Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 77 (2008) 570–577
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Peripherally alpha(α)-substituted novel phthalocyanines

Mahmut Durmuş [a], Mehmet Menaf Ayhan [a], Ayşe Gül Gürek [a], Vefa Ahsen [a,b,*]

[a] Gebze Institute of Technology, Department of Chemistry, P.O. Box 141, Gebze 41400, Kocaeli, Turkey
[b] TUBITAK – Marmara Research Centre, Materials Institute, P.O. Box 21, Gebze 41470, Kocaeli, Turkey

Received 4 June 2007; received in revised form 1 August 2007; accepted 9 August 2007
Available online 2 September 2007

Abstract

Two novel, nickel phthalocyanines bearing peripherally alpha(α)-substituents, namely octa(1,3-bis(dodecyloxy)propan-2-ol) and octa(1,3-bis[2-(2-ethoxyethoxy)ethoxy]propan-2-ol) were synthesized by cyclotetramerisation of the corresponding nitriles. At room temperature, the peripherally α-substituted Ni(II) phthalocyanine complexes exhibited a relatively viscous liquid state; their spectroscopic properties and aggregation behaviour were investigated in different solvents and at different concentrations in chloroform. The two compounds showed Q-bands in the near-IR region of the electronic spectrum and did not aggregate in all solvents and under a wide range of concentrations in chloroform.

Keywords: Liquid phthalocyanine; Nickel phthalocyanine; Synthesis; Non-aggregation; Peripherally (α) substitution

1. Introduction

Phthalocyanines, a family of aromatic macrocycles based on an extensive delocalized 18-π electron system, are known not only as classical dyes in practical use but also as modern functional materials in scientific research [1,2]. There has been growing interest in the use of phthalocyanines in a variety of new high technology fields including semiconductor devices [3,4], Langmuir–Blodgett films [5], electrochromic display devices [6], gas sensors [7–9], liquid crystals [10], non-linear optics [11] and various catalytic processes [12]. The attractive characteristics of phthalocyanines in these applications arise from their great diversity, thermal and chemical stability, redox versatility and intense colour. However, their insolubility in common organic solvents causes difficulties for many applications, rendering the syntheses of soluble derivatives an important task. Phthalocyanine derivatives of increased solubility have been obtained using substituents such as alkyl, alkoxy, alkylthio chains and bulky groups. Whereas, peripheral substitution with bulky groups or long alkyl, alkoxy or alkylthio chains leads to phthalocyanine products soluble in apolar solvents, sulfo or quaternary ammonium groups enhance solubility in aqueous media over a wide pH range of aqueous solutions. The size and the nature of the substituents are not the only criteria for the solubility of the substituted phthalocyanines; the change in symmetry caused by the substituents is also a key point. Generally, tetra-substituted phthalocyanines are more soluble than the symmetrically octa-substituted ones due to the formation of four positional isomers in the case of tetra-substituted analogues [13–15]. According to their substituent positions, two types of substituted macrocycles which show significant differences in their chemical and physical behaviour can be distinguished. Substitution at the more sterically crowded alpha(α) position show reduced aggregation tendencies more than substitution at β position [16,17]. It has been established that non-aggregated phthalocyanines are extremely important. Molecular aggregation of phthalocyanines, which is an intrinsic property of these large π-conjugated systems, provides an efficient non-radiative energy relaxation pathway. The nature of peripheral substituents influences the degree of aggregation, with bulky groups reducing this phenomenon [18].

Addition of groups to the peripheral positions of MPc complexes is known to influence the properties of the MPc to

* Corresponding author. Gebze Institute of Technology, Department of Chemistry, P.O. Box 141, Gebze 41400, Kocaeli, Turkey. Tel.: +90 262 605 31 06; fax: +90 262 653 84 90.
E-mail address: ahsen@gyte.edu.tr (V. Ahsen).

0143-7208/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2007.08.010

a large degree [19–23]. For instance, the peripheral substituents increase the distance between the planar macrocycle rings carrying the π-electrons thereby making solvation easier. Solvents also affect aggregation of phthalocyanine complexes. Organic solvents are known to reduce aggregation whereas aqueous medium results in highly aggregated complexes. However, many phthalocyanine complexes remain aggregated even in non-aqueous solutions [24–27]. Aromatic solvents such as benzene or toluene are known to give narrow Q-bands for phthalocyanines whereas broadening is observed in other non-aromatic solvents [28].

Morphologically, phthalocyanine compounds have traditionally been viewed as materials that have relatively high degrees of order in both the solid and the liquid crystalline states and that usually display melting points significantly above room temperature. While these morphologies are very interesting for scientific study and are useful in some applications, the existence of small ordered domains that mainly cause optical scattering can be an adversity. For applications requiring optical transparency and thin film processing, even a small amount of scattering can be detrimental. Therefore, liquid phthalocyanine derivatives have better properties than solid and liquid crystalline phthalocyanine derivatives. For example, liquid phthalocyanine derivatives are known to exhibit better non-linear optical properties [29]. Although there are a lot of studies about solid and liquid crystalline phthalocyanines, only a few studies described so far about liquid phthalocyanines [29–31].

Phthalocyanine derivatives possessing substituents in the 1,4,8,11,15,18,22,25 (peripherally α-substituted) sites are attractive for a number of reasons. First, alkyl and alkoxy substituents in these positions give rise to excellent solubility in organic solvents. Second, the phthalocyanines are produced as a single isomer due to the symmetry of the precursor. In addition, phthalocyanines with *n*-alkyl or *n*-alkyloxymethyl side chains longer than pentyl are liquid crystalline [32–34]. However, substituents, particularly when located at the peripherally α (1,4,8,11,15,18,22,25) sites of the macrocycle, can show a much more marked effect leading to significant bathochromic shifts. Indeed, examples of near infrared absorbing phthalocyanine dyes include derivatives bearing peripherally α substituents linked through oxygen atoms (λ_{max} ca. 760 nm) [35], and sulfur ($\lambda_{max} > 800$ nm) [36].

In this work, we have synthesized peripherally alpha(α) 1,3-bis(dodecyloxy)propan-2-ol and 1,3-bis[2-(2-ethoxyethoxy) ethoxy]propan-2-ol octa-substituted new liquid nickel phthalocyanine compounds (**5a** and **5b**) for the first time. We report on the effects of substituents on the spectroscopic and aggregation properties of nickel phthalocyanine derivatives in different solvents (toluene, dichloromethane, chloroform, THF, and DMSO) and different concentrations in chloroform.

2. Experimental

2.1. Materials

Pyridine, *n*-hexanol, 1-propanol, dimethylsulphoxide (DMSO), methanol, hexane, chloroform ($CHCl_3$), dichloromethane (DCM), tetrahydrofuran (THF), acetone, ethanol and dimethylformamide (DMF) were dried as described in Perrin and Armarego [37] before use. Dodecanol, 2,3-dicyanohydroquinone, K_2CO_3, NaOH, epichlorohydrin, 2(2-ethoxyethoxy)ethanol, nickel(II) chloride, $CDCl_3$, toluene-4-sulfonyl chloride and 1,8-diazabicyclo[5.4.0] undec-7-ene were purchased from Fluka. Column chromatography was performed on silica gel 60 (Merck, 0.040–0.063 mm) and preparative thin layer chromatography was performed on silica gel 60 P F_{254}. 1,3-Bis(dodecyloxy)propan-2-ol (**1a**) [38], 1,3-bis (dodecyloxy)propan-2-tosylate (**2a**) [38], 1,3-bis[2-(2-ethoxyethoxy)ethoxy]propan-2-ol (**1b**) [39] and 1,3-bis[2-(2-ethoxyethoxy) ethoxy] propan-2-tosylate(**2b**) [39] were synthesized and purified according to literature procedures.

2.2. Equipment

Elemental analyses were obtained with a Thermo Finnigan Flash 1112 Instrument. Infrared spectra in sodium chloride cells for oily compounds or KBr pellets for solid compounds were recorded on a Bio-Rad FTS 175C FT-IR spectrophotometer. Optical spectra in the UV–vis region were recorded with a Schimadzu 2001 UV Pc spectrophotometer using 1 cm path length cuvettes at room temperature. The mass spectra were acquired on a Bruker Daltonics (Bremen,Germany) MicrO-TOF mass spectrometer equipped with an orthogonal electrospray ionization (ESI) source. The instrument was operated in positive ion mode using a *m*/*z* range of 50–800. The capillary voltage of the ion source was set at 6000 V and the capillary exit at 190 V. The nebulizer gas flow was 3 bar and drying gas flow 10 L/min. The drying temperature was set at 200 °C. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions on a Varian 500 MHz spectrometer.

2.3. Synthesis

2.3.1. 3,6-Bis{2-(dodecyloxy)-1-[(dodecyloxy) methyl]ethoxy}phthalonitrile (4a)

Under nitrogen stream, 1,3-bis(dodecyloxy)propan-2-tosylate(**2a**) (7.97 g, 13.7 mmol) and 2,3-dicyanohydroquinone (**3**) (1.0 g, 6.24 mmol) were dissolved in dry DMF (30 mL) and the mixture stirred at room temperature for 15 min. Thereafter, finely ground K_2CO_3 (5.6 g, 41.1 mmol) was added portionwise over a period of 2 h and the reaction mixture left to stir for a further 48 h at 70 °C. The reaction was worked up by filtering the undissolved potassium carbonate, concentrating at reduced pressure to an approximate 2 mL volume and pouring into 50 mL stirred distilled water. The mixture was extracted with 3×50 mL portions of CH_2Cl_2, the combined organic phases were back extracted with 50 mL distilled water, and the CH_2Cl_2 phase dried over Na_2SO_4. After filtering and concentrating, the crude product was purified through a silica gel column with CH_2Cl_2/*n*-hexane (1:1) elution. Yield: 2.87 g (47%). E.N.: 59 °C. IR [(KBr) ν_{max}/cm^{-1}]: 3084 (Ar–CH), 2927 and 2857 (CH_2), 2234 (C≡N), 1575 (C=C), 1479, 1377, 1276, 1120 (C–O–C), 796, 724. ^{1}H NMR ($CDCl_3$): δH, ppm 0.89 (t, 12H, CH_3), 1.29 (m, 72H, CH_2), 1.56 (m, 8H, $OCCH_2$), 3.47 (t, 8H, OCH_2), 3.67 (d, 8H, OCH_2), 4.50

(m, 2H, CH), 7.41 (s, 2H, ArH). ^{13}C NMR (APT) ($CDCl_3$): δC, ppm 14.09 (CH_3), 22.87 (CH_2), 26.05 (CH_2), 29.36–29.62 (CH_2), 31.91 (CH_2), 70.63 (OCH_2), 72.01 (OCH_2–CHO), 81.37 (CH), 106.11 (ArC), 113.21 (C≡N), 122.45 (ArCH), 156.16 (ArCO). Calc. for $C_{62}H_{112}N_2O_6$: C 75.87, H 11.50, N 2.85; found: C 75.52, H 11.63, N 2.98. MS (FAB-MS) *m/z*: Calc. 980; found: 981.6 $[M+H]^+$.

2.3.2. 3,6-Bis(2-[2-(2-ethoxyethoxy)ethoxy]-1-{[2-(2-ethoxyethoxy)ethoxy]methyl}ethoxy) phthalonitrile (*4b*)

Synthesis and purification was as outlined for **4a** except 1,3-bis[2-(2-ethoxyethoxy)ethoxy] propan-2-tosylate (**2b**) was employed instead of 1,3-bis(dodecyloxy)propan-2-tosylate (**2a**). The amounts of the reagents employed were: **2b** (6.6 g, 13.7 mmol), 2,3-dicyanohydroquinone (**3**) (1.0 g, 6.24 mmol) and K_2CO_3 (5.6 g, 41.1 mmol) in DMF (20 mL). Yield: 3.0 g (62%). IR [(NaCl cell) ν_{max}/cm^{-1}]: 3089 (Ar–CH), 2974 and 2871 (CH_2), 2233 (C≡N), 1480, 1351, 1279, 1111 (C–O–C), 796, 724. ^{1}H NMR ($CDCl_3$): δH, ppm 1.14 (t, 12H, CH_3), 3.45–3.58 (m, 48H, CH_2), 4.51 (m, 2H, CH), 7.42 (s, 2H, ArH). ^{13}C NMR (APT) ($CDCl_3$): δC, ppm 15.36 (CH_3), 66.79 (CH_2), 69.96–71.33 (CH_2), 81.35 (CH), 106.13 (ArC), 113.51 (C≡N), 122.86 (ArCH), 156.24 (ArCO). Calc. for $C_{38}H_{64}N_2O_{14}$: C 59.05, H 8.35, N 3.62; found: C 59.37, H 8.19, N 3.88. MS (ES-MS) *m/z*: Calc. 772; found: 773.3 $[M+H]^+$.

2.3.3. 1,4-Octakis{(2-(dodecyloxy)-1-[(dodecyloxy)methyl]ethoxyphthalocyaninato)} nickel(II) (*5a*)

A solution of 3,6-bis{2-(dodecyloxy)-1-[(dodecyloxy)methyl]ethoxy}phthalonitrile (**4a**) (0.70 g, 0.71 mmol), anhydrous $NiCl_2$ (0.188 g, 1.45 mmol) and 1,8-diazabicylo[5,4,0]undec-7-ene(DBU) (0.162 mL, 1.10 mmol) in 10 mL dry *n*-hexanol was refluxed under argon atmosphere for 48 h, and then the solvent was removed under reduced pressure. The crude product was dissolved in CH_2Cl_2 and then filtered. After concentrating, the dark green waxy product was purified by passing through a silica gel column with CH_2Cl_2 elution. Furthermore this product was purified with preparative thin layer chromatography (silica gel) using CH_2Cl_2/*n*-hexane (5:2) solvent system. Yield: 0.45 g (16%). IR [(NaCl cell) ν_{max}/cm^{-1}]: 3082 (Ar–CH), 2926 and 2855 (CH_2), 1600 (C=N), 1496, 1465, 1377, 1263, 1120 (C–O–C), 1094, 747. ^{1}H NMR ($CDCl_3$): δH, ppm: 0.85 (t, 48H, CH_3), 1.11 (m, 288H, CH_2), 1.40 (m, 32H, OC–CH_2), 3.39 (m, 32H, OCH_2), 4.01 (br, 32H, OCH_2), 4.75 (m, 8H,CH), 7.68 (s, 8H, ArH). ^{13}C NMR (APT) ($CDCl_3$): δC, ppm 14.05, (CH_3), 22.65 (CH_2), 26.08 (CH_2), 29.35–29.62 (CH_2), 31.91 (CH_2), 70.42 (OCH_2), 71.61 (OCH_2–CH_2O), 81.95 (CH), 122.21 (ArCH), 127.64 (ArC), 145.56 (N=C–N), 150.62 (ArCO). UV–vis (chloroform): λ_{max}, nm (log ε): 732 (4.99), 657 (4.37), 340 (4.35), 300 (4.48). Calc. for $C_{248}H_{448}N_8O_{24}Ni$: C 74.75, H 11.33, N 2.81; found: C 74.93, H 11.66, N 2.89. MS (FAB-MS): *m/z* (%) Calc. 2984; found: 2985 $[M+H]^+$.

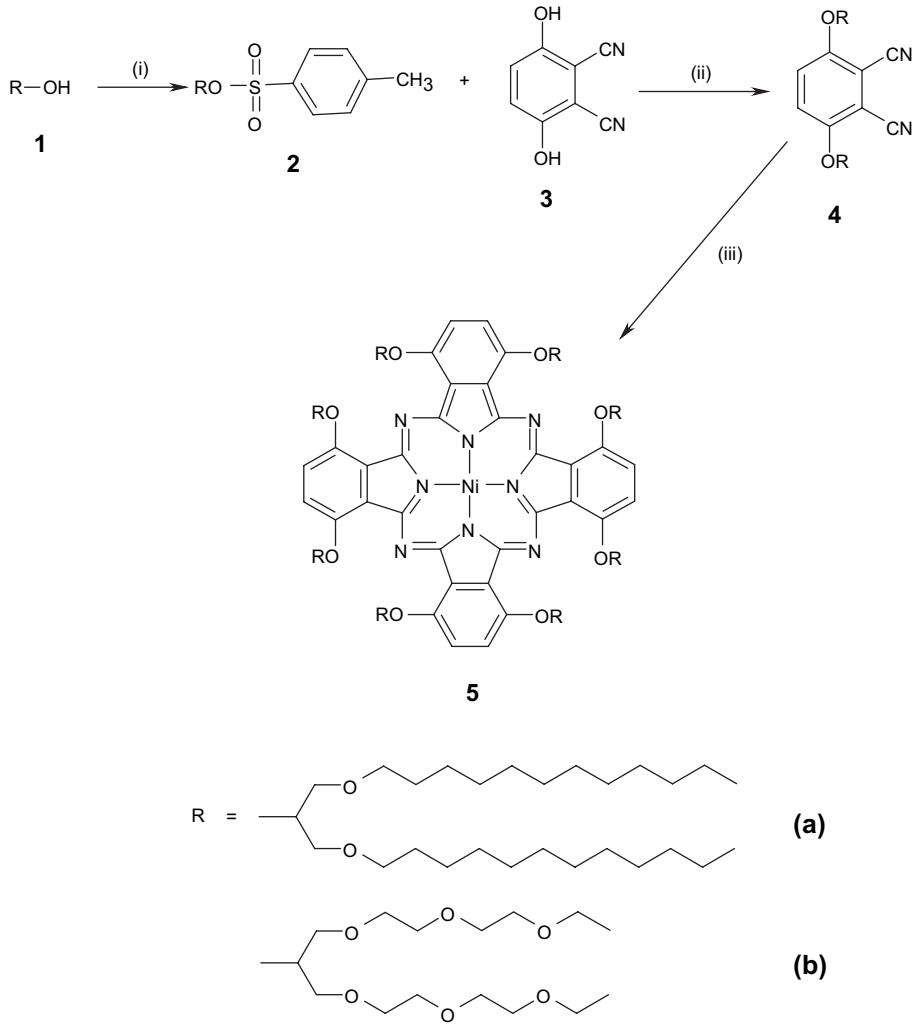
2.3.4. 1,4-Octakis{(2-[2-(2-ethoxyethoxy)ethoxy]-1-{[2-(2-ethoxyethoxy)ethoxy]methyl}ethoxyphthalocyaninato)} nickel(II) (*5b*)

Synthesis and purification was as outlined for **5a** except 3,6-bis(2-[2-(2-ethoxyethoxy)ethoxy]-1-{[2-(2-ethoxyethoxy)ethoxy]methyl}ethoxy)phthalonitrile (**4b**) was employed instead of 3,6-bis{2-(dodecyloxy)-1-[(dodecyloxy)methyl]ethoxy}phthalonitrile (**4a**). The amounts of the reagents employed were: **4b** (400 mg, 0.52 mmol), anhydrous $NiCl_2$ (104 mg, 0.8 mmol) and DBU (0.62 mL, 1.10 mmol) in *n*-hexanol (2.5 mL). Yield: 0.15 g (9%). IR [(NaCl cell) ν_{max}/cm^{-1}]: 3076 (Ar–CH), 2970 and 2867 (CH_2), 1600 (C=N), 1495, 1465, 1377, 1263, 1120 (C–O–C), 1094, 747. ^{1}H NMR ($CDCl_3$): δH, ppm: 1.04 (t, 48H, CH_3), 3.32–3.46 (m, 96H, CH_2), 3.51–3.61 (m, 64H, OC–CH_2), 4.00 (m, 32H, OCH_2), 4.69 (m, 8H, CH), 7.62 (s, 8H, ArH). ^{13}C NMR (APT) ($CDCl_3$): δC, ppm 14.10, (CH_3), 65.49 (CH_2), 68.70–69.80 (CH_2), 80.70 (CH), 121.22 (ArCH), 126.65 (ArC), 144.48 (N=C–N), 149.44 (ArCO). UV–vis (chloroform): λ_{max}, nm (log ε): 734 (5.18), 659 (4.56), 346 (4.57), 303 (4.69). Calc. for $C_{152}H_{256}N_8O_{56}Ni$: C 57.95, H 8.19, N 3.56; found: C 58.11, H 8.35, N 3.91. MS (ES-MS): *m/z* (%) Calc. 3150; found: 3151.2 $[M+H]^+$.

3. Results and discussion

3.1. Synthesis and characterization

Phthalocyanines are prepared by cyclotetramerization of phthalonitriles or 1,3-diimino-1*H*-isoindoles. 2,3,9,10,16,17,23,24-Octa-substituted (peripherally β) phthalocyanines can be synthesized from 4,5-disubstituted phthalonitriles [40] while 1,4,8,11,15,18,22,25-octa-substituted (peripherally α) phthalocyanines are obtained from 3,6-disubstituted phthalonitriles [41]. In our case, the starting phthalonitriles are reactive enough to obtain the expected phthalocyanines in classical template conditions. The syntheses of the peripherally alpha(α) octa-substituted phthalocyanines are achieved through two different routes. (i) Peripherally alpha(α) alkyl substituted phthalocyanines can be synthesized from the corresponding 3,6-dialkylphthalonitrile precursors. 3,6-Dialkylphthalonitrile precursors can be synthesized using appropriately substituted compounds in a Diels–Alder cycloaddition reaction. Two approaches satisfactorily exploited imply the use of dialkylfurans or dialkylthiophene dioxides as ''dienes'', fumaronitrile being the dienophile [41]. (ii) Peripherally alpha(α) alkyloxy substituted phthalocyanines can be synthesized from the corresponding 3,6-dialkyloxyphthalonitrile precursors. 3,6-Dialkyloxyphthalonitrile precursors are obtained from appropriate alcohols and 2,3-dicyanohydroquinone [42]. 2,3-Dicyanohydroquinone (**3**) was used recently to prepare 3,6-disubstituted phthalonitriles through base catalyzed nucleophilic aromatic displacement [31,40,43]. The same route was applied to prepare 3,6-bis{2-(dodecyloxy)-1-[(dodecyloxy)methyl]ethoxy}phthalonitrile (**4a**) from 1,3-bis (dodecyloxy)propan-2-tosylate (**2a**) and 2,3-dicyanohydroquinone (**3**) (Scheme 1). Similarly, the reaction of 3,6-bis{2-(dodecyloxy)-1-[(dodecyloxy) methyl]ethoxy}phthalonitriles (**4a**) under the same conditions with 2,3-dicyanohydroquinone (**3**) resulted in the expected compound 3,6-bis(2-[2-(2-ethoxyethoxy)ethoxy]-1-{[2-(2-ethoxyethoxy)ethoxy]methyl} ethoxy) phthalonitriles (**4b**) (Scheme 1). The reactions were



Scheme 1. Synthesis of peripherally alpha(α) 1,3-bis(dodecyloxy)propan-2-ol and 1,3-bis[2-(2-ethoxyethoxy)ethoxy]propan-2-ol substituted nickel(II) phthalocyanine complexes. (i) *p*-$MeC_6H_4SO_2Cl$, pyridine, room temperature; (ii) K_2CO_3, DMF; (iii) $NiCl_2$, DBU, *n*-hexanol.

carried out in dry dimethylformamide at 50 °C and gave yields 47% for **4a** and 62% for **5a**.

The preparation of phthalocyanine derivatives from the aromatic nitriles occurred under different reaction conditions [1]. A convenient high-yield synthesis requires for the further considerations. For various substituted dinitriles, the reaction is in the presence of strong non-nucleophilic bases such as 1,8-diazabicylo[5.4.0]undec-7-ene (DBU) or 1,5-diazabicylo[4.3.0]non-5-ene (DBN) in 1-pentanol [44–46]. The cyclotetramerization of dinitrile derivatives (**4a** and **4b**) in presence of anhydrous $NiCl_2$ and DBU in 1-hexanol gave the peripherally alpha(α) octa-substituted nickel(II) phthalocyanine derivatives (**5a** and **5b**).

The substituents' positions on the phthalocyanine ring affect its melting point. Generally, peripherally alpha(α)-substituted phthalocyanines have lower melting point than the corresponding peripherally β-substituted phthalocyanines [2]. Therefore, synthesized peripherally alpha(α) octa-substituted compounds (**5a** and **5b**) are optically clear, relatively viscous liquids at room temperature. When observed under crossed polarizers by optical microscope, no birefringence is observed. This enables us to be sure that the phthalocyanines are really liquids and not exhibiting a low viscous mesogenic state. This is fitting the observations of the melting point lowering of peripherally alpha(α)-substituted phthalocyanines.

Column and preparative thin layer chromatography with silica gel were employed to purify the products from the reaction mixtures. The intense green-blue relatively viscous products are very soluble in a number of solvents. They could thus be thoroughly investigated by ^1H and ^{13}C NMR and UV–vis spectroscopy in solution. In addition to elemental analysis result, mass spectra of the new organic intermediate compounds and phthalocyanines obtained by the FAB and ES-MS techniques show molecular ion peaks.

FT-IR spectra were recorded on KBr pellet for solid compound (**4a**) and NaCl cell for liquid compounds (**4b**, **5a**, **5b**), characteristic vibrations corresponding to ether groups (C–O–C) at ca. 1110–1120 cm^{-1} and CH_2 stretching at ca. 2927–2855 cm^{-1} for **4a** and **5a**, at ca. 2974–2867 cm^{-1} for **4b** and **5b** are common for the starting compounds (**4a**, **4b**) as well as for the phthalocyanines (**5a**, **5b**). The sharp peak

for the C≡N vibrations 2234 cm^{-1} for **4a** and 2233 cm^{-1} for **4b** disappears after phthalocyanine formation.

NMR investigation of the compounds **4a** and **4b** have provided the characteristic chemical shifts for the structures as expected. In the ^1H NMR analysis of all these compounds in deuterated chloroform, the methyl protons appear as triplet at 0.89 and 1.14 ppm integrating for 12 protons each, for phthalonitrile compounds **4a** and **4b**, respectively. The CH_2 protons appear as a multiplet at 1.29 ppm, a multiplet at 1.56 ppm, a triplet at 3.47 ppm and a doublet at 3.67 ppm integrating for 72, 8, 8, 8 protons each, making a total of 96 protons expected for compound **4a** and appear as a multiplet between 3.45 and 3.58 ppm integrating for a total of 48 protons as expected for compound **4b**. The aliphatic CH protons appear as multiplets at 4.50 and 4.51 ppm integrating for 2 protons each, for phthalonitrile compounds **4a** and **4b**, respectively. The aromatic protons appear as singlets at 7.41 and 7.42 ppm integrating for 2 protons each, for compounds **4a** and **4b**, respectively.

In the ^{13}C NMR spectra of dinitrile (**4a**), methyl carbon atoms show a signal at 14.09 ppm, the aliphatic CH_2 carbon atoms show different signals between 22.87 and 72.01 ppm, the aliphatic CH carbon atoms show a signal at 81.37 ppm. The aromatic carbon atoms of this compound were observed at 106.11 for ArC carbon atoms, 122.45 ppm for ArCH carbon atoms and 156.16 ppm for ArCO carbon atoms. The nitrile carbon atoms were observed at 113.21 ppm. The ^{13}C NMR spectra of other dinitril (**4b**), methyl carbon atoms show a signal at 15.36 ppm, the aliphatic CH_2 carbon atoms show different signals between 66.79 and 71.33 ppm, the aliphatic CH carbon atoms show a signal at 81.35 ppm. The aromatic carbon atoms of this compound were observed at 106.13 for ArC carbon atoms, 122.86 ppm for ArCH carbon atoms and 156.24 ppm for ArCO carbon atoms. The nitrile carbon atoms were observed at 113.51 ppm.

In the ^1H NMR analysis of peripherally alpha(α) octa-substituted nickel(II) phthalocyanine derivatives (**5a** and **5b**) in deuterated chloroform, Fig. 1 (using complex **5b** as an example in $CDCl_3$), the methyl protons appear as triplet at 0.85 ppm and 1.04 ppm integrating for 48 protons each, for phthalocyanine compounds **5a** and **5b**, respectively. The CH_2 protons appear as a multiplet at 1.11 ppm, a multiplet at 1.40 ppm, a multiplet at 3.39 ppm and a broad peak at 4.01 ppm integrating for 288, 32, 32, 32 protons each, making a total of 384 protons expected for compound **5a** and appear as a multiplet between 3.32 and 3.46 ppm, 3.51 and 3.61 ppm and as a multiplet at 4.00 ppm integrating for 96, 64 and 32 protons each, making a total of 192 protons expected for compound **5b**. The aliphatic CH protons appear as multiplets at 4.75 and 4.69 ppm integrating for 8 protons each, for phthalocyanine compounds **5a** and **5b**, respectively. Generally, the aromatic protons of peripherally alpha(α) octa-substituted phthalocyanines shift to upfield due to that the ring current effect is more shielded and comes into resonance at a stronger applied field, when compared with peripheral octa-substituted phthalocyanines [47,48]. A similar effect is seen for compounds **5a** and **5b**. The aromatic protons appear as singlets

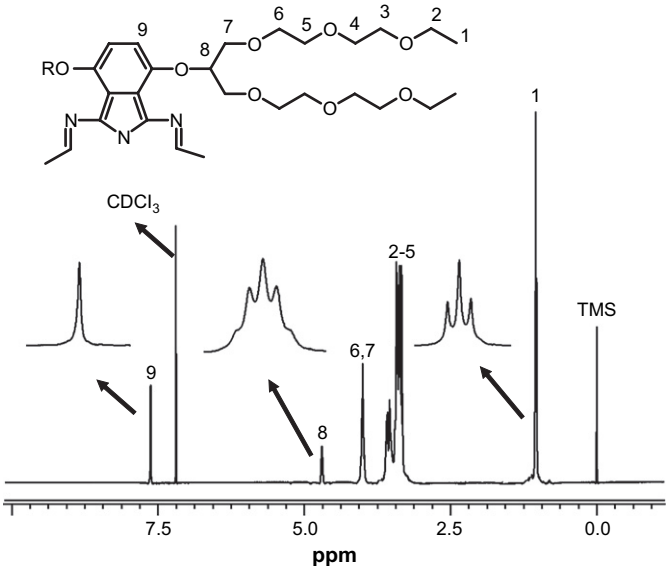


Fig. 1. ^1H NMR spectrum of complex **5b** in $CDCl_3$.

at 7.68 and 7.62 ppm integrating for 8 protons each, for compounds **5a** and **5b**, respectively.

The high solubility of the phthalocyanines has enabled us to obtain ^{13}C NMR spectra. The ^{13}C NMR spectra of the phthalocyanine derivatives are in agreement with the proposed structures. The chemical shift values in these spectra closely follow the empirically calculated ones [49]. The attached proton test (APT) technique was used for ^{13}C NMR studies.

In the ^{13}C NMR spectra of phthalocyanine compound (**5a**), Fig. 2 (using complex **5b** as an example in $CDCl_3$), methyl carbon atoms show a signal at 14.05 ppm, the aliphatic CH_2 carbon atoms show different signals between 22.65 and 71.61 ppm, the aliphatic CH carbon atoms show a signal at 81.95 ppm. The aromatic carbon atoms of this compound were observed at 122.21 ppm for ArCH carbon atoms, 127.64 ppm for ArC carbon atoms and 150.62 ppm for ArCO carbon atoms. The ^{13}C NMR spectra of other phthalocyanine compound (**5b**), methyl

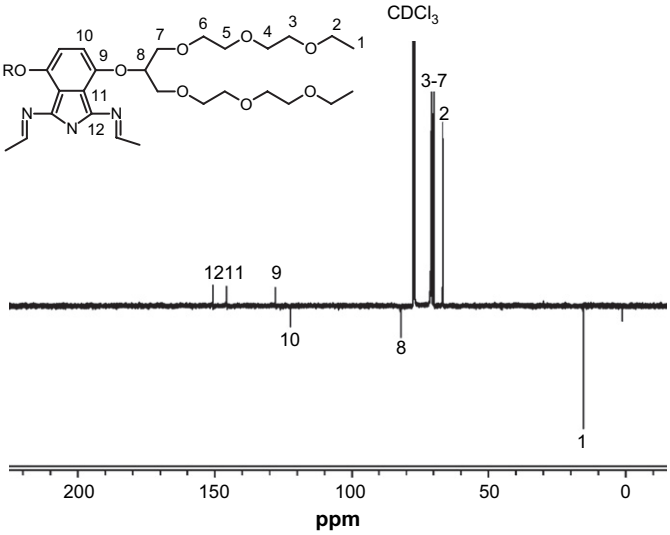


Fig. 2. ^{13}C NMR spectrum of complex **5b** in $CDCl_3$.

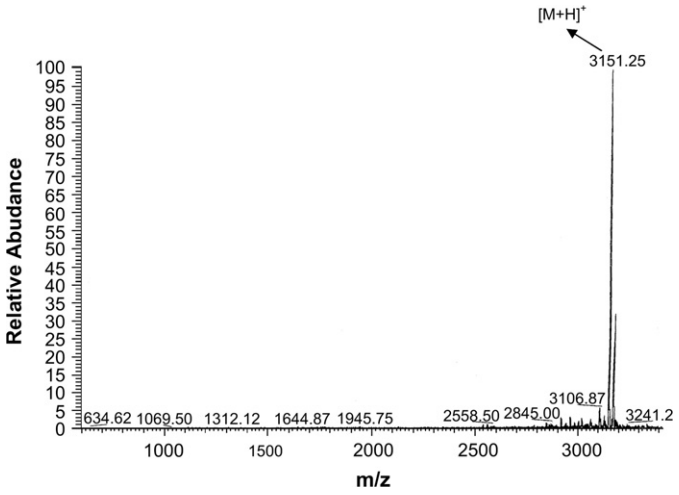


Fig. 3. Mass spectrum of complex **5b**.

Table 1
UV–vis spectral data of nickel(II) phthalocyanine complexes **5a** and **5b** in different solvents

Solvent[a]	Q-band/nm	B-band/nm	N-band/nm
5a			
Toluene	731	348	300
DCM	732	344	302
THF	732	343	300
$CHCl_3$	732	340	300
5b			
Toluene	734	346	303
DCM	731	344	301
THF	734	351	303
$CHCl_3$	734	346	303
DMSO	742	346	305
DMF	738	350	304
MeOH	734	351	304

[a] The compound **5a** is not soluble in DMF, DMSO and MeOH.

carbon atoms show a signal at 14.10 ppm, the aliphatic CH_2 carbon atoms show different signals between 65.49 and 69.80 ppm, the aliphatic CH carbon atoms show a signal at 80.70 ppm. The aromatic carbon atoms of this compound were observed at 121.22 ppm for ArCH carbon atoms, 126.65 ppm for ArC carbon atoms and 149.44 ppm for ArCO carbon atoms. In the ^{13}C NMR spectra the carbon atoms of the N=C–N group in the phthalocyanine core show at 145.56 and 144.48 ppm for compounds **5a** and **5b**, respectively.

A close investigation of the mass spectra of the phthalonitrile derivatives (**4a** and **5a**) and phthalocyanines (**5a** and **5b**) confirmed the proposed structures, Fig. 3 (using complex **5b** as an example). The mass spectra of these compounds were obtained by FAB and Electron Spray techniques. We observed the molecular ion peaks at *m/z*: 981.6 and *m/z*: 773.3 for phthalonitriles **4a** and **4b**, respectively. We observed the molecular ion peaks of phthalocyanines at *m/z*: 2985.0 for **5a** and *m/z*: 3151.2 for **5b**.

3.2. Ground state electronic absorption and aggregation behaviour

The ground state electronic absorption spectra showed monomeric behaviour evidenced by a single (narrow) Q-band, typical of metallated phthalocyanine complexes, Fig. 4 [50]. The Q-bands were observed at: 732 (**5a**) and 734 (**5b**) in DMSO, Table 1. The Q-bands of the α-substituted complexes (**5a** and **5b**) are red-shifted. The observed red spectral shift is typical of phthalocyanines with substituents at the peripherally alpha(α) positions and has been explained [51,52] to be due to linear combinations of the atomic orbitals (LCAO) coefficients at the peripherally alpha(α) positions of the HOMO being greater than those at the peripherally β positions. As a result, the HOMO level is destabilized more at the peripherally alpha(α) position that it is at the peripherally β position. Essentially, the energy gap (ΔE) between the HOMO and LUMO becomes smaller, resulting in a bathochromic shift.

Aggregation is usually depicted as a coplanar association and is dependent on the concentration, nature of the solvent, nature of the substituents, complexed metal ions and temperature [53]. In the aggregated state, the electronic structure of the complexed phthalocyanine rings is perturbed resulting in alternation of the ground and excited state electronic structures [54]. In this study, the aggregation behaviour of the phthalocyanine complexes (**5a** and **5b**) are investigated in different solvents (chloroform, dichloromethane, toluene and THF for complex **5a** and chloroform, dichloromethane, DMF, DMSO, MeOH, toluene, THF for complex **5b**) (Fig. 5 for complex **5b**). The complexes **5a** and **5b** showed a single peak in all studied solvents. The

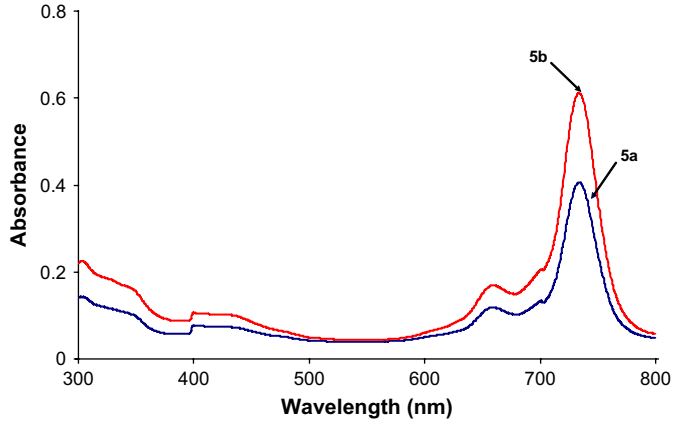


Fig. 4. Absorption spectra of phthalocyanine complexes (**5a** and **5b**) in $CHCl_3$. Concentration = 4×10^{-6} mol dm^{-3}.

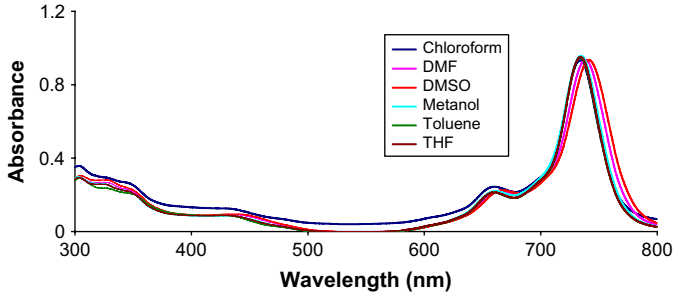


Fig. 5. Absorption spectra of phthalocyanine complex **5b** in different solvents. Concentration = 6.5×10^{-6} mol dm^{-3}.

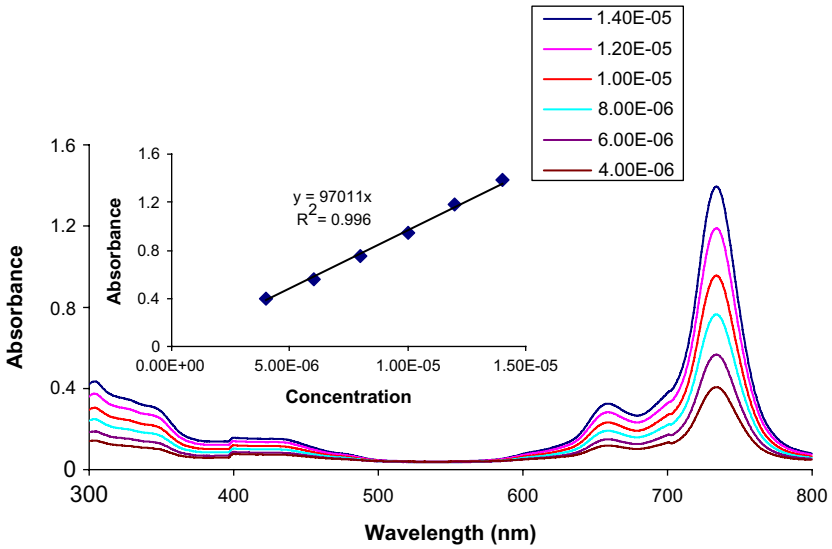


Fig. 6. Absorption spectra of **5a** in $CHCl_3$ at different concentrations. 14×10^{-6}, 12×10^{-6}, 10×10^{-6}, 8×10^{-6}, 6×10^{-6}, 4×10^{-6} mol dm^{-3}.

aggregation behaviour of the phthalocyanine complexes (**5a** and **5b**) were also investigated at different concentrations in chloroform. In chloroform, as the concentration was increased, the intensity of absorption of the Q-band also increased and there were no new bands (normally blue shifted) due to the aggregated species for all complexes (**5a** and **5b**) (Fig. 6 for complex **5a**). Beer–Lambert law was obeyed for all the compounds in the concentrations ranging from 1.4×10^{-5} to 4×10^{-6} mol dm^{-3}. The Beer–Lambert relationship is shown as an inset for **5a** in Fig. 6.

4. Conclusions

In this study, we synthesized and characterized new peripherally alpha(α) alkyloxy and polyoxy octa-substituted nickel phthalocyanine complexes. These Ni phthalocyanine complexes showed red-shift in the Q-band region of the electronic spectrum due to the peripherally alpha(α) substitution effect on the phthalocyanine framework. This work has also presented a comprehensive investigation of solvent effects on the aggregation of these octa-substituted nickel phthalocyanine complexes. The aggregation properties are studied for complexes **5a** in chloroform, dichloromethane, toluene and THF and for complex **5b** in chloroform, dichloromethane, DMF, DMSO, MeOH, toluene and THF. All complexes did not show aggregation in studied solvents (Fig. 5). And also, for these complexes the effect of the concentration on the aggregation properties was studied in chloroform. No aggregation was demonstrated in chloroform from concentration between 1.4×10^{-5} and 4×10^{-6} mol dm^{-3} (Fig. 6). The effect of the branched alkoxy and polyoxy-ethylene chains on aggregation is very similar, but if the solubility between the two substituents is compared, the polyoxy-ethylene substituent favours the solubility of the phthalocyanine complex in DMF, DMSO and MeOH. As the concentration is increased up to $\sim 5 \times 10^{-5}$ mol dm^{-3} in studied solvents, the phthalocyanine complexes (**5a** and **5b**) did not show any aggregation. This non-aggregative behaviour and the peripherally alpha(α) substitution enable us to obtain Pc liquid at room temperature, a promising property for many applications.

Acknowledgements

The authors wish to thank Colette Lebrun (CEA-Grenoble), Mine Tir Bilsel and Gökhan Bilsel (TÜBİTAK-UME) for the ES-MS and FAB mass spectra.

References

[1] Leznoff CC, Lever ABP, editors. Phthalocyanines: properties and applications, vols. 1–4. New York: VCH Publishers; 1989, 1993, 1996.
[2] McKeown NB. Phthalocyanine materials: synthesis, structure and function. Cambridge University Press; 1989.
[3] Simon J, Bassoul P. Design of molecular materials: supramolecular engineering. VCH Weinheim; 2000.
[4] Hanack M, Lang M. Adv Mater 1994;6:819–51.
[5] Cook MJ, McKeown NB, Simmons JM, Thomson AJ, Daniel MF, Harrison KJ, et al. J Mater Chem 1991;1:121–7.
[6] Schlettwein D, Wöhrle D, Jaeger NI. J Electrochem Soc 1989;136:2882–6.
[7] Dogo S, Germain JP, Maleysson C, Pauly A. Thin Solid Films 1992;219:251–6.
[8] Basova T, Tasaltin C, Gürek AG, Ebeoğlu MA, Öztürk ZZ, Ahsen V. Sens Actuators B 2003;96:70–5.
[9] Basova T, Kol'tsov E, Ray AK, Hassan AK, Gürek AG, Ahsen V. Sens Actuators B 2006;113:127–34.
[10] Simon J, Sirlin C. Pure Appl Chem 1989;61:1625–9.
[11] De la Torre G, Vazquez P, Agullo-Lopez F, Torres T. J Mater Chem 1998;8:1671–83.
[12] Lever ABP, Hempstead MR, Leznoff CC, Liu W, Melnik M, Nevin WA, et al. Pure Appl Chem 1986;58:1467–76.
[13] Leznoff CC, Marcuccio SM, Grinberg S, Lever ABP, Tomer KB. Can J Chem 1985;623–31.
[14] Durmuş M, Yeşilot S, Ahsen V. New J Chem 2006;30:675–8.
[15] Guo L, Meng FS, Gong XD, Xiao HM, Chen KC, Tian H. Dyes Pigments 2001;49:83–91.

[16] George RD, Snow AW, Shirk JS, Barger WR. J Porphyrins Phthalocyanines 1998;2:1–7.
[17] Cook MJ, McMurdo J, Miles DA, Poynter RH. J Mater Chem 1994;4:1205–13.
[18] FitzGerald S, Farren C, Stanley CF, Beeby A, Bryce MR. Photochem Photobiol Sci 2002;1:581–7.
[19] Louati A, Meray MEI, Andre JJ, Simon J, Kadish KM, Gross M, et al. Inorg Chem 1985;24:1175–9.
[20] Wöhrle D, Schmidt V. J Chem Soc Dalton Trans 1988;549–51.
[21] Hale PD, Pietro WJ, Ratner MA, Ellis DE, Marks TJ. J Am Chem Soc 1987;109:5943–7.
[22] Schlettwein D, Armstrong NR. J Phys Chem 1994;98:11771–9.
[23] Meier H, Albrecht W, Wöhrle D, Jahn A. J Phys Chem 1986;90: 6349–53.
[24] Maree S, Nyokong T. J Porphyrins Phthalocyanines 2001;5:782–92.
[25] Law WF, Liu RCW, Jiang J, Ng DKP. Inorg Chim Acta 1997;256: 147–50.
[26] Somashekarappa MP, Keshavayya J. Synth React Inorg Met-Org Chem 2001;31:811–27.
[27] Kobayashi N, Ogata H, Nonaka N, Luk'yanets EA. Chem Eur J 2003;9:5123–34.
[28] Ferencz A, Neher D, Schulze M, Wegner G, Viaene L, Schryver FC. Chem Phys Lett 1995;245:23–9.
[29] Snow AW, Shirk JS, Pong RGS. J Porphyrins Phthalocyanines 2000;4:518–24.
[30] Maya EM, Shirk JS, Snow AW, Roberts GL. Chem Commun 2001; 615–6.
[31] Durmuş M, Lebrun C, Ahsen V. J Porphyrins Phthalocyanines 2004;8:1175–86.
[32] Cherodian AS, Davies AN, Richardson RM, Cook MJ, McKeown NB, Thomson AJ, et al. Mol Cryst Liq Cryst 1991;196:103–14.
[33] Cook MJ, Daniel MF, Harrison KJ, McKeown NB, Thomson AJ. J Chem Soc Chem Commun 1987;1086–8.
[34] Cammidge AN, Cook MJ, Haslam SD, Richardson RM, Harrison KJ. Liq Cryst 1993;14:1847–62.
[35] Cook MJ, Dunn AJ, Howe SD, Thomson AJ, Harrison KJ. J Chem Soc Perkin Trans I 1988;2453–8.
[36] Burnham PM, Cook MJ, Gerrard LA, Heeney MJ, Hughes DL. Chem Commun 2003;2064–5.
[37] Perrin DD, Armarego WLF. Purification of laboratory chemicals. 2nd ed. Oxford: Pergamon Press; 1989.
[38] Gürek AG, Ahsen V, Heinemann F, Zugenmaier P. Mol Cryst Liq Cryst 2000;338:75–97.
[39] Gürek AG, Durmuş M, Ahsen V. New J Chem 2004;28:693–9.
[40] Wöhrle D, Eskes M, Shigehara K, Yamada A. Synthesis 1993;194–6.
[41] Cook MJ. Chem Rec 2002;2:225–36.
[42] Wu Y, Tian H, Chen K, Liu Y, Zhu D. Dyes Pigments 1998;37:317–25.
[43] Durmuş M, Nyokong T. Inorg Chem Commun 2007;10:332–8.
[44] Wöhrle D, Schnurpfeil G, Knothe G. Dyes Pigments 1992;18:91–102.
[45] Tomoda H, Saito S, Ogawa S, Shiraishi S. Chem Lett 1980;1277–80.
[46] Tomoda H, Saito S, Shiraishi S. Chem Lett 1983;313–6.
[47] Sleven J, Gorller-Walrand C, Binnemans K. Mater Sci Eng C 2001;18:229–38.
[48] Rihter BD, Kenney ME, Ford WE, Rodgers MAJ. J Am Chem Soc 1990;112:8064–70.
[49] Kalinowski HO, Berger S, Braun S. ^{13}C-NMR spektrokopie. New York: George Thime; 1984. p. 284–5.
[50] Stillman MJ, Nyokong T. In: Leznoff CC, Lever ABP, editors. Phthalocyanines: properties and applications, vol. 1. New York: VCH Publishers; 1989 [chapter 3].
[51] Anderson AB, Gorden TL, Kenney ME. J Am Chem Soc 1985;107: 192–5.
[52] Konami M, Hatano M, Tajiri A. Chem Phys Lett 1990;166:605–8.
[53] Engelkamp H, Nolte RJM. J Porphyrins Phthalocyanines 2000;4:454–9.
[54] Dominguez DD, Snow AW, Shirk JS, Pong RGS. J Porphyrins Phthalocyanines 2001;5:582–92.