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Pegylated phthalocyanines: synthesis and spectroscopic properties

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ABSTRACT

The syntheses and spectroscopic properties of a series of pegylated zinc(II)-phthalocyanines (Zn-Pcs) containing one, two, or eight tri(ethylene glycol) chains are described. The single molecular structure of a phthalonitrile precursor containing one hydroxyl and one PEG group, and its unique intermolecular hydrogen bonding are presented. The pegylated Pcs are highly soluble in polar organic solvents and have fluorescence quantum yields in the range 0.08–0.28.

Phthalocyanines (Pcs) are unique tetrapyrrolic macrocycles containing an extended aromatic 18-π electron system. Among the various applications of modified Pcs, they are promising photosensitizers for photodynamic therapy (PDT) of cancer[1,2] because of their intense absorptions at long wavelengths (>670 nm) and extraordinary ability for producing singlet oxygen. However, due to Pcs' intrinsic property of insolubility and high tendency for aggregation in aqueous solutions, research has centered on the synthesis of soluble Pcs and the tuning of their photophysical properties.[3,4] A general approach consists of attaching multiple hydrophilic or amphiphilic substituents to the periphery or the core of Pcs, such as carboxylates,[5] sulfonates,[6] phosphonates,[7] pyridinium ions,[8] hydroxyl groups,[9] peptides,[10] oligonucleotides,[11] and polyethylene glycol (PEG)[12] groups. In particular, the use of PEG as effective carriers[13–15] or covalently attached for drug delivery to target tissues,[16,17] is well documented. PEG-functionalized photosensitizers generally show improved serum life, reduced uptake by the reticuloendothelial system, enhanced cellular permeability and increased tumor accumulation.[18] Lutetium texaphyrin or Lutex®, containing two short PEG chains and two free hydroxyl groups, has demonstrated high photodynamic efficiency and has been evaluated in phase I/II clinical trials.[19,20] Recently, several groups[21–25,35,36] and us[8,26] reported the synthesis of PEG-substituted photosensitizers (porphyrins, chlorins, and Pcs) for application in PDT. Although such molecules generally show improved solubilities, their photophysical and biological properties depend on the length and number of PEG chains at the macrocycle periphery; two to four low molecular weight PEGs (<2000 amu) tend to minimize compound aggregation and improve tumor cellular uptake. Herein, we report the synthesis and photophysical properties of a new series of PEG-substituted zinc(II)-Pcs containing one, two or eight tri(ethylene glycol) chains, which are highly soluble in polar organic solvents. Furthermore, the new pegylated Zn-Pcs are pure compounds, rather than statistical mixtures of regioisomers, as previously reported.[21,36]

The synthetic route to tri(ethylene glycol) conjugated Pc **4**–**6** is shown in Scheme 1. Mono-, di-, and octa-tri(ethylene glycol) substituted Zn-Pcs **4**–**6** were obtained from the corresponding phthalonitrile precursors **1**–**3**. Phthalonitrile **1** was synthesized from 4,5-bis(2,5-di-*tert*-butyl-4-hydroxyphenoxy)phthalonitrile[9] and 2.3 equiv of 2-[2-(2-iodoethoxy)ethoxy]ethanol at 50 °C, in the presence of potassium carbonate, in 59% yield.[27] 2-[2-(2-Iodoethoxy) ethoxy]ethanol was synthesized from the commercially available 2-[2-(2-chloroethoxy)ethoxy] ethanol and sodium iodide, by refluxing in acetone for 24 h, in 90% yield. Pc **4** containing two PEG chains terminated with hydroxyl groups (PEGOH) was synthesized by a mixed macrocyclization using zinc(II) as template in the presence of excess of unsubstituted phthalonitrile. The reaction was heated to 140 °C and catalyzed by DBU to afford Pc **4** as a dark green solid in 8% yield.[28]

Several examples of α-substituted Pcs have been previously reported.[12,24,29–32] Such compounds are often observed to absorb and emit at longer wavelengths compared with their β-substituted analogs. This property could favor their application as photosensitizers for PDT due to the deeper penetration of long wavelength light into most human tissues. Furthermore, α-substituted Pcs in general show higher solubility in polar organic solvents and lower aggregation tendency than the corresponding β-substituted Pcs. The α-substituted octa-PEG-Pc **5**[33] containing eight PEGOMe

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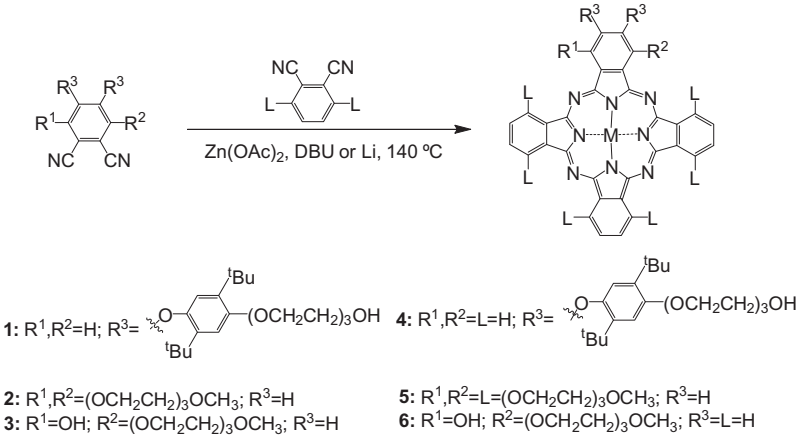

Scheme 1. Synthesis of Pcs **4**–**6**.

chains at the α positions of the Pc macrocycle, was synthesized from phthalonitrile **2** using a lithium template, followed by anhydrous zinc(II) acetate.[28] The precursor phthalonitrile **2** was synthesized by di-pegylation of 2,6-dihydroxyphthalonitrile using 1.2 equiv $CH_3(OCH_2CH_2)_3I$[8] by activation with 2 equiv potassium carbonate in 90% yield.[27] The synthesis of Pc **6** containing one hydroxyl group and one PEGOMe group at the α positions of the Pc was accomplished by mixed condensation of phthalonitrile **3** and unsubstituted phthalonitrile, similar to the method used for the synthesis of Pc **4**.[28] Phthalonitrile **3** was prepared by mono-pegylation of commercially available 2,6-dihydroxyphthalonitrile using 1 equiv $CH_3(OCH_2CH_2)_3I$[8] in DMF at room temperature, in 43% yield.[27] The structures of the two independent molecules of phthalonitrile **3** in the crystal are shown in Figure 1. They are very similar in conformation, except for the central ethylene glycol group. In both structures, the magnitude of the torsion angle about the C–C bond is the same, but opposite in sign, +65.5 and −65.9°. However, the torsion angles about the neighboring C–O bonds are such that the overall shape of the molecule does not change significantly. Torsion angles about those C–O bonds are −176.8 and +172.5° in one molecule and −84.2 and −84.9° in the other molecule. Each of the independent molecules forms an intermolecular hydrogen-bonded dimer about an inversion center, as shown in Figure 1. The acceptors are ether O, the O···O distances are 2.621(2) and 2.655(2) Å, and each dimer is a 26-membered ring.[34]

The PEG-substituted Pcs **4**–**6** are soluble in polar organic solvents, including DMF, DMSO, acetonitrile, and THF, as well as in less polar solvents such as dichloromethane and diethyl ether. The structures of these targeted Pcs were confirmed by NMR and MS spectroscopies. The ^{1}H NMR of Pc **4** in deuterated DMF shows the characteristic aromatic protons above 7 ppm, as we have previously reported.[9,31,32] Three sets of aromatic peaks at 9.45, 9.25, and 8.95 ppm in the downfield region were observed and assigned to the α-protons of this A_3B-type Pc: 9.45 ppm (broad, 4H) for the α-protons at the two symmetrical isoindole subunits (A′A′); 9.25 ppm (doublet, 2H) for the α-protons at the third isoindole subunit (A) and 8.95 ppm (singlet, 2H) for the α-protons at the substituted isoindole subunit (B). The signals in the range of 8.21–8.17 ppm (multiplet, 6H) are due to the β-ring protons in the 'A' part. The relative upfield protons at 7.31 (singlet, 2H) and 7.25 (singlet, 2H) ppm are due to the two β-substituted phenyl rings. The aliphatic proton signals in the PEG chain appear between 3.56–4.38 ppm, and the OH signals overlap with the solvent peak at around 3.5 ppm. Another two singlet peaks at 1.59 (18H) and 1.40 (18H) are assigned to the *tert*-butyl groups on the substituted phenyl rings. The symmetrical octa-pegylated Zn-Pc **5** has a simpler aromatic proton pattern due to the symmetry of the β-ring protons, appearing at 7.76 ppm (doublet, 8H). The aliphatic proton signals are in the range of 3.16–4.97 ppm. Pc **4** and **5** showed single or double molecular ion modes, respectively, at *m/z* 1281.5361 (Pc

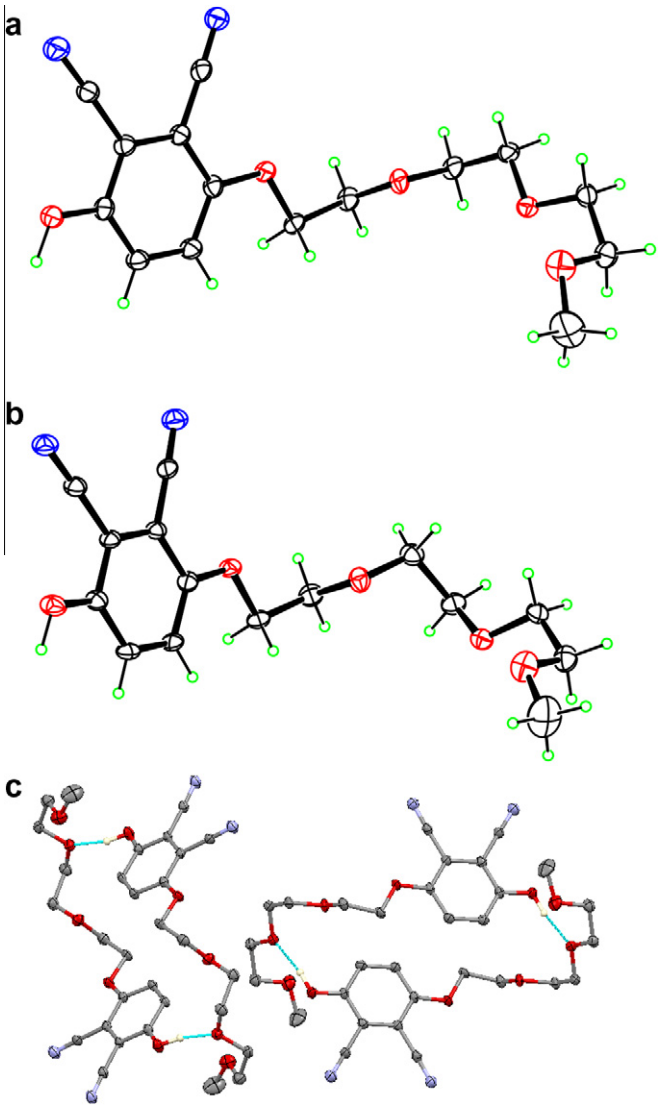

Figure 1. Molecular structure of the two independent molecules of phthalonitrile **3** (above), showing hydrogen bonding (below).

4) and 965.9939 (Pc **5**) with electrospray ionization method. Pc **6** containing one hydroxyl group and one PEGOMe group at the 1,4-α-positons showed a molecular fragment ion at *m/z* 723.6 $[M-OCH_3]^+$ in MALDI-MS.

The absorption spectrum of Pc **4** containing two PEGOH moieties in DMSO shows a characteristic strong Q band at 677 nm (Fig. 2) that strictly follows the Lambert–Beer law. This result indicates that Pc **4** exists in the monomeric form in DMSO. In acetone, Pc **4**'s Q band absorption is blue-shifted to 669 nm. Its fluorescence emission spectrum shows a peak at 680 nm in DMSO. The observed absorption and emission properties of Pc **4** are almost identical to those of 2,3-di-(2,5-di-*tert*-butyl-4-hydroxyphenoxy)-zinc(II)-phthalocyanine, previously reported by us.[9] This result indicates that the attachment of the PEGOH moieties at the phenoxy groups doesn't significantly change the photophysical properties of the Pc's conjugated core system, which is also in agreement with reports by others.[24,37,38] However, the fluorescence quantum yield of Pc **4** was found to be 0.28 (Table 1), which is higher than that reported for 2,3-di-(2,5-di-*tert*-butyl-4-hydroxyphenoxy)-zinc(II)-phthalocyanine (0.20).[9] This is probably due to the conjugation of the PEGOH chains, which makes the disubstituted Pc **4** more soluble and consequently forming monomeric species in DMSO. Interestingly, the OH group at the end of the PEG chain does not make the intermolecular hydrogen bonding a problem in this case. On the other hand, Pc **5** bearing eight PEGOMe groups has a significantly red-shifted Q band to the near-infrared (NIR) region at ~750 nm (Fig. 2). This phenomena is due to the attachment of the eight PEGOMe groups at the Pc's α positions, which reduces the Pc's HOMO-LUMO gap and causes longer absorption wavelength compared with the unsubstituted Zn(II)Pc (about 670 nm).[39] The observed absorption of octa-α-substituted Pc **5** is consistent with that reported for octa-α-alkyl-substituted zinc(II)-Pc.[40,41] Pc **5** has a weak emission peak at around 751 nm and lower

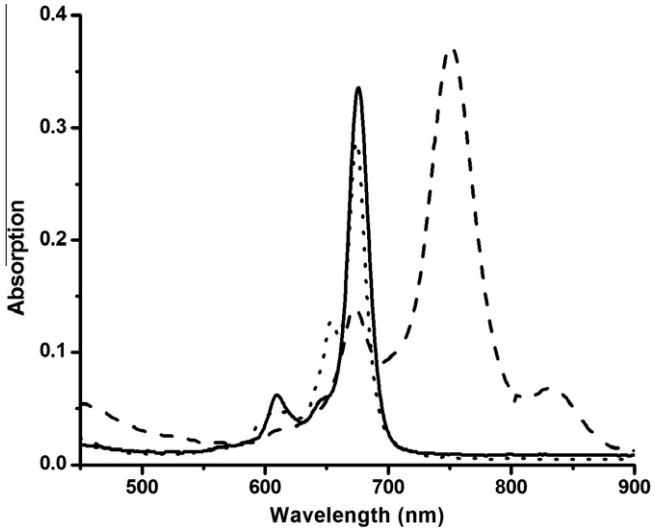

Figure 2. Absorption spectra of PEG-substituted Zn(II)-Pcs **4** (solid line), **5** (dash line) and **6** (dotted line) in DMSO at 2×10^{-6} M.

Table 1
Spectroscopic properties of Pcs **4**–**6** in DMSO at room temperature

Pc	Abs (λ_{max}, nm)	Em[a] (λ_{max}, nm)	Φ_f[b]	SS (nm)
4	677	680	0.28	3
5	749	751	0.08	2
6	676	677	0.13	1

Abs: absorption; Em: emission; SS: Stokes' shift.
[a] Excitation at 615 or 675 nm.
[b] Calculated using Zn(II)-phthalocyanine as the standard.

fluorescence quantum yield (Table 1); 0.08 is similar to the quantum yields reported for a series of cationic octa-PEG-alkylated-Zn(II)-Pcs (0.04–0.08).[8] Pc **6** containing one hydroxyl group and one PEGOMe chain has an absorption peak at 676 nm and a broad emission peak at 677 nm. Its fluorescence quantum yield is 0.13, probably as a result of intermolecular hydrogen bonding, as already observed in phthalonitrile **3** (Fig. 1). All of the Pcs **4**–**6** have small Stokes Shift of 1–3 nm.

In summary, we have successfully synthesized three pegylated zinc(II) Pcs **4**–**6** in 1–8% yields. All these PEG-Pcs are highly soluble in polar organic solvents such as acetone, DMF, and DMSO. Pc **4** containing two PEGOH chains at the *para*-position of β-substituted phenoxyl ring has similar absorption and emission peaks to the reported 2,3-di-(2,5-di-*tert*-butyl-4-hydroxyphenoxy)-zinc(II) Pc,[9] but significantly higher fluorescence quantum yield (0.28), probably due to its higher solubility in DMSO. Pc **5** containing eight PEGOMe chains at the α positions show pronounced red-shifted absorption and emission to ~750 nm. While Pc **5** has the lowest fluorescence quantum yield (0.08), Pc **6** bearing only one PEGOMe and one hydroxyl group shows similar absorption and emission wave lengths to Pc **4**, but significantly lower fluorescence quantum yield (0.13), probably due to intermolecular hydrogen bonding.

Acknowledgments

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27. *Selected spectroscopic data for phthalonitriles*: Compound **1**, ^{1}H NMR (acetone-d_6, 250 MHz): δ 7.32 (s, 2H, Ar-H), 7.06 (s, 2H, Ar-H), 6.91 (s, 2H, Ar-H), 4.23 (t, J = 4.4 Hz, 4H, OCH_2), 3.92 (t, J = 4.4 Hz, 4H, OCH_2), 3.70-3.51 (m, 18H, OCH_2, OH overlap), 1.37 (s, 18H, $C(CH_3)_3$), 1.35 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (acetone-d_6, 63 MHz): δ 155.7, 153.5, 146.3, 140.3, 138.5, 122.0, 120.6, 116.1, 112.7, 110.2 (Ar-C, CN), 73.4, 71.2, 71.1, 70.5, 68.5, 61.9 (CH_2O), 35.2, 35.1, 30.6, 29.9 ($C(CH_3)_3$). HRMS-ESI: m/z 833.4947 $[M+H]^+$, calcd for $[C_{48}H_{69}N_2O_{10}]^+$ 833.4946. Compound **2**, ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.18 (s, 2H, Ar-H), 4.12 (t, J = 4.6 Hz, 4H, OCH_2), 3.76 (t, J = 4.6 Hz, 4H, OCH_2), 3.63–3.59 (m, 4H, OCH_2), 3.54–3.49 (m, 8H, OCH_2), 3.43–3.39 (m, 4H, OCH_2), 3.23 (s, 6H, OCH_3). ^{13}C NMR ($CDCl_3$, 63 Hz): δ 155.0, 119.2, 112.8, 104.6 (Ar-C, CN), 71.5, 70.6, 70.2, 70.1, 69.7, 69.0 (OCH_2), 58.6 (OCH_3). HRMS-ESI: m/z 453.2230 $[M+H]^+$, calcd. for $[C_{22}H_{33}N_2O_8]^+$ 453.2231. Compound **3**, ^{1}H NMR (acetone-d_6, 250 MHz): δ 7.49 (d, J = 9.4 Hz, 1H, Ar-H), 7.36 (d, J = 9.4 Hz, 1H, Ar-H), 4.30 (t, J = 4.5 Hz, 2H, OCH_2), 3.84 (t, J = 4.5 Hz, 2H, OCH_2), 3.67–3.63 (m, 2H, OCH_2), 3.59–3.54 (m, 4H, OCH_2), 3.46–3.43 (m, 2H, OCH_2), 3.26 (s, 3H, OCH_3). ^{13}C NMR (acetone-d_6, 63 MHz): δ 155.80, 155.75, 123.66, 121.65, 114.37, 114.28, 104.30, 102.42 (Ar-C, CN), 72.53, 71.46, 71.14, 70.96, 70.81, 70.07 (OCH_2), 58.70 (OCH_3). HRMS-ESI: m/z 305.1140 $[M-H]^-$, 306.1169 $[M]^-$, calcd for $[C_{15}H_{17}N_2O_5]^-$ 305.1142, $[C_{15}H_{18}N_2O_5]^-$ 306.1216.
28. *Selected spectroscopic data for ZnPcs*: Compound **4**, ^{1}H NMR (DMF-d_7, 400 MHz): δ 9.45 (br, 4H, Ar-H), 9.25 (d, 2H, J = 7.4 Hz, Ar-H), 8.95 (s, 2H, Ar-H), 8.21–8.17 (m, 6H, Ar-H), 7.31 (s, 2H, Ar-H), 7.25 (s, 2H, Ar-H), 4.38 (t, J = 4.3 Hz, 4H, OCH_2), 4.00 (t, J = 4.3 Hz, 4H, OCH_2), 3.77 (t, J = 4.5 Hz, 4H, OCH_2), 3.70 (t, J = 4.5 Hz, 4H, OCH_2), 3.66–3.55 (m, 4H, OCH_2), 3.59–3.56 (m, 4H, OCH_2), 1.59 (s, 18H, $C(CH_3)_3$), 1.40 (s, 18H, $C(CH_3)_3$). HRMS-ESI: m/z 1281.5361 $[M+H]^+$, calcd for $[C_{72}H_{81}N_8O_{10}Zn]^+$ 1281.5362. UV–vis (DMSO): λ_{max} ($\log\varepsilon$) 677 (5.0), 611 (4.2) nm. Compound **5**, ^{1}H NMR (DMF-d_7, 400 MHz): δ 7.76 (d, J = 3.9 Hz, 8H, Ar-H), 4.97–4.91 (m, 32H, OCH_2), 4.15 (t, J = 4.9 Hz, 16H, OCH_2), 3.75 (t, J = 4.9 Hz, 16H, OCH_2), 3.58–3.56 (m, 16H, OCH_2), 3.36–3.34 (m, 16H, OCH_2), 3.16 (s, 24H, OCH_3). HRMS-ESI: m/z 965.9939 $[M+K+Na-4H]^{2-}$, calcd for $[C_{88}H_{124}N_8O_{32}ZnKNa]^{2-}$966.3582. UV–vis (DMSO): λ_{max} ($\log\varepsilon$) 749 (5.0), 674 (4.5) nm. Compound **6**, ^{1}H NMR (DMF-d_7, 400 MHz): δ 9.57–9.45 (m, 8H, Ar-H), 8.76–8.67 (m, 6H, Ar-H), 4.83 (br, 2H, OCH_2), 4.19 (br, 2H, OCH_2), 3.91–3.79 (m, 6H, OCH_2), 3.56 (br, 2H, OCH_2), 3.26 (s, 3H, OCH_3). MS (MALDI-TOF) m/z 723.6 $[M-OCH_3]^+$, calcd for $[C_{38}H_{27}N_8O_4Zn]^+$ 723.1. UV–vis (DMSO): λ_{max} ($\log\varepsilon$) 676 (3.6), 657 (3.3) nm.
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34. *Phthalonitrile* **3**: $C_{15}H_{18}N_2O_5$, M_r = 306.31, triclinic space group P-1, a = 8.9144(5), b = 10.9803(10), c = 15.9181(15) Å, α = 82.666(5), β = 89.322(5), γ = 87.909(5)°,V = 1544.3(2) Å^3, Z = 4, D_x = 1.317 g cm^{-3}, CuKα radiation, λ = 1.54178 Å, T = 90 K, μ = 0.84 mm^{-1}, θ_{max} = 68.2°, colorless lath 0.30 × 0.14 × 0.07 mm, Bruker Kappa Apex-II CCD diffractometer, 17,507 measured reflections, 5487 independent, 4228 with $I > 2\sigma(I)$, R_{int} = 0.046, R = 0.044, $wR(F^2)$ = 0.123 for 406 refined parameters and 5487 data, CCDC 826729.
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