



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

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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 ¹H 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.

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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 $\lambda \sim 680$ nm with high extinction coefficients $\epsilon > 10^5 \text{ M}^{-1} \text{ cm}^{-1}$. Substituted phthalocyanines, especially those containing electron-donating substituents, exhibit a bathochromic shift of their Q band up to $\lambda \sim 760$ nm.¹⁴ The position and bandwidth of the absorption bands of phthalocyanines can be adjusted

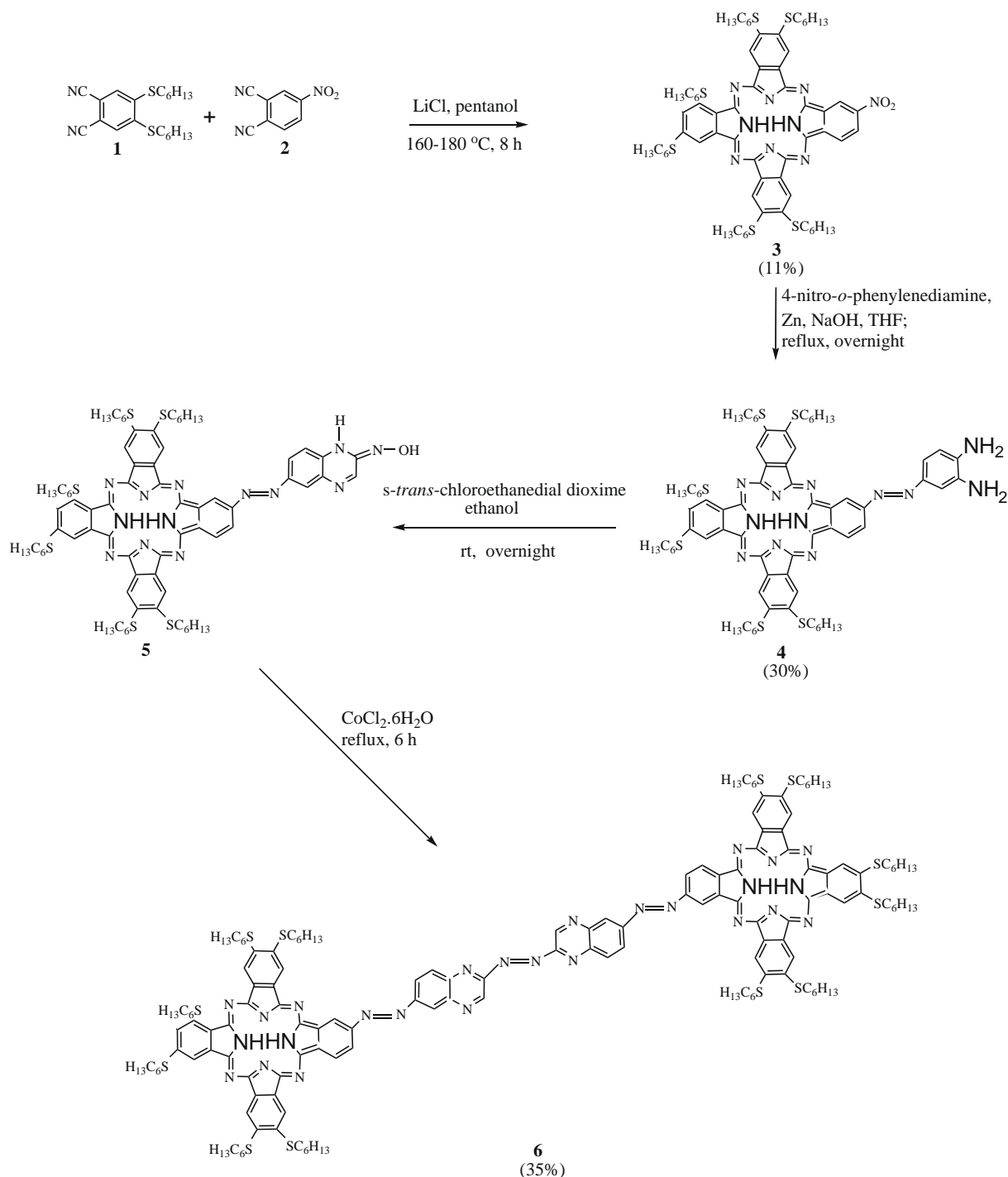
in several ways. On annulation of additional benzene rings to the phthalocyanine moiety, the π -system is extended such that strong red shifts of the Q band are observed for naphthalocyanines (Nc) at $\lambda \sim 740$ –810 nm, and anthracyanines (Ac) at $\lambda \sim 830$ –860 nm.^{15–17} Another method 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 annulated 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 $\text{NH}_2\text{-OH}$.^{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

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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 crystal 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 ni-

tro 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 $2\text{H}_2\text{O}$ 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 azo²⁴).

Synthesis of [(RS)₆PcNO₂] **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

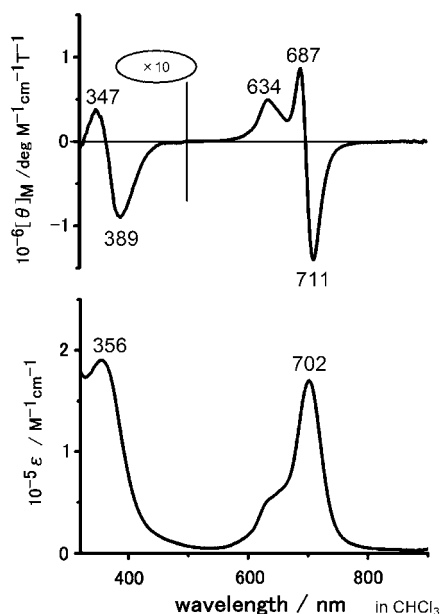


Figure 1. Electronic absorption (bottom) and magnetic circular dichroism (MCD) (top) spectra of compound **6**.

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) $\nu_{\text{max}}/\text{cm}^{-1}$ 730, 820, 840, 1020, 1070, 1110, 1140, 1342, 1381, 1458, 1523, 1595, 1610, 1640, 2854, 2925, 2954, 3060, 3417. Anal Calcd for $\text{C}_{68}\text{H}_{89}\text{N}_9\text{O}_2\text{S}_6$: 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) δ 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^+).

Synthesis of [(RS)₆PcN₂PhA] **4**

A mixture 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) $\nu_{\text{max}}/\text{cm}^{-1}$ 730, 820, 840, 1020, 1070, 1110, 1140, 1340, 1380, 1460, 1610, 1640, 2850, 2920, 2960, 3060, 3387, 3514. Anal Calcd for metal-free phthalocyanine $\text{C}_{74}\text{H}_{96}\text{N}_{12}\text{S}_6$: 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, $\text{DMF-}d_7$) δ 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]₂N₆AQ **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. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (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) $\nu_{\text{max}}/\text{cm}^{-1}$ 756, 840, 928, 1090, 1136, 1473, 1490, 1591, 1610, 2870, 2920, 3053, 3283. Anal Calcd for metal-free bisphthalocyanine $\text{C}_{152}\text{H}_{186}\text{N}_{26}\text{S}_{12}$: 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, $\text{DMF-}d_7$) δ 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^+).

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