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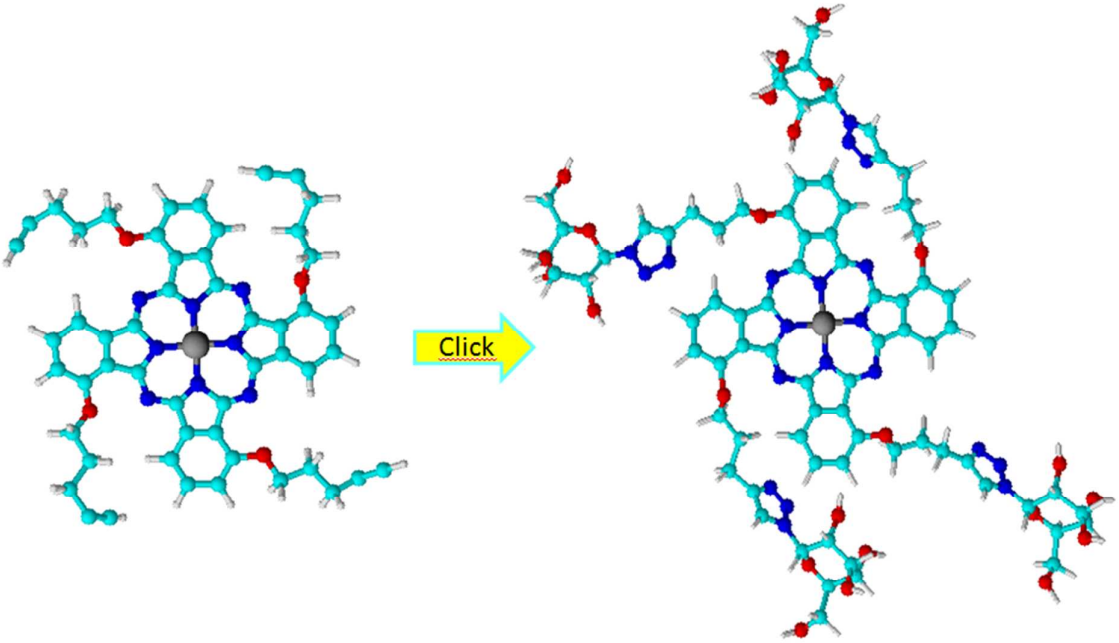

The synthesis of nonperipherally tetra terminalalkynyl substituted phthalocyanines and glycoconjugation of ZnPc derivative via click reaction and futher deacylation were carried out.

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Synthesis and Characterization of Nonperipherally Tetra Terminalalkynyl Substituted Phthalocyanines and Glycoconjugation via Click Reaction

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In order to obtain nonperipherally tetra terminalalkynyl substituted phthalocyanines (Pcs), new 3-pent-4-ynyloxy phthalonitrile (**3**) was prepared by the nucleophilic displacement reaction of 3-nitrophthalonitrile (**1**) and 4-pentyne-1-ol (**2**) and then cyclotetramerization attained in the presence of zinc acetate, cobalt acetate, and/or DBU in *n*-pentanol without protection/deprotection. For the first time, glycoconjugation of nonperipherally tetra terminalalkynyl substituted zinc phthalocyanine (ZnPc) (**6**) can be easily achieved via click reaction in high yield. The electronic absorption spectrum of the glucopyranosyl substituted ZnPc (**10**) derivative showed a red-shifted Q band at 751 nm in dichloromethane due to the protonation of meso nitrogens of pc macrocycle. Deacylation yielded ZnPc (**11**) bearing glucose substituents at nonperipheral positions with improved water-solubility and non-aggregation in DMSO. The chemical structures of new compounds were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, UV-Vis, mass spectrometry and elemental analysis. Moreover, the phthalonitrile compound was characterized using X-ray.

Introduction

Since the accidentally discovery of the phthalocyanines (Pcs), many efforts have been devoted on tailoring of their properties to produce molecular materials and technological devices. Recently they have found use as sensors [1,2], non-linear optics [3,4], dye sensitized solar cells [5,6], organic light emitting devices [7], molecular electronics [8,9], liquid crystals [10,11], semiconductors [12], catalysts [13,14], photodynamic reagents for cancer therapy (PDT) [15,16], among others. The properties of phthalocyanines are closely depended on their structure that can be modified by metallation or substitution variations: number, position, and nature. Incorporation of the substituents at the nonperipheral (np) sites as opposed to the peripheral (p) positions ensures good solubility and limited aggregation in most hydrophobic solvents and leads to significant bathochromic shifts of the Q absorption band. In addition, np-substituted compounds often crystallize well enough to enable X-ray crystallographic structure determinations [17]. Nonperipherally substituted octa- and tetra-alkyl, alkyloxy or alkylthiophthalocyanines were reported in the literature. However, studies on non-peripherally substituted Pc derivatives especially tetra substituted examples are still limited [18-22].

Click chemistry has been applied in a wide variety of research areas, including material science, polymer chemistry, and pharmaceutical sciences due to its being fast, quantitative, reproducible, resistant to side reactions and highly tolerant to reaction conditions [23]. The best known click reaction is the copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition between azides and alkynes is less used for the synthesis of substituted phthalocyanines [24-28]. Recently we have shown the syntheses of new symmetrical and unsymmetrical Pcs with teminalalkynyl substituents starting from phthalonitrile bearing terminalalkynyl moiety without protection/deprotection concept and their click reaction with azide-end functional polymers [29,30]. To the best of our knowledge, there is only one example of nonperipherally terminalalkynyl substituted phthalocyanine, that is 1,8,15,22-tetrakis(propargyloxy)phthalocyaninato-zinc(II) announced by Leznoff and coworkers in 1998. Besides, up to now, there are yet no any reports about the nonperipherally terminalalkynyl substituted phthalocyanines involved in click reaction.

Photodynamic therapy (PDT) has developed over last century and is now becoming a more widely used for the treatment of cancer. It involves the delivery of a nontoxic dyes known as photosensitizers (PS), followed by the irradiation with visible light of a specific wavelength, typically in the red region of the spectrum (620−690 nm). Activated photosensitizers transfer energy to molecular oxygen which results in the generation of reactive oxygen species mainly singlet oxygen ($^{1}O_2$) which in turn cause the destruction of tumors [31]. The development of efficient photosensitizers in terms of tumor-selectivity and reactive oxygen species (ROS)-producing ability is the main

topic of many ongoing research programs [32]. Phthalocyanine derivatives exhibit several optimal characteristics for being good PSs such as a high molar absorption coefficient in the visible region of the spectrum, a long lifetime of the triplet excited state, and an increased oxidative stability that allows their use as stable aqueous solutions. However, the lack of selective accumulation of these photo actively molecules within tumor tissue, the insolubility and aggregation in physiological fluids are major problems in PDT. The phthalocyanines conjugated with carbohydrate moieties have attracted considerable interest, with the aim of developing targeted photosensitizers and eventually the PDT efficacy [33-37].

The first carbohydrate substituted zinc(II) phthalocyanine was reported in 1989 by Maillard *et al*. [38] and its nonperipherally substituted analogue was synthesized in 2008 by Ng and *co*-workers [39]. Hanack, Ziegler *and co-workers* [40] prepared the first example of an anomerically glycosylated zinc (II) phthalocyanine in 2006 and after that several carbohydrate substituted phthalocyanines have been reported so far [41-46]. However, the synthesis of some of the glycosylated phthalocyanines can be rather complicated and not easy. Recently, carbohydrate conjugated phthalocyanines were synthesized by Click reaction as a novel method instead of traditional synthesis method [47-50].

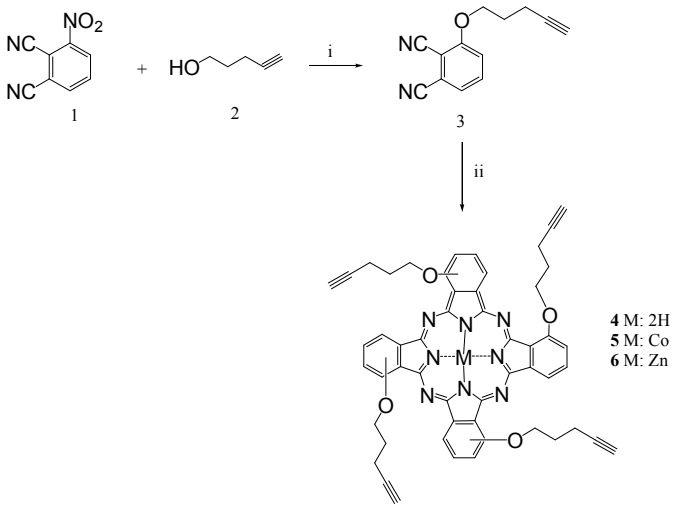
Based on the aforementioned statements, in this paper, firstly a novel phthalonitrile compound bearing an alkyne function in the C-3 position was designed to attain nonperipherally tetra terminalalkynyl substituted phthalocyanines by its cyclotetramerization in the presence of metal salts and/or DBU without protection/deprotection. In addition, to prove the viability of click reaction concept, we have chosen the resulting ZnPc derivative and the click reaction between nonperipherally tetra terminalalkynkyl substituted ZnPc (**6**) and 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl azide (**9**) then deacylation under Zemplén conditions provided water soluble nonperipherally tetra glucose substituted ZnPc (**11**) in high yield. The synthesis of nonperipherally tetra terminalalkynyl substituted phthalocyanines involved in click reaction with azido functional glucopyranosyl has never been reported so far to the best of our knowledge.

Results and discussion

Syntheses

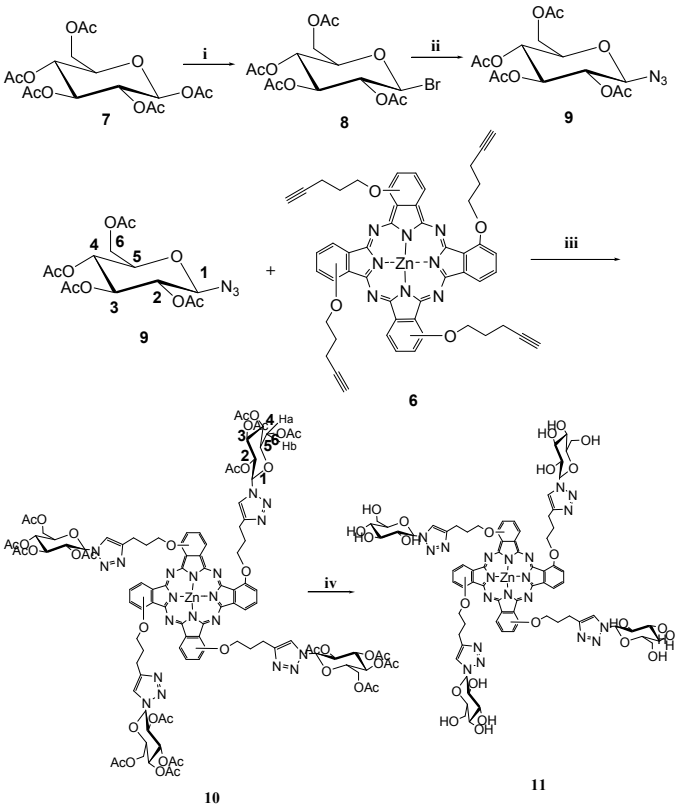
The terminalalkynyl substituted phthalocyanines are the common precursors for the preparation of functionalized analogues. This alkyne function can be introduced on the phthalocyanine precursor (usually a phthalonitrile), but are up to now more commonly introduced on the phthalocyanine itself. Recently, we have incorporated terminalalkynyl groups on the periphery of phthalocyanine compounds starting from terminalalkynyl substituted phthalonitrile precursor [29, 30]. In order to vary terminalalkynyl substituted phthalocyanines, we designed new phthalonitrile compound bearing an alkyne function in the C–3 position. The classical nucleophilic substitution of 3-nitrophthalonitrile (**1**) and 4-pentyn-1-ol (**2**) gave the targeted 3-pent-4-ynyloxy-phthalonitrile (**3**) in a satisfactory 74 % yield (Scheme 1).

We recently described the successful use of the cyclotetramerization of terminalalkynyl substituted phthalonitrile compound without protection/deprotection [29, 30]. This synthetic strategy which was adopted to prepare target 1,8(11),15(18),22(25)-tetra-terminalalkynyl substituted phthalocyanines (**4-6**) was carried out with reasonable yields by a direct cyclotetramerization of unprotected nonperipherally terminalalkynyl substituted phthalonitrile compound in the presence of zinc acetate, cobalt acetate, and/or DBU in pentanol (Scheme 1). Column chromatography was used to purify the following phthalocyanine compounds (**4-6**).



Scheme 1. Synthetic route of pent-4-ynyloxy substituted phthalocyanines. (i) DMSO, K_2CO_3, 50 °C, 48 h. (ii) *n*-pentanol, DBU, $Zn(CH_3COO)_2$, $Co(CH_3COO)_2$, 140 °C, 24 h

Phthalocyanine-carbohydrate conjugates are quite uncommon especially by click reaction. To our knowledge, title nonperipherally tetra glucose conjugated ZnPc (**11**) will be the first example of the conjugation of nonperipherally tetra terminalalkynyl substituted phthalocyanine with azido functional glucose via click reaction. For this purpose, 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (**7**) was transformed to 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl azide (**9**) as a white solid in 75% yield after bromination with hydrogen bromide in acetic acid and then reaction with NaN_3 in THF/water. The successful click reaction between glucopyranosyl azide (**9**) and nonperipherally tetra terminalalkynyl substituted ZnPc (**6**) in the presence of sodium ascorbate and copper sulfate resulted glycopyranosyl conjugated ZnPc (**10**) in satisfactory yield. Consequently, target compound, nonperipherally glucose conjugated ZnPc (**11**), was obtained by deprotection under Zémplen conditions in 87 % yield (Scheme 2).



Scheme 2. Synthetic route of glucose conjugated zinc phthalocyanine. (i) CH_2Cl_2, 33% HBr/AcOH, 0°C. (ii) THF/H_2O, NaN_3, 70 °C, 24 h. (iii) $Cu(SO_4).5H_2O$, Na ascorbate, THF/H_2O/MeOH, 50 °C, 48 h. (iv) CH_2Cl_2, MeONa, MeOH, rt., 24 h.

Structural characterizations

All new compounds (**3–11**) were fully characterized with various spectroscopic methods such as IR, ^{1}H NMR, ^{13}C NMR, UV-vis, mass spectrum, elemental analysis, and X-ray analysis. The IR spectrum of phthalonitrile compound (**3**) presents characteristic peaks such as the nitrile function at 2231 cm^{-1}, terminal alkyne function at 3286 cm^{-1} and 2116 cm^{-1}. The disappearance of the peak at 2231 cm^{-1} proves the occurrence of cyclotetramerization to phthalocyanine derivatives (**4-6**). Furthermore, the peaks at 3286 cm^{-1} and 2116 cm^{-1} were also disappeared in the case of "clicking" of ZnPc (**6**).

The structure of phthalonitrile compound (**3**) was confirmed by X-ray analysis (Table 1). The single crystals of this compound were grown by slow evaporation of methanol. ORTEP representation of the compound is shown in Fig. 1. The bond lengths and angles are all in normal range. The angle between the mean plane of the phenyl ring and the plane that goes through atoms O1, C5, C4, C3, C2 and C1 is 5.32(15)°. The C12–N1 and C13–N2 triple bond lengths are 1.143(3) A° and 1.146(3) A°, respectively, and agree with corresponding distances in the literature [55,56]. The value of the C6–O1–C5–C4 torsion angle of 178.08 (18)° is consistent with the value observed in the related 3-(prop-2-ynyloxy)phthalonitrile recently reported [56]. The intermolecular C-H···N interactions played an important role in stabilizing the packing of the molecules in the crystal.

Table 1. Crystal data and refinement parameters for **3**

Crystal Parameters	Phthalonitrile (3)
CCDC	978750
Empirical formula	$C_{13}H_{10}N_2O$
Formula weight (g mol^{-1})	210.23
Temperature (K)	100(2)
Wavelength (**Å**)	0.71073
Crystal system	triclinic
Space group	P -1
a (Å)	4.4256(6)
b (Å)	7.6883(10)
c (Å)	17.242(2)
α (°)	77.679(4)
β (°)	84.616(5)
γ (°)	74.348(4)
Crystal size (mm)	0.010 x 0.050 x 0.100
V (Å^3)	551.49(13)
Z	2
ρ calcd (g.cm^{-3})	1.266
μ (mm^{-1})	0.082
F(000)	220
□ range for data Collection (°)	2.42 to 28.36
h/k/l	-5/5, -10/10, -22/22
Reflections collected	19276
Independent reflections	2739
Data / restraints / parameters	2739 / 0 / 145
Goodness-of-fit on F^2	1.086
Final R indices [I>2σ(I)]	R_1 = 0.0702, wR_2 = 0.1792
R indices (all data)	R_1 = 0.0854, wR_2 = 0.1878
Largest diff. peak and hole (e.Å^{-3})	0.405 and -0.330

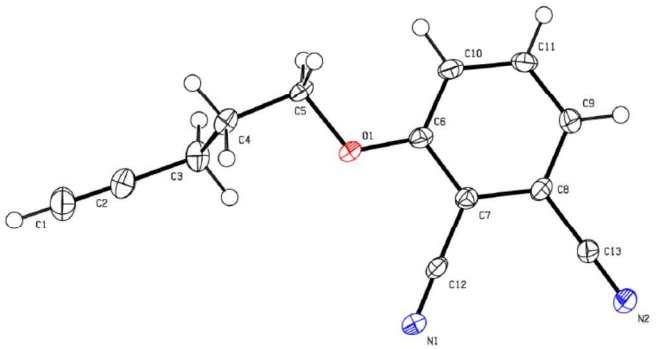


Figure 1. Molecular structure of phthalonitrile **3**.

In the ^{1}H NMR spectrum of **3**, the aromatic protons appeared as triplet, doublet and doublet at 7.64, 7.36 and 7.28, respectively, C*H*$_2$-O protons as triplet at 4.26 ppm, C*H*$_2$ protons multiplet at 2.48 and 2.10 ppm, C≡C*H* proton as triplet at 1.98 ppm. The ^{1}H NMR spectra of H_2Pc (**4**) and ZnPc (**6**) derivatives have almost the same chemical shifts and somewhat broader than the corresponding signals in the dinitrile compound (**3**). The inner

core –NH protons of the metal-free phthalocyanine (**4**) was observed at -2.82 ppm.

^{13}C NMR spectra of (**3**) show typical chemical shifts for aliphatic carbons (14.52, 27.21 ppm), O-*C*H$_2$ carbon (69.36 ppm), alkyne carbons (67.64, 82.52 ppm), aromatic carbons (100.40, 116.40, 117.07, 124.99, 134.56, 161.21 ppm), nitrile carbons (114.00, 115.12 ppm). H_2Pc (**4**) and ZnPc (**6**) show the typical ^{13}C NMR shifts as indicated in the experimental section.

In the mass spectra of phthalonitrile (**3**), phthalocyanines (**4-6**) and glucoconjugated phthalocyanines (**10, 11**), the molecular ion peaks were observed at m/z 210.00 $[M]^+$ for **3**, 842.78 $[M]^+$ for **4**, 899.67 $[M]^+$ for 5, 906.82 $[M]^+$ for **6**, 2400.00 $[M]^+$ for **10**, and 1741.92 $[M]^+$ for **11**.

The conversion of 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (**7**) to 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl azide (**9**) was confirmed with IR, ^{1}H NMR and ^{13} C NMR. The IR spectrum of glucopyranosyl azide (**9**) exhibits the expected specific peak at 2116.8 cm^{-1} due to the N_3 stretching vibration. In the ^{1}H NMR and ^{13} C NMR spectra of glucopyranosyl azide (**9**), signals at 4.29 ppm and 87.91 ppm indicate CH linked to the azido group.

The formation of glycopyranosyl conjugated ZnPc (**10**) was confirmed with the IR, ^{1}H NMR and ^{13} C NMR spectra. After the click reaction between glucopyranosyl azide (**9**) and terminalalkynyl substituted ZnPc (**6**), in the FT-IR spectra, the signal at 2116.8 cm^{-1} that observed for azido function of glucopyranosyl azide (**9**) and the signals at 2114.15 cm^{-1} and 3287.34 cm^{-1} that observed for alkyne function of ZnPc (**6**) have disappeared (Fig. 2). In the ^{1}H NMR spectrum, the peak at 4.29 ppm assigned to C*H*-N_3 shifted to 6.99 ppm and a new peak appeared at 8.06 ppm indicating triazole formation. In the ^{13}C NMR spectrum, the signals at 143.18 ppm and 125.50 ppm also confirm the formation of triazole ring.

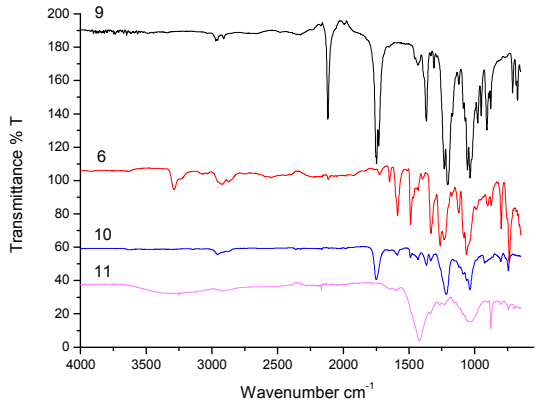


Figure 2. FT-IR spectra of **9, 6, 10,** and **11**.

Deprotection under Zemplén conditions afforded title glucose conjugated ZnPc (**11**) in quantitative yields. The presence of wide band around 3251 cm^{-1} and an intense band at 1423 cm^{-1} associated to the hydroxyl groups and the disappearance of the band corresponding to the carbonyl groups at 1748 cm^{-1} were observed in the IR spectrum of **11** (Fig. 2). In the ^{1} H NMR spectrum, the presence of the signal at 5.60-4.79 ppm was also attributed to the hydroxyl groups of glucose. In addition, deprotection was confirmed by the absence of signals between 2.08 and 1.81 ppm in the ^{1}H NMR spectrum corresponding to the acetyl groups.

Electronic absorption spectroscopy and aggregation behavior

UV-vis absorption is one of the most important properties of Pcs due to the spectral shape of an absorption spectrum is closely related to the molecular structures, central metals and substituents. The typical metallated phthalocyanines with D_{4h} symmetry have an unsiplit lowest energy band (Q band) in the visible region (650-700 nm) and less intense band (B band) in the 300-500 nm region. It is known that, the α-substituted Pc derivatives have their Q bands at longer wavelengths compared to the β-substituted derivatives [57].

Fig. 3 shows the UV-vis spectra of the nonperipherally tetra terminalalkynyl substituted metal free (**4**) cobalt (**5**) and zinc phthalocyanines (**6**) in THF. For nonperipherally tetra terminalalkynyl substituted Pcs (**4-6**), the Q-band absorptions appear at longer wavelength compared with phthalocyanines containing the same substituents on the peripheral positions that we have recently reported [29] (Table 2). The observed red shift of the Q-bands is a result of the nonperipheral substitution with pent-4-ynyloxy groups.

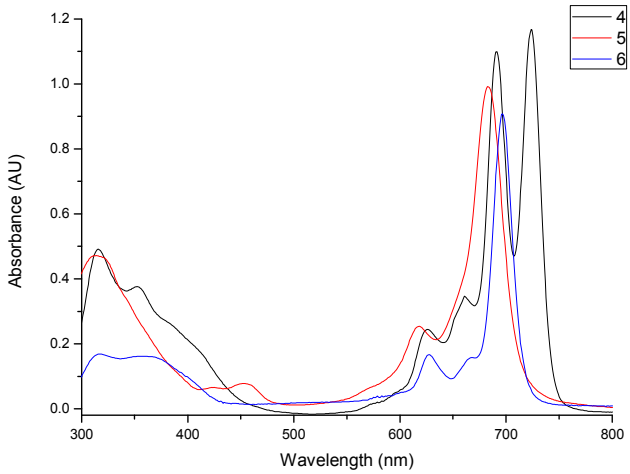


Figure 3. Electronic spectra of **4** (black line), **5** (red line), **6** (blue line) in THF (4x10^{-6} mol dm^{-3}).

Table 2. Spectral data for nonperipherally (**4-6**) and peripherally tetra pent-4-ynyloxy substituted Pcs [29] in THF.

Nonperipherally tetra pent-4-ynyloxy substituted Pcs (**4-6**)	λmax, nm	Peripherally tetra pent-4-ynyloxy substituted Pcs [29]	λmax, nm
H_2Pc	315, 691, 723	H_2Pc	335, 665, 702
CoPc	315, 682	CoPc	337, 671
ZnPc	315, 696	ZnPc	350, 675

The Pcs (**4-6**) present typical UV-vis spectra in THF, DCM and DMF for nonaggregated phthalocyanines showing an intense and sharp Q-band in the red visible region (Table 3) (Fig 4a-c). H_2Pc (**4**) shows split Q band components at *ca.*695 and 724 nm in THF, DCM and DMF (Fig. 4a). This splitting has been interpreted as due to the reducing the molecular symmetry from

D_{4h} to D_{2h}. As can be seen in Fig. 4b-c, CoPc (**5**) and ZnPc (**6**) show red shifted Q-bands (by 12 and 7 nm respectively) in DCM compared with their Q bands in THF. The phthalocyanine Q band shifts to the red with an increase in the refractive index of the solvent [58], hence a red shifting is observed in DCM which has a larger refractive index compared to the THF and DMF (Table 3).

Table 3. Spectral data for phthalocyanines (**4-6**) in different solvents

Phthalocyanines	Solvent	Q band λ_{max} (nm)
4	THF	723, 691
	DMF	725, 697
	DCM	724, 693
5	THF	682
	DMF	687
	DCM	694
6	THF	696
	DMF	700
	DCM	703

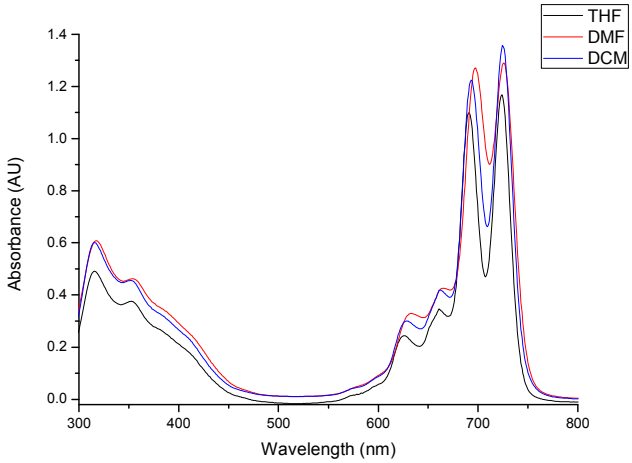


Figure 4a. Electronic spectra of **4** in THF (black line), DMF (red line), DCM (blue line) ($4x10^{-6}$ mol dm^{-3}).

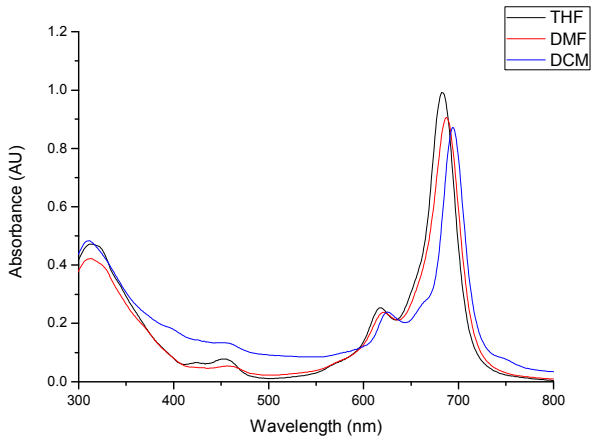


Figure 4b. Electronic spectra of **5** in THF (black line), DMF (red line), DCM (blue line) ($4x10^{-6}$ mol dm^{-3}).

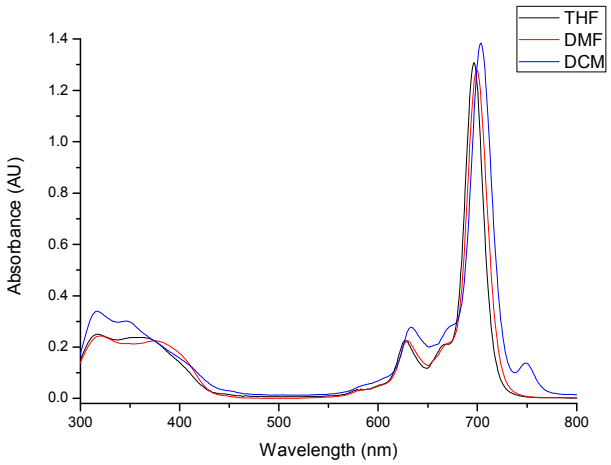


Figure 4c. Electronic spectra of **6** in THF (black line), DMF (red line), DCM (blue line) ($1.2x10^{-5}$ mol dm^{-3}).

Phthalocyanines have two types of aggregations called face-to-face H-aggregation and side-to-side J-aggregation [59]. J-type aggregation was rarely observed for the phthalocyanine molecules. The shift of the Q band to the red is desirable for applications of phthalocyanines as photosensitizers in photodynamic therapy (PDT). A red shifted Q band can be attributed to the J-aggregation of the Pcs [60, 61] or protonation of the meso-nitrogen atoms of the Pc ring due to acidic impurities in the solvents such as dichloromethane and chloroform, which leads to lowering of the symmetry and causes splitting and a bathochromic shift of the Q band [62-64]. The glycopyranosyl conjugated ZnPc (**10**) having Q band maxima at 698 nm in THF, 705 nm in DMSO did not show any aggregation in these solvents. On the other hand, this complex showed Q band at 705 nm and a new band at 751 nm in DCM (Fig. 5). To find out the cause of the extra red-shifted Q band (J-type aggregation or protonation of the Pc ring), the addition of increasing concentrations of trifluoroacetic acid (TFA) to a fixed concentration of **10** in DMSO was carried out (Fig. 6). It can be seen that in addition to the Q band at 705 nm, extra red-shifted band observed at 761 nm in DMSO by the addition of TFA. The incresing concentration of TFA diminishes the absorption at 705 nm while extra peak at 761 nm increases. It is suggesting that, the observed new red-shifted absorption band at 761 nm for nonperipherally tetra glycopyranosyl conjugated ZnPc (**10**) occurred due to the protonation of meso-nitrogens of pc macrocycle. Another evidence for the protonation of meso-nitrogens can be deduced from the UV-Vis spectra of **10** at different concentrations in DCM.

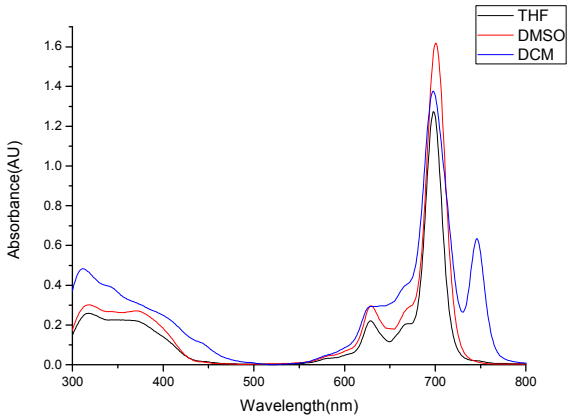


Figure 5. Electronic spectra of **10** in THF (black line), DMSO (red line), DCM (blue line) ($5x10^{-6}$ mol dm^{-3}).

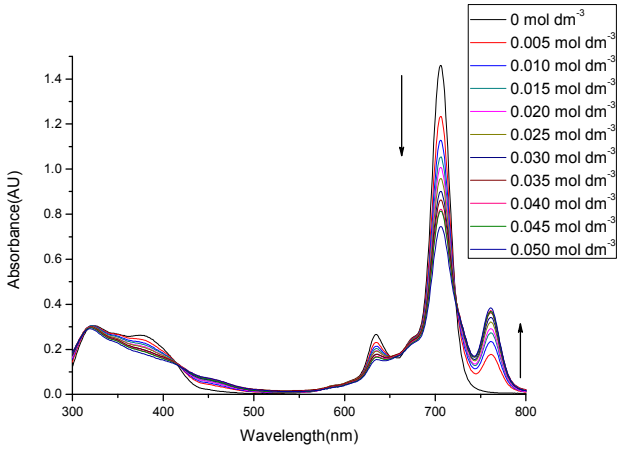


Figure 6. Change in the absorption spectrum of **10** (~$5x10^{-6}$ mol dm^{-3}) in DMSO seen upon the addition of increasing concentrations of TFA (0-0.050 mol dm^{-3}).

As shown in Fig. 7, when the solution of glycopyranosyl conjugated ZnPc (**10**) in DCM was diluted, the absorption of red shifted band at 751 nm increased.
The conversion of acetyl groups to hydroxyl groups has no influence on the electronic absorption spectrum. The nonperipherally tetra glucose conjugated ZnPc (**11**) dissolved in DMSO exhibits a strong Q-band at 705 nm, indicating that it is practically non-aggregated.

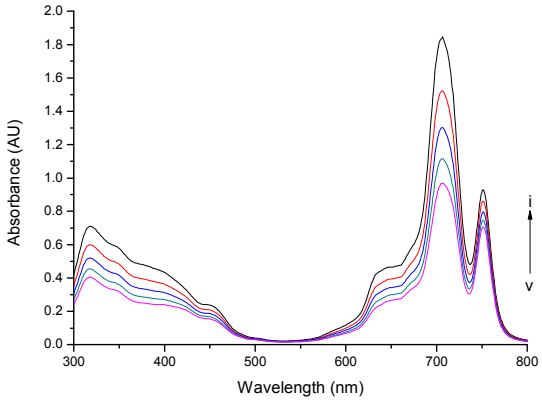


Figure 7. Electronic absorption spectra of **10** at various concentrations:(i) 1.3 $\times10^{-5}$, (ii) 9 $\times10^{-6}$, (iii) 6.5 $\times10^{-6}$, (iv) 5.2 $\times10^{-6}$, (v) 4.3 $\times10^{-6}$ mol dm^{-3} in DCM.

Fig. 8 shows that Lambert Beer law was obeyed for **11** at concentrations below 1.1 x 10^{-5} M. The solubility of tetra nonperipherally glucose conjugated ZnPc (**11**) in water was evidenced by its UV-vis spectrum. Compound **11** is aggregated in water and a new broader and blue shifted band at ~655 nm is observed. The shift to lower wavelengths is caused by H-type aggregates. Increasing the concentration of **11** in water leads to a increase of the blue shifted Q band demonstrating the formation of aggregated species. Fig. 9 shows that Lambert-Beer law was obeyed for non-peripherally tetra glucose conjugated ZnPc (**11**) in the concentrations ranging from 1.2 x 10^{-5} to 3.5 $x10^{-6}$ M in water.

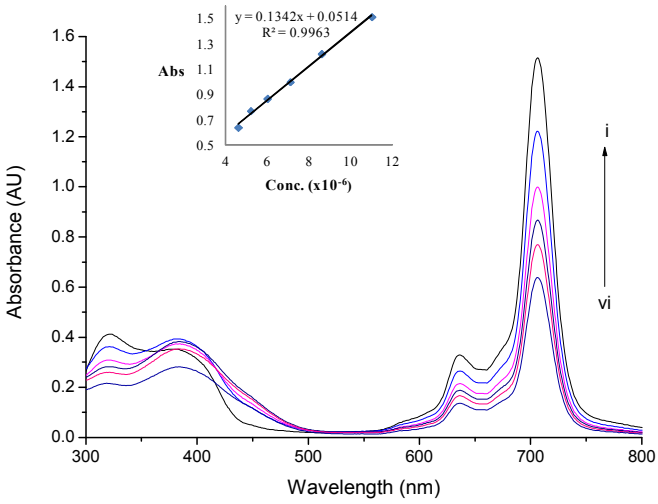


Figure 8. Electronic absorption spectra of **11** at various concentrations:(i) 1.1 $\times10^{-5}$, (ii) 8.6 $\times10^{-6}$, (iii) 7.1 $\times10^{-6}$, (iv) 6.0 $\times10^{-6}$, (v) 5.2 $\times10^{-6}$, (vi) 4.6 $\times10^{-6}$ mol dm^{-3} in DMSO.

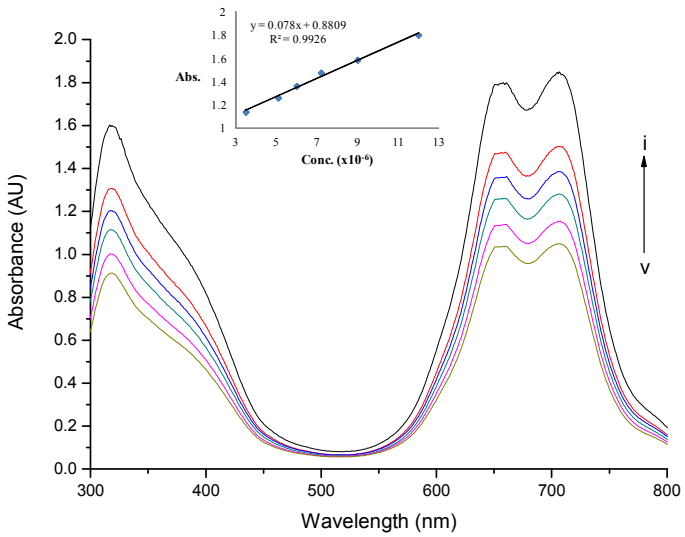


Figure 9. Electronic absorption spectra of **11** at various concentrations:(i) 1.2 $\times 10^{-5}$, (ii) 9.0 $\times 10^{-6}$, (iii) 7.2 $\times 10^{-6}$, (iv) 6.0 $\times 10^{-6}$, (v) 5.1 $\times 10^{-6}$, 3.5 $\times 10^{-6}$ mol dm^{-3} in water.

Conclusions

In summary, we have demonstrated the syntheses of nonperipherally tetra terminalalkynyl substituted phthalocyanines and the corresponding new precursor having terminal alkyne function at the C-3 position. Cyclotetramerizations were achieved in the presence of metal salts and/or DBU in *n*-pentanol without protection of the terminal alkyne function of the phthalonitrile compound. The combination of the click reaction between nonperipherally tetra terminalalkynyl substituted ZnPc (**6**) and azido functional glucopyranosyl (**9**) and the deacylation under Zemplén conditions yielded the title nonperipherally tetra glucose conjugated ZnPc (**11**). This is the first example of nonperipherally tetra terminalalkynyl substituted phthalocyanines involved in click reaction with azido functional glucose to the best of our knowledge.

In this study, we have varied the tetra terminalalkynyl substituted phthalocyanines with the nonperipheral substitution that are possible precursors for click chemistry. The water solubility promoted by the glucose moieties provides a potential application of ZnPc (**11**) derivative as photosensitizer in photodynamic therapy that we are currently investigating. These novel nonperipherally terminal alkynyl substituted phthalocyanines are now being used for a new electrode modification technique, "click electrochemistry". In addition, the synthesis of unsymmetrical phthalocyanine derivatives bearing terminal alkyne function at nonperipheral position is currently underway.

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Experimental

Materials

IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with ATR capability, electronic spectra were recorded on a Scinco SD 1000 singlebeam ultraviolet-visible (UV-vis) spectrophotometer using 1 cm path length cuvettes at room temperature. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 500 MHz spectrometer using TMS as internal reference. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. Mass spectra were performed on Bruker Microflex MALDI-TOF/MS and Perkin-Elmer Clarus 500 mass spectrometers. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. The homogeneity of the products was tested in each step by TLC (SiO_2). All reactions were carried out under nitrogen atmosphere in dried solvents. The solvents were stored over molecular sieves.

Synthesis

3-Pent-4-ynyloxy phthalonitrile (3) 3-nitrophthalonitrile (**1**) (1g, 5.77 mmol), 4-pentyn-1-ol (**2**) (0,873g, 10.39 mmol) and anhydrous potassium carbonate (K_2CO_3) (2.15g, 15.6 mmol) in DMSO (15 mL) were stirred two days at 50 °C. The reaction mixture was cooled to room temperature and poured into ice water to give a yellow-brown precipitate, which was filtered off and washed with water. After recrystallization from methanol, the title compound was obtained as a lustrous light bronze needle sufficiently pure for X-ray analysis. CCDC 978750 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Yield 0.90 g (74,19%), mp 127-129 °C, FT-IR γ (cm^{-1}): 3286.45 (≡C−H); 3099.21 (Ar-H); 2963.73-2844.82 (CH, aliphatic); 2231.18 (CN); 2116.37 (C≡C); 1284.93 (Ar-O-C). ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.64 (*Ar*-H, t, 1H), 7.36 (*Ar*-H, d, 1H), 7.28 (*Ar*-H, d, 1H), 4.26 (CH_2-O-, t, 2H), 2.48 (CH_2, m, 2H), 2.10 (CH_2, m, 2H), 1.98 (C≡C*H*, t, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm 161.21 (Ar-*C*-O), 134.56 (Ar-*C*), 124.99 (Ar-*C*), 117.07 (Ar-*C*), 116.40 (Ar-*C*), 115.12 (*C*≡N), 114.00 (*C*≡N), 100.40 (Ar-*C*), 82.52 (*C*≡CH), 69.36 (CH_2-O), 67.64 (C≡*C*H), 27.21 (CH_2), 14.52 (CH_2). GC-MS: m/z ($C_{13}H_{10}N_2O$) found= 210.00 (calcd. for $[M]^+$ 210.23).

1,8(11),15(18),22(25)-tetrakis(pent-4-ynoxy)phthalocyanine (4) A mixture of 3-pent-4-ynyloxy-phthalonitrile (0.1 g, 0.48 mmol) and 30 µl of DBU in *n*-pentanol (2 mL) were heated to 140 °C with stirring for 24 h under N_2. The dark blue mixture was cooled to room temperature and then precipitated with hexane. The precipitate was filtered off and washed with hexane. The crude product was purified by column chromatography on silica gel using THF/hexane 100:70 as the

eluent to afford metal free phthalocyanine as a blue solid. Yield 0.023 g (23%). FT-IR γ (cm^{-1}): 3637.93 (N-H); 3290.63 (≡C−H); 3014 (Ar-H); 2954.71-2870.68 (CH, aliphatic); 2107.75 (C≡C); 1267.83 (Ar-O-C). UV-Vis (THF) λ_{max}/nm: 723, 691, 315. ^{1}H NMR (500 MHz, DMSO d_6):δ ppm 8.52 (Ar-*H*, m 4H), 8.29 (Ar-*H*, m, 4H), 7.65 (Ar-*H*, m, 4H), 4.27 (C*H*$_2$-O-, m, 8H), 2.82 (C*H*$_2$, m, 8H), 2.34 (C*H*$_2$, m, 8H), 1.92 (C≡C*H*, m, 4H), -2.82 (N-*H*, s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm 161.23 (Ar-*C*-O), 136.34, 126.23, 118.99, 116.22, 115.81, 114.01 (Ar-*C*), 83.66 (*C*≡CH), 72.35 (*C*H$_2$-O), 68.61 (C≡*C*H), 27.73 (*C*H$_2$), 14.73 (*C*H$_2$). MS: m/z ($C_{52}H_{40}N_8O_4$) found= 842.782 (calcd. for $[M]^+$ 842.94). Calcd. for C 74.63, H 4.73 N 13.14 %; found C 74.05, H 4.68, N 13.21.

1,8(11),15(18),22(25)-tetrakis(pent-4-ynoxy)phthalocyaninato cobalt(II) (5) A mixture of 3-pent-4-ynyloxy-phthalonitrile (0.1 g, 0.48 mmol), $Co(CH_3COO)_2$ (0.028 g, 0.16 mmol) and 30 µl of DBU in *n*-pentanol (2 mL) was heated to 140 °C with stirring for 24 h under N_2. The dark blue mixture was cooled to room temperature and then precipitated with hexane. The precipitate was filtered off and washed with hexane. The crude product was purified by column chromatography on silica gel using THF:hexane 1:1 as the eluent to afford cobalt phthalocyanine as a blue solid. Yield 0.026 g (18.24%), FT-IR γ (cm^{-1}): 3293.10 (≡C−H); 3040 (Ar-H); 2954.59-2870.68 (CH, aliphatic); 2112.06 (C≡C); 1272.10 (Ar-O-C). UV-Vis (THF) λ_{max}/nm: 682, 315. MS: m/z ($C_{52}H_{40}N_8O_4Co$) found= 899.672 (calcd. for $[M]^+$ 899.86). Calcd. for $C_{52}H_{40}N_8O_4Co$: C 69.41, H 4.48, N 12.45, O 7.11, Co 6.55% ; found C 69.33, H 4.39, N 12.451 %.

1,8(11),15(18),22(25)-tetrakis(pent-4-ynoxy)phthalocyaninatozinc(II) (6) A mixture of 3-pent-4-ynyloxy-phthalonitrile (0.1 g, 0.48 mmol), $Zn(CH_3COO)_2$ (0.029 g, 0.16 mmol) and 30 µl of DBU in n-pentanol (2 mL) was heated to 140 °C with stirring for 24 h under N_2. The dark blue mixture was cooled to room temperature and then precipitated with hexane. The precipitate was filtered off and washed with hexane. The crude product was purified by column chromatography on silica gel using THF as the eluent to afford zinc phthalocyanine as a blue solid. Yield 0.077 g (53.84%), FT-IR γ (cm^{-1}): 3287.34 (≡C−H); 3034.48 (Ar-H); 2921.42-2870.68 (CH, aliphatic); 2114.15 (C≡C); 1262.90 (Ar-O-C). UV-Vis (THF) λ_{max}/nm: 696, 315. ^{1}H NMR (500 MHz, DMSO d_6): δ ppm 8.88 (Ar-H, m 4H), 8.10 (Ar-*H*, m, 4H), 7.40 (Ar-H, m, 4H), 4.56 (C*H*$_2$-O-, m, 8H), 2.82 (C*H*$_2$, m, 8H), 2.37 (C*H*$_2$, m, 8H), 1.90 (C≡C*H*, m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm 156.37, 152.94, 152.82, 152.68 (Ar-C-O), 141.48, 130.86, 126.49, 125.36, 116.08 (Ar-C), 84.59 (*C*≡CH), 72.03 (*C*H$_2$-O), 69.67 (C≡*C*H), 28.65 (CH$_2$), 15.19 (CH$_2$). MS: m/z ($C_{52}H_{40}N_8O_4Zn$) found= 906.818 (calcd. for $[M]^+$ 906.32). Calcd. for $C_{52}H_{40}N_8O_4Zn$: C 68.91, H 4.45, N 12.36 % ; found C 68.80, H 4.39 N 12.39 %.

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl azide (9) To a vigorously stirred solution of 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (**7**) (2.4 g, 6.1 mmol) in $CHCl_2$ (20mL) was added carefully a solution of 33% hydrobromic acid in glacial acetic acid (10 mL) at 0 °C. The resulting solution was stirred for 7 h. The orange solution was poured in ice-water. The combined organic phases were consecutively washed with sat. aq. $NaHCO_3$ (2 × 600 mL), dist. water (300 mL), and brine (2 ×300 mL) and dried over Na_2SO_4. Filtration and evaporation gave the crude glycosyl bromide (**8**) as yellow oil. The recrystallization from ethanol yielded the pure bromide as white solid (1.34 g 53%). Sodium azide (1.49 g, 23 mmol) and 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl bromide (**8**) (0.95 g, 2.31 mmol) were suspended in a mixture THF/water 10/1 (22 mL) and stirred at 70 °C for 24 h. Evaporation to dryness afforded a yellow-white residue that was dissolved in chloroform (500 mL) and water (200 mL). The phases were separated and the organic layer was washed consecutively with dist. water (300 mL), sat. aq. $NaHCO_3$ (400 mL), brine (200 mL) and dried over Na_2SO_4. The crude yellowish product obtained after filtration and evaporation, was washed with cold ethanol. After recrystallization from ethanol, the title compound 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl azide (**9**) was obtained as a white solid. Yield: (0.64g), 74.53%. FT-IR γ (cm^{-1}): 2968.60-2906.60 (CH, aliphatic); 2116.8 (N_3), 1748.2 (C=O); 1206 (C-O-C). ^{1}H-NMR (500 MHz, $CDCl_3$): δ ppm 5.23 (1H, t, H-3), 5.11 (1H, t, H-4), 4.97 (1H, t, H-2), 4.66 (1H, d, H-6a), 4.29 (1H, dd, H-1), 4.19 (1H, dd, H-6b) 3.82-3.79 (1H, m, H-5), 2.11 (3H, s, -OC(O)C*H*3), 2.09 (3H, s, -OC(O)C*H*3), 2.04 (3H, s, -OC(O)C*H*3), 2.02 (3H, s, -OC(O)C*H*3). ^{13}C-NMR (125 MHz, $CDCl_3$): δ ppm 170.58, 170.10, 169.29, 169.18 (4 × -O*C*(O)CH3), 87.91 (C-1), 74.03 (C-5), 72.60 (C-3), 70.64 (C-2), 67.88 (C-4), 61.65 (C-6), 20.69, 20.55, 20.53, 20.53 (4 × -OC(O)*C*H3). Calcd. for $C_{14}H_{19}N_3O_9$: C 45.04, H 5.13, N 11.26 % ; found C 44.97, H 5.03, N 11.33 %.

1,8(11),15(18),22(25)-tetrakis[((1-N-(2,3,4,6-tetra-*O*-acetyl-β-Dglucopyranosyl)-1H-1,2,3-triazol-4-yl)propoxy)] phthalocyaninatozinc(II) (10) To a solution of terminalalkynyl substituted ZnPc (**6**) (0.030g, 0.033 mmol) and 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl azide (**9**) (0.061 g, 0.165 mmol) in THF/H_2O/MeOH 3:1:1 (10 mL) was added consecutively $CuSO_4.5H_2O$ (0.021 g, 0.132 mmol) and sodium ascorbate (0.078 g, 0.396 mmol). The mixture was stirred vigorously at 50°C for 48 h under nitrogen. The solvent was removed under reduced pressure, and the residue was taken-up in dichloromethane, washed with water and dried over $MgSO_4$. After the filtration and evaporation of the solvent, the crude product was purified by column chromatography with silica gel using first THF/hexane (1:1) then THF as eluent. Yield: (0.042.g), 52 %. FT-IR γ (cm^{-1}): 2952.58-2866.63 (CH, aliphatic); 1748.84 (C=O); 1587.23, 1431.96 (C=C phenyl); 1216.05 (Ar-O-C). UV-Vis (THF) λ_{max}/nm: 698, 317. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 9.15 (12H, br, Ar-*H*), 8.06 (4H, br, C*H*-N_3), 6.99 (4H, br, H-1), 5.38-5.02 (24H, br, aliphatic protons of glucopyranosyl), 4.11 (8H, br, OC*H*$_2$CH$_2$CH$_2$), 2.28 (8H, d, OCH$_2$C*H*$_2$CH$_2$), 2.18 (8H, d, -OCH$_2$CH$_2$C*H*$_2$), 2.08, 2.02, 1.89, 1.81 (4 × 12H, s, -OC(O)C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 170.52, 169.90 (-O*C*(O)CH$_3$), 156.27, 135.77, 132.58, 128.07 (Ar-*C*), 143.18 (*C*CHN$_3$), 125.50 (C*C*HN$_3$),

85.68 (C-1), 74.87 (O-CH_2), 72.74 (C-5), 70.47 (C-3), 68.62 (C-2), 67.66 (C-4), 61.59 (C-6), 34.96 (OCH_2CH_2), 24.39 ($OCH_2CH_2CH_2$), 21.17, 20.68, 20.50, 20.07 (4 × -OC(O)*C*H3). MS: m/z ($C_{108}H_{116}N_{20}O_{40}Zn$) found = 2400 (calcd. for [M]$^+$ 2399.58). Calcd. for $C_{108}H_{116}N_{20}O_{40}Zn$: C 54.06, H 4.87, N 11.67 %; found C 53.93, H 4.81, N 11.72 %.

1,8(11),15(18),22(25)-tetrakis[((1-N-(β-D-glucopyranosyl)-1H-1,2,3-triazol-4-yl)propoxy)] phthalocyaninatozinc(II)(11)

The compound **10** (0.030g 0,012 mmol) was dissolved in DCM (2.5ml) containing 2.5ml of MeONa solution in methanol and stirred at room temperature 24h. After the evaporation of solvent, the solid product was washed with THF, DCM and methanol respectively. Product was chromatographically pure. Yield: (0.019 g) 87 %. FT-IR γ (cm^{-1}): 3251.61 (O-H, glucopyranosyl); 2923.39-2864.02 (CH, aliphatic); 1423.34 (C-O-H). UV-Vis (DMSO) λ_{max}/nm: 705, 319 ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 9.03, 8.34-8.14 (12H, br, Ar–*H*), 7.77 (4H, br, C_2HN_3), 5.74 (4H, br, H-1), 5.60-4.79 (16H, br, -OH), 4.11 (8 H, br, -O-CH_2), 3.58-3.16 (24H, br, aliphatic protons of glucopyranosyl), 2.63 (8H, m, O-CH_2-CH_2-), 2.36 (8H, m, O-CH_2-CH_2-CH_2) .MS: m/z ($C_{77}H_{87}N_{20}O_{24}Zn$) found = 1741.92 (calcd. for [M]$^+$ 1742.02). Calcd. for $C_{77}H_{87}N_{20}O_{24}Zn$: C 53.09, H 5.03, N 16.08 %; found C 52.99, H 4.93, N 16.15.

X-ray crystallographic details of 3-Pent-4-ynyloxy phthalonitrile (3) Crystal data and details of data collection and structure refinement are given in Table 1. Unit cell measurements and intensity data collection was performed on an Bruker D 8 Venture three-circle diffractometer using monochromatized Mo Kα X-radiation (k = 0.71073 A °). The data reduction included a correction for Lorentz and polarization effects, with an applied multiscan absorption correction (SADABS) [51]. Space groups were determined using XPREP implemented in APEX [52]. The structure was solved using the direct methods procedure in SHELXS-97 [53] and then refined by full matrix least-squares refinements on F2 using the SHELXL-2013. All non-hydrogen atoms were refined anisotropically using all reflections with $I > 2\sigma(I)$ C-bound H atoms were positioned geometrically and refined using a riding mode. The final geometrical calculations and the molecular drawings were carried out with MERCURY [55] program.

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