 [C-4], 153.27, 153.30, 153.33, 153.35, 153.53, 153.66 [C-7], 153.24, 153.73, 154.56, 154.79, 154.84, 155.02 [C-1], 157.47, 158.10, 158.47, 158.66, 158.69 [C-5] (ppm). MS MALDI-TOF: see results and discussion. $C_{117}H_{134}F_3N_{11}O_8SZn$ (1976.87): calcd. C 71.09, H 6.83, N 7.79, S 1.62; found C 70.88, H 6.77, N 7.47, S 0.00.

Phthalocyaninatozinc Complex 3: NaH (3 mg, 60% suspension in oil) was added to a stirred solution of β-naphthol (11 mg, 75 μmol) in anhydrous toluene (3 mL) at room temperature. After 15 min, **2** (50 mg, 25.3 μmol) was added. The mixture was stirred for 10 min while monitoring the progress of the reaction by TLC. At the end of this period 0.5 mL of acetic acid was added. The organic phase was evaporated, and the crude product was purified by chromatography over silica gel [eluent: chloroform containing 1% AcOH] to afford **3** (46 mg, 86%).**3:** FTIR (KBr), $\tilde{\nu}$ = 459 vw, 507 vw, 597 w, 706 m, 719 w, 748 m, 866 m, 902 m, 961 s, 1002 vw, 1037 s, 1087 s, 1119 m, 1139 m, 1198 vs, 1226 m, 1247 m, 1269 s, 2361 vw, 1297 vs, 1364 m, 1402 vs, 1422 vs, 1450 vs, 1479 vs, 1586 s, 1608 s, 2868 m, 2906 m, 2963 vs, 3071 vw cm^{-1}. UV/Vis (THF, $c = 2.70 \times 10^{-6}$ M) λ (logε) = 287 (4.72), 356 (4.94), 569 (4.44), 628 (4.67), 691 (5.27), 711 (5.13) nm. (CH_2Cl_2, $c = 5.82 \times 10^{-6}$ M) λ (logε) = 290 (4.59), 352 (4.77), 520 (4.16), 565 (4.09), 689 (4.89), 728 (4.78) nm. ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 1.34 s, 1.35 s, 1.36 s, 1.40 s (90 H, H-10), 1.45 (s, 18 H, H-10′), 6.77 (d, J = 9.63 Hz, 1 H, H-c), 7.17–7.30 (m, 17 H, H-6, 6′, 8), 7.46 (t, J = 1.82 Hz, 1 H, H-8′), 7.53 (dd, J = 6.97, J = 7.72 Hz, 1 H, H-f), 7.67 (dd, J = 6.97, J = 7.35 Hz, 1 H, H-g), 7.73 (d, J = 7.80 Hz, 1 H, H-e), 7.96 (d, J = 9.55 Hz, 1 H, H-d), 8.94 (d, J = 8.08 Hz, 1 H, H-h), 9.10 (s, 5 H, H-3), 9.31 (s, 1 H, H-3′), 9.48 (s, 1 H, H-γ′), 9.92 (s, 1 H, H-γ), 16.98 (s, 1.4 H, OH, NH) ppm. ^{1}H NMR (250 MHz, [D$_8$]THF + Et$_3$N): δ = 1.34 s, 1.35 s, 1.36 s, 1.37 s (90 H, H-10), 1.45 (s, 18 H, H-10′), 7.05 (d, J = 9.57 Hz, 1 H, H-c), 7.17–7.30 (m, 17 H, H-6, 6′, 8), 7.35 (t, J = 1.20 Hz, 1 H, H-8′), 7.44 (dd, J = 7.63, J = 7.23 Hz, 1 H, H-f), 7.61 (m, 2 H, H-e, g), 7.79 (d, J = 9.62 Hz, 1 H, H-d), 8.87 (d, J = 8.03 Hz, 1 H, H-h), 9.08 s, 9.11 s, 9.14 s (5 H, H-3), 9.34 (s, 1 H, H-3′), 9.57 (s, 1 H, H-γ′), 9.87 (s, 1 H, H-γ), 16.98 (s, 1 H, NH) ppm. ^{13}C NMR (250 MHz, [D$_8$]THF + Et$_3$N): δ = 31.71, 31.90, 31.96 [C-10], 35.73, 35.78, [C-9], 109.72 (C-γ), 113.05, 113.08, 113.16, 113.20, 113.52 [C-6], 114.05, 114.24, 114.72, 114.96, 115.02 [C-3], 115.35 (C-3′), 117.44, 117.66, 117.70 [C-8], 118.12 (C-γ′, C-8), 123.07 (C-h), 123.28 (q, J = 327 Hz, CF_3), 127.74 (C-c), 129.08 (C-i), 129.61 (C-e), 130.19 (C-g), 131.80 (C-j), 134.09 (C-β′), 135.23 (C-a), 135.81, 135.83, 135.85, 135.98, 136.19 [C-4], 138.21 (C-β), 139.42 (C-δ′), 141.26 (C-δ), 141.59 (C-d), 150.55, 150.64, 150.91, 150.99, 151.10, 151.27 [C-4], 153.25, 153.45 [C-7], 153.50, 153.55, 154.26, 154.39 [C-1], 155.99 (C-α′), 156.17 (C-α), 158.17, 158.57, 158.61, 158.67, 158.72, 158.74 [C-5], 178.69 (C-b) ppm. MS MALDI-TOF: See results and discussion. $C_{127}H_{142}F_3N_{11}O_9SZn$ (2121.05): calcd. C 71.92, H 6.75, N 7.26, S 1.51; found C 72.17, H 6.81, N 6.97, S 0.03.

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