Tetrahedron Letters 50 (2009) 6775–6778

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

# Effect of peripheral substitution on the electronic absorption and magnetic circular dichroism (MCD) spectra of metal-free azo-coupled bisphthalocyanine

Ümit Salan[a], Nagao Kobayashi[b,*], Özer Bekaroğlu[c,*]

[a] Department of Chemistry, Marmara University, Göztepe-İstanbul 34722, Turkey
[b] Department of Chemistry, Graduate School of Science Tohoku University, Sendai 980-857, Japan
[c] Department of Chemistry, Technical University of İstanbul, Maslak, Turkey

ARTICLE INFO

*Article history:*
Received 4 May 2009
Revised 7 September 2009
Accepted 18 September 2009
Available online 24 September 2009

ABSTRACT

A new azo-coupled bisphthalocyanine is synthesized from the corresponding quinoxaline oxime which can be obtained by the reaction of *s-trans*-chloroethanedial with N=N conjugated metal-free phthalocyanine. The phthalocyanine is synthesized by the reaction of 4-nitro-*o*-phenylenediamine with 2-nitro-9,10,16,17,23,24-hexa(hexylthio)phthalocyanine. Novel compounds are characterized by elemental analysis, UV/vis, IR and $^1$H NMR, and MALDI-TOF spectroscopy. The effect of the azo units on the position and intensity of the electronic absorption and magnetic circular dichroism (MCD) spectra of the bisphthalocyanine are examined for the N=N conjugated metal-free phthalocyanine.

## Introduction

Phthalocyanines are a class of macrocyclic compound possessing a conjugated system of 18 π-electrons. They exhibit a number of unique properties, which make them of great interest in various scientific and technological areas ranging from nanotechnology to medicine. Phthalocyanines, which were first developed as dyes and pigments have been explored in numerous technological applications, such as photovoltaic solar cells,[1] electrophotography,[2] molecular electronics,[3] Langmuir–Blodgett films,[4,5] electrochromism in display devices,[6] gas sensors,[7,8] liquid crystals,[9–11] nonlinear optics,[12] and medical applications.[13]

Phthalocyanines have received significant attention particularly because of their use in photodynamic cancer therapy. For this application, the wavelength of the major $\pi\rightarrow\pi^*$ transitions in the UV/vis region is of critical importance. The phthalocyanines show typical electronic spectra with two strong absorption regions, one in the UV region at about 300–350 nm (the B band) and the other in the visible region at about 600–700 nm (the Q band). The characteristic Q-band transition of metal-free phthalocyanines with $D_{2h}$ symmetry is observed as a split band of high intensity in the visible region. Monomolecular phthalocyanines show Q band absorptions at $\lambda$ ~680 nm with high extinction coefficients $\varepsilon$ >$10^5$ M$^{-1}$ cm$^{-1}$. Substituted phthalocyanines, especially those containing electron-donating substituents, exhibit a bathochromic shift of their Q band up to $\lambda$ ~760 nm.[14] The position and bandwidth of the absorption bands of phthalocyanines can be adjusted in several ways. On annulation of additional benzene rings to the phthalocyanine moiety, the π-system is extended such that strong red shifts of the Q band are observed for naphthalocyanines (Nc) at $\lambda$ ~740–810 nm, and anthracyanines (Ac) at $\lambda$ ~830–860 nm.[15–17] Another method for extending the π-electron system and thus shifting the Q band into the near infrared (NIR) region is the dimerization of phthalocyanines and related macrocycles via common annelated benzene rings or other fully conjugated linkages.[17]

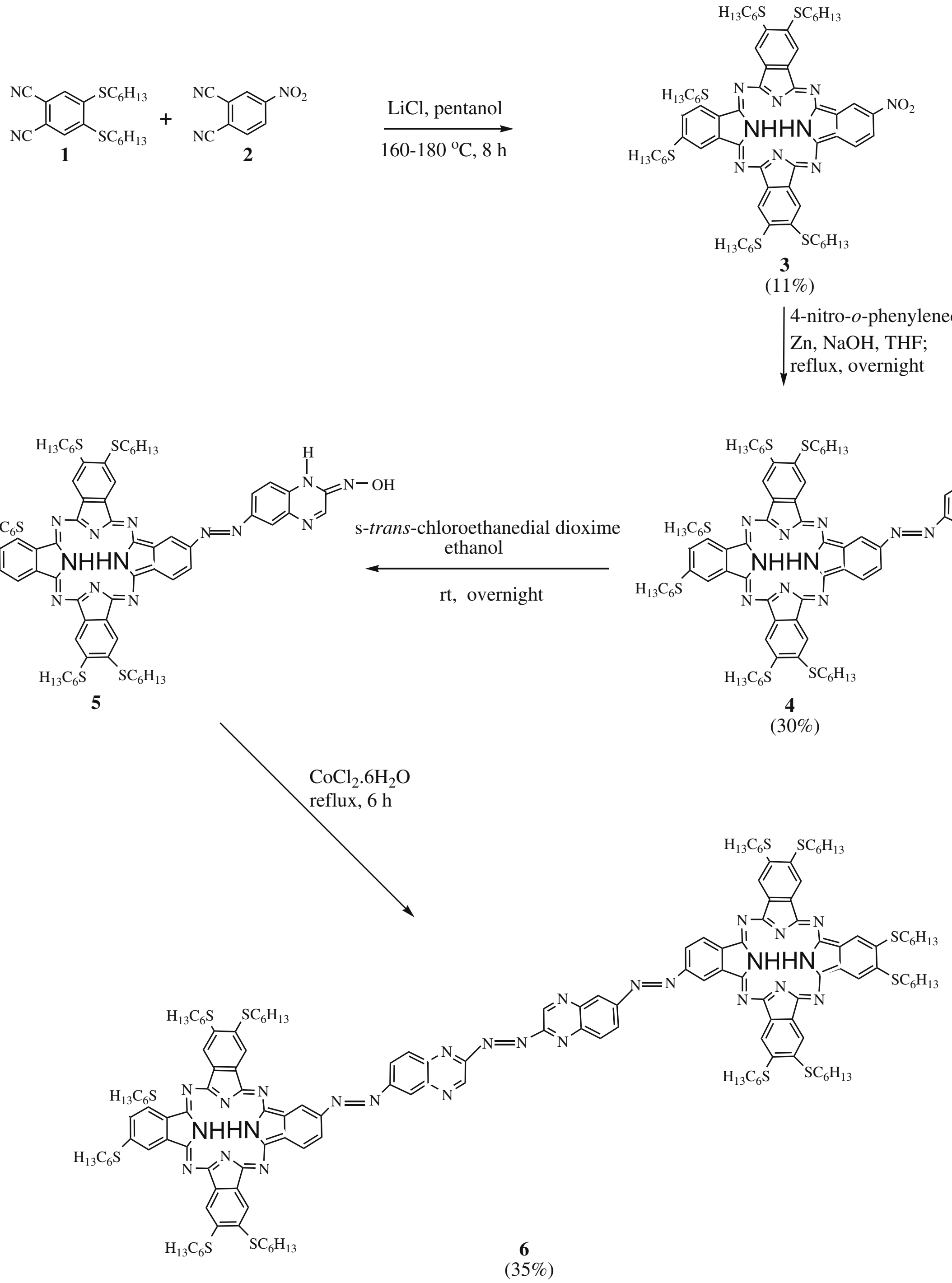
While numerous syntheses and applications of azo dyes have been reported,[18] the relationship between molecular structure and absorption wavelengths has also received significant interest.[19] However, publications on phthalocyanines containing an azo chromophore are limited.[20] Herein, we report the synthesis, characterization, and electronic absorption and magnetic circular dichroism (MCD) spectra of a novel metal-free bisphthalocyanine containing three azo groups in a linking unit.

In this study, we aimed to synthesize a new *trans*-azo-coupled bisphthalocyanine starting from the corresponding quinoxaline oxime by making use of the template effect of cobalt(II) ions. The synthesis of azo-coupled metal-free bisphthalocyanine **6** is shown in Scheme 1. When a solution of the quinoxaline oxime and cobalt(II) chloride in absolute DMF was refluxed for 6 h, compound **6** was isolated as a green precipitate. The mechanism for the coupling process from **5** to **6** is not explained as yet.[21] The quinoxaline oxime was synthesized in one step by reaction of *s-trans*-chloroethanedial dioxime with compound **4** and elimination of $NH_2$–OH.[21–23] Compound **4** was synthesized by the reaction of 4-nitro-*o*-phenylenediamine with 2-nitro-9,10,16,17,23,24-hexa(hexylthio)phthalocyanine **3**, which was obtained from 4,5-bis(hexylthio)phthalonitrile **1** and 4-nitrophthalonitrile **2** (Scheme 1). The coupling reaction between **3** and 4-nitro-*o*-phenylenediamine

---

* Corresponding authors. Tel.: +90 216 3590130; fax: +90 216 3860824 (Ö.B.).
*E-mail addresses:* nagaok@mail.edu.tains.tohoku.ac.jp (N. Kobayashi), obek@itu.edu.tr (Ö. Bekaroğlu).

0040-4039/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2009.09.108



**Scheme 1.**

was regioselective resulting in the trans-form product. The regioselectivity arises from the fact that the resonance energy of the trans-form is approximately 3.5 kcal/mol lower than the cis-form. It was shown to be *trans*-2,2-azoquinoxaline unequivocally by X-ray single cystal analysis.[22] The spectroscopic data confirmed the proposed structures of all of the new compounds.

The elemental analysis results for compounds **3**, **4,** and **6** were in good agreement with the calculated values. A diagnostic feature of phthalocyanine formation from compounds **1** and **2** is the disappearance of the sharp intense CN vibrational bands in the IR spectra. Other IR bands of compound **3** include C–H stretching bands at 2854, 2925, 2954, and 3060 $cm^{-1}$ and the bending bands of the nitro group at 1342 and 1523 $cm^{-1}$. The band at around 3417 $cm^{-1}$ can be attributed to the N–H stretching frequency of the inner core of the metal-free phthalocyanine **3**. The chemical shifts in the $^1H$ NMR spectra of compounds **3**, **4,** and **6** were found to be in agreement with the values reported for similar compounds.[22,23] In the IR spectrum of compound **3**, the intense absorption bands at 1520 and 1340 $cm^{-1}$ corresponding to the $NO_2$ bending vibrations disappeared after its conversion into compound **4**. The IR spectrum of compound **4** included $NH_2$ stretching bands at 3387 and 3514 $cm^{-1}$. Comparison of the IR spectral data of compounds **4** and **6** clearly indicated the conversion of the $NH_2$ groups into N=N moieties by the disappearance of the $NH_2$ bands and the appearance of new imine bands at 1473 and 1490 $cm^{-1}$ in **6**. MALDI-TOF samples were prepared by mixing the appropriate complex (2 mg/mL in chloroform) with the matrix, α-cyano-4-hydroxycinnamic acid (10 mg/mL in chloroform) solution (1:20 v/v) in a 0.5 mL Eppendorf® micro-tube. Finally 1 μL of this mixture was deposited on the sample plate, dried at room temperature, and then analyzed. The molecular ion peaks of **3**, **4,** and **6** were observed at 1255, 1344, and 2758 Da, respectively. Apart from the molecular ion peaks, $H_2O$ and $2H_2O$ adducts were also present.

Figure 1 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of compound **6** in $CHCl_3$. The Q and Soret bands appeared at 702 and 356 nm, respectively. The bands are at slightly longer wavelength than those of phthalocyanines (Pcs) without peripheral substituents. One notable feature is that the Q band is not split, although metal-free Pcs generally show split peaks which can be assigned to Qx and Qy transitions. This is quite a rare phenomenon in metal-free Pcs, although metal-free Pcs having a Q band at a wavelength longer than ca. 780 nm are known to have unsplit Q bands.[24] As a summation of the effect of the peripheral azo and alkylthio groups, the Qx and Qy splitting is thought to decrease, to produce an apparently single Q band which is characteristic of metal Pc species. The MCD spectrum is also similar to that of metal Pcs, such that dispersion-type *pseudo* Faraday *A* terms were recorded corresponding to the Q and Soret absorption peaks. The intramolecular interaction of the two Pc units appears small, since both the Q and Soret bands are similar in shape to those of typical monomeric Pc species. Although the relative intensity of the Soret band compared to the Q band is larger than in normal Pcs, this may be due to the superimposition of the absorption due to the connecting chromophore units (quinoxaline and azo[24]).

### Synthesis of $[(RS)_6PcNO_2]$ 3

A powdered mixture of compound **1** (1600 mg, 4.44 mmol), **2** (192 mg, 1.10 mmol), and LiCl (46 mg, 1.10 mmol) was dissolved in pentanol under an argon atmosphere. The mixture was heated at 160–180 °C for 8 h to give unsymmetrically substituted metal-free phthalocyanines consisting of various ratios of **1** and **2**. The reaction mixture was cooled to room temperature and precipitated by adding water. After filtration, the product was washed with cold ethanol and diethyl ether. The residue was fractionated on a silica gel column, eluting with $CHCl_3$, and a gradient of $CHCl_3$–THF up to 100% THF. Yield: 172 mg (11%). This compound is soluble in $CHCl_3$ and $CH_2Cl_2$. Mp >350 °C. IR (KBr) $\nu_{max}/cm^{-1}$ 730, 820, 840, 1020, 1070, 1110, 1140, 1342, 1381, 1458, 1523, 1595, 1610, 1640, 2854, 2925, 2954, 3060, 3417. Anal Calcd for $C_{68}H_{89}N_9O_2S_6$: C, 65.01; H, 7.10; N, 10.04; S, 15.30. Found: C, 64.93; H, 7.22; N, 10.15; S, 15.20. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.20 (t, $J = 6$ Hz, 18H), 1.25–1.70 (m, 48H), 2.80 (t, $J = 6$ Hz, 12H), 6.80–7.90 (m, 9H). (MALDI-TOF): *m/z* 1255 ($M^+$).

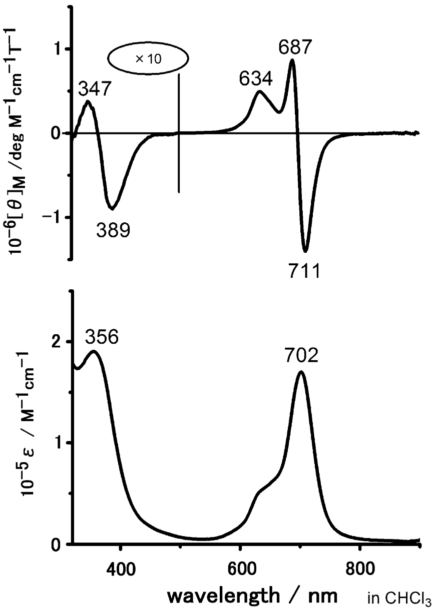


**Figure 1.** Electronic absorption (bottom) and magnetic circular dichroism (MCD) (top) spectra of compound **6**.

### Synthesis of $[(RS)_6PcN_2PhA]$ 4

A mixure of metal-free phthalocyanine **3** (300 mg, 0.24 mmol) and 4-nitro-*o*-phenylenediamine (37 mg, 0.08 mmol) was dissolved in THF. NaOH [0.2 mL (19.5 g NaOH in 45 mL)] and activated Zn (0.48 mmol) were added to this solution and the reaction mixture was refluxed overnight. The resultant product was filtered off and acidified using HCl (10%). The residue was evaporated in vacuo. Yield: 96 mg (30%). Mp >350 °C. IR (KBr) $\nu_{max}/cm^{-1}$ 730, 820, 840, 1020, 1070, 1110, 1140, 1340, 1380, 1460, 1610, 1640, 2850, 2920, 2960, 3060, 3387, 3514. Anal Calcd for metal-free phthalocyanine $C_{74}H_{96}N_{12}S_6$: C, 66.07; H, 7.14; N, 12.50; S, 14.29. Found: C, 65.95; H, 7.25; N, 12.60; S, 14.20. $^1H$ NMR (400 MHz, DMF-$d_7$) $\delta$ 0.90 (br s, 2H), 0.96 (t, 18H), 1.32 (br s, 2H), 1.42–1.70 (m, 48H), 2.90 (t, 12H), 6.80–7.80 (m, 12H). MS (MALDI-TOF): *m/z* 1344 ($M^+$).

### Synthesis of $[(RS)_6Pc]_2N_6AQ$ 6

Compound **4** (80 mg, 0.06 mmol) was dissolved in DMF (2 mL) and added to absolute ethanol (18 mL). This solution, was simultaneously added dropwise over 30 min to a solution of *s-trans*-chloroethanedial dioxime (8 mg, 0.06 mmol in 2 mL of ethanol) at room temperature under an argon atmosphere, and stirring was continued overnight. The reaction mixture containing **5** was evaporated and the residue stirred in dry DMF (3 mL) at 90 °C under an argon atmosphere. $CoCl_2 \cdot 6H_2O$ (0.07 mmol, 0.016 g) in dry DMF (1 mL) was added to the stirred solution and the mixture was refluxed for 6 h under argon. The resulting dark-green precipitate was filtered off and washed with absolute ethanol. The crude product **6** was purified by column chromatography over silica gel, eluting with $CHCl_3$. Yield: 57 mg (35%). This compound was soluble in $CHCl_3$ and $CH_2Cl_2$. Mp >350 °C. IR (KBr) $\nu_{max}/cm^{-1}$ 756, 840, 928, 1090, 1136, 1473, 1490, 1591, 1610, 2870, 2920, 3053, 3283. Anal Calcd for metal-free bisphthalocyanine $C_{152}H_{186}N_{26}S_{12}$: C, 66.13; H, 6.75; N, 13.20; S, 13.92. Found: C, 65.80; H, 6.85; N, 13.55; S, 14.10. $^1H$ NMR (400 MHz, DMF-$d_7$) $\delta$ 0.96 (t, $J = 6$ Hz, 36H), 1.26–1.70 (m, 96H), 2.90 (t, $J = 6$ Hz, 24H), 6.80–7.80 (m, 24H), 9.60 (s, 2H). MS (MALDI-TOF): *m/z* 2758 ($M^+$).

### Acknowledgments

We would like to thank The Research Foundation of Marmara University and the Commission of Scientific Research Project (BAP-KO) [FEN-D-030408-0083] and the Turkish Academy of Sciences (TUBA).

### References and notes

1. Wohrle, D.; Meissner, D. *Adv. Mater.* **1991**, *3*, 129–138.
2. Loutfy, R. O.; Hor, A. M.; Hsiano, C. K.; Barayi, G.; Kazmaier, P. *Pure Appl. Chem.* **1989**, *60*, 1047–1054.
3. Simic-Glavaski, B.. In *Phthalocyanines—Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1993; Vol. 3, pp 119–166. Chapter 2.

4. Cook, M. J.; Dunn, A.; Daniel, M. F.; Hart, R. C. O.; Richardson, R. M.; Roser, S. J. *Thin Solid Films* **1988**, *159*, 395–404.
5. Palacin, S.; Lesieur, P.; Stefanelli, I.; Barraud, A. *Thin Solid Films* **1988**, *159*, 83–90.
6. Nicholson, M. M.. In *Phthalocyanines—Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1993; Vol. 3, pp 71–117. Chapter 2.
7. Lefevre, D.; Porteu, F.; Balog, P.; Roulliay, M.; Zalczer, G.; Palacin, S. *Langmuir* **1993**, *9*, 150.
8. Shi, C.; Anson, F. C. *Inorg. Chim. Acta* **1994**, *225*, 215.
9. Van der Pol, J. F.; Neeleman, E.; Zwikker, J. W.; Nolte, R. J. M.; Drenth, W.; Aerths, J.; Visser, R.; Picken, S. J. *Liq. Cryst.* **1989**, *6*, 577–592.
10. Simon, J.; Sirlin, C. *Pure Appl. Chem.* **1989**, *61*, 1625–1629.
11. Swarts, J. C.; Langner, E. H. G.; Krokeide-Hove, N.; Cook, M. J. *J. Mater. Chem.* **2001**, *11*, 434–443 and references cited therein.
12. De la Torre, G.; Torres, T.; Agullo-Lopez, F. *Adv. Mater.* **1997**, *9*, 265–269.
13. Ali, H.; Lier, J. E. *Chem. Rev.* **1999**, *99*, 2379–2450.
14. Kobayashi, N.; Ogata, H.; Nonaka, N.; Luk'yanets, E. A. *Chem. Eur. J.* **2003**, *9*, 5123–5134.
15. Kobayashi, N.; Nakajima, S.; Ogata, H.; Fukuta, T. *Chem. Eur. J.* **2004**, *10*, 6294–6312.
16. Mack, J.; Stillman, M. J.; Kobayashi, N. *Coord. Chem. Rev.* **2007**, *251*, 429–453.
17. Kobayashi, N.; Nakai, K. *Chem. Commun.* **2007**, 4077–4092.
18. Zollinger, H. *Color Chemistry*; VCH: Weinheim, 1987.
19. Herbst, W.; Hunger, K. *Industrielle Organische Pigmente*; VCH: Weinheim, 1987.
20. Yazici, A.; Ates, D.; Bekaroglu, O.; Kobayashi, N. *J. Porphyrins Phthalocyanines* **2006**, *10*, 1140–1144.
21. Ertaş, M.; Gürek, A.; Gül, A.; Belaroğlu, Ö. *J. Chem. Res. (S)* **1988**, *109*, 1157–1167.
22. Koçak, A.; Bekaroğlu, Ö. *Helv. Chim. Acta* **1985**, *68*, 581.
23. Salan, Ü.; Altındal, A.; Bulut, M.; Bekaroğlu, Ö. *Tetrahedron Lett.* **2005**, *46*, 6057–6061.
24. Kobayashi, N.; Osa, T. *Carbohydr. Res.* **1989**, *192*, 147–157.