Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 48 (2007) 6326–6329

Synthesis, characterization and electrical properties of novel mono- and cofacial bisphthalocyanines bridged with four [1a,8b-dihydronaphtho[*b*]naphthofuro[3,2-*d*]furan-7,10-diyl] units

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

[a]*Department of Chemistry, Marmara University, 34722 Göztepe-İstanbul, Turkey*
[b]*Department of Physics, Marmara University, 34722 Göztepe-İstanbul, Turkey*
[c]*Department of Chemistry, Hacettepe University, 06532 Ankara, Turkey*
[d]*Department of Chemistry, Technical University of İstanbul, Maslak-İstanbul, Turkey*

Received 6 April 2007; revised 22 June 2007; accepted 5 July 2007
Available online 30 July 2007

Abstract—Novel mono phthalocyanines and cofacial bisphthalocyanines were synthesized from 4,4′-(1a,8b-dihydronaphtho[*b*]-naphthofuro-[3,2-*d*]furan-7,10-diyl)bis(oxy)diphthalonitrile **1**. The products were characterized by elemental analysis, UV–vis, IR, ^{1}H NMR and mass spectroscopy. Both the direct current (dc) and alternating current (ac) electrical properties of the product films were investigated as a function of temperature in the frequency range 40–10^5 Hz. It was observed that the ac response of the films can be represented by the ω^s law. The temperature dependence of dc conductivity showed typical Arrhenius behavior for all compounds.

1. Introduction

For many years phthalocyanines (Pcs) have been widely used as organic pigments and dyestuffs. In addition to a large amount of fundamental academic research, interest has also expanded in applied fields such as electrodichroism, optical disk, laser dyes, liquid crystals, molecular metals, electrocatalysis, photodynamic cancer therapy,[1] nonlinear optics,[2–4] photoelectrochemistry[5–8] and gas sensors.[9–14] From this point of view, the synthesis and the electrical and gas-sensing properties of several Pc derivatives have been investigated. We have reported recently on the synthesis, characterization and electrical, electrochemical and gas-sensing properties of a novel sandwich dilutetium tetra Pc,[15–17] a *trans*-2,2′-azoquinoxa-line bridged bis Pc,[18] a cyclic borazine derivative containing three phthalocyaninato Zn(II) macrocycles[19] and four *t*-butylcalix[4]arene, 1,1′-methylenedinaphthalen-2-ol and 1a,8b-dihydronaphtho[*b*]-naphthofuro[3,2-*d*]furan-7,10-diol bridged binuclear zinc(II) and cobalt(II) ball types Pcs, as well as metal-free clamshell Pc.[20–22] These novel compounds showed interesting electrical and electrochemical properties.

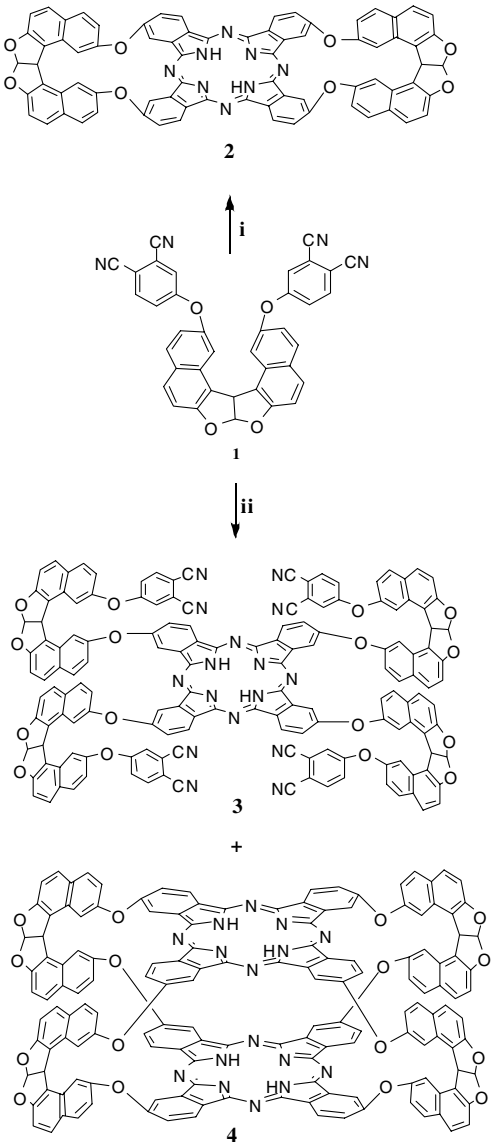
In the present Letter, we have used the 'heating of the solid phase' method for the synthesis of the novel cofacial bisphthalocyanine tetra 1a,8b-dihydro-naphtho [*b*]naphtha-furo[3,2-*d*]furan-7,10-diol bridged Pc **4**. We found that this reaction also produced compounds **2** and **3** as was initially evident by thin layer chromotography. Since the yield of **2** was very low, we did not isolate it from the reaction mixture. Instead, **2** was synthesized independently using Li as a catalyst in hexanol at 170 °C. Impedance spectroscopy and dc techniques were used to characterize the electrical properties of films **2**–**4**. Temperature dependent measurements revealed that the dc behavior of the films can be described by activated conductivity dependence on temperature. It was also observed that the operating temperature had a considerable effect on the impedance spectra of the films. The ac conductivity $\sigma(\omega)$ varied as ω^s, where the exponent s is the temperature dependent variable and is always less than unity.

Starting material **1** was obtained via reaction of 4-nitrophthalonitrile and 1a,8b-dihydronaphtho[*b*]naphtha-furo[3,2-*d*]furan-7,10-diol in dry DMSO in the presence

* Corresponding author. Tel.: +90 216 359 01 30; fax: +90 216 386 08 24; e-mail: obek@itu.edu.tr

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.07.013

of dry K_2CO_3.[22,23] Compound **2** could be synthesized by reaction of **1** with Li in dry *n*-hexanol at 170 °C. Phthalocyanines **3** and **4** were synthesized by heating **1** with $Mg(OAc)_2{\cdot}4H_2O$ in a sealed tube under an N_2 atmosphere (Scheme 1). Elemental analysis and IR, ^1H NMR, mass and UV–vis spectra confirmed the structures of **2**–**4**. A diagnostic feature of the formation of Pcs **2** and **4** from compound **1** was the disappearance of the sharp CN vibration at 2231 cm^{-1} in the IR spectrum. The IR spectra of compounds **2**–**4** showed C–O–C peaks at 1220–1285 cm^{-1}, C=C (phenyl and naphthalene) peaks at 1560–1655 cm^{-1}, aromatic CH peaks at 3060–3070 cm^{-1} and aliphatic CH absorptions at 2840–2945 cm^{-1}. The weak bands around 3380–3450 cm^{-1} for **2**, **3** and **4** can be attributed to the N–H stretching frequency of the metal-free inner core. The ^1H NMR spectrum was also in good correlation with the structure of **2**. The aromatic protons appeared at 6.80–7.95 ppm, the –O–CH–O– protons at 7.15 ppm and the Ar–CH–Ar protons at 5.30 ppm. The NH protons were not observed, probably due to the broad nature of these signals in the presence of the intense resonances of the Pc ring.[24] The UV–vis spectra of **2**, **3** and **4** in THF showed characteristic absorptions between 610 and 710 nm in the Q-band region. The Q band observed for the compounds 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. The observed bands (B) at 300–350 nm were due to the transitions from the deeper π levels to the LUMO. The UV spectra of **2**, **3** and **4** showed double Q bands which are quite typical for metal-free Pcs (Fig. 1).



Scheme 1. Synthesis of compounds **2**, **3** and **4**. Reagents and conditions: (i) Li, *n*-hexanol, N_2,170 °C; (ii) $Mg(CH_3COO)_2{\cdot}4H_2O$, N_2, 300 °C.

Planar devices consisting of thin films of compounds with interdigital electrodes were used for dc and ac measurements. The dc conductivity of the films were determined from the slopes of the measured current–voltage characteristics. The electrical conductivity values obtained for **2**, **3** and **4** at room temperature were 7.72×10^{-11} S/cm, 1.05×10^{-8} S/cm and 3.21×10^{-11} S/cm, respectively. Linear temperature dependence was observed for all the films in the temperature range of 290–425 K. This indicates that conduction occurred through an activated process having a single activation energy in the operating range of temperatures. The activation energies were derived from the slope of the ln σ_{dc} versus $1/T$ graphs and were found to be 0.80 eV for **2**, 0.57 eV for **3** and 0.86 eV for **4**.

The frequency dependence of the ac conductivity for different temperatures between 290 and 425 K were also

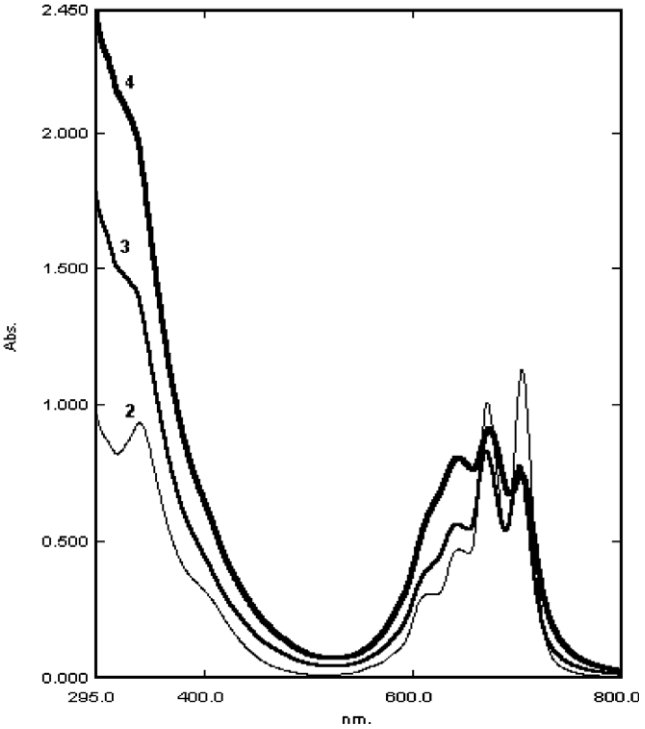


Figure 1. UV spectra of compounds **2**, **3** and **4** in THF.

investigated. By evaluating the ac behavior of the films, the measured ac conductivity data can be described by the power law behavior[25] $\sigma_{ac} = C(T)\omega^s$ for all the compounds, where C is a constant and ω is the angular frequency. The measured ac conductivity data exhibited a strong dependence upon frequency at high frequencies, with weaker dependence at low frequency for all the temperatures investigated. The values of the frequency exponents s were obtained from the slopes of logarithmic conductivity versus frequency graphs. The derived values of s were less than unity for all the temperature and frequency ranges. It was also observed that the exponent s decreased with increasing temperature from 290 K to 425 K for all the compounds. A similar frequency dependence on the ac conductivity in metal-free phthalocyanine was observed by Amar et al.[26] Various models such as tunneling and hopping have been proposed to explain this type of behavior. The dependence of the frequency exponent s on temperature suggests correlated barrier hopping. The measured impedance spectra for all compounds at 370 K is shown in Figure 2 where, the impedance spectra consist of a quasi-vertical line for compounds **2** and **4** even at 370 K. On the other hand a full semicircle for compound **3** was obtained at the same temperature. A semicircular shaped curve in the Nyquist plot indicates that the impedance becomes capacitive. In this case, the measured impedance data can be modeled as a capacitor in parallel with a resistor in series with another resistor. An ideal semicircle in a complex plane plot appears only in Debye dispersion relation for a single relaxation time process. However, the majority of actual materials exhibit a pronounced deviation from the simplified Debye treatment. Depressed semicircles indicate that the maximum of the imaginary part of impedance is smaller than the half of the real part of impedance. The effect of temperature on the impedance spectra of the films becomes clearly visible with a rise in temperature. At 425 K, only depressed semicircles with different radii were observed for compounds **2**–**4**.

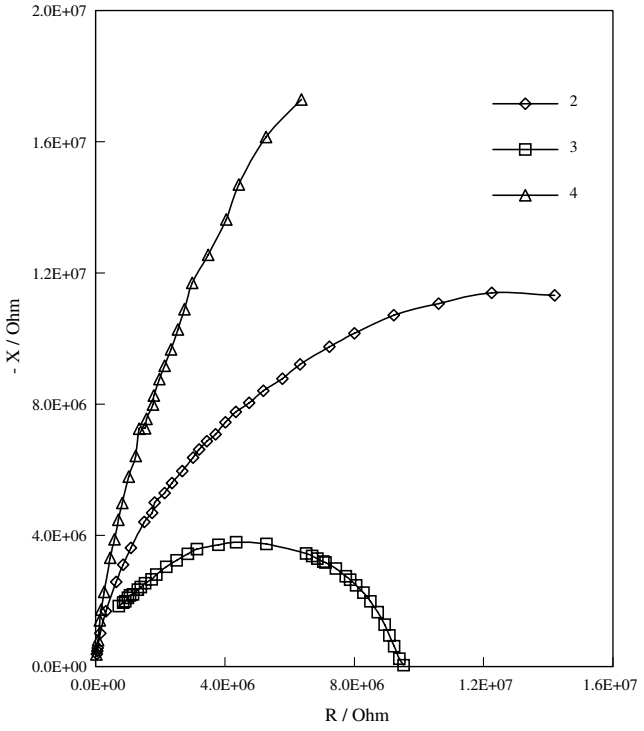


Figure 2. Impedance spectra of films **2**–**4** at 370 K.

2. Experimental

For the electrical and impedance measurements, thin films of **2**–**4** were obtained on photolithographically patterned interdigital electrodes by spin-coating. Dc conductivity and impedance spectra measurements were performed between 290 and 425 K using a Keithley 617 electrometer. Ac conductivity and impedance measurements were carried out with a Keithley 3330 LCZ meter in the frequency range 40–10^5 Hz and in the temperature range from 290 to 425 K. The measurement procedure for the temperature dependent dc and ac conductivity and impedance spectra was as described.[27]

2.1. Synthesis of [3,9,17,23-bis(1′a,8′b-oxynaphtho[*b*]-naphthofuro[3,2-*d*]-7,10-diyl)phthalocyanine] 2

A suspension of compound **1** (0.2 g, 0.3×10^{-3} mol) in 3.0 mL of dry *n*-hexanol was heated under N_2 in a sealed tube at 80 °C. After addition of lithium (0.035 g, 5.043 mmol) to the reaction mixture, a dark green color appeared over 15 min. The reaction mixture was stirred at 170 °C for 8 h. After cooling to room temperature, methanol (20 mL) was added to the precipitate and the product was filtered. The residue was washed successively with hot methanol, hot acetic acid, ethanol, acetonitrile and acetone before drying in vacuo (70 °C). The residue was fractionated on a silica gel column eluting with chloroform and a gradient of chloroform–methanol up to 5% methanol. Yield: 25 mg (13 %). This compound was soluble in THF, DMF, and DMSO. Mp > 350 °C. IR (KBr pellet) $\nu_{max/cm^{-1}}$: 838, 926, 1094, 1179, 1227, 1361, 1383, 1454, 1472, 1510, 1614, 1717, 2850, 2925, 3054, 3433. Elemental analysis, element % found (% calculated for $C_{76}H_{38}N_8O_8$): C 76.25 (76.63) H 3.57 (3.22) N 9.78 (9.41). UV–vis (THF), nm ($\log\varepsilon$): 337 (4.971), 613 (4.486), 644 (4.673), 671 (5.004), 704 (5.053). ^{1}H NMR (DMSO-d_6) δ 5.30 (d, $J = 5.85$ Hz 2H), 6.80–7.95 (m, 32H), 7.15 (d, $J = 5.85$ Hz, 2H), (MALDI-TOF): m/z (%) = 1191(100) $[M+H]^+$.

2.2. Synthesis of [2,10,16,24-tetrakis(1a-hydronaptho-[*b*]-napthofuro[3,2-*d*]-7,10-diyl-4-oxyphthalonitrile)phthalocyanine] 3 and [1′a, 8′b-tetrakis-bis{(2′,10′,16′,24′)-phthalocyaninyl} dioxynaptho-[*b*]-naphthofuro[3,2-*d*]-furan-7,10-diyl] 4

A mixture of compound **1** (0.2 g, 0.3×10^{-3} mol) and $Mg(OAc)_2{\cdot}4H_2O$ (0.100 g, 4.67×10^{-4} mol) was powdered in a quartz crucible and heated in a sealed glass tube for 5 min under an N_2 atmosphere at 300 °C. After cooling to room temperature, 5 mL of DMF was added to the residue to dissolve the product. The reaction mixture was precipitated by adding water. The precipitate was filtered, washed with hot water and ethanol in order to remove unreacted starting materials. Then, the crude

product was boiled in acetic acid and hydrochloric acid mixture (19:1 volume ratio). After filtration the product was washed with acetic acid, methanol, ethanol, acetonitrile and acetone for 12 h, respectively, in a soxhlet apparatus then dried in vacuo. The residue was fractionated on a silica gel column eluting with chloroform and a gradient of chloroform–methanol up to 100% methanol.

Compound **3** was slightly soluble in DCM, $CHCl_3$ and was soluble in THF, DMF and DMSO Mp >350 °C. Yield: 10 mg (5%) IR (KBr pellet) $v_{max/cm^{-1}}$: 831, 964, 1016, 1180, 1184, 1257, 1365, 1450, 1521, 1598, 1628, 1718, 2231, 2850, 2925, 3074, 3448. Elemental analysis, element % found (% calculated for $C_{152}H_{74}N_{16}O_{16}$): C 76.42 (76.70) H 3.22 (3.13) N 9.23 (9.42). UV–vis (THF), nm (log ε): 331 (4.770), 643 (4.262), 671 (4.466), 703 (4.426). MS (MALDI-TOF): $m/z = 2379$ (M+H).

Compound **4** was soluble in THF, DMF, DMSO. Mp > 350 °C. Yield: 30 mg (15%). IR (KBr pellet) $v_{max/cm^{-1}}$: 834, 952, 1008, 1094, 1179, 1223, 1339, 1365, 1454, 1472, 1506, 1610, 1715, 2850, 2925, 3059, 3381. Elemental analysis, element % found (% calculated for $C_{152}H_{76}N_{16}O_{16}$): C 74.47 (74.71) H 3.02 (2.97) N 9.21 (9.17). UV–vis (THF), nm (log ε): 335 (4.511), 643 (4.119), 672 (4.172), 704 (4.085), MS (MALDI-TOF): m/z (%) =1192 (100) $[M+2H]^{2+}$, 851 (59), 2381 (28) $[M+H]^{+}$ and 1531 (23).

Acknowledgments

This work was supported partly by the Turkish Academy of Sciences (TUBA), The State Planning Organization (Project Number: 2003 K 120810) and The Research Fund of Marmara University.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.07.013.

References and notes

1. Kobayashi, N.; Kobayashi, Y.; Osa, T. *Am. Chem. Soc.* **1993**, *115*, 10994.
2. Tolbin, A. Y.; Ivanov, A. V.; Tomilova, L. G.; Zefirov, N. S. *Mendeleev Commun.* **2003**, *7*, 162.
3. De Wulf, D. W.; Leland, J. K.; Wheeler, B. L.; Bard, A. J.; Batzel, D. A.; Dininny, D. R.; Kenney, M. E. *Inorg. Chem.* **1987**, *26*, 266.
4. Merey, Ş.; Bekaroğlu, Ö. *J. Chem. Soc.* **1999**, 4503.
5. Koike, N.; Uekusa, H.; Ohashi, Y.; Harnoode, C.; Kitamura, F.; Ohsaka, T.; Tokuda, K. *Inorg. Chem.* **1996**, *35*, 5798.
6. Jiang, J.; Arnold, D. P.; Yu, H. *Polyhedron* **1999**, *18*, 2129.
7. (a) Leznoff, C. C.; Lam, H.; Nevin, W. A.; Kobayashi, N.; Janda, P.; Lever, A. B. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1021; (b) Lam, H.; Marcuccio, S. M.; Svirskaya, P. I.; Greenberg, S.; Leznoff, C. C.; Cerny, R. L. *Can. J. Chem.* **1989**, *67*, 1087.
8. Kobayashi, N.; Yanagisawa, Y.; Osa, T.; Lam, H.; Leznoff, C. C. *Anal. Chem.* **1990**, *6*, 813.
9. Kobayashi, N.; Lam, H.; Nevin, W. A.; Janda, P.; Leznoff, C. C.; Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 3415.
10. Kobayashi, N.; Lam, H.; Nevin, W. A.; Janda, P.; Leznoff, C. C.; Koyama, T.; Monden, A.; Shirai, H. *J. Am. Chem. Soc.* **1994**, *116*, 879.
11. Kobayashi, N.; Numao, M.; Kondo, R.; Nakajima, S.; Osa, T. *Inorg. Chem.* **1991**, *30*, 2241.
12. Kobayashi, N. *J. Chem. Soc., Chem. Commun.* **1991**, 1203.
13. Kobayashi, N.; Higashi, Y.; Osa, T. *Chem. Lett.* **1994**, *10*, 1813.
14. Garcia; Frutos, E. M.; Fernandez; Lazaro, F.; Maya, E. M.; Vazquez, P.; Torres, T. *J. Org. Chem.* **2000**, *65*, 6841.
15. Abdurrahmanoğlu, Ş.; Altındal, A.; Özkaya, A. R.; Bulut, M.; Bekaroğlu, Ö. *Chem. Commun.* **2004**, 2096.
16. Altındal, A.; Abdurrahmanoğlu, Ş.; Bulut, M.; Bekaroğlu, Ö. *Synth. Met.* **2005**, *150*, 181.
17. Abdurrahmanoğlu, Ş.; Özkaya, A. R.; Bulut, M.; Bekaroğlu, Ö. *Dalton Trans.* **2004**, 4022.
18. Salan, Ü.; Altındal, A.; Bulut, M.; Bekaroğlu, Ö. *Tetrahedron Lett.* **2005**, *46*, 6057.
19. Özer, M.; Altındal, A.; Özkaya, A. R.; Bulut, M.; Bekaroğlu, Ö. *Synth. Met.* **2005**, *155*, 222.
20. Ceyhan, T.; Altındal, A.; Özkaya, A. R.; Erbil, M. K.; Salih, B.; Bekaroğlu, Ö. *Chem. Commun.* **2006**, 320.
21. Odabaş, Z.; Altındal, A.; Özkaya, A. R.; Bulut, M.; Salih, B.; Bekaroğlu, Ö. *Polyhedron* **2007**, *26*, 695.
22. Odabaş, Z.; Altındal, A.; Özkaya, A. R.; Salih, B.; Bulut, M.; Bekaroğlu, Ö. *Polyhedron* **2007**. doi:10.1016/j.poly.2007.03.047.
23. Odabaş, Z.; Talınlı, N. *Heterocycl. Commun.* **2000**, *6*, 437.
24. Matlaba, P.; Nyokong, T. *Polyhedron* **2002**, *21*, 2463.
25. Elliot, S. R. *Adv. Phys.* **1987**, *36*, 135.
26. Amar, N. M.; Saleh, A. M.; Gould, R. D. *Appl. Phys. A* **2003**, *76*, 77.
27. Özer, M.; Altındal, A.; Özkaya, A. R.; Bulut, M.; Bekaroglu, Ö. *Polyhedron* **2006**, *25*, 3593.