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FULL PAPER

Helical Self-Assembly of Optically Active Glycoconjugated Phthalocyanine *J*-Aggregates

Felix Bächle,[a] Cäcilia Maichle-Mössmer[b] and Thomas Ziegler*[a]

Abstract: Four galactoconjugated zinc(II) phthalocyanines (Pcs) have been prepared and fully characterized. The carbohydrate-containing phthalonitrile precursors of the Pcs were synthesized through a copper-catalyzed azide-alkyne cycloaddition (CuAAC). The Pcs show a remarkable aggregation behaviour in solution, depending on the nature of the solvent, the temperature and the substitution position on the phthalocyanine. Solvent dependent CD-spectroscopy experiments shows that these Pcs aggregate as chiral helices in solution. Crystal structure data of a phthalocyanine bearing two carbohydrate units substantiate the properties shown by CD spectroscopy. Furthermore, the 1,2,3-triazole moieties of the Pcs play a decisive role in the formation of supramolecular aggregates. The glycoconjugated zinc(II) phthalocyanines described here show molar extinction coefficients $\varepsilon_{max} > 10^5$ M^{-1} cm^{-1} and absorption maxima λ_{max} > 680 nm, which make them attractive photosensitizers for Photodynamic Therapy (PDT).

Introduction

In 1909, S. E. Sheppard discovered concentration-dependent anomalies concerning the Beer-Lambert law in isocyanine dyes. However, he could not find a conclusive explanation for this aggregation phenomenon.[1] As we know today, aggregation of tetrapyrrol derivates can occur in most organic or aqueous solvents. The aggregation of Pcs, on the other hand, can have an uncontrolled and unforeseeable effect on the photophysical properties and considerably influences these properties as well. For example, absorption, fluorescence quantum yield and photosensitizer activity of Pcs may drastically decrease upon aggregation.[2] In general, aggregation can be divided into two different types (Figure 1). On one hand, tetrapyrrol macrocycles can form face to face aggregates with the molecular transition dipole moments connected perpendicular to the line connecting their centres. In this case, the aggregation type is called *H*-aggregate. The absorption maxima of this kind of aggregate is hypsochromically shifted in comparison to the monomer and the emission is completely quenched.[3] On the other hand, aggregates with the transition dipole moments parallel to the line connecting the centres of each molecule are called *J*-aggregates or *Scheibe*-aggregates.[4] This type of aggregate is named after its discoverers E. E. Jelley[5] and G. Scheibe[6] who independently found this special macromolecular phenomenon. *J*-aggregates are characterized by bathochromic shifted absorption maxima in comparison to the monomer. Furthermore, the emission is not quenched in this case.[4b, 7]

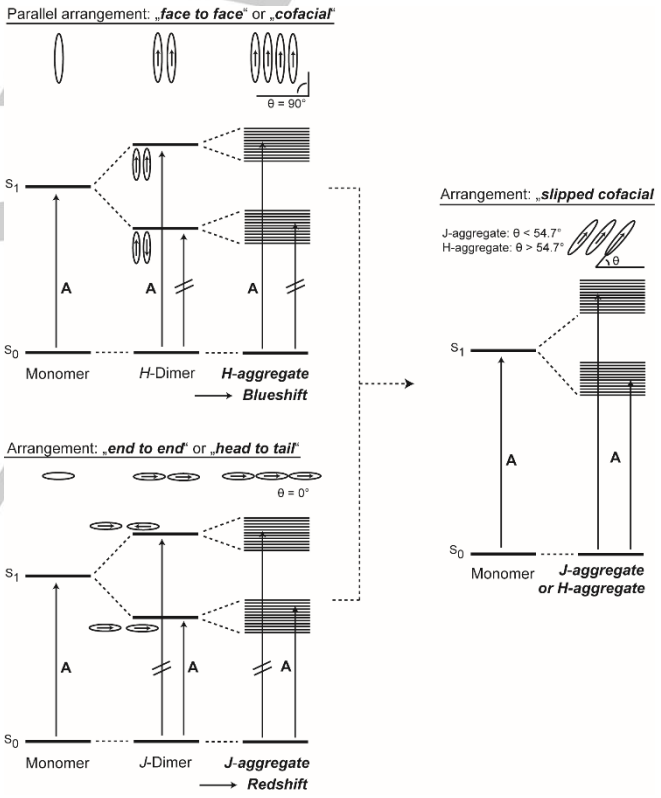

Figure 1. Schematic representation of the photophysical absorption properties (A) of a *J*- or *H*- aggregate. Slipped facial aggregates are tilted aggregates. In this case it depends on the staggering angle of which aggregation type is formed.

Porphyrins are widespread in nature. Besides the crucial function in heme complexes, many substance classes closely related to the porphyrin structure can be found in nature. These include for example the chlorophylls (Chls) and bacteriochlorophylls (BChls) found in the natural light-harvesting complex (LHC) as the most prominent chromophores.[8] These two substance classes belong to the group of chlorines and bacteriochlorines. Examples for

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naturally occurring BChls are the purple bacteria Rhodopseudomonas acidophila and Rhodospirillum molischianum which contain 27 and 24 BChls as chromophores in their light collection complexes II (LH II) and which aggregate in a *J*-aggregational arrangement.[9]

Porphyrins and phthalocyanines normally form *H*-aggregates in solution. The reason for this behaviour is the fact that the angle in a face-to-face arrangement of molecules in H-aggregates is favoured due to the electrostatic repulsion or attraction of a staggered arrangement of molecules. In this case, driven by π-π van der Waals interactions, the aromatic core of the tetrapyrrole molecules overlap strongly with each other and results in columnar stacks.[10] *J*-aggregates are more sparse in this substance class and when they occur, they can be caused by a metal ligand coordination.[11] In addition to the two non-covalent interactions mentioned above, aggregation can also occur through hydrogen bonding[11f, 12] and donor-acceptor interactions,[13] respectively. Factors additionally influencing the aggregation of porphyrins and phthalocyanines in solution are the concentration[10b], temperature[14], nature of attached substituents[10b, 10c, 15], nature of solvent[14], additives[16] and the nature of the metal ion in the centre of the tetrapyrrol.[16-17] The aggregation can range from a low molecular to a supramolecular size. Aggregates can even form on the nm scale.[7b] Consequences of aggregation are lower solubility, problems with purification and characterization, reduction of singlet oxygen yield and triplet lifetime. Wherefore, aggregation severely affects the applicability of such compounds and has to be studied thoroughly. Since in addition to the first targeted application in 1977 for a photographical process[18], phthalocyanines are an essential component of many modern applications such as Photodynamic Therapy (PDT) and thus, require careful investigation of their aggregation behaviour.

PDT is a non-invasive treatment modality to destroy malignant tissue and cells through oxidation processes. It is based on a combination of molecular oxygen, a photosensitizer and light. A photosensitizer (PS) can be seen as a compound activable by light. Irradiation at a specific wavelength of light excites the photosensitizer. Subsequently, energy is transferred to other molecules in its direct surrounding.[19] When the photosensitizer is used for PDT, cytotoxic species such as singlet oxygen ($^1O_2$) or hydroxyl radicals are generated from oxygen which is present in the respective tissues. Approximately 4000 years ago the Egypt's used sunlight and bishop's weed (*ammi majus*) containing psoralen to cure skin diseases such as vitiligo. Today, psoralen is still used in combination with UV-light as a treatment of various skin diseases.[20] Modern photosensitizers should have long wavelength absorption maxima, they should display high $^1O_2$ quantum yields, have high molar extinction coefficients and a non-existent dark toxicity.[21] Porphyrin type photosensitizers such as phthalocyanines comply with these requirements. PCs usually have absorption maxima (Q-Band) in the range of 670-800 which allows for the light to penetrate human tissue up to 2 cm.[22] They also have very high extinction coefficients ($\varepsilon_{max} > 10^5\ m^{-1}\,cm^{-1}$) and low dark toxicities.[22-23] First successful and commercially available examples of porphyrin type photosensitizers in this respect are Foscan, Visodyne and Photofrin.[24] The goal for a successful development of efficient PSs, and also one of the most challenging goals for modern PDT as a medical treatment option against cancer, lies in the ability to maximize the selective uptake in the malignant tumorous tissue.

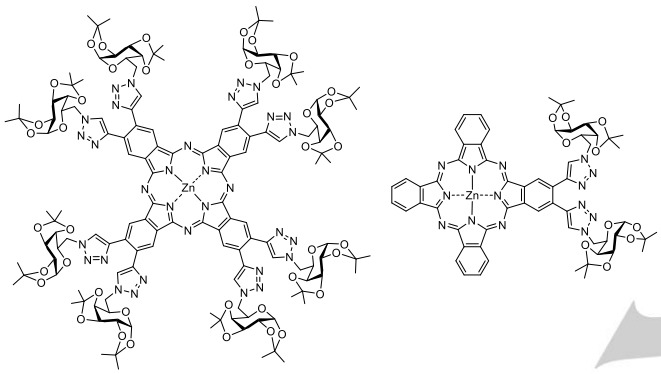
Photosensitizers which are able to accumulate in the targeted tissue are called "third generation photosensitizers".[21] They are either modified by polar groups modulating their amphiphilicity or linked covalent to a special bioactive carrier.[22] For an organic chemist though, a plethora of different bioactive carriers are available, such as amino acids, peptides, antibodies, steroids or carbohydrates.[25] Especially, glycoconjugated phthalocyanines are auspicious candidates as third generation photosensitizers in this respect. The carbohydrate moiety of these types of PCs provides for the desired hydrophilicity and also increases the overall amphiphilicity of the PS in combination with the hydrophobic aromatic phthalocyanine core.[25a, 26] This intrinsic amphiphilicity should facilitate the unspecific transport through the cell membrane as much as the for instance D-galactose increases the specific transport through the membrane via monosaccharide transport proteins (GLUT proteins).[27] Such hexose-transportproteins are overexpressed in several types of cancer.[28] The transport into the cell can also be influenced by the size of a molecule. Therefore, it is important to understand the influence of the aggregation of such molecules in this context. Substitution at the periphery of the phthalocyanine core by chiral groups like sugars leads to an asymmetry of the chromophore of the respective Pc and can be measured by circular dichroism (CD) spectroscopy.[11h, 29] On one hand, CD-spectroscopy can identify chirality transfer from the substituent to the chromophore which occurs on the molecular scale and results in sharp negative or positive peaks in the CD spectrum.[30] On the other hand, when the chromophore forms chiral supramolecular aggregates in solution, such as helices, the CD-spectrum shows signals with a well-defined bisignate Cotton effect.[31] The substance class of phthalocyanines includes only a few examples where supramolecular chiral aggregates had been detected in solution. However, in some cases it has been shown that Pcs with chiral substituents are able to form the desired helical aggregates.[11h, 30a, 32] The driving force for such chiral aggregates can be viewed as a combination of π-π- and metal-ligand interactions as was mentioned above.

After having studied various sugar-decorated phthalocyanines as potential photosensitizer for photodynamic therapy in the past,[19, 25c, 33] we now came across an extraordinary phenomenon regarding the supramolecular properties of 1,2,3-triazole substituted phthalocyanines which we wish to report here today.

Results and Discussion

In continuation of our work in the field of glycoconjugated zinc(II) phthalocyanines and their derivatives as photosensitizers for PDT, we now present four new isopropylidene protected D-galactose bearing zinc(II) phthalocyanines **1**-**4** (Scheme 1). In order to develop ideal photosensitizers for PDT, we focused in this present work on the aggregation behaviour of such compounds and on

understanding it at the molecular level. Furthermore, we synthesized two octamethoxy substituted Pcs **5a** and **5b** (Scheme 1) for which we presumed that they might be helpful model compounds for understanding the crystallization behaviour of the glycosylated PCs. In detail, compounds **1-4** consist of a zinc(II) phthalocyanine core and protected D-galactose units. Phthalocyanines **1** and **2** are substituted by galactosyltriazole moieties at the exterior position (peripheral or β-position) whereas phthalocyanines **3** and **4** are functionalized at the "inner" peripheral position of the Pc (non-peripheral or α-position). The sugars are linked via 1,2,3-triazole units to the aromatic phthalocyanine core. The phthalocyanine moiety was chosen as the photoactive part of the molecule for its outstanding photophysical properties needed for PDT.



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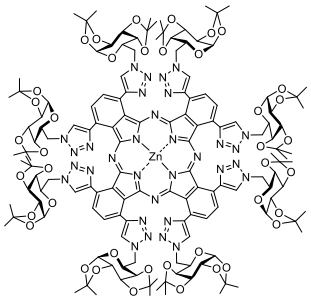

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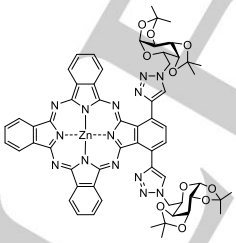

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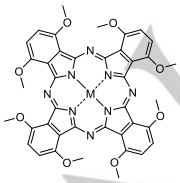


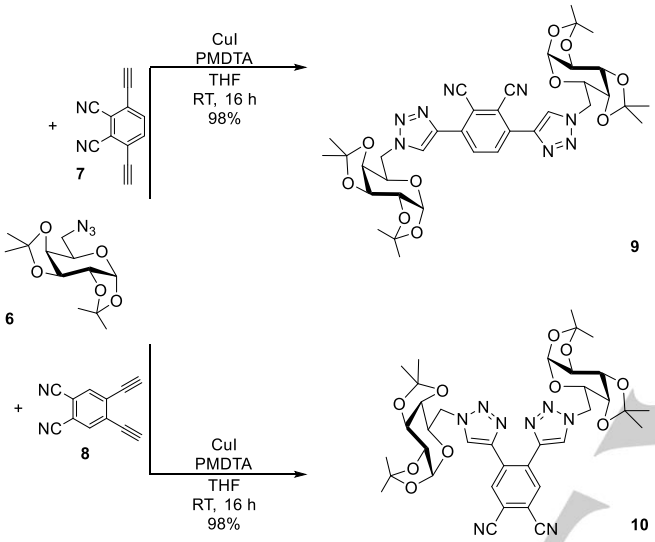
5a M = Zn
5b M = Mg

Scheme 1. Overview of the novel galactoconjugated, 1,2,3-triazole linked zinc(II)phthalocyanines **1**-**4** and octamethoxy substituted phthalocyanines **5a** and **5b**.

Zinc(II) as the central metal ion was chosen because of its biocompatibility and its ability to further increase the $^1O_2$ quantum yield (φ_Δ) in comparison to other metal ions.[34] The 1,2,3-triazole was chosen as a linker between the sugar and the dye for its simple accessibility via "Click Reactions" and for its high stability against enzymatic cleavage and biocompatibility referring to a minimal dark toxicity.[35] Furthermore, 1,2,3-triazoles increase the polarity of the molecule and thus the solubility in water. D-Galactose was chosen as the carbohydrate residue due to its compatibility with GLUT proteins. Another factor not to be underestimated when using D-galactose is the convenient access of suitably protected sugar building blocks (*i.e*. diactetone-D-galactose and derivatives thereof) which withstand the harsh basic conditions necessary for the tetramerization of the respective glycoconjugated phthalonitrile precursors. Carbohydrate substituents at a PC core structure do not only influence the physiological properties of the resulting photosensitizer. They also ensure the solubility in virtually all common solvents like, for instance, diethyl ether, methylene chloride, benzene and DMF which is beneficial for the purification of the prepared material by column chromatography or crystallization. Likewise, glycosylation of Pcs makes it significantly easier to determine the photophysical properties of these otherwise mostly insoluble molecules in many different solvents. In general, we intended to investigate whether the two different substitution positions (α or β) in addition to their influence on the photophysical properties also affect the aggregation behaviour in solution. Likewise, we also intended to evaluate any possible significant differences in the physical behaviour of octa- and disubstituted phthalocyanines, respectively for we assumed eightfold substituted Pcs to show a less distinct aggregation than the twofold substituted counterparts.

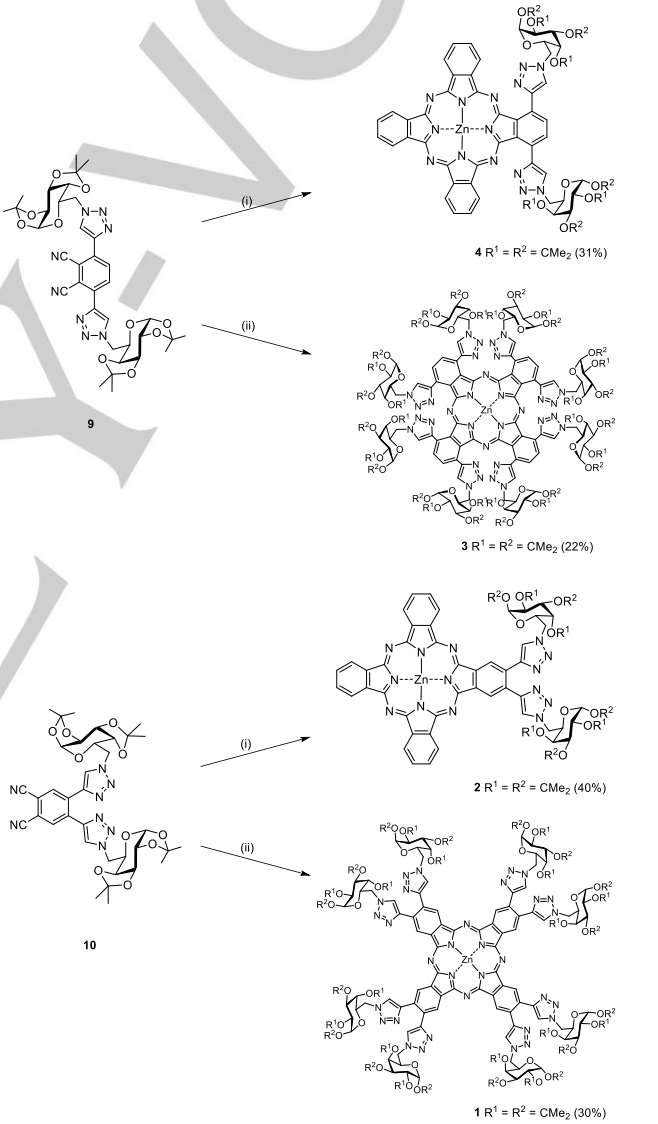
Synthesis. Schemes **2**-**4** summarize the synthetic route to the four novel zinc(II)-phthalocyanines **1**-**4**. We choose position 6 at the galactose part for its attachment to the phthalocyanine core via 1,2,3-triazole units for the convenient preparation of the required carbohydrate building blocks and the reduced tendency of such modified PCs to form intermolecular aggregates in solution.[19] Despite the fact that the tendency of forming aggregates in solution is almost unpreventable for phthalocyanines it should be ensured that it remains as unlikely as possible because aggregated phthalocyanines lead to photophysical self-quenching (more precisely impaired light absorption) what significantly decreases their photosensitizing ability. Our synthesis starts with D-galactose which is first protected with acetone and a catalytic amount of iodide to afford diacetonegalactose.[36] Subsequently, the free hydroxyl group at position 6 was tosylated (77% yield) followed by nucleophilic substitution of the tosylate by azide to afford **6** in 96% yield (see supporting information).[37] Both glycoconjugated phthalonitriles **9** and **10** were prepared by copper catalyzed alkyne-azide cycloaddition (CuAAC or "Click" reaction) in THF as the solvent with copper(I)iodide as catalyst and *N*,*N*′,*N*″,*N*‴,*N*‴-pentamethyldiethylenetriamine (PMDTA) as base (Scheme 2).[33d, 38] The isomeric bis ethynyl phthalonitriles **7** and **8** were prepared according to literature procedures.[33d] The 1,2,3-triazole ring

formation proceeded smoothly in both cases and respective phthalonitrile derivatives **9** and **10** were both obtained in 98% yield. It should be noted that the CuAAC reaction only succeeded under strictly anhydrous conditions. Commonly applied procedures for CuAAC reactions like copper(II)sulfat and sodium ascorbate in a mixture of water and methanol only lead to unidentified side-products. Next, phthalocyanines **1-4** were prepared starting from the precursors **9** and **10** using Tomoda's[39] general method for the synthesis of phthalocyanines from phthalonitriles (Scheme 3). Specifically, zinc(II) chloride, DBU as the base and *n*-pentanol as the solvent were used here.



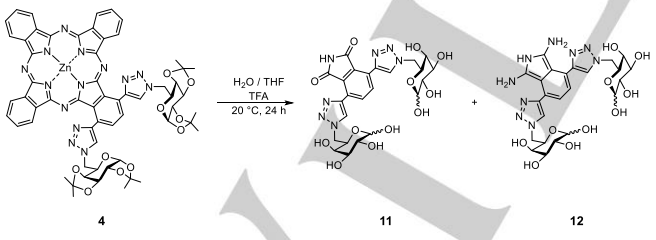
Scheme 2. Synthesis of the glycoconjugated phthalonitriles **9** and **10.**

It is important to note that all compounds should be completely dissolved at 90 °C in a minimal amount of solvent before the DBU is added. For the less sterically hindered octasubstituted phthalocyanine **1** the typical green colour of the product occurred within 5 minutes after the DBU was added. The solution of the bulkier Pc **3** only appeared after approximately 1 h what is most likely due to the fact that its substituents are arranged in sterically more challenging way. The higher steric demand also explains the lower yield for the synthesis of α-substituted phthalocyanine **3** in comparison to **1**. For the synthesis of the dissymmetric AB_3-type phthalocyanines **2** and **4** a large excess of phthalonitrile was necessary in order to obtain the products in good yields and to prevent the formation of differently composed phthalocyanines such as for instance A_2B_2-type and A_3B-type phthalocyanines.[40] In this way, only less polar unsubstituted phthalocyanine and some byproducts due to decomposition had to be removed by column chromatography on silica gel. The protected glycoconjugated phthalocyanines **2** and **4** were obtained in good 40% and 31% yields, respectively. Next, we tried to deprotect the galactose moieties by hydrolytically removing the isopropylidene groups at the galactose moieties using trifluoracetic acid (TFA) in a mixture of water and THF. Other acidic deprotection conditions, such as HCl_{aq}, *p*TsOH or acetic acid only resulted in re-isolation of the starting material. To our surprise, the deep green or blue coloured Pc solutions turned completely transparent upon treatment with aqueous THF and a white precipitate formed after evaporation of the solvent. As it turned out after isolation of the deprotected compound, the white substance was the deprotected diaminoisoindole **12** and the deprotected phthalimid **11** shown in Scheme 4. Both compounds were unambiguously confirmed by UV-spectroscopy and HRESI-MS. It appears to be rather surprising that the virtually nearly "indestructible" phthalocyanine core showed a clean decyclization while the triazole linked sugars only got deprotected but otherwise remained intact.



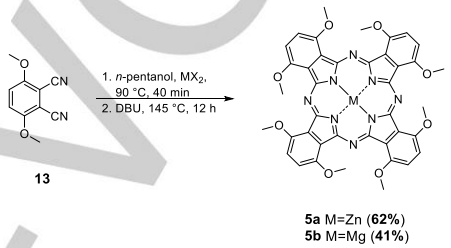
Scheme 3. Top: Synthesis of the two non-peripheral (α-position) glycoconjugated phthalocyanines **3** to **4** from the phthalonitrile precursor **9** using the Tomada method. Bottom: Synthesis of the two peripheral (β-position) glycoconjugated phthalocyanines **1** and **2** from the phthalonitrile precursor **10** using the Tomada method. Reaction conditions: (i) phthalonitrile, $ZnCl_2$, DBU, *n*-pentanol 145 °C, 16 h; (ii) $ZnCl_2$, DBU, *n*-pentanol, 145 °C, 16 h.

The same unexpected hydrolysis was also observed for the two dissymmetrically galactoconjugated phthalocyanines **2** and **4** as well as for the sterically more crowded octasubstituted glycophthalocyanines **1** and **3**. It has previously been described in the literature that phthalocyanines are first protonated at the ring nitrogen-atoms by strong mineral acids like sulfuric acid and that the stability of metal phthalocyanines toward mineral acids increases in the order: ZnPc < CuPc < CoPc < NiPc. In our case, this protonation lead to the 1,3-diiminoisoindole derivative (**12**) which was immediately hydrolysed by water giving phthalimide **11** as well. Ghani et al. showed that TFA alters the UV spectra of the Pcs compared to those obtained for conventional solvents.[41] Ellis et al. proposed that TFA protonates all four nitrogen atoms on the porphyrin ring.[42] Studies of Ledson et al. showed that protonation of a Pc effects only the outer bridge nitrogen atoms. The authors further discuss that the outer nitrogen may play a role in the protonation and that the molecule can be slightly deformed.[43] The deformation of the phthalocyanine ring system could lead to a debilitated aromatic stability what could initiate the breakup of the phthalocyanine ring. Nevertheless, the surprizing finding that the phthalocyanine core is preferentially hydrolysed upon treatment with acid supports the fact that the 1,2,3-triazole linker is rather difficult to cleave and holds the sugar and the aromatic moiety strongly together. We repeated the PC-decyclization several times and found that the corresponding phthalimides were isolated for all four AB_3 and A_4 phthalocyanines. To the best of our knowledge, this is the first example for a clean cleavage of a phthalocyanine leading to the respective monomeric starting compounds. The fact that glycoconjugated zinc(II) phthalocyanines are cleaved under conditions necessary for removing the isopropylidene protecting groups shows how harsh the conditions have to be for this deprotection reaction. All things considered, it seems reasonable to assume that the carbohydrates increase the aggregation by forming hydrogen bonds between the molecules. The aggregated molecules are thus sterically more demanding and the protective groups more difficult to be cleaved off.



Scheme 4. Deprotection of the isopropylidene groups lead to detetramerization of the phthalocyanine core. Phthalimid **11** and diaminoisoindole **12** were formed.

As mentioned above, the two octamethoxy substituted phthalocyanines **5** were also synthesized (Schemes 1 and 6). The reason for their preparation was due to our intention to use these two "simple" phthalocyanines for optimization of the methods for growing single crystals suitable for x-ray crystallography. Specifically, we prepared two non-peripheral octamethoxy substituted phthalocyanines **5a** and **5b** with Mg(II) and Zn(II) as central metal ions (see discussion below). The respective phthalonitrile precursors were synthesized according to a literature procedure from 2,3-dicyanohydroquinone and dimethyl sulfate.[44] In order to obtain **5a** and **5b**, the cyclotetramerization was carried out under the same conditions as shown above for the galactoconjugated A_4 zinc(II) phthalocyanines **1** and **3** (*i.e.* in *n*-pentanol and DBU with magnesium(II) acetate or zinc(II) chloride). The suitable AB_3-type derivatives were not prepared in this case because of the difficult purification caused by the minimal difference in polarity between the AB_3-type Pc and the unsubstituted metal phthalocyanine.



Scheme 6. Synthesis of **5a** and **5b** from dimethyl 3,6-dimethoxyphthalonitrile.

Spectroscopic properties and aggregation behaviour. The spectroscopic data of the glycoconjugated Pcs **1**-**4** are shown in Table 1. The focus of the aggregation studies was placed on the AB_3 phthalocyanines **2** and **4** because of the fact that these compounds have a much more pronounced aggregation behaviour than the A_4 Pcs **1** and **3**. They even form aggregates at low concentrations ($<6\cdot10^{-6}$ M). Nevertheless, in DMSO no aggregation at all was observed for all four phthalocyanines and the Beer-Lambert law was obeyed for concentrations ranging from $1\cdot10^{-6}$ to $18\cdot10^{-6}$ M in DMSO. The fluorescence quantum yields (Φ_F) in DMSO were determined by measuring the fluorescence emission (E) and the absorbance (A) of each compound. By comparison with a standard (ZnPc[45]), the Φ_F could be determined using the following equation (1). The refractive indices are named n and n_{Std}.

$$(1) \qquad \phi_F = \phi_F(Std) \cdot \frac{E \cdot A_{Std} \cdot n^2}{E_{Std} \cdot A \cdot n_{Std}^2}$$

The fluorescence lifetimes (τ_F) were directly measured with laser spectroscopy. τ_F refers to the average time a molecule stays in its excited state before emission. The rate constant for fluorescence k_F (eq. 2) and the natural radiative lifetimes (τ_0) (eq. 3) were determined using fluorescence quantum yields and the fluorescence lifetimes.[7a]

$$(2) \quad k_F = \frac{\phi_F}{\tau_F} \qquad (3) \quad \phi_F = \frac{\tau_F}{\tau_0}$$

Table 1. Photophysical properties of the galactoconjugated phthalocyanines **1**-**4** in DMSO.

Compound	λ_{max} nm (log ε)	$\lambda_{em,\ max}$ (nm) [a]	$\lambda_{exc,\ max}$ (nm) [b]	Δ_{Stokes} (nm)	τ_F (ns)[c]	Φ_F [d]	τ_0 (ns) [e]	k_F ($\cdot 10^8$ s^{-1}) [f]
1	700 (5.47) 670 (4.63) 630 (4.68) 370 (5.01)	709	700	9	2.5	0.18	13.9	0.72
2	679 (5.24) 612 (4.49) 352 (4.78)	691	675	12	2.8	0.18	15.6	0.64
3	737 (5.15) 700 (4.41) 660 (4.39) 341 (4.71)	741	735	4	-	0.06	-	-
4	687 (5.03) 636 (4.59) 619 (4.57) 342 (4.75)	700	685	13	2.4	0.13	18.5	0.54
ZnPc[g]	672 (5.14)	672	682	10	1.22	0.20	6.8	1.47

[a] Emission at λ_{ma}. [b] Excitation at λ_{max}. [c] measured in DMSO (3 µM) [d] Φ_F: fluorescence quantum yield [e] τ_0: natural radiative lifetime [f] k_F: rate constant for fluorescence [g] photophysical data for ZnPc (DMSO) from Gürol et al.[45]

The fluorescence lifetime for Pc **3** could not be determined due to the low fluorescence emission of this molecule. The fluorescence quantum yields of the substituted Pcs are lower than the Φ_F of unsubstituted ZnPc. Possibly, the substitution leads to an increased chance that the excited singlet state is quenched.[7a] The corresponding UV-, emission- and τ_F-spectra are listed in the supplement material. Figure 2 and 3 show an excerpt of the UV spectra (Q band: $\pi \rightarrow \pi^*$) of AB_3-type Pc **2** and **4** in the non-aggregated form (DMSO). The two galacto-conjugated Pcs show a Q band with expected λ_{max} values for **2**: 679 nm and **4**: 687 nm. The reason for the bathochromic shift of the Q band of **4** in comparison to **2** is probably due to the fact that the linear combinations of the atomic orbitals (LCAO) of the HOMO at the α-positon of the Pc are larger than the LCAOs at the β-position. As a result, the HOMO of **4** is destabilized and the HOMO-LUMO gap decreases.[46] When the less polar, non-coordinating solvent chloroform is used, both Pcs show new absorption bands. In detail, the peripherally substituted Pc **2** shows a new absorption band, red shifted to the monomer band. This band can be considered as the *J*-band since it results from the formation of a *J*-aggregate. Such behaviour of phthalocyanines has already been described in the literature by several groups.[3a, 11b, 11j]

In order to rule out the possibility that the new red-shifted band is not due to protonation by traces of HCl in the chloroform solution we added Huenigs base (DIPEA) and trifluoroacetic acid (TFA) to the chloroform solution since protonation can lead to a change in the absorption properties of the phthalocyanine as the symmetry is reduced. By adding a base, no disappearance of the *J*-band occurred whereas by adding TFA a new band appeared. All these findings confirm our assumption that Pc **2** formed *J*-aggregates in chloroform. The appearance of the novel band in chloroform-TFA solution is a result of the protonation of the nitrogen atoms of the phthalocyanine ring. By adding coordinating solvents, such as pyridine or DMSO, the *J*-band slowly vanishes. Coordinating solvents or coordinating additives break the aggregate by separating the molecules from each other. To our surprise, the absorption spectrum of phthalocyanine **4** (α-substituted) showed three main bands in chloroform. In comparison of the solutions of the monomeric form of **4** in chloroform with pyridine and in DMSO, in pure chloroform a red shifted and a slightly blue shifted band were observed. This behavior is highly unusual though. We assume that the reason for the differences in the absorption spectra of **2** and **4** lay in the different substitution positions (β- or α-) on the phthalocyanine ring.

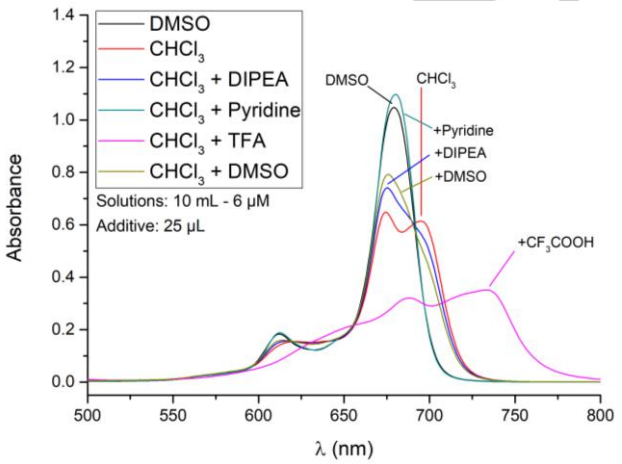


Figure 2. UV/Vis spectra (Q band) of **2** measured in different solvents.

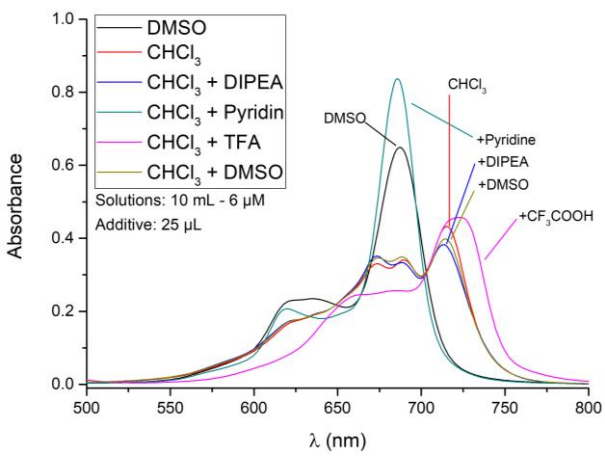


Figure 3. UV/Vis spectra (Q band) of **4** measured in different solvents.

The fact that both regioisomers show a red-shifted band in the UV spectrum is less surprising to us than the formation of an additional blue-shifted band in the case of **4**. We believe that the red-shifted bands (*J*-band) can be attributed to the formation of a slipped cofacial aggregate (*J*-aggregate) which may be caused by a metal-ligand coordination. This is clearly the case for compound **2**. In case of compound **4**, we also suppose a slipped cofacial stack. Here, we assume a higher θ-angle (compared to Figure 1) and a slightly more parallel arrangement of the Pcs. Lin et al. showed that phthalocyanines with chiral substituents can form aggregates which show red- and blue-shifted absorption bands.[47] ^{1}H-NMR spectroscopic studies showed that the aggregation behavior of such phthalocyanines is highly dependent on the nature of the solvent and the temperature. Octa-substituted phthalocyanines **1** and **3** showed well-resolved NMR spectra in $CDCl_3$ with traces of pyridine-d5. Without pyridine-d5, aggregation was observed though. The AB_3-type phthalocyanines **2** and **4** showed significantly stronger aggregations in solution than the octa-substituted Pcs. Only with strongly coordinating solvents, such as DMF-d7, well-resolved peaks could be obtained. Figure 4 shows the ^{1}H-NMR spectra of **4** in $CDCl_3$, $CDCl_3$ with pyridine-d5 and DMF-d7. To obtain a well resolved ^{1}H- or ^{13}C-NMR spectrum of **2** and **4** the NMR spectra had to be measured even at 100 °C in DMF-d7. Dimers and trimers of **2** and **4** could also be identified with MALDI-TOF spectroscopy (see supplementary material) which illustrates the strength of the interactions within the aggregates. The ^{1}H-NMR spectra of the two isomeric AB_3-phthalocyanines **2** and **4** are identical except for one difference. The ^{1}H-signal of the 1,2,3-triazole of the α-substituted Pc **4** is shifted downfield by 0.7 ppm in comparison to **2**.

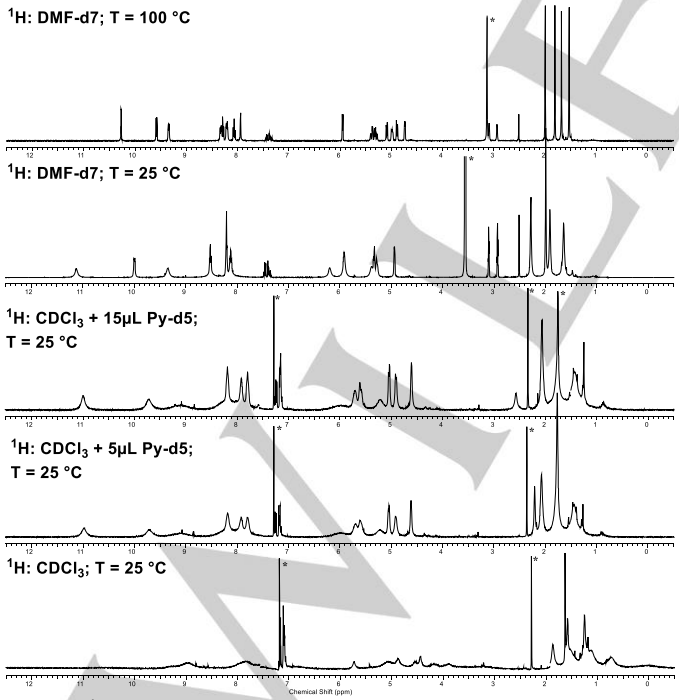


Figure 4. ^{1}H-NMR spectra spectra of **4** in $CDCl_3$ (at the bottom), $CDCl_3$ with pyridine-d5 and DMF-d7 at room temperature and 100 °C. *Signals are shortened due to lucidity reasons.

This relatively large shift is likely due to the different spatial orientation of the triazoles caused by the higher steric hindrance in phthalocyanine **4**. This leads to a different anisotropic effect caused by the large π-system of the Pc. The UV- and ^{1}H-NMR spectra led us to the assumption that the position of the substitution on the Pc (α- or β-) in combination with the nature of the 1,2,3-triazole moiety must have a decisive role in the formation of the different types of aggregates. In order to investigate this phenomenon in greater detail, we also performed CD spectroscopic and crystallization studies. Supramolecular behavior in solution, such as helical aggregation, can be identified with CD spectroscopy, as already mentioned in the introduction. A positive bisignate Cotton-effect represents a right-handed helix and a negative cotton effect a left-handed helix.[31] The helical chirality of the phthalocyanine chromophores in the aggregates is physically defined by the direction and coupling of the respective monomer dipoles. According to Nakanishi's semi-empirical method, the type of cotton effect (positive or negative) can be directly related to the helical direction of rotation in the supramolecular aggregate. The CD spectra for **2** and **4** are shown in Figure 5 and 6. The CD spectra were measured in chloroform, chloroform with additional pyridine and in DMSO. As expected, a CD signal was received exclusively in chloroform. However, to our great surprise, the two different isomers of the AB_3 Pcs (α- or β-) obviously form helices with different helical configurations.

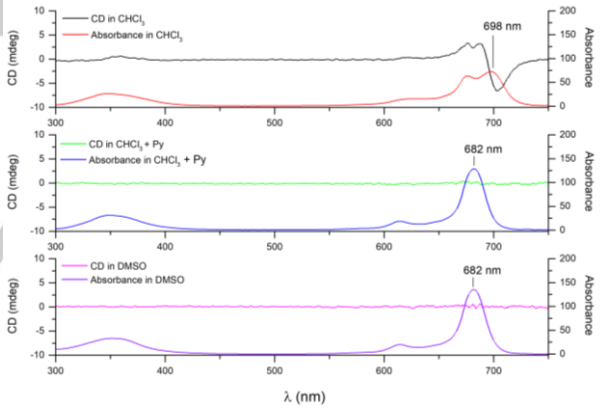


Figure 5. CD and absorbance spectra of **2** measured in chloroform, chloroform with pyridine and in DMSO.

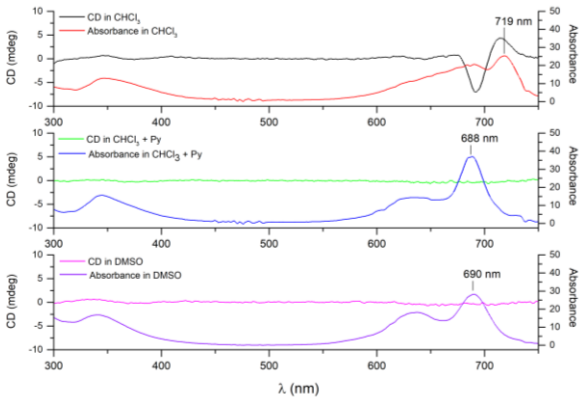


Figure 6. CD and absorbance spectra of **4** measured in chloroform, chloroform with pyridine and in DMSO.

Due to the negative bisignate Cotton-Effect, shown in Figure 5, the peripherally (β-), disubstituted phthalocyanine **2** forms a left-handed helix in chloroform and, in contrast, the non-peripherally (α-), disubstituted phthalocyanine **4** forms a right-handed helix which is evident due to the positive bisignate Cotton-Effect (Fig. 6). Similar dependences of the handiness of supramolecular helices on the position of the substitution at the phthalocyanine has already been observed by Lin et al.[47] The observation of a Cotton-Effect in both cases indicates the successful chiral expression on the Pcs **2** and **4** at the supramolecular level. Table 2 summarizes CD spectroscopic data for phthalocyanines **1**-**4**. The bisignate Cotton-Effects for **2** [704(-)/687(+)] with a crossover at 693 nm and for **4** [714(+)/691(-)] with a crossover at 704 nm are in accordance with the respective *J*-bands in their UV spectra. The octasubstituted phthalocyanines **1** and **3** also behave differently regarding their circularly dichroism (see supporting information). In these cases, only peripherally substituted Pc **1** shows a bisignate Cotton-Effect in chloroform and therefore forms supramolecular helical arrangements. PC **3** shows a pronounced chiral transfer at the molecular level (Table 2) in all three solvents but no helical arrangement (Q- and soret band). This effect may be attributed to the higher steric inhibition of PC **3** and the herewith associated stronger steric rejection of individual molecules.

Table 2. Values for the CD-spectra of the galactoconjugated Pcs **1-4**.

Pc	Solvent	CD-Signal	UV/Vis peak form[a]	UV/Vis λ_{max} (nm)
1	$CHCl_3$	729(+)/708/693(-)	*J*-aggregate	710+702
	$CHCl_3$ + Py	-	M	702
	DMSO	-	M	702
2	$CHCl_3$	704(-)/693/687(+)	*J*-aggregate	698+675
	$CHCl_3$ + Py	-	M	682
	DMSO	-	M	682
3	$CHCl_3$	737(-)	M	744
	$CHCl_3$ + Py	738(-)	M	744
	DMSO	736(+)	M	743
4	$CHCl_3$	714(+)/704/691(-)	*J*-aggregate	729+691
	$CHCl_3$ + Py	-	M	688
	DMSO	-	M	690

[a]M: monomer peak.

Crystallization. In general, we could not theoretically exclude the possibility that the carbohydrate moiety also has a decisive role in the formation of the aggregates. Therefore, we tried to crystallize the galactoconjugated phthalocyanines **1**-**4**. This has proved to be a difficult task though. We used several different techniques for growing single crystals, such as slow evaporation, lamination or slow diffusion. Over a period of two years, we were only able to obtain ultra-thin needles which did not scatter and were therefore not measurable. In the solid state such Pcs are usually not aggregated in an ordered manner.[48] Another problem with glycoconjugated phthalocyanines is the high mobility of the carbohydrate moieties. In order to overcome these problems, we prepared the two octamethoxy substituted phthalocyanines **5a** and **5b** which could be synthesized in large quantities and thus, were much better suited for optimizing crystallization methods than the glycosylated phthalocyanines. Consequently, in both cases (Zn(II)Pc **5a** and Mg(II)Pc **5b**) we obtained measurable single crystals (Figure 7). The main reason for obtaining crystals suitable for x-ray crystallography was the addition of pyridine to the solution.

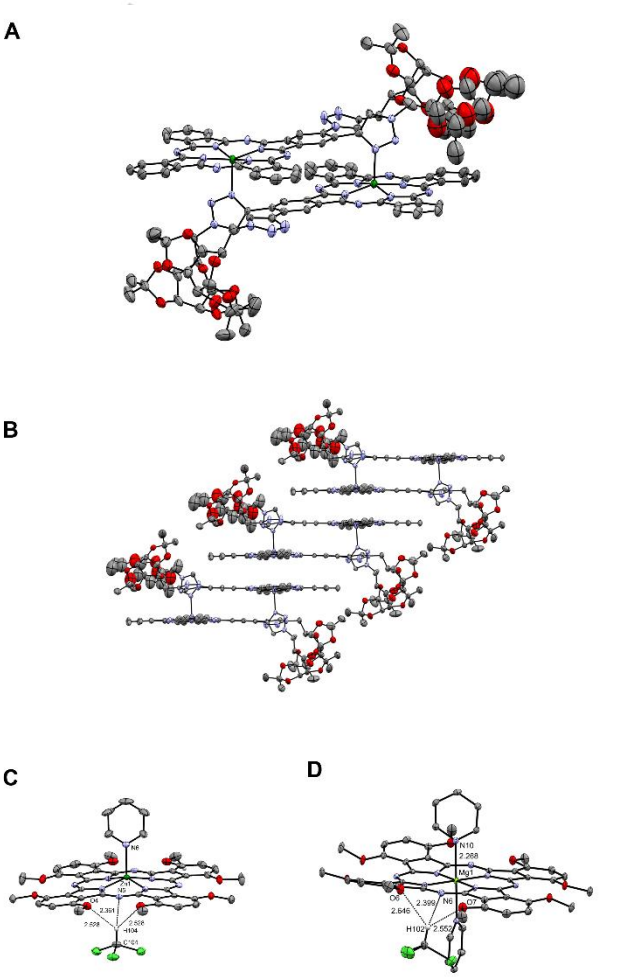


Figure 7. Crystal structures of **2** (A and B, R-value: 6.6), **5a** (C, R-value: 4.4) and D: **5b** (D, R-value: 4.5). The hydrogen atoms are not shown for clarity reasons.

As a result, **5a** crystallized with one and **5b** with two pyridine molecules attached to the metal ion. The fact that zinc prefers to be present in porphyrins and phthalocyanines in a fivefold coordination is well known.[49] The presence of chloroform in the crystallizing solution was also indispensable as it turned out that each chloroform molecule contributes an essential trigonal hydrogen bond to the crystal arrangement (Figure 7, C and D and supporting information). In case of the glycoconjugated phthalocyanines **1**-**4**, however, we did not want to prevent the triazole-zinc interaction in the single crystal by the addition of pyridine. Therefore, this crystallization method could not be transferred to the glycoconjugated phthalocyanines. Nevertheless, by slow evaporation of DMF over a period of 6 months we were finally able to obtain a measurable single crystal of phthalocyanine **2**. The resulting crystal structure is shown in Figure 7 and is the first crystal structure of a glycoconjugated phthalocyanine. The R-value of 6.6 is acceptably good for such a large and mobile molecule. This crystal structure clearly confirms our assumption that the 1,2,3-triazoles play a decisive role in the formation of this kind of aggregates. In the solid state, phthalocyanine **2** is present as a dimer. This dimer is formed by a non-covalent, double zinc-triazole interaction. The dimers connect with each other in the previously suggested slipped cofacial arrangement. The “stairs” of this stack are connected through π-π interactions. Furthermore, the crystal structure of **2** shows another remarkable property of the disubstituted phthalocyanine. One triazole coordinates with the zinc(II) central atom of the dimeric neighbour and the other triazole is turned into the plane and therefore part of the aromatic system of the phthalocyanine core. The distance between the interacting N-(triazole) and the zinc(II) ion is 2.2 Å. The distances between the phthalocyanine planes within a dimer (metal-ligand) and from dimer to dimer (π-π) are both 3.4 Å. Unfortunately, we could not obtain a crystal structure from the regioisomeric phthalocyanine **4**, nor from the octa glycoconjugated Pcs **1** and **3**.

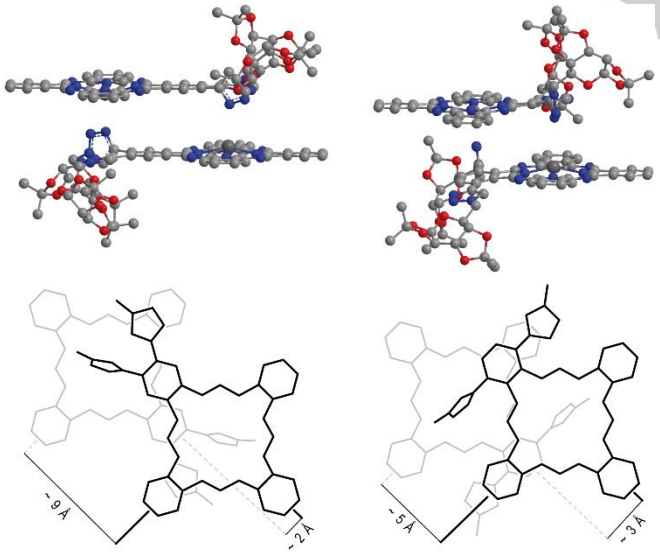


Figure 8. Top: 3D-models of the dimeric Pcs **2** (top left) and **4** (top right). The hydrogen atoms are not displayed in this case. Bottom: Graphical representation of the distances within the two dimers. The carbohydrate moiety is hidden for clarity reasons.

Nevertheless, the crystal structure of **2** provides decisive information on the arrangement of this molecules in solution. It is impressive that the π-π-interaction between two dimers is very well defined and directed. For this reason, it may also be possible that such phthalocyanines can form chiral helices in solution by a similar interplay of metal ligand and π - π -interactions. The difference between the two isomeric AB_3 phthalocyanines **2** and **4** in their helical direction of rotation in solution may be due to the different distances between the triazole substituents and the phthalocyanine. The molecular distances within a dimer of **2** and **4** are shown in Figure 8 (bottom). A different distance has a direct effect on the staggering angle θ (Figure 1 in the introduction). This angle determines which aggregate form is present, whereby the transition from the *H*- to the *J*- aggregate is fluid. Staggering angles θ > 54.7° lead to a more parallel arrangement of the aggregate (*H*-aggregate). By contrast, a staggering angle θ < 54.7° results in the formation of a *J*-aggregate. α-regioisomer **4** will probably form more linear stacks due to the smaller distance within a dimer. This explains the *H*- and *J*-aggregation band in the UV spectrum, described above, and the lower fluorescence quantum yield of **4** compared to **2**. A short overview of the possible dimeric arrangements is given in Figure 9A. There are three orientations possible for the molecules within the dimer, which are based on metal ligand interactions. In our case, closed type arrangement A-2 (Figure 9) is present. Based on this dimeric arrangement, the supramolecular interaction between the dimers have to be due to π - π -interactions. A model for the helical arrangement for **2** and **4** in solution is illustrated in Figure 9B. This model shows one possible arrangement of the dimers in non-coordinating solvents.

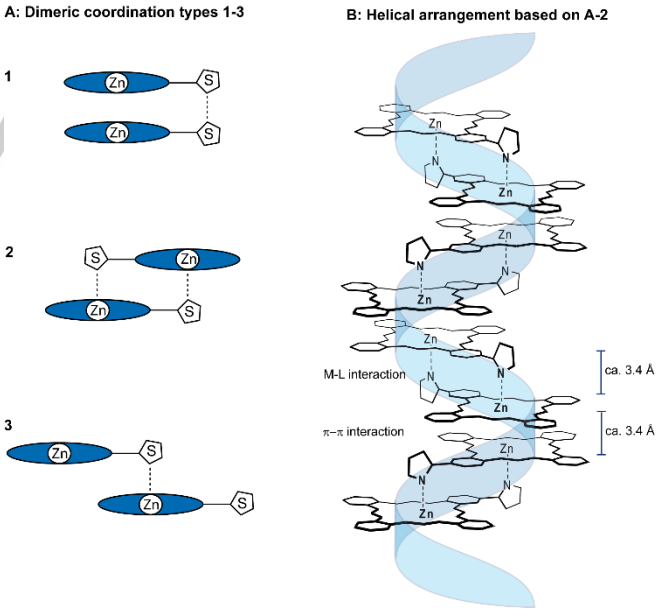


Figure 9. A: Schematic representation of possible dimeric arrangements: A-1: mirror type dimer, A-2: closed type dimer, A-3: angled dimer (S: substituent).[50] **B** shows a graphical illustration of the helical stacks, the disubstituted phthalocyanines **2** and **4** can form. The dimeric form A-2 is assumed within the helix. In both cases**,** we suppose a slipped cofacial arrangement between the dimers as it is shown in the picture. In case of **2** the staggering is more distinct due to the less sterically hindered arrangement.

We suggest a slipped cofacial arrangement for both AB_3 phthalocyanines. The stacks of α-regioisomer **4** seem to be more columnar than the stacks of β-regioisomer **2**. But even **4** does not form a perfect linear column (pure *H*-aggregate).

Conclusion

Four novel galactoconjugated zinc(II) phthalocyanines were synthesized and fully characterized. The 1,2,3-triazole heterocycle was chosen as the linker between the sugar moieties and the phthalocyanine core due to its biocompatibility. The isopropylidene protected carbohydrate moiety made the phthalocyanine soluble in many different organic solvents, which was necessary for the spectroscopic studies. The Q bands of all phthalocyanines in DMSO laid in the red visible light region (679-737 nm) and the molar absorption coefficents ε_{max} were > 10^5 M^{-1} cm^{-1}. Overall, the photochemical properties were promising for the usage of these phthalocyanines as photosensitizers in PDT. From the spectroscopic behavior in solution it could be concluded that the synthesized phthalocyanines form *J*-aggregates. For the examination of the self-assembly in solution, temperature dependent NMR-spectroscopy, UV- and CD-spectroscopy in various solvents were applied. The circular dichroism of the disubstituted phthalocyanines **2** and **4** showed that both disubstituted phthalocyanines form chiral helices in solution with opposite handedness. These findings showed that the position of the substitutents on the phthalocyanine periphery influences the chiral transfer and the self-assembly in solution. The crystal structure of Pc **2** revealed the effect of the interplay of metal ligand coordination and π-π interactions on the morphology and chiral arrangement of the aggregated supramolecular structures. In this case, the 1,2,3-triazole linker played a decisive role in the metal ligand coordination within the Pc dimers. Specifically, it coordinated the zinc(II) central metal ion of the adjacent Pc, inducing a slipped cofacial arrangement in the helical arrangement. The octasubstituted Pcs **1** and **3** are sterically more crowded than the disubstituted Pcs. Only β-substituted Pc **1** showed a helical arrangement in solution. In summary, it could be shown that the binding of carbohydrates to phthalocyanines via a triazole was successful in terms of photosensitizing properties. Furthermore, extraordinary supramolecular properties were found which could be useful for material science applications.

Experimental Section

General Methods and Information. All starting materials and reagents were purchased from Sigma-Aldrich, TCI, ABCR GmbH and GLYCON Biochemicals GmbH and were of the highest purity available. All reactions were carried out under anhydrous conditions using flame dried glassware in anhydrous, freshly distilled solvents, unless otherwise noted. TLC was performed on Macherey-Nagel Polygram SIL G/UV_{254} plastic plates, precoated with 0.2 mm thickness of silica gel containing fluorescent indicator. Silica gel 60 (particle size 0.04-0.063 mm) was used for column chromatography. NMR spectra were measured on a Bruker Avance 400 or on a Bruker AMX 600 spectrometer. The ^{1}H- and ^{13}C-NMR spectra in DMF-d7 were measured at 25 °C and 100 °C. Coupling constants are listed in Hz. UV-Vis spectra were recorded on a Perkin Elmer Lambda 35 spectrometer using a 1 cm quartz cuvette. IR spectra were recorded with a Bruker Tensor 27. CD-Spectra were measured on a Jasco J-720 spectrometer. Elemental analyses were performed on a HEKAtech Euro EA Analyzer using sulfanylamide as standard. Optical rotation measurements were obtained with a Perkin Elmer Model 341 polarimeter. High-resolution ESI-TOF mass spectra were measured on a Bruker Daltonics Maxis G4. MALDI-TOF spectra were measured on a Bruker Daltonics Apex 2 using 2,5-dihydroxybenzoic acid (DHB) or *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) as matrix. FTICRMS was performed with a Bruker Daltonics APEX 2.

4,5-Bis(trimethylsilylethynyl)phthalonitrile, 3,6-Bis(trimethylsilylethynyl)-phthalonitrile, 4,5-Bis-(ethynyl)phthalonitrile, 3,6-Bis(ethynyl)phthalonitrile and 6-azido-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose were prepared according to literature procedures.[33d]

[1,4,8,11,15,18,22,25-Octamethoxyphthalocyaninato]zinc(II) (**5a**): Under an atmosphere of nitrogen, 500 mg (2.66 mmol) 3,6-dimethoxyphthalonitrile, 544 mg (3.99 mmol) dry $ZnCl_2$, were suspended in freshly distilled *n*-pentanol (3 mL). The reaction mixture was stirred at 90 °C for 30 minutes. Next, 596 µL (3.99 mmol) DBU were added and the solution was heated to 145 °C and stirred for 16 h until TLC (chloroform containing 8 % methanol and 2,5 % triethylamine) indicated the consumption of the starting material. The dark green reaction mixture was cooled to room temperature and concentrated under reduced pressure. Purification was done by successive column chromatography on silica gel and eluting with a) chloroform containing 6 % methanol and 2,5 % trimethylamine and b) chloroform containing 8 % acetone and 2,5 % triethylamine) to afford **5a** (335 mg, 62 %) as a green amorphous solid. IR (KBr): 3462, 3253, 2925, 2831, 2662, 2544, 1599, 1502, 1464, 1437, 1378, 1317, 1271, 1207, 1157, 1094, 1071 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$ + pyridine-d5): δ (ppm) = 7.51 (s, 8H, H-aryl), 4.56 (s, 24H, CH_3). ^{13}C-NMR (101 MHz, $CDCl_3$ + Pyridine-d5): δ (ppm) = 153.7 (C-Pc), 151.4 (*C*-OMe), 127.7 (C-Pc), 111.8 (CH-Pc), 57.0 (CH_3); LDI-MS *m/z* 853 $[(M+HCl)+H]^+$; HRESIMS *m/z* 817.17068 (calcd for $[C_{40}H_{33}N_8O_8Zn]^+$, 817.17073); anal. C 58.92, H 4.06, N 13.29, calcd for $C_{40}H_{32}N_8O_8Zn$, C 58.72, H 3.94, N 13.70.

Single crystals for X-ray crystallography could be received through slow evaporation from a saturated solution of **5a** in chloroform containing 1 % of pyridine at room temperature. CCDC 1920654 (**5a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[1,4,8,11,15,18,22,25-Octamethoxyphthalocyaninato]magnesium(II) (**5b**): Under an atmosphere of nitrogen, 700 mg (3.72 mmol) 3,6-dimethoxyphthalonitrile, 760 mg (5.58 mmol) dry $ZnCl_2$, were suspended in freshly distilled *n*-pentanol (3 mL). The reaction mixture was stirred at 90 °C for 30 minutes. Afterwards, 833 µL (5.58 mmol) DBU were added, and the solution was heated to 145 °C and stirred for 16 h until TLC (chloroform containing 8 % methanol and 2,5 % triethylamine) indicated the consumption of the starting material. The dark green reaction mixture was cooled to room temperature and concentrated under reduced pressure. Purification as described for the preparation of **5a** gave **5b** (296 mg, 41 %) as a green amorphous solid. IR (KBr) 3435, 3257, 2926, 2832, 2533, 2339, 1560, 1501, 1464, 1435, 1378, 1318, 1272, 1206, 1185, 1157, 1071 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$ + Pyridine-d5): δ (ppm) = 7.38 (s, 8H, H_{Ar}), 4.44 (s, 24H, CH_3). ^{13}C-NMR (101 MHz, $CDCl_3$ + Pyridine-d5): δ (ppm) = 152.6 (8C, NC_q), 150.7 (8C, COMe), 127.5 (8C, C_q), 110.9 (8C, CH_{Ar}), 56.1 (8C, CH_3); MALDI-MS *m/z* 777 $[M+H]^+$; HRESIMS *m/z* 777.22692 (calcd for $[C_{40}H_{33}N_8O_8Mg]^+$, 777.22663).

Single crystals for X-ray crystallography were obtained through slow evaporation of the solvent from a saturated solution of **5b** in chloroform

containing 1 % of pyridine at room temperature. CCDC 1920653 (**5b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

3,6-Bis-[1-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galacto-pyranosyl)1H-1,2,3-triazole-4-yl]-phthalonitrile (**9**): Under an atmosphere of nitrogen, 150 mg (0.85 mmol) 3,6-Bis(ethynyl)phthalonitrile, 583 mg (2.04 mmol) 6-azido-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **6** und 179 mg (0,94 mmol) Cu(I)I were dissolved in dry THF (10 mL) and 248 µL (1.19 mmol) *N,N,N′,N″,N‴*-pentamethyldiethylenetriamine were added to the solution. The reaction mixture was stirred for 12 h at room temperature until TLC (toluene / acetone 5:1) indicated the complete consumption of the starting material. Within the 12 h of stirring, the reaction mixture changed its colour from red to green. The reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (toluene / acetone 6:1), affording **9** (620 mg, 98 %) as a colourless, amorphous solid. $[\alpha]^{25}_{D}$: –89.3 (c = 1.0 $CHCl_3$); IR (KBr): 3156, 3086, 2990, 2937, 2230 cm^{-1}; ^{1}H-NMR (in $CDCl_3$): δ (ppm) = 8.71 (s, 2H, *H*-triazole), 8.63 (s, 2H, *H*-aryl), 5.53 (d, 2H, $J_{1,2}$ = 5.0, *H*-1), 4.72-4.59 (m, 6H, *H*-6a, *H*-6b, *H*-3), 4.35 (dd, 2H, $J_{2,3}$ = 2.5, *H*-2), 4.30-4.28 (m, 2H, *H*-5), 4.27-4.24 (m, 2H, *H*-4), 1.53, 1.44, 1.38, 1.29 (4s, 24H, C*H*$_3$). ^{13}C-NMR (in $CDCl_3$): δ (ppm) = 141.9 (C-triazole), 135.0 (C-aryl), 132.5 (CH-aryl), 124.9 (CH-triazole), 116.3 (CN), 112.3 (*C*-CN), 110.3, 109.3 (C-isopropylidene), 96.4 (C-1), 71.2 (C-4), 71.0 (C-3), 70.5 (C-2), 67.1 (C-5), 51.1 (C-6), 26.2, 25.1, 24.6 (CH_3). FTICRMS *m/z* 769.29176 (calcd for $[C_{36}H_{42}N_8O_{10}Na]^+$, 769.29161).

4,5-Bis-[1-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galacto-pyranosyl)1H-1,2,3-triazole-4-yl]-phthalonitrile (**10**): Under an atmosphere of nitrogen, 250 mg (1.42 mmol) 4,5-Bis(ethynyl)phthalonitrile, 970 mg (3.40 mmol) 6-azido-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **6** and 297 mg (1.56 mmol) Cu(I)I were dissolved in dry THF (12 mL) and 415 µL (1.99 mmol) *N,N,N′,N″,N‴*-pentamethyl-diethylenetriamine were added to the solution. The reaction mixture was stirred for 12 h at room temperature until TLC (toluene / acetone 5:1) indicated the complete consumption of the starting material. Within the 12 h of stirring, the reaction mixture changed its colour from red to green. The reaction mixture was worked up as described for the preparation of **9** to afford **10** (1.05 g, 98 %) as a colourless, amorphous solid. $[\alpha]^{25}_{D}$: –66.5 (c =1.0 $CHCl_3$); IR (KBr): 3146, 2989, 2937 cm^{-1}; ^{1}H-NMR (in $CDCl_3$): δ (ppm) = 8.34 (s, 2H, *H*-aryl), 7.73 (s, 2H, *H*-triazole), 5.53 (d, 2H, $J_{1,2}$ = 4.8, *H*-1), 4.66-4.60 (m, 4H, $J_{6a,6b}$ = 14.2, *H*-3, *H*-6a), 4.47 (dd, 2H, *H*-6b), 4.30 (dd, 2H, $J_{2,3}$ = 2.4, *H*-2), 4.25-4.23 (m, 4H, $J_{5,6b}$ = 9.0, *H*-5, *H*-4), 1.47, 1.37, 1.36, 1.28 (4s, 24H, C*H*$_3$). ^{13}C-NMR (in $CDCl_3$): δ (ppm) = 142.6 (C-triazole), 135.4 (CH-aryl), 134.3 (C-aryl), 124.9 (CH-triazole), 115.3 (CN)*, 114.9 (*C*-CN)*, 110.0, 109.3 (C-isopropylidene), 96.1 (C-1), 71.1 (C-5)*, 70.8 (*C*-3), 70.6 (*C*-2), 67.4 (C-4)*, 51.1 (C-6), 26.1, 26.0, 25.0, 24.3 (CH_3). FAB-MS *m/z* 747 $[M+H]^+$; FTICRMS *m/z* 769.291706 (calcd for $[C_{36}H_{42}N_8O_{10}Na]^+$, 769.291611); anal. C 57.67, H 5.84, N 14.77, calcd for $C_{36}H_{42}N_8O_{10}$, C 57.90, H 5.67, N 15.01. * Signals can be interchanged.

[2,3-Bis(1-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galacto-pyranose-6-yl)-1H-1,2,3-triazole-4-yl)-phthalocyaninato]zinc(II) (**2**): Under an atmosphere of nitrogen, 240 mg (0.32 mmol) 4,5-Bis-[1-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranosyl)1H-1,2,3-triazole-4-yl]-phthalonitrile **10**, 453 mg (3.54 mmol) phthalonitrile, and 482 mg (3.54 mmol) dry $ZnCl_2$ were suspended in freshly distilled *n*-pentanol (8 mL). The reaction mixture was stirred at 90 °C for 40 minutes until a yellow solution was formed. Afterwards, 530 µL (3.54 mmol) DBU were added and the solution was heated to 145 °C and stirred for 16 h until TLC (chloroform containing 5 % methanol and 1 % triethylamine) indicated the consumption of the starting material. The dark blue reaction mixture was cooled to room temperature and concentrated under reduced pressure. Purification of the crude product, carried out by successive column chromatographies and eluted with a) chloroform containing 2 % methanol and 1 % trimethylamine and b) toluene containing 15 % acetone and 0.5 % triethylamine), afforded **2** (153 mg, 40 %) as a blue amorphous solid. IR: (KBr) 3443, 3059, 2987, 2934, 2625, 2547, 1729, 1611, 148, 1456, 1410, 1383, 1334, 1285, 1258, 1212, 1164, 1116, 1093, 1070; ^{1}H-NMR (in DMF-d7): δ (ppm) = 9.40 (s, 2H, *H*-Pc-(triazole)), 9.24-9.19 (m, 6H, *H*-Pc), 8.15-8.13 (m, 6H, *H*-Pc), 8.03-8.00 (m, 2H, *H*-Pc), 7.88 (2H, s, *H*-triazole), 5.63 (d, 2H, $J_{1,2}$ = 4.9, *H*-1), 4.80-4.74 (m, 4H, *H*-6$_a$, *H*-3), 4.63 (dd, 2H, $J_{6a,6b}$ = 13.9, $J_{5,6b}$ = 8.4, *H*-6b), 4.81-4.78 (m, 6H, *H*-2, *H*-4, *H*-5), 1.61, 1.58, 1.48, 1.42 (4s, 24H, C*H*$_3$); ^{13}C-NMR (in DMF-d7): δ (ppm) = 154.8 (C-Pc), 154.6 (C-Pc), 152.3 (C-Pc), 153.7 (C-Pc), 147.4 (C-triazole), 139.7 (C-Pc), 139.6 (C-Pc), 139.6 (C-Pc), 138.8 (C-Pc), 131.6 (C-Pc), 130.2 (CH-Pc), 130.2 (CH-Pc), 125.4 (CH-triazole), 124.9 (CH-Pc-(Triazole)), 123.6 (CH-Pc), 123.5 (CH-Pc), 123.5 (CH-Pc), 110.7 (C-isopropylidene), 109.9 (C-isopropylidene), 96.7 (C-1), 72.8 (C-2)*, 72.5 (C-3)*, 72.3 (C-4)*, 68.9 (C-5)*, 51.5 (C-6), 26.9, 26.9, 25.7, 25.4 (CH_3-isopropylidene); MALDI-MS m/z 1194 $[M]^+$; HRESIMS *m/z* 1217.33322 (calcd for $C_{60}H_{54}N_{14}O_{10}ZnNa$ $[M+Na]^+$, 1217.33310); UV/Vis (DMSO): λ_{max} (log ε) = 352 (4.78), 612 (4.49), 679 (5.24) nm. *These signals can be interchanged.

Single crystals for X-ray crystallography were obtained through slow evaporation of the solvent from a saturated solution of **2** in DMF at room temperature. CCDC 1920655 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre..

[1,4-Bis(1-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galacto-pyranose-6-yl)-1H-1,2,3-triazole-4-yl)phthalocyaninato]zinc(II) (**4**): Under an atmosphere of nitrogen, 400 mg (0.54 mmol) 3,6-Bis-[1-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranosyl)1H-1,2,3-triazole-4-yl]-phthalonitrile **9**, 755 mg (5.89 mmol) phthalonitrile, 803 mg (5.89 mmol) dry $ZnCl_2$, were suspended in freshly distilled *n*-pentanol (8 mL). The reaction mixture was stirred at 90 °C for 40 minutes until a yellow solution was formed. Afterwards, 880 µL (5.89 mmol) DBU were added, and the solution was heated to 145 °C and stirred for 16 h until TLC (chloroform containing 5 % methanol and 1 % triethylamine) indicated the consumption of the starting material. The dark blue reaction mixture was cooled to room temperature and concentrated under reduced pressure. Purification of the crude product was carried out as described for the preparation of **2** to afford **4** (202 mg, 31 %) as a blue amorphous solid. IR: (KBr) 2988, 2935, 1729, 1486, 1454, 1256, 1212, 1166, 1068, 1006 cm^{-1}; ^{1}H-NMR (in DMF-d7): δ (ppm) = 10.08 (s, 2H, *H*-triazole), 9.40-9.38 (m, 2H, *H*-Pc), 9.16-9.14 (m, 2H, *H*-Pc), 8.15-8.08 (m, 4H, *H*-Pc), 8.03-8.00 (m, 2H, *H*-Pc), 7.89-7.86 (m, 2H, *H*-Pc), 7.75 (s, 2H, *H*-Pc-(triazole)), 5.76 (d, 2H, $J_{1,2}$ = 4.7, *H*-1), 5.22-5.08 (m, 4H, *H*-6$_{a,b}$), 4.90 (2H, dd, $J_{2,3}$ = 2.0, $J_{3,4}$ = 7.9 Hz, *H*-3), 4.81-4.78 (2H, m, *H*-5), 4.70 (2H, d, $J_{3,4}$ = 7.9, *H*-4), 4.55 (2H, dd, $J_{1,2}$ = 4.6, $J_{2,3}$ = 2.2, *H*-2), 1.81, 1.62, 1.49, 1.34 (4s, 24H, C*H*$_3$); ^{13}C-NMR (in DMF-d7): δ (ppm) = 154.6 (C-Pc), 154.3 (C-Pc), 152.4 (C-Pc), 151.8 (C-Pc), 145.4 (C-triazole), 139.5 (C-Pc), 139.4 (C-Pc), 139.2 (C-Pc), 134.1 (C-Pc), 130.3 (CH-Pc-(Triazole)), 129.9 (CH-Pc), 129.7 (CH-Pc), 129.7 (CH-triazole), 127.3 (C-Pc), 123.6 (CH-Pc), 123.4 (CH-Pc) 123.0 (CH-Pc), 110.9 (C-isopropylidene), 109.9 (C-isopropylidene), 96.9 (C-1), 72.8 (C-4), 72.5 (C-3), 72.3 (C-2), 68.9 (C-5), 51.5 (C-6), 26.4, 26.0, 24.8, 24.4 (CH_3-isopropylidene); MALDI-MS m/z 1194 $[M]^+$; HRESIMS *m/z* 1195.35133 (calcd for $C_{120}H_{110}N_{28}O_{20}Zn_2$ $[2M+2H]^{2+}$, 1195.35115); anal. C 60.59, H 4.68, N 15,72, calcd for $C_{60}H_{54}N_{14}O_{10}Zn$, C 60,23, H 4,55, N 16,39. UV/Vis (DMSO): λ_{max} (log ε) = 342 (4.75), 619 (4.57), 636 (4.59), 687 (5.03) nm.

[2,3,9,10,16,17,23,24-Octakis(1-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranosyl)-1H-1,2,3-triazole-4-yl)-phthalocyaninato]-zinc(II) (**1**): Under an atmosphere of nitrogen, 500 mg (0.67 mmol) 4,5-

Bis-[1-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-d-galactopyranosyl)1H-1,2,3-triazol-4-yl]-phthalonitrile **10**, 45.6 mg (0.33 mmol) dry $ZnCl_2$, were suspended in freshly distilled *n*-pentanol (2 mL). The reaction mixture was stirred at 90 °C for 30 minutes until a colourless solution was formed. Afterwards, 200 µL (1,34 mmol) DBU were added, and the solution was heated to 145 °C and stirred for 16 h until TLC (ethylacetate containing 8 % methanol) indicated the consumption of the starting material. The dark green reaction mixture was cooled to room temperature and concentrated under reduced pressure. Purification was carried out by successive column chromatography with elution by a) ethylacetate containing 5 % methanol on silica gel, b) methylenchloride containing 15 % ethylacetate on neutral Al_2O_3 and c) methylenchloride on Biobeads S-X1 (Bio-Rad), to afford **1** (150 mg, 29 %) as a green amorphous solid. IR (KBr): 3149, 2986, 2936, 1734, 1622 cm^{-1}; ^{1}H-NMR (in chloroform and pyridine-d5): δ (ppm) = 9.89 (s, 8H, *H*-Pc), 7.84 (s, 8H, *H*-triazole), 5.55 (d, 8H, $J_{1,2}$ = 4.9, *H*-1), 4.73 (dd, 8H, $J_{6a,6b}$ = 13.9, *H*-6a), 4.67 (dd, 8H, $J_{3,4}$ = 7.9, *H*-3), 4.60 (dd, 8H, *H*-6b), 4.42-4.39 (m, 8H, $J_{5,6a}$ = 5.1, $J_{5,6b}$ = 7.9, *H*-5), 4.34 (dd, 8H, $J_{2,3}$ = 2.4, *H*-2), 4.25 (dd, 8H, $J_{4,5}$ = 1.5, *H*-4), 1.52, 1.50, 1.37, 1.30 (4s, 96H, CH_3). ^{13}C-NMR (in chloroform and pyridine-d5): δ (ppm) = 154.3 (C-Pc), 146.8 (C-triazole), 138.4 (C-Pc), 131.0 (C-Pc), 125.1 (CH-Pc), 124.6 (CH-triazole), 109.9 (C-isopropylidene), 109.2 (C-isopropylidene), 96.3 (C-1), 71.0 (C-4), 70.8 (C-3), 70.6 (C-2), 67.3 (C-5), 50.4 (C-6), 26.2, 26.1, 25.0, 24.5 (CH_3-isopropylidene). MALDI-MS m/z 3051 $[2M]^{2+}$; HRESIMS *m/z* 785.27349 (calcd for $[C_{144}H_{168}N_{32}O_{40}ZnNa_4]^{4+}$, 785.27390); anal. C 56.79, H 6.07, N 14.48, calcd for $C_{144}H_{168}N_{32}O_{40}Zn$, C 56.66, H 5.55, N 14.68. UV/Vis (DMSO): λ_{max} (log ε) = 700 nm (5.47), 670 (4.63), 630 (4.68), 370 (5.01) nm.

[1,4,8,11,15,18,22,25-Octakis(1-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose-6-yl)-1H-1,2,3-triazole-4-yl)-phthalocyaninato]zinc(II) (**3**): Under an atmosphere of nitrogen, 693 mg (0.93 mmol) 3,6-Bis-[1-(6-deoxy-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranosyl)1H-1,2,3-triazole-4-yl]-phthalonitrile **9**, 192 mg (1.41 mmol) dry $ZnCl_2$, were suspended in freshly distilled *n*-pentanol (3 mL). The reaction mixture was stirred at 90 °C for 60 minutes until a colourless solution was formed. Afterwards, 200 µL (1,34 mmol) DBU were added, and the solution was heated to 145 °C and stirred for 16 h until TLC (ethylacetate containing 5 % methanol and 1 % triethylamine) indicated the consumption of the starting material. The dark green reaction mixture was cooled to room temperature and concentrated under reduced pressure. Purification was carried out by successive column chromatography on silica gel with elution by a) chloroform containing 1 % methanol and 1 % trimethylamine, b) methylenchloride containing 10 % acetone and 0.5 % trimethylamine, and c) ethylacetate containing 33 % toluene), gave **3** (153 mg, 22 %) as a green amorphous solid. IR (KBr) 3448, 3169, 2985, 2935, 2910, 1729, 1634, 1456, 1380, 1311, 1256, 1214, 1166, 1105, 1070, 1006, 859 cm^{-1}; ^{1}H-NMR (in chloroform and pyridine-d5): δ (ppm) = 9.00 (s, 8H, *H*-Pc), 8.73 (s, 8H, *H*-triazole), 4.95 (d, 8H, $J_{1,2}$ = 4.9, *H*-1), 4.78 (d, 8H, $J_{6a,6b}$ = 14.4, *H*-6a), 4.51 (dd, 8H, $J_{2,3}$ = 8.0, $J_{3,4}$ = 1.8, *H*-3), 4.40-4.30 (m, 16H, *H*-4, *H*-6b), 4.22-4.20 (m, 8H, *H*-5), 4.06-4.04 (dd, 8H, *H*-2), 1.30, 1.29, 1.23, 0.99 (4s, 96H, CH_3). ^{13}C-NMR (in chloroform and pyridine-d5): δ (ppm) = 153.3 (C-Pc), 143.3 (C-triazole), 134.8 (C-Pc), 130.9 (CH-Pc), 127.7 (C-Pc), 127.4 (CH-triazole), 109.8 (C-isopropylidene), 108.8 (C-isopropylidene), 95.8 (C-1), 71.5 (C-4), 70.8 (C-3), 70.5 (C-2), 67.8 (C-5), 51.7 (C-6), 26.0, 26.0, 24.9, 24.2 (CH_3-isopropylidene). MALDI-MS m/z 3051 $[M]^+$; HRESIMS *m/z* 1525.57668 (calcd for $[C_{144}H_{170}N_{32}O_{40}Zn]^{2+}$, 1525.57668); anal. C 56.64, H 5.86, N 14.22, calcd for $C_{144}H_{168}N_{32}O_{40}Zn$, C 56.66, H 5.55, N 14.68. UV (DMSO): λ_{max} (log ε) = 341 (4.71), 660 (4.39), 700 (4.41), 737 (5.15) nm.

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Keywords: glycoconjugation • helical self-assembly • *J*-aggregates • phthalocyanines • 1,2,3-triazole

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