Available online at www.sciencedirect.com

ScienceDirect

Tetrahedron Letters 49 (2008) 896–900

Tetrahedron Letters

Synthesis and characterization of novel cofacial bis-phthalocyanines containing 16-crown-5 ether groups

Metin Özer [a], Ahmet Altındal [b], Bekir Salih [c], Mustafa Bulut [a], Özer Bekaroğlu [d,*]

[a] Department of Chemistry, Marmara University, Istanbul 34722, Turkey
[b] Department of Physics, Marmara University, Istanbul 34722, Turkey
[c] Department of Chemistry, Hacettepe University, Ankara 06532, Turkey
[d] Department of Chemistry, Istanbul Technical University, Istanbul 34469, Turkey

Received 13 June 2007; revised 20 November 2007; accepted 27 November 2007
Available online 4 December 2007

Abstract

Four crown ether substituted cofacial bis-phthalocyanines were prepared by the cyclic condensation of dihydroxy groups of pentaerythritol moieties of phthalocyanine with tetraethyleneglycol ditosylate in the presence of NaH as base in refluxing THF.

The core metal ion and peripheral substituents in phthalocyanines (Pcs) are the two most important variables. If the possibility of introducing a large number of different metal ions into the Pc center is combined with the unlimited number and type of substituents, the diversity of novel compounds becomes unlimited. Many kinds of Pcs with various substituents and central metal ions have been reported.[1,2] However, the synthesis and properties of cofacial bis-Pcs with a number of cross-links have only been reported occasionally in the literature.[3–7] These complexes have inflexible structures and often show spectroscopic, electrochemical, and physical properties that vary significantly from the parent monomers.[5–7]

The combination of a Pc and a crown ether has led to soluble products, which include additional functionalities, bind alkali metal ions or form stacked structures in the presence of certain cations.[8–11]

Recently, our efforts have been focused on the preparation of cofacial bis-Pc derivatives with new functionalities.[5–7] Our primary target has been to improve the physical and chemical properties of this type of Pcs by the addition of macrocyclic groups on the periphery.

In the present Letter, we report novel cofacial bis-Pc derivatives with four crown ether substituents attached to the periphery through dihydroxy pentaerythritol groups. The interaction of the crown ether groups with K^+ ions leading to intramolecular sandwich complexes has been employed to evaluate the conductivity properties of these novel cofacial bis-Pcs.

To the best of our knowledge, only a few cofacial bis-Pc complexes have been reported so far.[3–7] However, in none of the cases is this type of Pc linked to crown ether moieties through the hydroxy groups of a pentaerythritol group.

Precursor cofacial dimers of Pcs **1** and **2** were prepared and well characterized by the reported method.[7] The synthesis of cofacial **1** and **2** was achieved by heating a homogenized mixture of the corresponding bisphthalonitrile with $Zn(OAc)_2{\cdot}2H_2O$ or $Co(OAc)_2{\cdot}4H_2O$ in the ratio 1:1 leading to cyclotetramerization in a sealed tube at 300 °C in 10 min. The mixture of Pc(Zn) or Pc(Co) with four acetal moieties was hydrogenated with 10% Pd/C in DMF at room temperature under 1 atmosphere hydrogen pressure for 8 h according to the published procedure.[12] The catalyst was filtered off and the mixture was precipitated by the addition of ethanol to give **1** (76%) or **2** (63%). Next, the novel crown ether substituted Pcs **3** and **4** were

---

[*] Corresponding author. Tel.: +90 216 3590130; fax: +90 216 3860824.
E-mail address: obek@itu.edu.tr (Ö. Bekaroğlu).

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.11.168

prepared by condensation of the dihydroxy groups of the four pentaerythritol moieties with tetraethyleneglycol ditosylate (TEGDTos) as described in the literature.[12] To make the crown ether rings, Na^+ or K^+ ions were used as a template. Thus, two hydroxyl groups of the pentaerythritol moiety were used in crown ether formation. Therefore it is suggested that the crown ether units are perpendicular to the Pc planes. The reaction was accomplished in tetrahydrofuran (THF) at reflux in the presence of sodium hydride (NaH) as base. The crown ethers **3** and **4** were purified by silica gel chromatography using a gradient of $CHCl_3$/THF as eluent. The structures of **3** and **4** were confirmed by elemental analysis, FTIR, NMR, UV–vis, and (MALDI-TOF)-mass spectroscopy (Scheme 1).

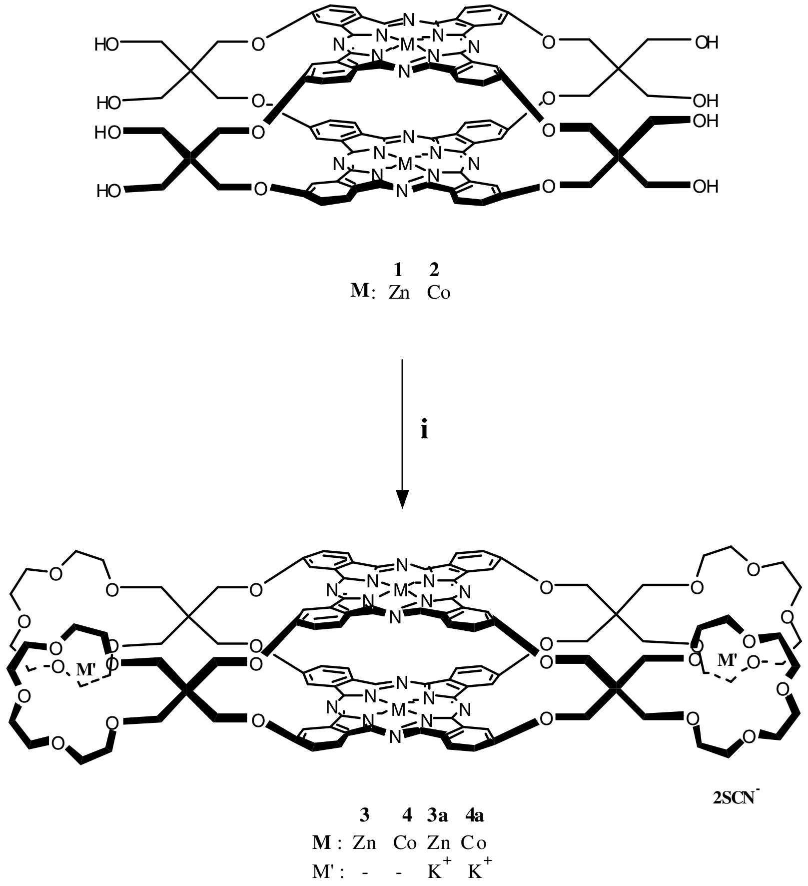
The synthesis of alkali metal (K^+) adducts (**3a** and **4a**) of **3** and **4** was achieved by stirring in THF/MeOH (5:2) with excess KSCN in MeOH at 50 °C for 15 min. The mixture was cooled to rt, then the precipitate was filtered off, washed successively with methanol and ether, and dried under vacuum.

The FT-IR spectra of **3** and **4** indicated typical aliphatic-CH vibrational bands at 2947–2851 cm^{-1} and at 2962–2874 cm^{-1}, which were assigned to the crown ethers of the Pc assemblies. The broad vibrational OH band seen at about 3402 cm^{-1} in **1** and **2** was not present in the FTIR spectra of **3** and **4**.

The ^1H NMR spectrum of **3** showed typical chemical shifts for the protons of the crown ether and pentaerythritol groups (δ: 3.93–3.32 ppm) as well as those due to the Pc aromatic protons (δ: 7.64–7.27 ppm). Formation of the crown ether derivative **3** was also confirmed by the loss of the broad singlet proton signal due to the aliphatic OH substituents of the pentaerythritol moieties at 11.35 ppm in the ^1H NMR of **1**. For **3**, the resonances of the protons of the four crown ether groups appeared as multiplets in the high field region.

On the other hand, the UV–vis spectra of **3** and **4** in THF displayed typical absorptions around 675 nm and 660 nm in the *Q* band region (Fig. 1). The *Q* band was attributed to the $\pi \rightarrow \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. Other bands (*B*) in the UV region at 349 nm and 334 nm were observed due to transitions from the deeper π levels to the LUMO. When aggregation occurs, a band at ca. 630 nm arises in the electronic spectrum as a result of intramolecular interactions between the Pc units.[6,7,13] Thus, the bands at around 638 nm and 602 nm can be attributed to intramolecular interactions of the cofacial structures of the macrocycles, although the *Q* band is not split.

With the aim of assessing the effect of alkali cations on the aggregation behaviour of the crown ether substituted



Scheme 1. Reagents and conditions: (i) TEGDTos, NaH, THF. Yields: (**1**, 76%); (**2**, 63%); (**3**, 26%); (**4**, 22%); (**3a**, 92%); (**4a**, 88%).

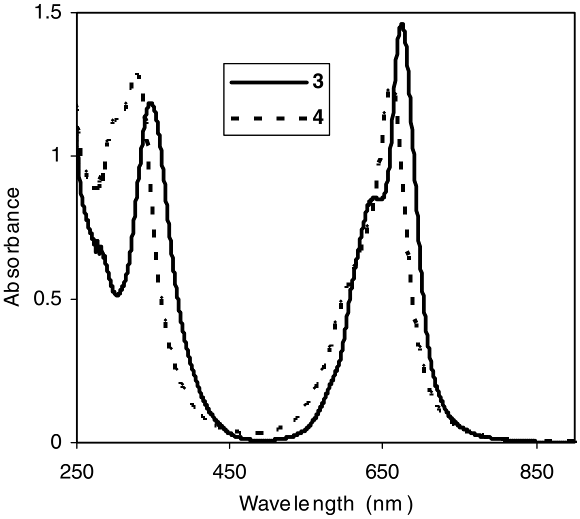


Fig. 1. UV–vis spectra of cofacial crown ether substituted bis-Pc derivatives **3** and **4** in THF.

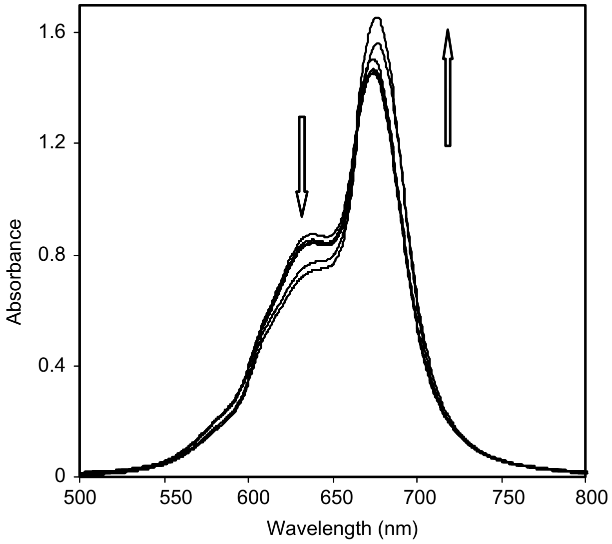


Fig. 2. Changes in the absorption spectrum of **3** upon addition of KSCN solution.

phthalocyanines by spectral methods, **3** and **4** were dissolved in THF, and an alkali metal salt (NaSCN or KSCN) dissolved in methanol was added. To avoid any effect arising from dilution due to the addition of the metal salt to the phthalocyanine solution, the phthalocyanines and metal salts were prepared at concentrations of 10^{-5} M and 10^{-3} M, respectively.

During the gradual addition of NaSCN, no appreciable difference in the *Q* band spectra was observed. However, the KSCN addition raised the *Q* band absorption maxima suggesting that the aggregation had decreased.

In phthalocyanines, it is known that the intense absorption in the lower energy side of the *Q* band is a measure of the monomeric units in solution, while aggregated species (dimer, trimer, etc.) lead to a shoulder at shorter wavelengths.[14] In the case of phthalocyanines with fused crown ether groups, it has been reported that addition of alkali metals of sufficiently large radii enhances aggregation as a result of intermolecular sandwich formation, observed by the decrease in the intensity of the *Q* band maximum.[9] In our case, interaction of K^+ ions with the crown ether moieties of **3** or **4** creates a contrary effect and increases the *Q* absorption maximum. This means that alkali metal complexation increases the concentration of the monomeric units by intramolecular sandwich formation (Fig. 2), and this also reveals that the distance between the two Pc planes increases.

The insolubility of **3** and **4** in water immiscible solvents such as chloroform or dichloromethane hindered alkali metal extraction experiments from the aqueous phase to the organic phase.[9,15,16]

MALDI-TOF-MS has proved to be an excellent tool for systematically studying this kind of complex, which is otherwise difficult to characterize. The MS spectra of **3** and **4** provided definitive characterization. For the zinc complex, only a linear mode positive ion MALDI mass spectrum could be obtained in α-cyano-4-hydroxycinnamic acid MALDI matrix even though other novel MALDI matrices were tested. The protonated molecular ion peak of the zinc complex was observed at 2315 Da mass which overlapped with the theoretical calculated molecular ion of the zinc complex. Beside the protonated molecular ion peak, no other peak was observed in the spectrum and this shows that no impurity was present in the sample and that the complex molecule is reasonably stable under MALDI-MS conditions. Positive ion and reflectron mode MALDI spectra of the cobalt complex could be obtained in an α-cyano-4-hydroxycinnamic acid MALDI matrix. The isotopic peak distribution of the protonated molecular ion peak was due to the carbon and cobalt isotopes and the experimental isotopic peak distribution (shown as inset) corresponded to the theoretical calculations. This showed that the complex had been synthesized successfully. Beside the protonated molecular ion peak of the cobalt complex, very few peaks were observed being mainly those resulting from fragmentation of the complex (Figs. 3 and 4).

Yield **3**: 0.048 g, 26%. Mp >300 °C. UV–vis (DMF) λ, nm (log ε): 675 (5.79), 638 (5.56), 348 (5.71) (Fig. 1). ^{1}H NMR (DMSO-d_6) δ, ppm: 7.27–7.64 (m, 24H, arom-CH), 3.32–3.93 (m, 32H, aliph-CH_2 and m, 64H, crown ether). IR (KBr pellet) ν, cm^{-1}: 3059 (arom-CH), 2947–2851 (aliph-CH), 1728–1716 (C=N), 1605 (Ar-C=C), 1466, 1230 (Aliph-O-Ar), 1088, 1050. MS (MALDI-TOF), *m*/*z*: 2315 $[M+H]^+$ (Fig. 3). Anal. Calcd for $C_{116}H_{120}N_{16}O_{28}Zn_2$: C, 60.13; H, 5.22; N, 9.67. Found: C, 60.32; H, 5.18; N, 9.33.

Yield **4**: 0.037 g, 22%. Mp >300 °C. UV–vis (DMF) λ, nm (logε): 660 (5.43), 602 (4.83), 333 (5.32) (Fig. 1). IR (KBr pellet) ν, cm^{-1}: 3043(arom-CH), 2962–2874 (aliph-CH), 1735–1718 (C=N), 1595 (Ar-C=C), 1474, 1246 (Aliph-O-Ar), 1094, 1057. MS (MALDI-TOF), *m*/*z*: 2305 $[M+H]^+$ (Fig. 4). Anal. Calcd for $C_{116}H_{120}N_{16}O_{28}Co_2$: C, 60.47; H, 5.25; N, 9.73. Found: C, 60.91; H, 5.11; N, 9.58.

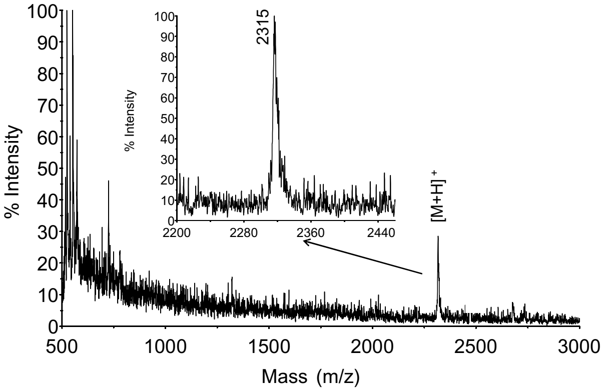


Fig. 3. The positive ion and linear mode MALDI-MS spectrum of **3** was obtained in an α-cyano-4-hydroxycinnamic acid (ACCA) (15 mg/mL 1:1 water–acetonitrile) MALDI matrix using nitrogen laser accumulating 50 laser shots. Inset spectrum shows expanded molecular mass region of the complex.

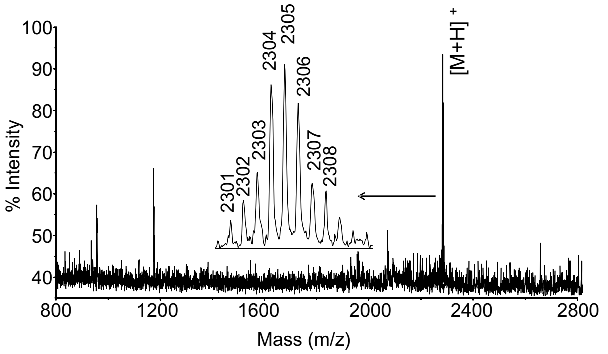


Fig. 4. Positive ion and reflectron mode MALDI-MS spectrum of **4** was obtained in an α-cyano-4-hydroxycinnamic acid (ACCA) (15 mg/mL 1:1 water–acetonitrile) MALDI matrix using nitrogen laser accumulating 50 laser shots. The inset spectrum shows the expanded molecular mass region of the complex.

Temperature dependent dc conductivity studies were performed to obtain information on the processes taking place in **3**, **4**, **3a**, and **4a**. The conductivity measurements of the films of **3**, **4**, **3a**, and **4a** were carried out in the temperature range 290–476 K, using an interdigital transducer structure with gold electrodes. Thin films of the compounds were obtained by spin-coating over the electrode arrays. The variation of the dc conductivity of compounds **3** and **4** as a function of reciprocal temperature in the temperature range 290–476 K (Fig. 5) suggested the presence of only one conduction mechanism. Thus, the conduction behaviour of **3** and **4** can be interpreted as the usual Arrhenius type. The values of the activation energies were derived from the slope of $\log \sigma_{dc}$ versus $1/T$ graph and were 0.56 eV and 0.52 eV for compounds **3** and **4**, respectively.

With the insertion of an alkali metal (K^+), a deviation from linearity of the $\log \sigma_{dc}$ versus $1/T$ plot at approximately 391 K was observed for compounds **3a** and **4a**. It was also observed that the insertion of alkali metals increased the dc conductivity. The observed electrical conductivity values at room temperature for **3**, **4**, **3a**, and **4a** are 1.5×10^{-11} S/cm, 4.7×10^{-11} S/cm, 1.7×10^{-10} S/cm and 2.6×10^{-10}, respectively. The order of dc conductivities observed for these compounds was **4a** > **3a** > **4** > **3** for all temperatures investigated. It can be clearly seen from Figure 5 that the graph splits into two different linear regions. Each region can be ascribed a different activation energy corresponding to a different dominant excitation. This type of temperature dependence can be interpreted as a transition from extrinsic to intrinsic conduction due to the introduced acceptor level within the band gap by adsorbed O_2 molecules. The same type of temperature dependence of dc conductivity was observed for multinuclear metallo phthalocyanines (Zn) with alkylthio substituents by Ceyhan et al.[17] The activation energies obtained for the films of **3a** and **4a** for the first linear region are the same (0.40 eV). The values of the activation energies for the second linear region were 0.72 eV and 0.81 eV for compounds **3a** and **4a**, respectively.

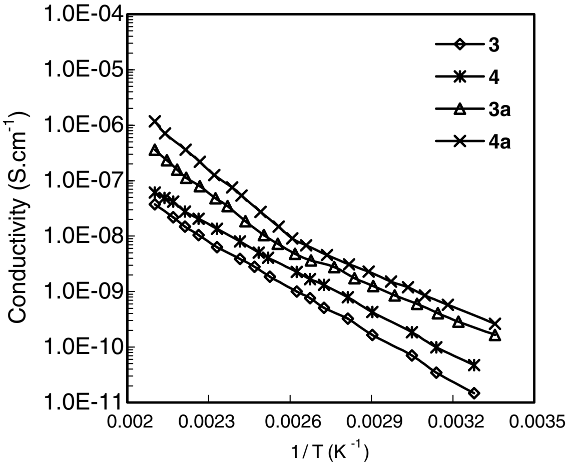


Fig. 5. Dependence of the dc conductivity on the inverse of temperature for films of compounds **3**, **4**, **3a** and **4a**.

Acknowledgments

This work was supported partly by the Turkish Academy of Sciences (TUBA), TÜBİTAK (Project No: 106T326) and the Research Fund of DPT (Project No: 2003K120810).

References and notes

1. Bekaroğlu, Ö. *Appl. Organomet. Chem.* **1996**, *10*, 605.
2. Kobayashi, N. *Coord. Chem. Rev.* **2002**, *227*, 129.
3. Tolbin, A. Y.; Ivanov, A. V.; Tomilova, L. G.; Zefirov, N. S. *Mendeleev Commun.* **2002**, 96.
4. Tolbin, A. Y.; Ivanov, A. V.; Tomilova, L. G.; Zefirov, N. S. *J. Porphyrins Phthalocyanines* **2003**, *7*, 162.
5. Ceyhan, T.; Altındal, A.; Özkaya, A. R.; Erbil, M. K.; Salih, B.; Bekaroğlu, Ö. *Chem. Commun.* **2006**, 320.
6. Odabaş, Z.; Altındal, A.; Özkaya, A. R.; Salih, B.; Bulut, M.; Bekaroğlu, Ö. *Polyhedron* **2007**, *26*, 695.
7. Özer, M.; Altındal, A.; Özkaya, A. R.; Salih, B.; Bulut, M.; Bekaroğlu, Ö. *Eur. J. Inorg. Chem.* **2007**, 3519.

8. Koray, A. R.; Ahsen, V.; Bekaroglu, Ö. *J. Chem. Soc. Chem. Commun.* **1986**, 932.
9. Ahsen, V.; Yılmazer, E.; Ertaş, M.; Bekaroglu, Ö. *J. Chem. Soc. Dalton Trans.* **1988**, 401.
10. Ahsen, V.; Yılmazer, E.; Gürek, A.; Gül, A.; Bekaroglu, Ö. *Helv. Chim. Acta* **1989**, *71*, 1616.
11. Okur, A. I.; Gül, A.; Cihan, A.; Tan, N.; Bekaroglu, Ö. *Synth. React. Inorg. Met. Org. Chem.* **1990**, *20*, 1399.
12. Lukyanenko, N. G. O.; Melnik, T.; Kirichenko, T. I. *Synth. Commun.* **1986**, 930.
13. Manivannan, V.; Nevin, W. A.; Leznoff, C. C.; Lever, A. B. P. *J. Coord. Chem.* **1988**, *19*, 139.
14. Leznoff, C. C.; Lever, A. B. P. *Phthalocyanines Properties and Applications*; VCH: Weinheim, 1989. p 183.
15. Haines, A. H.; Hodgkisson, I.; Smith, C. *J. Chem. Soc., Perkin Trans. 1* **1983**, 311.
16. Ahsen, V.; Gürek, A.; Musluoğlu, E.; Bekaroglu, Ö. *Chem. Ber.* **1989**, *122*, 1073.
17. Ceyhan, T.; Altındal, A.; Erbil, M. K.; Bekaroğlu, Ö. *Polyhedron* **2006**, *25*, 737.