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Syntheses of novel unsymmetrically tetrasubstituted phthalocyaninato vanadyl and zinc complexes with a nitro or amino group

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Abstract

Four new unsymmetrical metallophthalocyanines were synthesized. The vanadium trichloride-mediated statistical condensation of 5-nitro-1,3-diiminoisoindoline with 5-*tert*-butyl-1,3-diiminoisoindoline or with 5-neopentoxy-1,3-diiminoisoindoline in anhydrous 2-(*N*,*N*-dimethylamino)ethanol under reflux did not yield the desired 2-nitro-9,16,23-tri(*tert*-butyl)phthalocyaninato or 2-nitro-9,16,23-tri(neopentoxy)phthalocyaninato vanadyl complexes, but yielded the unexpected 2-amino-9,16,23-tri(*tert*-butyl)phthalocyaninato or 2-amino-9,16,23-tri(neopentoxy)phthalocyaninato vanadyl complexes. 2-Nitro-9,16,23-tri(*tert*-butyl)phthalocyaninato vanadyl complex was prepared by a statistical condensation of 4-*tert*-butylphthalonitrile and 4-nitrophthalonitrile in the presence of vanadium trichloride and dry urea at 175–180 °C, while zinc 2-nitro-9,16,23-tri(neopentoxy)phthalocyaninate was synthesized by the zinc acetate-mediated statistical condensation of the two corresponding 1,3-diiminoisoindolines in 2-(*N*,*N*-dimethylamino)ethanol under reflux. All the target unsymmetrical phthalocyanines were separated by common column chromatography and characterized by elemental analysis, IR and ^{1}H-NMR, UV-visible and fast-atom-bombardment mass spectroscopies.

Keywords: Unsymmetrical; Metallophthalocyanine; Synthesis; Vanadium trichloride; Tri(*tert*-butyl)-substituted; Tri(neopentoxy)-substituted

1. Introduction

Phthalocyanines have been used as excellent dyes and pigments for 10s of years. They have also found practical applications in many other fields such as semiconductors, catalysts, chemical sensors, liquid crystals and nonlinear optics [1–3]. To date a great variety of symmetrical or pseudo-symmetrical phthalocyanines have been comprehensively studied [1–3]. However, less knowledge of unsymmetrically substituted phthalocyanines has been accumulated, mainly because they are much more difficult to synthesize and purify. Recent researches have indicated that unsymmetrical

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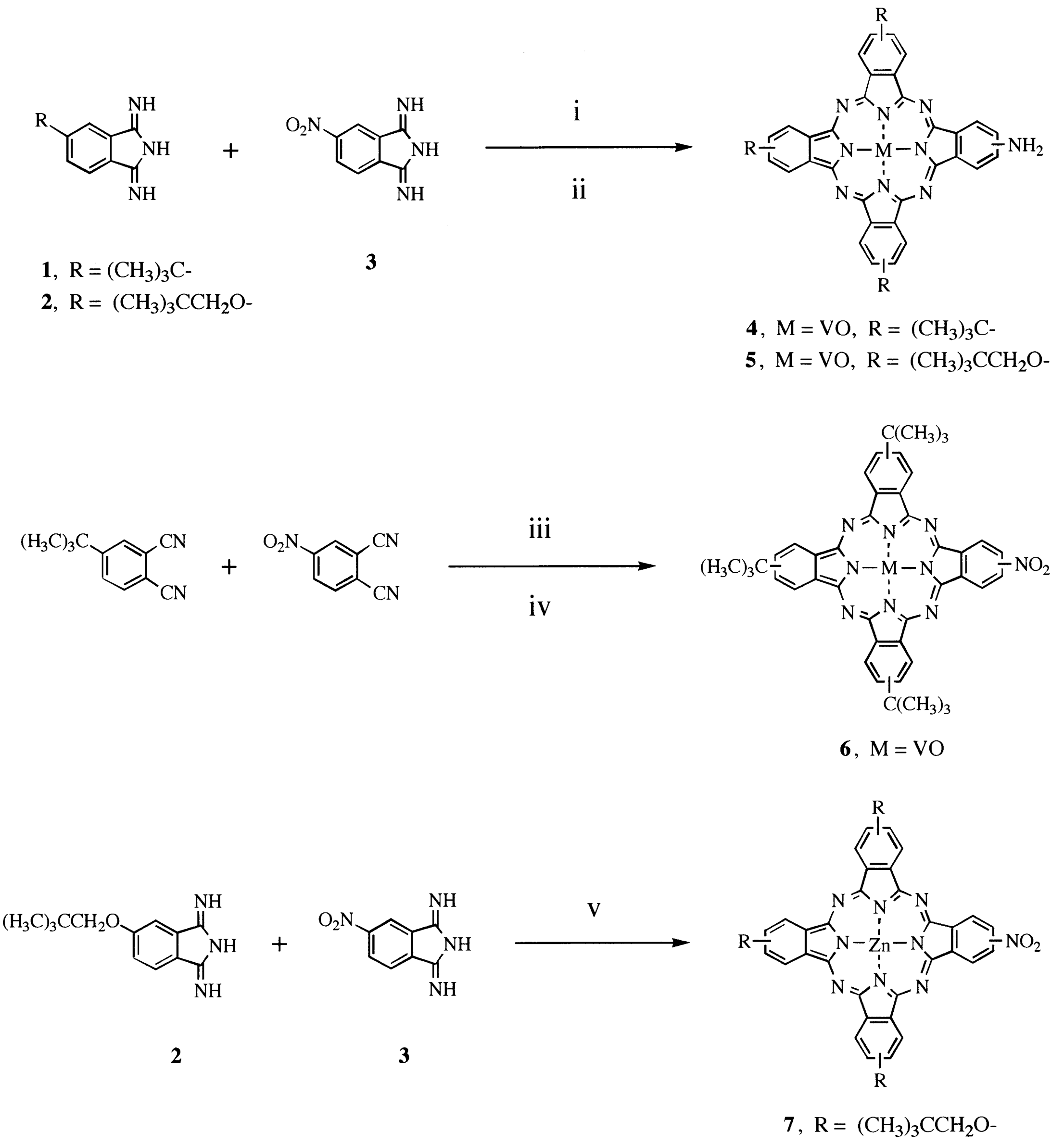
phthalocyanines possess interesting properties in various areas like liquid crystals [4–7], Langmuir–Blodgett (LB) film formation [8–10], photodynamic therapy of cancer [11–13], and second-order nonlinear optics [14]. In particular, monofunctional phthalocyanines with only one reactive functional group such as one sulfo [15,16], carboxyl [16,17], amino [15,16] or hydroxyl [5,18] group are important intermediates for the syntheses of many new mononuclear, binuclear and polynuclear phthalocyanines.

Unsymmetrical phthalocyanines are usually prepared by statistical synthesis employing two differently substituted phthalonitriles or corresponding 1,3-diiminoisoindolines [15,16,19–22], reaction of a polymer-bonded phthalonitrile (or 1,3-diiminoisoindoline) with an excess of another differently substituted phthalonitrile (or 1,3-diiminoisoindoline) followed by liberation of the formed phthalocyanine [23–25], or ring expansion of a so-called subphthalocyanine with a substituted 1,3-diiminoisoindoline [26–30]. Each method has its advantages and disadvantages which will not be discussed here. In general, the statistical condensation route is most commonly used.

Although donor-acceptor substituted phthalocyanines with polarized electron distribution have been theoretically proposed as novel materials for second-order nonlinear optics [31], only a limited number of unsymmetrical push-pull phthalocyanines have been reported in this area so far [14]. During the last decade, we have been engaged in the preparation and study of nonlinear optical properties of unsymmetrically substituted phthalocyanines carrying donors and acceptor groups [32–39]. Previously we have reported the synthesis and second-order nonlinear optical properties of metal-free nitro-tri(*tert*-butyl)phthalocyanine [32–34] and its copper complex [35,36]. Later zinc nitro-tri(*tert*-butyl)phthalocyanine [15], metal-free [40], zinc and copper amino-tri(*tert*-butyl)phthalocyanine [15] have also been reported. As an extension of our previous research, this paper reports the synthesis and characterization of some new tri(*tert*-butyl)- or tri(neopentoxy)-substituted unsymmetrical metalphthalocyanines (see Scheme 1). There are several reasons why we designed and synthesized such unsymmetrical phthalocyanines. First, in order to achieve a molecular polarity of the target phthalocyanines, we introduced three *tert*-butyl or neopentoxy groups on three of the benzene units and a nitro or amino group on the fourth one. In the presence of electron-withdrawing nitro group, three *tert*-butyl or neopentoxy groups serve as donor substituents, whereas they are acceptor substituents in the case of electron-donating amino group. Thus those target unsymmetrical phthalocyanines can be expected to be good candidates for second-order nonlinear optics. Secondly, we focused on the preparation of unsymmetrical vanadylphthalocyanines, because previously we found out the vanadyl phthalocyanine films have large third harmonic susceptibilities $\chi^{(3)}(-3\omega, \omega,\omega,\omega)$ among different metallophthalocyanine films [41,42]. Therefore, the target unsymmetrical phthalocyanines are also expected to be third order nonlinear optical materials. Moreover, the different central metal ions are also very important in understanding the spectral and nonlinear optical properties of phthalocyanines [42], so an unsymmetrical zinc phthalocyanine was also prepared for a comparison. In the present paper, the preparation, characterization and spectral properties of these novel unsymmetrical phthalocyanines are described.

2. Results and discussion

Scheme 1 shows the syntheses of the target unsymmetrical phthalocyanines **4**–**7**. 5-*tert*-Butyl-1,3-diiminoisoindoline (**1**) [43,44], 5-neopentoxy-1,3-diiminoisoindoline (**2**) [45], and 5-nitro-1,3-diiminoisoindoline (**3**) [43] were prepared by the reaction of the corresponding phthalonitrile with ammonia gas in the presence of sodium methoxide in methanol. The vanadium trichloride-mediated statistical condensation of a 3:1 molar ratio of 5-*tert*-butyl-1,3-diiminoisoindoline (**1**) and 5-nitro-1,3-diiminoisoindoline (**3**) in anhydrous 2-(*N*,*N*-dimethylamino)ethanol under reflux for 21 h and the subsequent treatment with water under reflux for 4 h did not yield the desired 2-nitro-9,16,23-tri(*tert*-butyl)phthalocyaninato vanadyl complex (**6**), but yielded the unexpected 2-amino-9,16,23-tri(*tert*-butyl)phthalocyaninato vanadyl complex



Scheme 1. Reagents and conditions: (i) vanadium trichloride, 2-(*N*,*N*-dimethylamino)ethanol, reflux, 16–21 h; (ii) water, reflux, 3–4 h; (iii) vanadium trichloride, urea, 175–180 °C, 4 h; (iv) water, reflux, 2 h; (v) zinc acetate, 2-(*N*,*N*-dimethylamino)ethanol, reflux, 16 h.

(**4**) in 16.5% yield after purification. This fact may be explained by the strong reducing ability of an excess of vanadium trichloride in a protic solvent. Similarly, the vanadium trichloride-mediated statistical condensation of a 3:1 molar ratio of 5-neopentoxy-1,3-diiminoisoindoline (**2**) and 5-nitro-1,3-diiminoisoindoline (**3**) in anhydrous 2-(*N*,*N*-dimethylamino)ethanol under reflux for 16 h and the subsequent treatment with water under reflux for 3 h produced the unexpected 2-amino-9,16,23-

tri(neopentoxy)phthalocyaninato vanadyl complex (**5**) instead of the desired 2-nitro-9,16,23-tri (neopentoxy)phthalocyaninato vanadyl complex. After purification, compound **5** was obtained in 10.5% yield.

The desired unsymmetrical vanadylphthalocyanine **6** was prepared by a different route. The statistical condensation of a 3:1 molar ratio of 4-*tert*-butylphthalonitrile and 4-nitrophthalonitrile in the presence of an excess of vanadium trichloride and dry urea at 175–180 °C for 4 h and the subsequent treatment with water under reflux for 2 h yielded a mixture of 2,9,16,23-tetra(*tert*-butyl)phthalocyaninato vanadyl complex, **6** and other statistical products. The unsymmetrical vanadylphthalocyanine **6** was separated by common column chromatography on silica gel using different solvents as eluents and obtained in 9.2% yield after soxhlet extraction with methanol. Nevertheless, zinc 2-nitro-9,16,23-tri(neopentoxy)phthalocyaninate (**7**) was synthesized by the zinc acetate-mediated statistical condensation of a 3:1 molar ratio of 5-neopentoxy-1,3-diiminoisoindoline (**2**) and 5-nitro-1,3-diiminoisoindoline (**3**) in anhydrous 2-(*N*,*N*-dimethylamino)ethanol under reflux for 16 h and obtained in 27.4% yield after purification.

We have also tried to synthesize 2-nitro-9,16,23-tri(neopentoxy)phthalocyaninato vanadyl complex by the statistical condensation of a 3:1 molar ratio of 4-neopentoxyphthalonitrile and 4-nitrophthalonitrile in the presence of an excess of vanadium trichloride and dry urea at 175–180 °C, however, we have not succeeded in the separation of the desired compound, because of the little difference in solubility between the desired unsymmetrical vanadylphthalocyanine and other statistical product mixtures.

All final products were obtained as pure samples after numerous purifications via column chromatography on silica gel and then by recrystallization. Unsymmetrically tetrasubstituted metallophthalo cyanines **4**–**7** were prepared as structural isomer mixtures. They were characterized by ^{1}H-NMR, IR and fast-atom-bombardment MS spectroscopic methods, as well as by elemental analysis. All the analytical and spectral data are consistent with the predicted structures. It should be noted that the ^{1}H-NMR spectra of unsymmetrical vanadyl phthalocyanines **4**–**6** are extremely broad because of the presence of the paramagnetic vanadium atom and the constitutional isomers [46]. Owing to the broad ^{1}H-NMR spectra, the aromatic protons of those unsymmetrical vanadylphthalocyanines can not be expected to be clearly resolved. Attempts to record the well-resolved ^{13}C-NMR spectra of those unsymmetrical vanadylphthalocyanines were not successful. On the other hand, the ^{1}H-NMR spectrum of unsymmetrical zincphthalocyanine **7** is better resolved than those of unsymmetrical vanadylphthalocyanines due to the diamagnetism of zinc atom.

All tri(*tert*-butyl)- or tri(neopentoxy)-substituted unsymmetrical phthalocyanines **4**, **5**, **6** and **7** show good solubility in common organic solvents such as dichloromethane, chloroform, diethyl ether and tetrahydrofuran. The unsymmetrical zincphthalocyanine **7** also shows good solubility in more polar solvents like ethyl acetate and acetone.

Figs. 1 and 2 show the UV–visible absorption spectra of compounds **4**, **5**, **6** and **7** in 1,4-dioxane, respectively. These new unsymmetrical metallophthalocyanines show the typical absorptions in the B-band region of around 350 nm, however, their Q-band absorptions of around 700 nm are quite different. The unsymmetrical phthalocyanines **4** and **5** show a Q-band absorption without splitting,

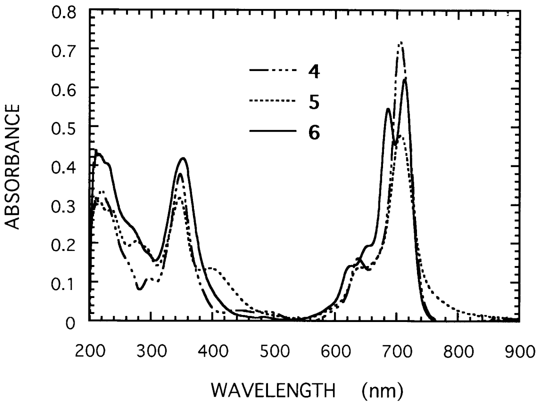


Fig. 1. Ultraviolet–visible absorption spectra of vanadyl 2-amino-9,16,23-tri(*tert*-butyl)phthalocyaninate **4** (5.30×10^{-6} M), vanadyl 2-amino-9,16,23-tri(neopentoxy)phthalocyaninate **5** (9.29×10^{-6} M) and vanadyl 2-nitro-9,16,23-tri(*tert*-butyl)-phthalocyaninate **6** (5.13×10^{-6} M) in 1,4-dioxane.

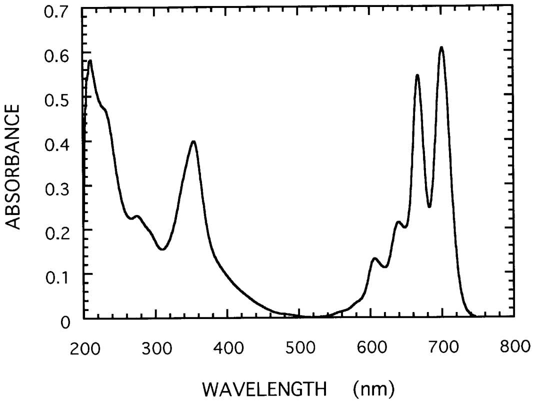


Fig. 2. Ultraviolet–visible absorption spectrum of zinc 2-nitro-9,16,23-tri(neopentoxy)phthalocyaninate 7 (4.58×10^{-6} M) in 1,4-dioxane.

while the corresponding metallophthalocyanines **6** and **7** show a splitted Q-band absorption. The unusual spectroscopic behavior of compounds **6** and **7** may be attributed to the influence of peripheral donor and acceptor groups. The substitution of the phthalocyanine rings of compounds **6** and **7** with one electron-withdrawing nitro group and three electron-donating *tert*-butyl or neopentoxy groups perturbs the excited state energy levels of the molecules. This kind of perturbation leads to a splitted Q-band absorption in their UV–visible absorption spectra. On the other hand, the molecules of compounds **4** and **5** do not possess strong *donor→acceptor* dipole moments, so their Q-band absorptions were not significantly perturbed by peripheral substituents. However, compounds **4** and **5** show weak absorptions in the window region between 450 and 600 nm. These absorptions might be attributed to the intermolecular aggregation that is caused by the intermolecular hydrogen bonding between the amino groups and the oxygen atoms of the central vanadyl groups.

In summary, tri(*tert*-butyl)- or tri(neopentoxy)-substituted unsymmetrical metallophthalocyanines **4**, **5**, **6** and **7** were synthesized by a statistical condensation route. The vanadium trichloride-mediated statistical condensation in anhydrous 2-(*N*,*N*-dimethylamino)ethanol resulted in the reduction of the peripheral nitro group of the desired unsymmetrical vanadylphthaloacyanine. All the target unsymmetrical phthalocyanines were separated by common column chromatography and fully characterized. Their solubility and spectral properties in a certain solvent depends strongly not only on the peripheral substituents but also on the central metal ion. Second harmonic generation of spin-coated thin films of poly(methyl methacrylate) doped with compound **6** or **7** was observed after electric poling at 110 °C for 30 min at a fundamental wavelength of 1.064 μm. The detailed results of their nonlinear optical and other physical and chemical properties will be published elsewhere.

3. Experimental

IR spectra were recorded on a Shimadzu FTIR-4100 Fourier transform infrared spectrophotometer, using potassium bromide pellets. ^{1}H-NMR and ^{13}C-NMR spectra with tetramethylsilane as internal standard were recorded on a Jeol JNM-EX270 Fourier transform nuclear magnetic resonance spectrometer (270 MHz). Electron ionization mass spectra were recorded on a Hitachi M-80A mass spectrometer. Fast-atom-bombardment mass spectra (FAB–MS) with *m*-nitrobenzyl alcohol as a matrix were recorded on a Jeol JMS-HX110 mass spectrometer. Elemental analyses were carried out by the Microanalysis Laboratory of RIKEN (The Institute of Physical and Chemical Research). UV-visible absorption spectra were measured by a Shimadzu UV-3100 spectrophotometer in a quartz cell of path length 10 mm. Column chromatography was performed using silica gel of particle size 63–200 μm which was produced by Merck Company.

4-*tert*-Butylphthalonitrile (97%) and 4-nitrophthalonitrile (98%) were purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. The solvents for UV–visible absorption measurement were of spectral grade and used without further purification. Other chemicals were of reagent grade and used as supplied.

5-*tert*-Butyl-1,3-diiminoisoindoline (**1**) [43,44], 5-neopentoxy-1,3-diiminoisoindoline (**2**) [45] and 5-nitro-1,3-diiminoisoindoline (**3**) [43] were prepared following methods described in the references.

3.1. Vanadyl 2-amino-9,16,23-tri(tert-butyl)phthalocyaninate (4)

A typical procedure: In a 100-ml round-bottomed three-neck flask equipped with a nitrogen gas inlet, a reflux condenser and a magnetic stirring bar, were placed a mixture of 5-*tert*-butyl-1,3-diiminoisoindoline **1** (604 mg, 3.0 mmol) and 5-nitro-1,3-diiminoisoindoline **3** (190 mg, 1.0 mmol). To this mixture, under dry nitrogen gas, were added anhydrous vanadium trichloride (403 mg, 2.56 mmol) and anhydrous 2-(*N*,*N*-dimethylamino)ethanol (6 ml). The resulting mixture was stirred at room temperature for 15 min and then refluxed for 21 h in an atmosphere of dry nitrogen gas. A dark blue mixture was formed in the process of heating. The reaction mixture was cooled, then refluxed with 40 ml of water for 4 h, and finally poured into 100 ml of water. The resulting dark-blue precipitate was suction filtered and washed with water until the filtrate became clear, then washed with methanol to remove yellow-blue by-product, and air-dried. The resulting residue was purified by column chromatography on silica gel with toluene/hexane (2:1, volume ratio) as the first eluent to give the first fraction of 2,9,16,23-tetra(*tert*-butyl)vanadylphthalocyanine (141 mg, 23.4%), followed by eluting with toluene to remove the pale blue impurities, then with toluene/tetrahydrofuran (50:1, volume ratio) as the third eluent to give a green-blue fraction which was checked by FAB–MS to be **4**. The crude unsymmetrical product was further purified by column chromatography on silica gel once with dichloromethane as the first eluent to remove pale-blue impurities, and then with chloroform as the second eluent to give a dark blue solid, 126 mg (16.5%). IR: ν_{max}/cm^{-1} 3374, 3229 (NH_2), 3065 (=CH), 2957, 2902, 2863 (CH_3), 1611 (C=C ring), 1504, 1485, 1465 (C=C ring), 1394, 1362 (CH_3), 1331, 1281, 1255 (C–C), 1200, 1147, 1087 (ring), 1047, 1003, 930, 830, 754 (CH_3). ^{1}H-NMR ($CDCl_3$): δ 1.20–2.30 (*m*, 27H, 9×CH_3), 4.25–4.46 (*m*, NH_2), 7.50–9.60 (*br*, H_{arom}). FAB–MS: *m*/*z* (%) 764.2 (M^+ +1, 53.8), 763.2 (M^+, 100.0), 747.2 (M^+ - CH_4, 29.3). UV–visible (1,4-dioxane): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 705.0 (5.14), 637.5 (4.48), 488.0 (3.66), 443.5 (3.72), 347.5 (4.85), 297.5 (4.32), 220.5 (4.81). Anal. calcd. for $C_{44}H_{41}N_9OV$ (762.81): C, 69.28; H, 5.42; N, 16.53. Found: C, 69.42; H, 5.70; N, 16.11.

3.2. Vanadyl 2-amino-9,16,23-tri(neopentoxy)-phthalocyaninate (5)

Quantities: 5-neopentoxy-1,3-diiminoisoindoline **2** (231 mg, 1.0 mmol), 5-nitro-1,3-diiminoisoindoline **3** (63 mg, 0.33 mmol), anhydrous vanadium trichloride (105 mg, 0.67 mmol) and anhydrous 2-(*N*,*N*-dimethylamino)ethanol (2 ml); reaction conditions: room temperature, 15 min; reflux, 16 h; subsequent reflux with 10 ml of water, 3 h. The experimental procedure was as described for the preparation of compound **4**. The crude product was purified by column chromatography on silica gel using toluene/hexane (2:1, volume ratio) and toluene as the eluents to give the first fraction of 2,9,16,23-tetra(neopentoxy)vanadylphthalocyanine (70 mg, 30.3%), followed by eluting with toluene/tetrahydrofuran (50:1, volume ratio) to give a yellow-green fraction of **5**. The crude unsymmetrical product was further purified by column chromatography on silica gel once with hexane/tetrahydrofuran (3:1–1:1, volume ratio) as an eluent, and then once with chloroform and chloroform/tetrahydrofuran (10:1, volume ratio) as the eluents to give a dark green solid. The final purification was achieved by column chromatography on silica gel with toluene as the first eluent and toluene/tetrahydrofuran (10:1, volume ratio) as the second eluent to give the product as a dark green solid, 31 mg (10.5%). IR: ν_{max}/cm^{-1} 3385, 3222 (NH_2), 3065 (=CH), 2955 (CH_3), 2925 (CH_2), 2869 (CH_3), 1609 (C=C ring), 1504, 1491 (C=C ring), 1473, 1398, 1367 ($C(CH_3)_3$), 1343, 1286, 1239 (C–C), 1129, 1087 (ring), 1057, 1009, 949, 876, 853, 825, 753, 737 (CH_2). ^{1}H-NMR ($CDCl_3$): δ 1.10–1.60 (*m*, 27H, 9×CH_3), 3.80–4.60 (*br m*, 6H, 3×OCH_2), 4.30 (*m*, NH_2), 6.90–8.50 (*br*, H_{arom}). FAB–MS: *m*/*z* (%) 854.3 (M^+ +1, 56.3), 853.3 (M^+, 100.0), 852.3 (M^+-1, 57.1), 783.2 (M^+–C_5H_{10}, 18.3). UV–visible (1,4-dioxane): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 706.5 (4.71), 641.5 (4.17), 397.0 (4.16), 347.0 (4.53), 276.5 (4.35), 235.0 (4.49), 210.0 (4.53). Anal. calcd. for $C_{47}H_{47}N_9O_4V$ (852.91): C, 66.19; H, 5.55; N, 14.79. Found: C, 66.86; H, 6.15; N, 14.21.

*3.3. Vanadyl 2-nitro-9,16,23-tri(*tert*-butyl)phthalocyaninate (**6**)*

Quantities: 4-*tert*-butylphthalonitrile (2.21 g, 12.0 mmol), 4-nitrophthalonitrile (6.93 g, 4.0 mmol), anhydrous vanadium trichloride (1.44 g, 9.15 mmol) and dry urea (15 g); reaction conditions: 110–120 °C, 30 min; 175–180 °C, 4 h; subsequent reflux with 150 ml of water, 2 h. The experimental procedure was as described for the preparation of compound **4**. The crude product was extracted with dichloromethane through the dissolution-filtration process, and the extract solution was condensed. The resulting black-blue residue was purified by column chromatography on silica gel with dichloromethane as an eluent to give the first dark blue fraction consisting of both symmetrical and unsymmetrical products. This product was purified again by column chromatography on silica gel with toluene/hexane (4:1–3:2, volume ratio) as an eluent to give the first fraction of 2,9,16,23-tetra(*tert*-butyl)vanadylphthalocyanine, followed by eluting with toluene to give a blue fraction consisting largely of **6**. The crude unsymmetrical product was further purified by column chromatography on silica gel with 3:2 and 2:1 (volume ratio) dichloromethane/hexane as the eluents to give a dark blue solid of 6. The product was soxhlet extracted with methanol for 7 h to yield a dark blue solid, 291 mg (9.2%). IR: ν_{max}/cm^{-1} 3072 (=CH), 2958, 2902, 2863 (CH_3), 1613 (C=C ring), 1526 (NO_2), 1498, 1485 (C=C ring), 1394, 1365 ($C(CH_3)_3$), 1333 (NO_2), 1282, 1255 (C–C), 1201, 1153, 1077 (ring), 1007, 930, 833, 759 (CH_3), 731. ^{1}H-NMR ($CDCl_3$): δ 1.40–2.40 (*m*, 27H, 9×CH_3), 7.50–9.70 (*br*, H_{arom}). FAB–MS: *m*/*z* (%) 793.2 (M^+, 100.0), 777.2 (M^+–CH_4, 45.5), 762.2 (M^+–CH_4–CH_3, 20.0), 747.2 (M^+-CH_4–C_2H_6, 25.4). UV–visible (1,4-dioxane): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 712.5 (5.08), 685.5 (5.03), 484.0 (3.29), 352.5 (4.91), 210.5 (4.93). Anal. calcd. for $C_{44}H_{39}N_9O_3V$ (792.79): C, 66.66; H, 4.96; N, 15.90. Found: C, 66.91; H, 5.18; N, 15.48.

*3.4. Zinc 2-nitro-9,16,23-tri(neopentoxy)phthalocyaninate (**7**)*

Quantities: 5-neopentoxy-1,3-diiminoisoindoline **2** (231 mg, 1.0 mmol), 5-nitro-1,3-diiminoisoindoline **3** (63 mg, 0.33 mmol), anhydrous zinc acetate (95%, 125 mg, 0.65 mmol) and anhydrous 2-(*N*,*N*-dimethylamino)ethanol (2 ml); reaction conditions: room temperature, 15 min; reflux, 16 h. The experimental procedure was as described for the preparation of compound **4**. The crude product was extracted with acetone through the dissolution–filtration process, and the extract solution was condensed under reduced pressure. The resulting dark blue residue was purified by column chromatography on silica gel with hexane/ethyl acetate (6:1–5:1, volume ratio) as an eluent to give the first fraction of symmetrical 2,9,16,23-tetra (neopentoxy)zincphthalocyanine, and the second blue fraction consisting largely of **7**. The crude unsymmetrical product was further purified by column chromatography on silica gel twice with hexane/ethyl acetate (8:1–5:1, volume ratio) as an eluent to give a shining blue solid, 80 mg (27.4%). IR: ν_{max}/cm^{-1} 3072 (=CH), 2955 (CH_3), 2928 (CH_2), 2870 (CH_3), 1609 (C=C ring), 1523, 1486 (C=C ring), 1475, 1395, 1365 ($C(CH_3)_3$), 1336, 1283, 1237 (C–C), 1123, 1086 (ring), 1055, 1011, 935, 874, 854, 826, 742, 726 (CH_2). ^{1}H-NMR (CD_3COCD_3): δ 1.15–1.30 (*m*, 27H, 9×CH_3), 3.45–4.20 (*br m*, 6H, 3×OCH_2), 6.45–8.15 (*br*, 12H, H_{arom}). FAB–MS: *m*/*z* (%) 879.3 (M^+-1, 76.1), 880.3 (M^+, 100.0, ^{64}Zn-7 requires M^+ 879.93), 881.3 (M^+ +1, 94.0), 882.3 (M^+, 78.9, ^{66}Zn-7), 883.3 (M^+ +1/^{66}Zn-7, M^+/^{67}Zn-7, 65.9), 884.3 (M^+, 50.8)/885.3 (M^+ +1, 27.2) (^{68}Zn-7), 886.3 (M^+, 12.0, ^{70}Zn-7). UV–visible (1,4-dioxane): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 701.0 (5.12), 667.5 (5.07), 640.0 (4.67), 606.0 (4.46), 354.0 (4.94), 275.0 (4.70), 211.5 (5.10). Anal. calcd. for $C_{47}H_{45}N_9O_5Zn$ (881.32): C, 64.05; H, 5.15; N, 14.30. Found: C, 64.07; H, 5.17; N, 14.07.

References

[1] Moser FH, Thomas AL. The phthalocyanines, vols. 1 and 2. Boca Raton, FL: CRC Press, 1983.

[2] Leznoff CC, Lever ABP, editors. Phthalocyanines, properties and applications, vols. 1–4. New York, Weinheim, Cambridge: VCH Publishers, 1996.
[3] Hanack M, Lang M. Advan Mater 1994;6:819.
[4] Piechocki C, Simon J. J Chem Soc Chem Commun 1985: 259.
[5] Van der Pol JF, Neeleman E, Nolte RJM, Zwikker ZW, Drenth W. Makromol Chem 1989;190:2727.
[6] Bryant GC, Cook MJ, Haslam SD, Richardson RM, Ryan TG, Thorne AJ. J Mater Chem 1994;4:209.
[7] Clarkson GJ, McKown NB, Treacher KE. J Chem Soc Perkin Trans 1 1995;1817
[8] Cook MJ, Daniel MF, Harrison KJ, McKeown NB, Thomson AJ. J Chem Soc Chem Commun 1987:1148.
[9] Cook MJ, McKeown NB, Simmons JM, Thomson AJ, Daniel MF, Harrison KJ, Richardson RM, Roser SJ. J Mater Chem 1991;1:121.
[10] Poynter RH, Cook MJ, Chesters MA, Slater DA, McMurdo J, Welford K. Thin Solid Films 1994; 243:346.
[11] Rosenthal I. Photochem Photobiol 1991;53:859.
[12] Winkelman JW, Arad D, Kimel S. J Photochem Photobiol B Biol 1993;18:181.
[13] Morgan J, Lottman H, Abbou CC, Chopin DK. Photochem Photobiol 1994;60:486.
[14] De la Torre G, Vázquez P, Agulló-López F, Torres T. J Mater Chem 1998;8:1671.
[15] Kudrevish SV, Ali H, van Lier JE. J Chem Soc Perkin Trans 1 1994;2767
[16] Kliesh H, Weitemeyer A, Müller S, Wöhrle D. Liebigs Ann Chem 1995:1269.
[17] Hirth A, Sobbi AK, Wöhrle D. J Porphyrins Phthalocyanines 1997;1:275.
[18] Bryant GC, Cook MJ, Ryan TG, Thorne AJ. Tetrahedron 1996;52:809.
[19] Schmid G, Sommerauer M, Geyer M, Hanack M. In: Leznoff CC, Lever ABP, editors. Phthalocyanines, properties and applications, vol. 4. New York, Weinheim, Cambridge: VCH Publishers, 1996. p. 1–18.
[20] De la Torre G, Torres T. J Porphyrins Phthalocyanines 1997;1:221.
[21] Ding X, Shen S, Zhou Q, Xu H. Dyes and Pigments 1999; 40:187.
[22] Makhseed S, Cook A, McKeown NB. Chem Commun 1999:419.
[23] Leznoff CC, Hall TW. Tetrahedron Lett 1982;23:3023.
[24] Wöhrle D, Krawczyk G. Polym Bull 1986;15:193.
[25] Leznoff CC, Svirskaya PI, Khouw B, Cerny RL, Seymour P, Lever ABP. J Org Chem 1991;56:82.
[26] Geyer M, Plenzig F, Rauschnabel J, Hanack M, del Rey B, Sastre A, Torres T. Synthesis 1996:1139.
[27] Kobayashi N, Kondo R, Nakajima S, Osa T. J Am Chem Soc 1990;112:9640.
[28] Dabak S, Gül A, Bekaroglu Ö. Chem Ber 1994;127:2009.
[29] Weitemeyer A, Kliesh H, Wöhrle D. J Org Chem 1995; 60:4900.
[30] Kudrevich SV, Gilbert S, van Lier JE. J Org Chem 1996; 61:5706.
[31] Li DQ, Ratner MA, Marks TJ. J Am Chem Soc 1988; 110:1707.
[32] Liu Y, Zhu D, Wada T, Yamada A, Sasabe H. J Heterocyclic Chem 1994;31:1017.
[33] Liu Y, Xu Y, Zhu D, Wada T, Sasabe H, Liu L, Wang W, Thin Solid Films 1994;244:943.
[34] Liu Y, Xu Y, Zhu D, Wada T, Sasabe H, Zhao X, Xie X. J Phys Chem. 1995;99:6957.
[35] Liu YQ, Zhu DB. Synth Met 1995;71:1853.
[36] Liu Y, Xu Y, Zhu D, Zhao X. Thin Solid Films 1996; 289:282.
[37] Tian M, Wada T, Sasabe H. J Heterocyclic Chem 1997; 34:171.
[38] Tian M, Wada T, Kimura-Suda H, Sasabe H. Mol Cryst Liq Cryst 1997;294:271.
[39] Tian M, Wada T, Kimura-Suda H, Sasabe H. J Mater Chem 1997;7:861.
[40] Liu SG, Liu YQ, Xu Y, Zhu DB, Zhao X, Yu AC, Zhao XS. Langmuir 1998;14:690.
[41] Hosoda M, Wada T, Yamada A, Garito AF, Sasabe H. Jpn J Appl Phys 1991;30:L1486.
[42] Nalwa HS, Shirk JS. In: Leznoff CC, Lever ABP, editors. Phthalocyanines, properties and applications, vol. 4. New York, Weinheim, Cambridge: VCH Publishers, 1996. p. 79–181.
[43] Brach PJ, Grammatica SJ, Ossanna OA, Weinberger L. J Heterocyclic Chem 1970;7:1403.
[44] Hanack M, Metz J, Pawlowski G. Chem Ber 1982; 115:2836.
[45] Marcuccio SM, Svirskaya PI, Greenberg S, Lever ABP, Leznoff CC, Tomer KB. Can J Chem 1985;63:623.
[46] Law KY. Inorg Chem 1985;24:1778.