

# The first synthesis and characterization of new metal-free and metallophthalocyanine containing 33-membered crown ether moieties

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Dedicated to Professor Özer Bekaroğlu on the occasion of his 80th birthday

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## INTRODUCTION

Phthalocyanines and metallophthalocyanines have attracted considerable attention owing to their variety, optical, electronic, structural and coordination properties. They exhibit a number of extraordinary characteristics leading to potential applications in various scientific, technological and medical areas such as pigments, catalysts, non-linear optical devices, liquid crystals, Langmuir-Blodgett films, electrochromic devices, gas sensors and photosensitizers for photodynamic therapy [1]. Metal cations over 70 different elements have been used as central atoms in the phthalocyanine cavity: therefore, a large number of different metallophthalocyanines could be synthesized [2]. Coordination chemistry of phthalocyanines has encouraged researchers to specific products with certain properties required for applications such as photocatalysts or electrocatalysts in the reduction of carbon dioxide and oxygen [3]. The synthesis of the

peripherally substituted phthalocyanines with macrocycle moieties have been well studied, but the non-peripheral ones have received considerably less attention since their first synthesis almost twenty-seven years ago [4].

Since crown ethers were first recognized by Pedersen as a relatively new class compounds, they have received tremendous interest, especially in the fields of host-guest chemistry [5], ion binding with metal and organic cations and applications in the preparation of chemosensors, molecular machines and supramolecular polymers [6]. Self-assembly is a powerful tool for the creation of extremely large and functioning supramolecular systems [7]. Rotaxanes are very convenient structures for ordering self-assembly processes. This kind of molecular assemblies have potential applications in the areas of nanoscience switches and shuttles [8]. The most of the rotaxanes involving huge crown ether moieties such as dibenzo-24-crown-8 or dibenzo-34-crown-10 have been templated by the hydrogen bonding between seconder dialkylammonium ions and cyclic studied over the past 28 years in this area. Unfortunately, only a limited study achieved to synthesize extremely huge crown ether

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units linked non-peripheral positions so far. Moreover, there are a few examples of crown ethers containing macrocycles more than 30-membered rings attached to phthalocyanine structure [10].

In contrast with the phthalocyanines containing peripherally macrocyclic donor sets, there are relatively fewer studies on phthalocyanines involving non-peripheral macrocyclic donor sets. In this paper, we report the synthesis of the novel metal-free and metallophthalocyanines which contain non-peripherally substituted four 33 membered macrocyclic polyethers.

## **EXPERIMENTAL**

#### General methods and materials

Unless otherwise stated, all preparations were carried out in argon atmosphere in a vacuum line using standard Schlenk techniques. Tetraethylenglycolditosylate (2) [11] was prepared according to the method described in the literature. 2,3-Dicyanohydroquinone and other chemicals were purchased from Aldrich and used without purification. All solvents were freshly purified by standard procedures before use [12] and stored over molecular sieves (4 Å). The purity of the novel products was tested in each step by thin layer chromatography (TLC Silica gel 60  $F_{254}$  plate). <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on Varian Mercury 200-NMR and Varian Mercury Plus 300-MHz spectrometers in CDCl<sub>3</sub> solutions, with Me<sub>4</sub>Si as the internal standard. Infrared spectra were recorded on a Perkin Elmer Spectrum FT-IR spectrometer. Mass spectra were measured on micrOTOF and Micromass Quattro Ultima LC-MS/ MS instruments. Electronic spectra were recorded on a Shimadzu UV-1601 spectrophotometer which is doublebeamed with thermostatically controlled cell block. The elemental analysis was performed on a Costech ECS 4010 instrument. Melting points were determined in open glass capillaries using a Buchi apparatus and are uncorrected.

#### Synthesis

**3,6-bis[2-(2-{2-[2-(toluene-4-sulphonyl)-ethoxy]-ethoxy}-ethoxy]phthalonitrile (3).** A solution of tetraethyleneglycolditosylate (30.5 g, 60.75 mmol) in dry acetonitrile (70 mL) was added dropwise to a suspension of 2,3-dicyanohydroquinone (1.6 g, 10 mmol) in dry acetonitrile (200 mL) under argon atmosphere at 60 °C for 45 min. The reaction mixture was heated and stirred at reflux temperature for 10 days and monitored by a thin layer chromatography [silica gel (chloroform:ethanol) (95:5)]. At the end of this period, the mixture was cooled to room temperature and filtered off, washed with dry ethyl acetate and then evaporated to dryness under reduce pressure. The waxy crude product was extracted with the

mixture of toluene (120 mL) and the aqueous solution of NaOH (10%, 150 mL). The organic phase was washed with water  $(4 \times 50 \text{ mL})$  and dried over CaCl<sub>2</sub>. The mixture was filtered off, washed with toluene and evaporated to dryness under reduced pressure. The yellow oily product was purified by column chromatography [silica gel (chloroform:ethyl acetate) (95:5)], to yield (3.78 g, 46%) of pale yellow waxy product (3). Anal. calcd. for C<sub>38</sub>H<sub>48</sub>N<sub>2</sub>S<sub>2</sub>O<sub>14</sub>: C, 55.60; H, 5.85; N, 3.41%. Found C, 55.77; H, 5.53; N, 3.29. IR: v, cm<sup>-1</sup> 3040 (Ar-H), 3025 (Ar-H), 2881–2784 (C-H), 2232 (C≡N), 1597 (tosyl), 1486, 1353, 1286, 1189, 1137–1105, 1018, 925. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 7.79–7.71 (4H, m, ArH), 7.43-7.34 (4H, m, ArH), 6.72 (2H, s, ArH) 4.18-4.3 (4H, m, -OCH<sub>2</sub>), 3.84-3.74 (4H, m, -OCH<sub>2</sub>), 3.65-3.42 (24H, m, -OCH<sub>2</sub>) 2.46 (6H, s, -CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz;  $CDCl_3$ ):  $\delta_C$ , ppm 155.00, 144.61, 132.48, 129.64, 127.62. 122.13, 112.95, 104.46, 70.66, 70.31, 70.15, 69.70, 69.12, 68.78, 68.24, 21.36. MS (ES): m/z 821 [M + 1]<sup>+</sup>.

2,5,8,11,14,20,23,26,29,32-Decaoxa-tricyclo- $[31.2.2.1^{15,19}]$  octatriconta-1(36),15,17,19-(38),33(37),34-hexaene-34,35-dicarbonitrile (5). 1,3dihydroxybenzene (0.77 g, 7 mmol) was added directly to a suspension of Cs<sub>2</sub>CO<sub>3</sub> (10.50 g, 46.90 mmol), CsOTos (3.0 g, 13.4 mmol) and tetrabutylammonium iodide (TBAI) (0.7 g, 1.925 mmol) in dry DMF (450 mL) at 80 °C under argon atmosphere and the mixture was stirred at this temperature for 1 h. A mixture of the degassed solution of **3** (5.74 g, 7 mmol) and CsOTos (5.39 g, 24.15 mmol) in dry DMF (100 mL) was added dropwise to the above mixture for 90 min. The reaction mixture was heated and stirred at 100 °C for 7 days and monitored by a thin layer chromatography [silica gel (hexane:acetone) (60:40)]. At the end of this period, the mixture was cooled to room temperature and filtered off, washed with dry chloroform. The combined organic phases were evaporated to dryness under reduced pressure. The crude product was dissolved with dichloromethane (150 mL) and washed with water  $(2 \times 75 \text{ mL})$  and dried over MgSO<sub>4</sub>. The mixture was filtered off, washed with dry dichloromethane and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography [silica gel (hexane:acetone) (60:40)], to yield (0.77 g, 22%) as a pale yellow clear oil. Anal. calcd. for  $C_{30}H_{38}N_2O_{10}$ : C, 61.43; H, 6.48; N, 4.77%. Found C, 61.25, H, 6.74, N, 4.53. IR: v, cm<sup>-1</sup> 3080 (Ar–H), 3037 (Ar–H), 2945–2874 (C-H), 2230 (C≡N), 1585, 1482, 1448, 1351, 1281, 1184, 1126–1065, 983. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 7.18 (2H, s, ArH), 7.04 (1H, t, ArH), 6.48 (3H, m, ArH), 4.15-3.96 (4H, m, OCH<sub>2</sub>), 3.80-3.71 (4H, m, OCH<sub>2</sub>), 3.65–3.46 (20H, m, OCH<sub>2</sub>), 3.36–3.28 (4H, m, OCH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ<sub>C</sub>, ppm 159.11, 154.65, 128.47, 116.05, 112.90, 107.56, 103.00, 71.46, 70.77, 69.11, 68.25, 67.13. MS (ES): m/z 587 [M + 1]<sup>+</sup>, 604  $[M + H_2O]^+$ 

Metal-free phthalocyanine ( $H_2Pc$ ). A standard Schlenk tube was charged with a solution of 4 (0.293 g,

0.5 mmol) in dry n-pentanol (2.5 mL) and five drops of 1,8-di-azabicyclo[5.4.0]undec-7-ene (DBU) under argon atmosphere and degassed several times. The temperature was gradually increased up to 155 °C and refluxed at this temperature for 8 h. During this time, the mixture became dark green. After cooling to room temperature, dry methanol was added and stirred for 3 h to precipitate completely. The mixture was filtered off, washed with dry methanol and diethyl ether and then dried in vacuo. The dark green product was purified by column chromatography [silica gel (chloroform:methanol) (98:2)] as eluent and gave green solid product. Yield 0.089 g (15%), mp > 300 °C. Anal. calcd. for  $C_{120}H_{154}N_8O_{40}$ : C, 61.38; H, 6.56; N, 4.77%. Found C, 61.19; H, 6.79; N, 4.95. IR: v, cm<sup>-1</sup> 3320 (N–H), 3085 (Ar–H), 3052 (Ar-H), 2928–2864 (C-H), 1641 (C=N)<sub>meso</sub>, 1601, 148.8, 1353, 1262, 1186, 1114-1092, 976. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>): δ<sub>H</sub>, ppm 7.32 (12H, s, Ar–H), 7.17 (8H, m, Ar-H), 6.48 (4H, t, Ar-H), 4.48-4.31 (64H, m, -CH<sub>2</sub>-), 3.88-3.71 (32H, m, -CH<sub>2</sub>-), 3.45-3.36 (32H, m, -CH<sub>2</sub>-), -1.97 (2H, s, NH). <sup>13</sup>C NMR (75 MHz; CDCl<sub>3</sub>): δ<sub>c</sub>, ppm 158.78, 154.47, 155.17, 129.11, 112.51, 107.05, 103.29, 72.18, 71.89, 71.06, 69.83, 68.55. UV-vis (CHCl<sub>3</sub>):  $\lambda_{max}$ , nm (log ε) 800 (3.81), 732 (3.93), 354 (4.34). MS (ES): m/z 2386.08 [M + K + 1]<sup>+</sup>.

**Cobalt(II) phthalocyanine (CoPc).** Dicyano derivative **5** (0.293 g, 0.5 mmol) in dry *N*,*N*-dimethyle-thanolamine (2 mL) and anhydrous  $CoCl_2$  (0.065 g, 0.5 mmol) was placed into a Standard Schlenk tube under

argon atmosphere, and reaction mixture was evacuated several times and refilled with argon. Under this reaction condition, the reaction mixture was heated and stirred at 155 °C for 8 h. The reaction mixture was then cooled to room temperature, filtered and the residue was washed with water, methanol and diethyl ether. The purification of crude product was performed by column chromatography [silica gel (chloroform:methanol) (98:2)] affording desired product in 13.6% yield (0.082 g) as a dark green solid. mp > 300 °C. Anal. calcd. for  $C_{120}H_{152}N_8O_{40}Co: C$ , 59.92; H, 6.32; N, 4.66; Co, 2.45%. Found C, 60.14; H, 6.07; N, 4.89; Co, 2.20. IR: v, cm<sup>-1</sup> 3076 (Ar–H), 3043 (Ar-H), 2956-2863 (C-H), 1624 (C=N)<sub>meso</sub>, 1599, 1491, 1350, 1258, 1211, 1092–1052, 971. UV-vis (CHCl<sub>3</sub>):  $\lambda_{max}$ , nm (log  $\epsilon$ ) 726 (4.94), 653 (4.37), 320 (4.67). MS (ES): m/z 2421.29 [M + H<sub>2</sub>O + 1]<sup>+</sup>.

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## **RESULTS AND DISCUSSION**

In this study, we give a full account of the synthesis and characterization of novel metal-free ( $H_2Pc$ ) and cobalt (**CoPc**) phthalocyanines by the cyclotetramerization reaction of the dicyano compound containing *p*-phenylene*m*-phenylene-33-crown-10 moieties. Synthesis of 3,6-bis-[2-(2-{2-[2-(toluene-4-sulphonyl)-ethoxy]-ethoxy}ethoxy)-ethoxy]-phthalonitrile (**3**) was performed as shown in Scheme 1. The purification of **3** required column chromatography on silica gel using chloroform:ethyl acetate



**Scheme 1.** (i) K<sub>2</sub>CO<sub>3</sub>, dry CH<sub>3</sub>CN, Ar, 60 °C, 10 days; (ii) Cs<sub>2</sub>CO<sub>3</sub>, CsOTos, TBAI, dry DMF, Ar, 80 °C, 7 days; (iii) dry *n*-pentanol, DBU, reflux, 8 h. (**H<sub>2</sub>Pc**); anhyd. CoCl<sub>2</sub>, dry *N*,*N*-dimethylethanolamine, reflux, 8 h (**CoPc**)

(95:5) as an eluent and gave 46% yield. In the <sup>1</sup>H NMR spectrum of 3, the presence of significant resonances for tosyl and hydroquinone groups as dublets and multiplets at  $\delta = 7.79 - 7.71$  and 7.43 - 7.34 ppm, respectively, is one of the verification of condensation reaction (Scheme 1). This spectrum displayed relatively well-defined resonance signals in the polyetheric moieties corresponding as expected to the typical signals of the precursor compound (2). The  ${}^{13}C$  NMR spectrum of the same compound clearly indicated the presence of cyano ( $\delta = 112.95$  ppm), tosyl  $(\delta = 144.61, 132.48, 129.64, 127.62 \text{ ppm})$  and aliphatic carbons at  $\delta = 70.66, 70.31, 70.15, 69.70, 69.12, 68.78,$ 68.24, 21.36 ppm, respectively. The IR spectrum of compound 3 also exhibited characteristic vibrations related C=N and tosyl groups at 2232 and 1598 cm<sup>-1</sup>. The ES mass spectrum at  $m/z = 821 [M + 1]^+$  and elemental analysis of this compound supported the condensation reaction between the starting materials (1 and 2).

The synthesis of the cyano compound **5** (Scheme 1) containing 33-membered decaoxa macrocycle was performed by condensation reaction between compound **3** and 1,3-dihydroxy benzene (**4**). Treatment of **3** with **4** in dry DMF in the presence of  $Cs_2CO_3$ , CsOTos and TBAI *via* high dilution technique resulted in the formation of desired decaoxa macrocycle **5** in 22% yield as pale yellow oily product after purification by column chromatography [silica gel (hexane:acetone)(60:40)]. In the <sup>1</sup>H NMR spectrum of **5**, the chemical shifts of tosyl protons in the precursor compound (**3**) disappeared after

the macrocyclization reaction. On the other hand, the presence of new resonances for 1,3-dihydroxybenzene moiety as triplet and multiplet at  $\delta = 7.04$  and 6.48 ppm, respectively, is one of the verifications of macrocyclization reaction. Observed characteristic signals of proton-decoupled <sup>13</sup>C NMR spectrum of the compound for the novel aromatic carbon atoms at  $\delta = 159.11$ , 128.47, 107.56 and 103.00 ppm clearly suggested the macrocyclization reaction has occurred. The results of NMR spectra are shown in Figs S1 and S2 (Supporting information). In the IR spectrum of 5, very specific stretching vibrations of tosyl groups at 1598 cm<sup>-1</sup> disappeared after the macrocyclization formation. The mass spectrum of 5 contained an intense peak at m/z =587  $[M + 1]^+$  for the parent ion, which can be attributed to the formation of dicyano derivative (5).

Condensation of four molecules of dicyano compound (5) containing 33-membered macrocyclic polyether moiety into the metal-free phthalocyanine were carried out in dry *n*-pentanol and a catalytic amount of DBU as the ring-forming catalyst [13]. After purification by column chromatography, the desired compound  $H_2Pc$  was obtained in 15% yield. The <sup>1</sup>H NMR spectrum of this compound in CDCl<sub>3</sub> exhibits the characteristic signals of macropolycycle and phthalocyanine moieties. The strong shelding of the inner core protons of this compound was manifested by a broad resonance at  $\delta = -1.97$  ppm [14] at high concentration which could be attributed to the NH resonance and identified easily with deuterium exchange.



Fig. 1. Mass spectrum of H<sub>2</sub>Pc

In <sup>13</sup>C NMR spectrum of this compound, all resonances are identical for the precursor non-peripherally substituted dicyano derivative except for the C=N carbons as expected. The chemical shift appeared at  $\delta = 155.17$  ppm of this compound should be related to inner core C=N signals [15]. Cyclotetramerization of the dicyano derivative was confirmed by the disappearance of the significant C=N vibrations at 2230 cm<sup>-1</sup> in the IR spectrum of H<sub>2</sub>Pc. The difference between the IR spectra of **5** and H<sub>2</sub>Pc are clear from the presence of some characteristic vibrations such as N–H and C=N at 3320 and 1641 cm<sup>-1</sup>, respectively. The structure of metal-free phthalocyanine were confirmed by elemental analysis, as well as mass spectral (ES-MS) data at 2386.08 [M + K + 1]<sup>+</sup> (Fig. 1).

Cyclotetramerization of macrocyclic polyether substituted dicyano compound (5) to give the cobalt(II) phthalocyanine (CoPc) was carried out in dry N,Ndimethylethanolamine in the presence of anhydrous CoCl<sub>2</sub> [13, 16] at 155 °C for 8 h afforded the corresponding tetra-substituted metallophthalocyanine (CoPc) in 13.6% yield as dark green solid after purification by column chromatography. Cyclotetramerization of the dicyano compound (5) was confirmed by the disappearance of the sharp C=N stretching vibration at 2230 cm<sup>-1</sup> of the precursor dicyano derivative (5) and the presence of C=N resonance at 1624 cm<sup>-1</sup> also confirmed the formation of cobalt(II) phthalocyanine. The rest of the IR spectrum of CoPc closely resemble that of 5, including the characteristic vibrations of the aromatic and polycyclic etheric groups. The mass spectrum of CoPc, which showed the expected peak at  $m/z = 2421.29 [M + H_2O + 1]^+$ , also confirmed the proposed structure.

The synthesized metal-free phthalocyanine displayed noticeable electronic spectrum in chloroform (Fig. 2) with two significant absorption bands, one of them in the visible region at about 800–732 nm corresponding to the split Q-band due to its  $D_{2h}$  symmetry, as  $Q_x$  and  $Q_y$  bands [17], attributed to the  $\pi \rightarrow \pi^*$  transition from HOMO to the LUMO orbitals. The other band is B band in the UV part of the spectrum at about 354 nm, arising from the deeper  $\pi \rightarrow \pi^*$  transition [18]. The Q-band of the non-peripherally crown ether substituted metal-free phthalocyanine is redshifted-significantly compared to peripherally substituted analogs [19]. Bathochromic shift of Q-band is also known in symmetric phtalocyanines bearing non-peripheral chalcogenic donors such as sulphur, selenium [20] and, rarely oxygen [21]. However, in this study we observed bahtochoromic shift in the synthesized 33-membered symmetrical phtalocyanine bearing macrocyclic oxygen donors [22]. This situation has been explained to be due to LCAO coefficient as its being greater than those at the peripheral positions [23]. The shape of this absorption spectrum is also similar to that of core-modified phthalocyanine analogs with a seven membered ring moiety [24]. In contrast to the cobalt(II) phthalocyanine, as it is shown in Fig. 2, the metal-free phthalocyanine is strongly aggregated in chloroform solution due to the



**Fig. 2.** Electronic absorbtion spectra of  $H_2Pc$  (—) and **CoPc** (—) in chloroform (concentration =  $1.10^{-5}$  M)

typical decreasing of intensity and widening of Q-band absorptions. The lower energy bands at  $\lambda_{max} = 726$  and 653 nm belonging to the cobalt(II) phthalocyanine are due to the monomeric species at the non-peripheral positions, which have increased values at the longest wavelength Q-band absorption compared to its analogs and demonstrate less aggregation, prevent macrocycles from getting too close to each other [25]. The typical monomeric behavior evidenced by a single absorptions species with  $D_{4h}$  symmetry [26]. The disaggregation of cobalt(II) phthalocyanine can be referred to the presence of central metal ion.

#### CONCLUSION

In this study, novel metal-free and phthalocyaninato cobalt(II) complex containing symmetrically four 33-membered crown ether units were synthesized by cyclotetramerization reaction of 2,5,8,11,14,20,23,-26,29,32-decaoxatricycle[ $31.2.2.1^{15,19}$ ]octatriconta-1(36),15,17,19(38),33(37),34-hexaene-34,35-dicarbonitrile (**5**) in the presence of a strong organic base and anhydrous CoCl<sub>2</sub>. The new compounds were characterized by standard methods including elemental analysis, <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, UV-vis and MS techniques. The ground state electronic absorption spectra of the phthalocyanines were also described in chloroform. Metal-free phthalocyanine (**H**<sub>2</sub>**Pc**) showed noticeable

Q-band absorption at 800 nm compared to the peripherally substituted phthalocyanines analog in chloroform. The noticeable red-shifted band at 800 nm for  $H_2Pc$  and 726 nm for **CoPc** are due to monomeric and non-aggregated species. This absorption band can be shifted to the  $Q_{\Delta}$  (singlet oxygen quantum yield) values for photodynamic therapy (PDT) applications. This significant red-shift band is also important and will receive further attention for various near-IR investigations. The intensity of this absorption in  $H_2Pc$  has also decreased as expected.

### **Supporting information**

<sup>1</sup>H and <sup>13</sup>C NMR spectra of **5** in CDCl<sub>3</sub> are given in the supplementary material (Figs S1–S2). This material is available free of charge *via* the Internet at http://www. worldscinet.com/jpp/jpp.shtml.

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