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The synthesis and characterization of nonperipherally tetra terminal alkynyl substituted phthalocyanines and glycoconjugation *via* the click reaction†

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In order to obtain nonperipherally tetra terminal alkynyl substituted phthalocyanines (Pcs), new 3-pent-4-ynyloxy phthalonitrile (**3**) was prepared by the nucleophilic displacement reaction of 3-nitrophthalonitrile (**1**) and 4-pentyn-1-ol (**2**) and then cyclotetramerization was attained in the presence of zinc acetate, cobalt acetate, and/or DBU in *n*-pentanol without protection/deprotection. For the first time, the glycoconjugation of the nonperipherally tetra terminal alkynyl substituted zinc phthalocyanine (ZnPc) (**6**) can be easily achieved *via* the click reaction in a 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 the *meso* nitrogens of the Pc macrocycle. Deacylation yielded ZnPc (**11**) bearing glucose substituents at nonperipheral positions with an improved water-solubility and non-aggregation in DMSO. The chemical structures of the 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 to the 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] and 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. The incorporation of substituents at the nonperipheral (np) sites as opposed to the peripheral (p) positions ensures a good solubility and limited aggregation in most hydrophobic solvents and leads to significant bathochromic shifts of the Q absorption band. In addition, the 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 and is less used for the synthesis of substituted phthalocyanines.[24–28] Recently we have shown the syntheses of new symmetrical and unsymmetrical Pcs with terminal alkynyl substituents starting from phthalonitrile bearing a terminal alkynyl moiety without the 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 terminal alkynyl substituted phthalocyanine, that is 1,8,15,22-tetrakis(propargyloxy)phthalocyaninato-zinc(II) announced by Leznoff and coworkers in 1998.[65] In addition, up to now, there are no reports about nonperipherally terminal alkynyl substituted phthalocyanines involved in the click reaction.

Photodynamic therapy (PDT) has developed over the last century and is now becoming more widely used for the treatment of cancer. It involves the delivery of a nontoxic dyes known as photosensitizers (PS), followed by irradiation with visible light of a specific wavelength, typically in the red region

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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 ($^1O_2$) which in turn cause the destruction of tumors.[31] The development of efficient photosensitizers in terms of the 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 the tumor tissue, the insolubility and the 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]

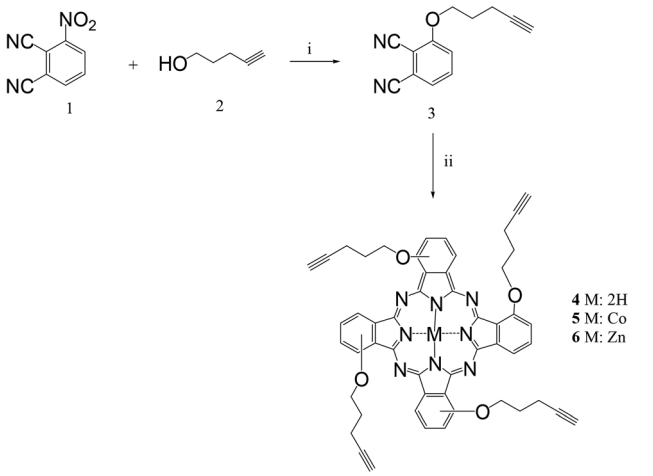
The first carbohydrate substituted zinc(II) phthalocyanine was reported in 1989 by Maillard *et al.*[38] and its nonperipherally substituted analogue was synthesized in 2008 by Ng and co-workers.[39] Hanack, Ziegler and co-workers[40] prepared the first example of an anomerically glycosylated zinc(II) 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 the click reaction as a novel method instead of the 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 terminal alkynyl substituted phthalocyanines by its cyclotetramerization in the presence of metal salts and/or DBU without protection/deprotection. In addition, to prove the viability of the click reaction concept, we have chosen the resulting ZnPc derivative and the click reaction between nonperipherally tetra terminal alkynyl 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 a high yield. The synthesis of nonperipherally tetra terminal alkynyl substituted phthalocyanines involved in the click reaction with azido functional glucopyranosyl has never been reported so far to the best of our knowledge.

Results and discussion

Syntheses

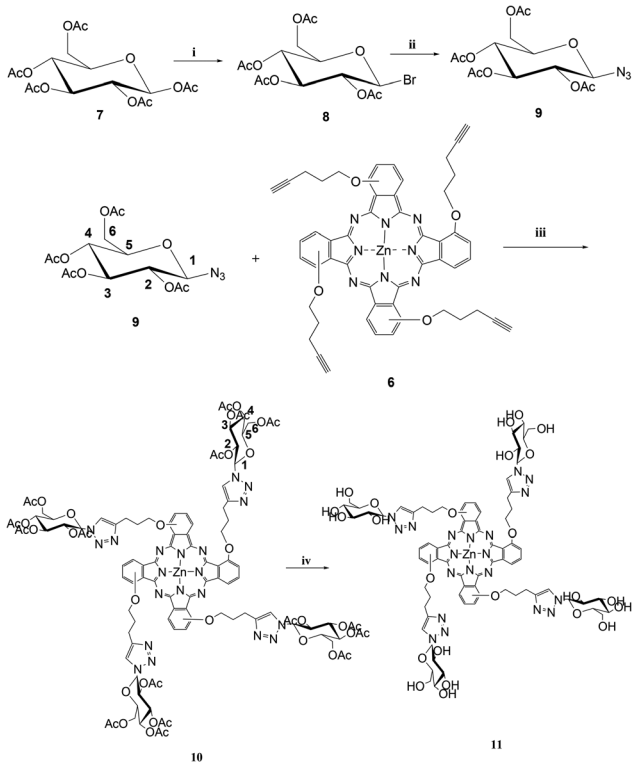
The terminal alkynyl substituted phthalocyanines are the common precursors for the preparation of functionalized analogues. This alkyne function can be introduced on the phthalocyanine precursor (usually a phthalonitrile), but are up to now more commonly introduced on the phthalocyanine itself. Recently, we have incorporated terminal alkynyl groups on the periphery of phthalocyanine compounds starting from a terminal alkynyl substituted phthalonitrile precursor.[29,30] In order to vary the terminal alkynyl substituted phthalocyanines, we designed a 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).



Scheme 1 The synthetic route for 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.

We recently described the successful use of the cyclotetramerization of terminal alkynyl substituted phthalonitrile compounds without protection/deprotection.[29,30] This synthetic strategy which was adopted to prepare target 1,8(11),15(18),22-(25)-tetra-terminal alkynyl substituted phthalocyanines (**4–6**) was carried out with reasonable yields by the direct cyclotetramerization of an unprotected nonperipherally terminal alkynyl 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**).

Phthalocyanine–carbohydrate conjugates are quite uncommon especially by the click reaction. To the best of our knowledge, title nonperipherally tetra glucose conjugated ZnPc (**11**) will be the first example of the conjugation of a nonperipherally tetra terminal alkynyl substituted phthalocyanine with azido functional glucose *via* the 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 a 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 the nonperipherally tetra terminal alkynyl substituted ZnPc (**6**) in the presence of sodium ascorbate and copper sulfate resulted glycopyranosyl conjugated ZnPc (**10**) in a satisfactory yield. Consequently, the target compound, nonperipherally glucose conjugated ZnPc (**11**), was obtained



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

by deprotection under Zémplen conditions in an 87% yield (Scheme 2).

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 spectroscopy, 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}, and the 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 the phthalocyanine derivatives (**4–6**). Furthermore, the peaks at 3286 cm^{-1} and 2116 cm^{-1} also disappeared in the case of the "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 the slow evaporation of methanol. The ORTEP representation of the compound is shown in Fig. 1. The bond lengths and angles are all in the 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) Å and 1.146(3) Å, respectively, and agree with the corresponding distances in the literature.[55,56] The value of the C6–O1–C5–C4 torsion angle of 178.08 (18)° is consistent with

Table 1 The 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	$P\bar{1}$
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 × 0.050 × 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
θ 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 [$I > 2\sigma(I)$]	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

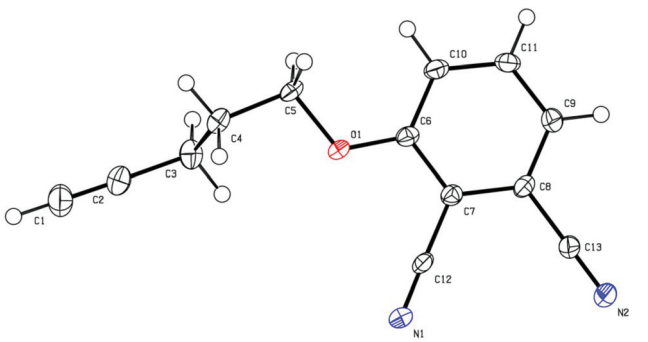


Fig. 1 The molecular structure of phthalonitrile (**3**).

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.

In the ^{1}H NMR spectrum of **3**, the aromatic protons appeared as a triplet, doublet and doublet at 7.64, 7.36 and 7.28, respectively, the CH_2–O protons appeared as a triplet at 4.26 ppm, the CH_2 protons appeared as a multiplet at 2.48 and 2.10 ppm and the C≡C*H* proton appeared as a triplet at 1.98 ppm. The ^{1}H NMR spectra of the H_2Pc (**4**) and ZnPc (**6**) derivatives have almost the same chemical shifts and are 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.

The ^{13}C NMR spectra of (**3**) shows typical chemical shifts for the aliphatic carbons (14.52 and 27.21 ppm), the O–*C*H_2

carbon (69.36 ppm), the alkyne carbons (67.64 and 82.52 ppm), the aromatic carbons (100.40, 116.40, 117.07, 124.99, 134.56 and 161.21 ppm) and the nitrile carbons (114.00 and 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**), the phthalocyanines (**4–6**) and the 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, ^1H 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 ^1H NMR and ^{13} C NMR spectra of glucopyranosyl azide (**9**), signals at 4.29 ppm and 87.91 ppm indicate the CH linked to the azido group.

The formation of glycopyranosyl conjugated ZnPc (**10**) was confirmed with the IR, ^1H NMR and ^{13} C NMR spectra. After the click reaction between glucopyranosyl azide (**9**) and the terminal alkynyl substituted ZnPc (**6**), in the FT-IR spectra, the signal at 2116.8 cm^{-1} that was observed for the azido function of glucopyranosyl azide (**9**) and the signals at 2114.15 cm^{-1} and 3287.34 cm^{-1} that were observed for the alkyne function of ZnPc (**6**) have disappeared (Fig. 2). In the ^1H 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 a triazole ring.

Deprotection under Zemplén conditions afforded the title glucose conjugated ZnPc (**11**) in quantitative yields. The presence of a 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 ^1H 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 ^1H 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 fact that 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 unsplit lowest energy band (Q band) in the visible region (650–700 nm) and a 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 terminal alkynyl substituted metal free (**4**) cobalt (**5**) and zinc phthalocyanines (**6**) in THF. For the nonperipherally tetra terminal alkynyl substituted Pcs (**4–6**), the Q band absorptions appear at a longer wavelength compared with the 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.

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 being due to the reduction of 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 visible region with an increase in the refractive index of the

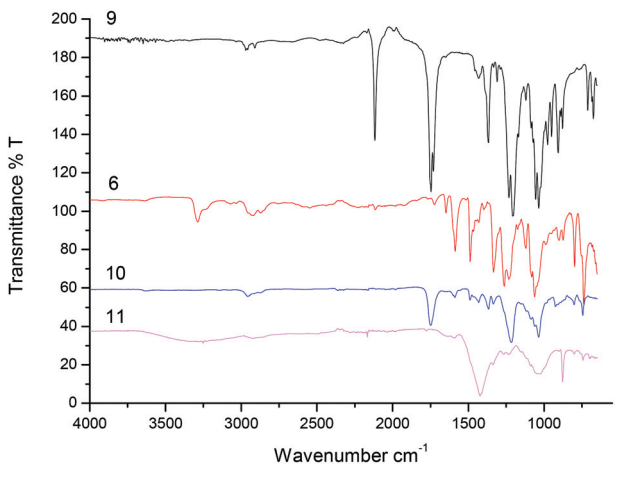


Fig. 2 FT-IR spectra of **9**, **6**, **10** and **11**.

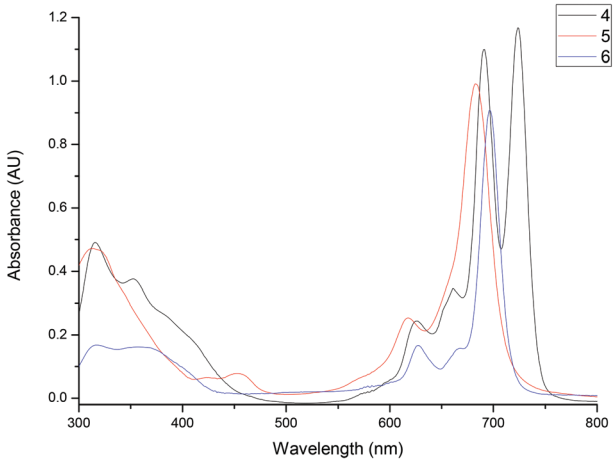


Fig. 3 The electronic spectra of **4** (black line), **5** (red line) and **6** (blue line) in THF (4×10^{-6} mol dm^{-3}).

Table 2 The spectral data for the nonperipherally (**4–6**) and peripherally tetra pent-4-ynyloxy substituted Pcs[29] in THF

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

Table 3 The 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

solvent,[58] hence a red shifting is observed in DCM which has a larger refractive index compared to that in THF and DMF (Table 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 visible region 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 the 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 the lowering of the symmetry and causes splitting and a bathochromic shift of the Q band.[62–64]

The glycopyranosyl conjugated ZnPc (**10**) having a Q band maxima at 698 nm in THF and 705 nm in DMSO did not show any aggregation in these solvents. On the other hand, this complex showed a 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, there is an extra red-shifted band observed at 761 nm in DMSO by the addition of TFA. The increasing concentration of TFA diminishes the absorption at 705 nm while the 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 the *meso*-nitrogens of the pc macrocycle. Another evidence for the protonation of the

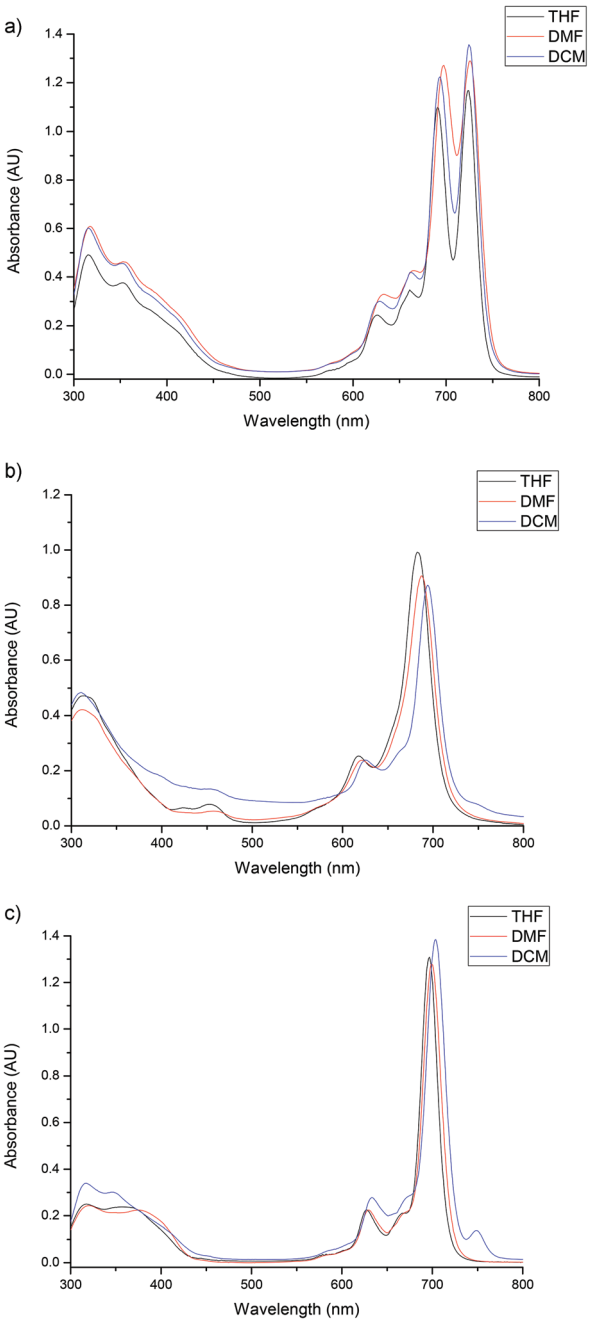


Fig. 4 (a) The electronic spectra of **4** in THF (black line), DMF (red line) and DCM (blue line) (4×10^{-6} mol dm^{-3}). (b) The electronic spectra of **5** in THF (black line), DMF (red line) and DCM (blue line) (4×10^{-6} mol dm^{-3}). (c) The electronic spectra of **6** in THF (black line), DMF (red line) and DCM (blue line) (1.2×10^{-5} mol dm^{-3}).

meso-nitrogens can be deduced from the UV-vis spectra of **10** at different concentrations in DCM.

As shown in Fig. 7, when the solution of glycopyranosyl conjugated ZnPc (**10**) in DCM was diluted, the absorption of the red shifted band at 751 nm increased.

The conversion of the acetyl groups to the hydroxyl groups has no influence on the electronic absorption spectrum. The nonperipherally tetra glucose conjugated ZnPc (**11**) dissolved

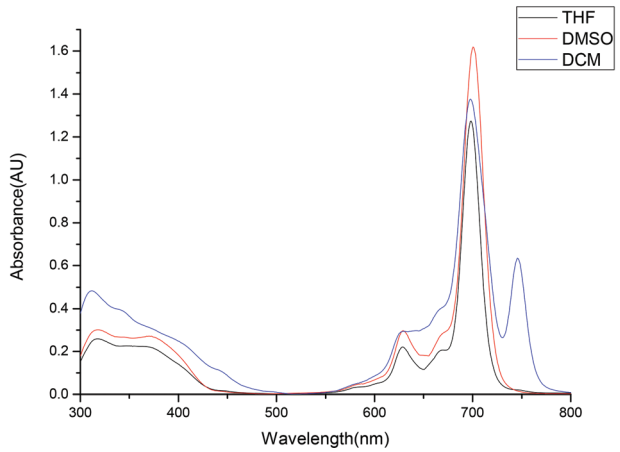


Fig. 5 The electronic spectra of **10** in THF (black line), DMSO (red line) and DCM (blue line) (5×10^{-6} mol dm^{-3}).

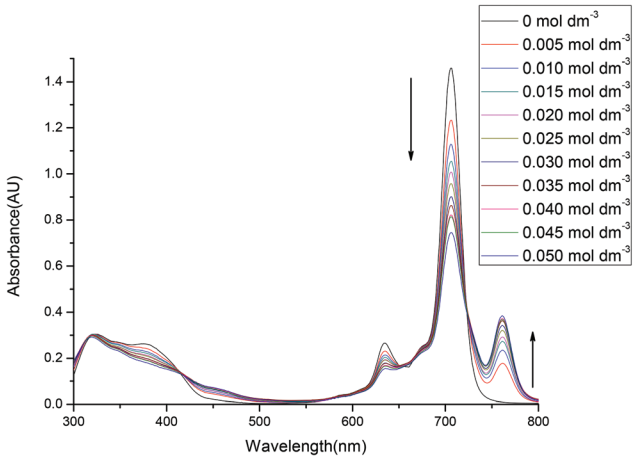


Fig. 6 The change in the absorption spectrum of **10** (~5×10^{-6} mol dm^{-3}) in DMSO seen upon the addition of increasing concentrations of TFA (0–0.050 mol dm^{-3}).

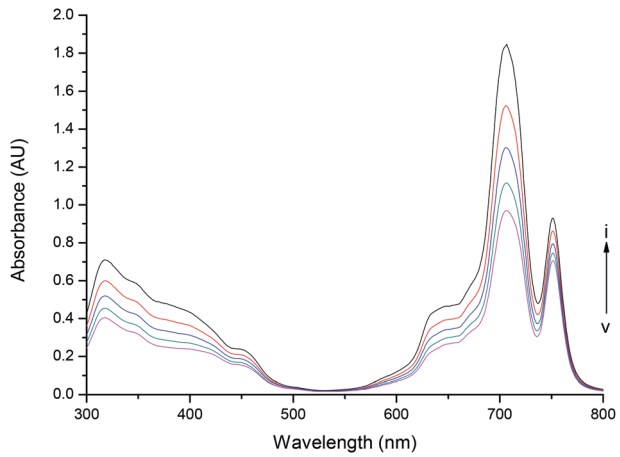


Fig. 7 The electronic absorption spectra of **10** at various concentrations: (i) 1.3×10^{-5}, (ii) 9×10^{-6}, (iii) 6.5×10^{-6}, (iv) 5.2×10^{-6} and (v) 4.3×10^{-6} mol dm^{-3} in DCM.

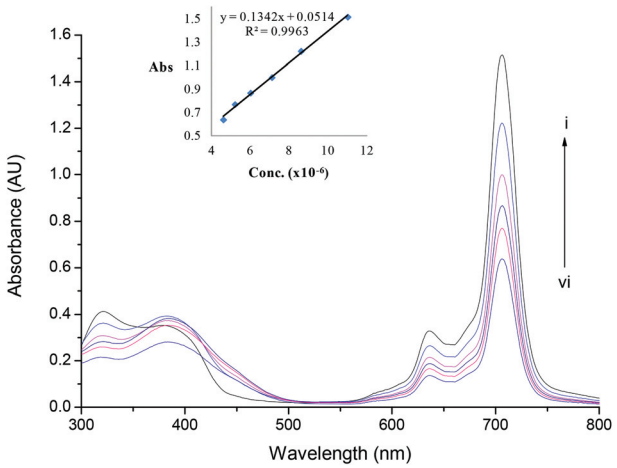


Fig. 8 The electronic absorption spectra of **11** at various concentrations: (i) 1.1×10^{-5}, (ii) 8.6×10^{-6}, (iii) 7.1×10^{-6}, (iv) 6.0×10^{-6}, (v) 5.2×10^{-6} and (vi) 4.6×10^{-6} mol dm^{-3} in DMSO.

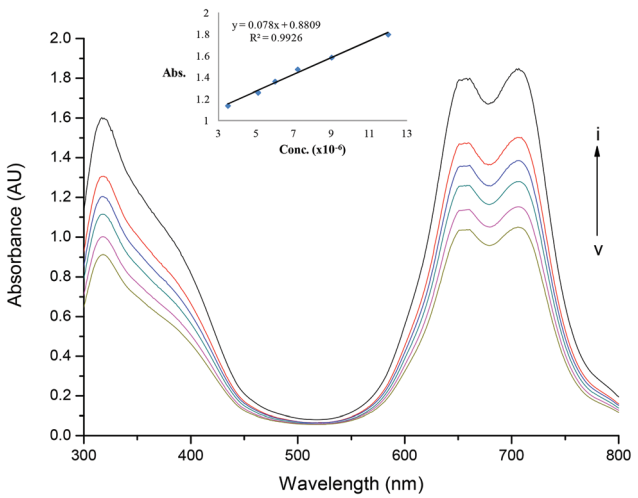


Fig. 9 The electronic absorption spectra of **11** at various concentrations: (i) 1.2×10^{-5}, (ii) 9.0×10^{-6}, (iii) 7.2×10^{-6}, (iv) 6.0×10^{-6}, (v) 5.1×10^{-6}, 3.5×10^{-6} mol dm^{-3} in water.

in DMSO exhibits a strong Q band at 705 nm, indicating that it is practically non-aggregated.

Fig. 8 shows that the Lambert-Beer law was obeyed for **11** at concentrations below 1.1×10^{-5} M. The solubility of the 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 an increase of the blue shifted Q band demonstrating the formation of aggregated species. Fig. 9 shows that the Lambert-Beer law was obeyed for the non-peripherally tetra glucose conjugated ZnPc (**11**) in concentrations ranging from 1.2×10^{-5} to 3.5×10^{-6} M in water.

Conclusions

In summary, we have demonstrated the syntheses of non-peripherally tetra terminal alkynyl 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 the protection of the terminal alkyne function of the phthalonitrile compound. The combination of the click reaction between the nonperipherally tetra terminal alkynyl 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 terminal alkynyl substituted phthalocyanines involved in the click reaction with azido functional glucose to the best of our knowledge.

In this study, we have varied the tetra terminal alkynyl 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 the ZnPc (**11**) derivative as a 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 the nonperipheral position is currently underway.

Experimental

Materials

The IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with ATR capability and the electronic spectra were recorded on a Scinco SD 1000 singlebeam ultraviolet-visible (UV-vis) spectrophotometer using 1 cm path length cuvettes at room temperature. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 500 MHz spectrometer using TMS as the internal reference. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. The mass spectra were obtained using 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 in a nitrogen atmosphere in dried solvents. The solvents were stored over molecular sieves.

Synthesis

3-Pent-4-ynyloxy phthalonitrile (3). 3-Nitrophthalonitrile (**1**) (1 g, 5.77 mmol), 4-pentyn-1-ol (**2**) (0.873 g, 10.39 mmol) and anhydrous potassium carbonate (K_2CO_3) (2.15 g, 15.6 mmol) in DMSO (15 mL) were stirred for 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 number 978750 contains the supplementary crystallographic data for this paper.

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 (*C*H$_2$–O), 67.64 (C≡*C*H), 27.21 (*C*H$_2$), 14.52 (*C*H$_2$). 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) 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 100 : 70 as the eluent to afford the 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 (CH_2–O–, m, 8H), 2.82 (CH_2, m, 8H), 2.34 (CH_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 (CH_2–O–, m, 8H), 2.82 (CH_2, m, 8H), 2.37 (CH_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 $CHCI_2$ (20 mL) a solution of 33% hydrobromic acid in glacial acetic acid (10 mL) at 0 °C was added carefully. 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 a 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 of 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) and 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: (0.64 g), 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-D-glucopyranosyl)-1*H*-1,2,3-triazol-4-yl)propoxy)] phthalocyaninatozinc(II) (10). To a solution of terminal alkynyl substituted ZnPc (**6**) (0.030 g, 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), $CuSO_4{\cdot}5H_2O$ (0.021 g, 0.132 mmol) and sodium ascorbate (0.078 g, 0.396 mmol) were added consecutively. 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 the 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, OCH_2CH_2CH_2), 2.28 (8H, d, OCH_2CH_2CH_2), 2.18 (8H, d, –OCH_2CH_2CH_2), 2.08, 2.02, 1.89, 1.81 (4 × 12H, s, –OC(O)CH_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–*C*H_2), 72.74 (C-5), 70.47 (C-3), 68.62 (C-2), 67.66 (C-4), 61.59 (C-6), 34.96 (OCH_2*C*H_2), 24.39 (OCH_2CH_2*C*H_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)-1*H*-1,2,3-triazol-4-yl)propoxy)] phthalocyaninatozinc(II)(11). Compound **10** (0.030 g, 0.012 mmol) was dissolved in DCM (2.5 mL) containing 2.5 mL of MeONa solution in methanol and stirred at room temperature for 24 h. After the evaporation of the solvent, the solid product was washed with THF, DCM and methanol, respectively. The 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–*C*H_2–), 2.36 (8H, m, O–CH_2–CH_2–*C*H_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). The crystal data and details of the data collection and structure refinement are given in Table 1. The unit cell measurements and intensity data collection were performed on an Bruker D 8 Venture three-circle diffractometer using monochromatized Mo Kα X-radiation (*k* = 0.71073 Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multiscan absorption correction (SADABS).[51] The 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 F^2 using the

SHELXL-2013. All non-hydrogen atoms were refined anisotropically using all reflections with $I > 2\sigma(I)$. The 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 the MERCURY[54] program.

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