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Synthesis and spectral properties of new soluble naphthalocyaninatometal derivatives

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Abstract

Several naphthalocyanines, including soluble asymmetrical derivatives, were prepared by conventional condensation methods or by ring-expansion of the corresponding subnaphthalocyanine. the latter method offers two major advantages, over the mixed condensation method, viz., convenient purification and relatively high yield. electronic absorption spectral data indicate that the majority of the new colorants have Q-bands above 750 nm. the substituent effect at peripheral sites was small with respect to the position of the Q-bands, but the nature of the central metal atoms significantly affected the Q-bands. In addition, asymmetrical tri-*t*-butyl naphthalocyaninatozinc shows interesting spectral properties in solvents without heteroatoms, due to the formation of plane-to-plane and head-to-tail aggregated dimers simultaneously, which can be prevented in solvents such as ether, alcohol and amines.

Keywords: Naphthalocyaninatometal; Asymmetry; Synthesis; Ring-expansion method; Electronic absorption spectra; Aggregation

1. Introduction

Continued interest in phthalocyanines (Pcs) results from their wide application as substrates for semiconductors, gas-detectors, photovoltaic devices, photodynamic cancer therapy, and nonlinear optical (NLO) devices [1]. To fully exploit the potential of phthalocyanines as functional materials, it is necessary to solve two major problems. The first challenge is to control their structure and optical and electrical properties, which is usually achieved by appropriate chemical modification. This requires making chemical substitutions at peripheral sites and proper choices for metal atoms at the axial center. The second problem pertains to device fabrication. Most devices require smooth, uniform thin films. Consequently, excellent dye solubility in common solvents is needed in the fabrication step [2].

Naphthalocyanines (Ncs) have experienced increasing interest since the discovery of their unusual spectral properties [3]. Compared to the corresponding metallo-phthalocyanines, the larger aromatic systems of Ncs offer additional π-electron delocalisation. The extended π-conjugation and the presence of terminal groups afford different optical absorption properties to metallonaphthalocyanines [4]. In particular, the extension

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of their delocalised system makes them possible candidates for NLO devices.

NLO materials are attracting much attention because of their potential application in optical communication, data storage, optical computing, dynamic holography, harmonic generations, frequency mixing and optical switching [5–7]. Useful NLO materials should display large optical nonlinearity, low optical losses and ultrafast response time. Personal computers have been shown to be the thrust of nonlinear optical effects [8,9]. Furthermore, theoretical calculations have suggested that push–pull asymmetrically substituted phthalocyanines, with suitable donor and acceptor groups and efficient intramolecular charge transfer, should yield interesting compounds for SHG (second-harmonic generation) [10,11].

With the previous point in mind, attention has been given to the synthesis of novel push–pull asymmetrically substituted phthalocyanines, and many asymmetrical personal computers have been developed [12–14]. However, few reports on asymmetrical naphthalocyanine derivatives have been published, due to their inherent insolubility in organic solvents, and difficulties associated with their synthesis.

Our interest in the synthesis of novel naphthalocyanine derivatives arises from their potential optical application as NLO materials, with emphasis on asymmetrical naphthalocyanines containing donor or acceptor moieties for SHG properties. In the present paper, several symmetrical and soluble asymmetrical naphthalocyanine derivatives were prepared by conventional condensation methods or by using structurally distorted subnaphthalocyanine. The absorption properties of the resultant compounds were also evaluated.

While symmetrical phthalocyanines can be conveniently prepared by the condensation method, the preparation of asymmetrically substituted phthalocyanines has employed the following strategies: (a) attachment of a substituted diiminoisoindoline to an insoluble polymer, reaction with a large excess of a second differently substituted diiminoisoindoline, and subsequent liberation of the Pc from the polymer [15]; (b) cross condensation of a diiminoisoindoline derivative with a 1,3,3-trichloroisoindolenine or with another sterically crowded iminoisoindoline [16]; (c) ring expansion of a pre-organized subphthalocyanine with a substituted diiminoisoindoline [17]; (d) mixed condensation of two differently substituted phthalonitrile-precursors or diiminoisoindolines in appropriate stoichiometric ratios, followed by chromatographic separation of the statistical mixtures.

In the latter method, two difficulties are encountered. First, condensation of two different precursors can give a statistical distribution of mono-, di-, tri-, and tetra-substituted phthalocyanines, which leads to a very low yield of the desired product. Secondly, their similar properties preclude the purification of the desired product by column chromatography.

In this paper, the latter two methods were used to prepare asymmetrical tri-*t*-butyl naphthalocyanine, and other symmetrical and asymmetrical naphthalocyanines were prepared by the condensation method.

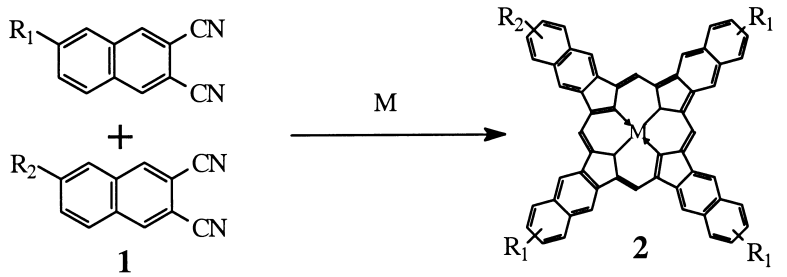
2. Results and discussion

2.1. Synthesis of symmetrical and asymmetrical naphthalocyanines

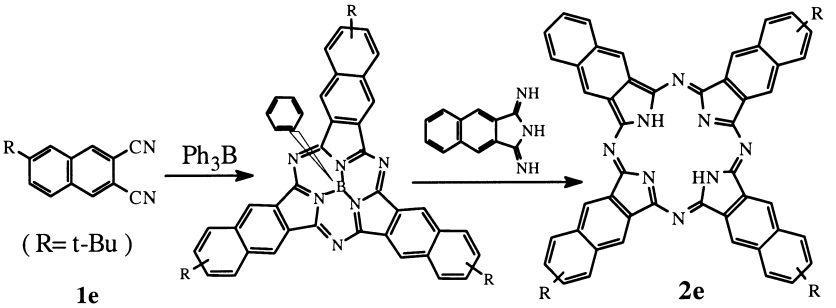
The synthetic routes employed in this study are shown in Schemes 1 and 2. Cyano and nitro groups were used as electron acceptors, and tetracyanonaphthalocyanine (**2a**) was readily obtained from 2,3,6-tricyanonaphthalene [18]. Similarly, tetra-cyano naphthalocyaninatometal derivatives (**2b–c**) were prepared in the presence of metal salts. Tetra-nitronaphthalocyaninatozinc (**2d**) could not be obtained by the same method, but could be synthesized by the reaction of 6-nitro-2,3-dicyanonaphthalene with zinc chloride in the presence of urea and ammonium molybdate in refluxing nitrobenzene.

The four products had poor solubility in most solvents, except for DMF, DMSO and pyridine. However, hydrolysis of tetra-cyanonaphthalocyaninatozinc, gave tetra-carboxynaphthalocyaninatozinc (**2i**) as a water-soluble product.

New soluble asymmetrical compounds (**2e–h**) were prepared using the appropriate molar ratio



Scheme 1. Synthetic route for naphthalocyanine derivatives via the condensation method.



Scheme 2. Synthetic route for compound **2e** via the ring-expansion method.

of two different precursors, by using the mixed condensation method shown in Scheme 1. At least four by-products were also obtained, and the presence of di- and tetra-*t*-butyl products increased the difficulty of the purification step. Therefore, multiple-stage column chromatography was necessary for each product, giving very low yields. All compounds showed satisfactory elemental analysis, and the results of MALDI-TOF-MS (matrix-assisted laser desorption ionization-time of flight-MS) and IR analyses are shown in Table 1.

Tri-t-butyl naphthalocyanine (**2e**) was also synthesized by the reaction of 1,3-diiminobenzoisoindole with phenyl-(2,11,20)-tri-*t*-butyl subnaphthalocyaninatoboron [19], which was prepared by the reaction of 6-*tert*-butyl-2,3-dicyanonaphthalene with triphenylboron in 1-bromonaphthalene (Scheme 2). separation of the resultant mixture was readily accomplished by column chromatography. This method proved advantages over the mixed condensation method, because only the desired product was obtained and the yield of target compound was higher. In addition, final purification by column chromatography was easier, due to fewer by-products and better resolution of each band on the column. On the other hand, this method was unsuitable for the preparation of those asymmetrical Pcs that either contained a central metal atom (e.g. compound **2f**) or were sensitive to the reaction conditions (e.g. compound **2g**).

2.2. Absorption spectra

The absorption spectra of compounds **2a–i** are shown in Figs. 1-4, and a list of the associated B-bands and Q-bands is given in Table 2. From

Table 2, it is clear that most of these compounds have Q-bands above 750 nm. Results in Fig. 1 indicate that compounds **2a–c,** which have the same substituents at the periphery of the molecule and different central metal atoms, exhibited a Q-band shift from 681 to 764 nm. This indicates that the nature of the central metal atom significantly affected the Q-band position. Tetra-*t*-butyl-naphthalocyaninatozinc, with a Q-band at 763 nm in DMF, and compounds **2b**, **2d** and **2i,** with the same central metal atom but with different substituents at the periphery of the molecules, have very similar Q-bands. This indicates that substituents have a small influence on the Q-band positions of the title compounds.

When the spectrum of compound **2f** was measured, an interesting behavior was observed. Fig. 4 shows the visible absorption spectral changes in nitrogen-purged chloroform as a function of time. The fresh solution (0 h) gave a Q-band at 769 nm and a small peak at 716 nm. After

Table 1
MALDI-TOF-MS and FT–IR data for **2a–i**

Compound	MS (M^+)	FT–IR (KBr, selected data, cm^{-1})
2a	814	2223s, 1620m, 1347s, 1078m
2b	876	2222s, 1634m, 1351s, 1086m-s
2c	871	2222s, 1615m, 1537m, 1080m
2d	956	1611m, 1529m-s, 1338vs, 1079m
2e	882	2955m, 1610m, 1475s, 1361m-s
2f	944	2949m, 1390m, 1352m, 1085m
2g	907	2951m, 2851m, 2222s, 1386s, 1362m
2h	927	2955m, 1611m, 1530m, 1335vs
2i	952	1709vs, 1611m, 1354s, 1334s, 1080m

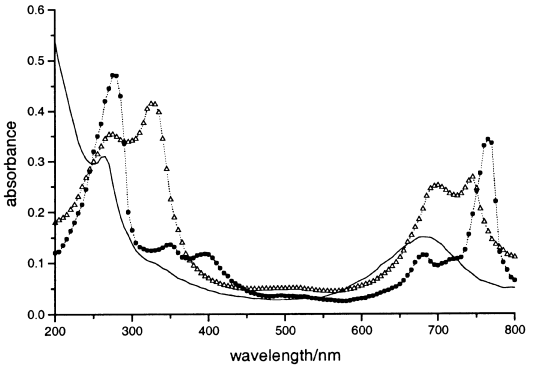


Fig. 1. Electronic spectra of compounds **2a** (−), **2b** (•), and **2c** (Δ) in DMF.

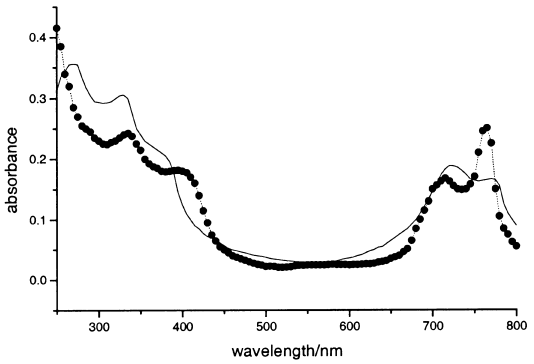


Fig. 2. Electronic spectra of compounds **2d** (−) and **2i** (•) in DMF.

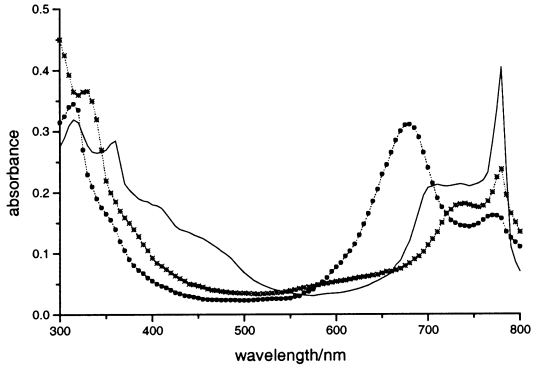


Fig. 3. Electronic spectra of compounds **2e** (−), **2g** (•), and **2h** (*) in $CHCl_3$.

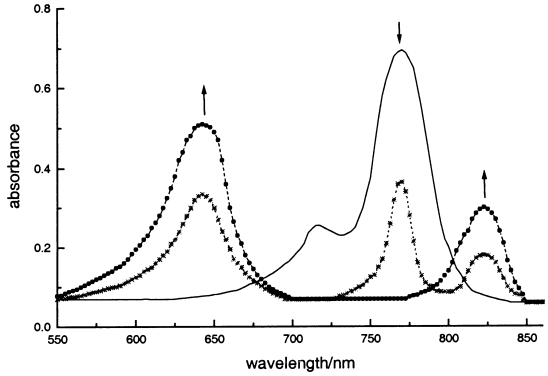


Fig. 4. Electronic spectral changes of compound **2f** in $CHCl_3$ after 0 h (−), 24 h (*) and 52 h (•).

Table 2
Summary of absorption spectral data for compounds **2a–i**

Compound	Solvent	Soret band B (nm)	Visible band Q (nm)
2a	DMF	263	681 (shoulder)
2b	DMF	347	764
2c	DMF	324	744
2d	DMF	328	768
2e	$CHCl_3$	358	782
2f	$CHCl_3$ (fresh)	324	769
2g	$CHCl_3$	312	772
2h	$CHCl_3$	328	778
2i	DMF	333	764

24 h, the small peak had disappeared, the peak at 769 nm had greatly decreased, and new peaks at 642 and 822 nm appeared. After 52 h, the Q-band had completely disappeared, and the new peaks approached their maximum intensity. The same behavior was found in solvents without heteroatoms (e.g. benzene or cyclohexane). However, when pyridine was added dropwise, the peak at 769 nm reappeared and increased in intensity with the further addition of pyridine. Simultaneously, the peaks at 642 and 822 nm decreased and finally disappeared. These results are summarized graphically in Fig. 5.

Although oxidation and protonation mechanisms [20,21] have been reported to explain similar behavior from several phthalocyanines and biphthalocyanines, they do not account for the behavior of compound **2f**. If such mechanisms were operating in chloroform, the behavior of **2f** would have been the same in solvents such as ether, alcohol and amines. In fact, even oxygen-purged solutions of the latter solvents did not display the behavior observed in chloroform. Therefore, it is believed that the Q-band changes resulted from the formation of two-types of aggregations.

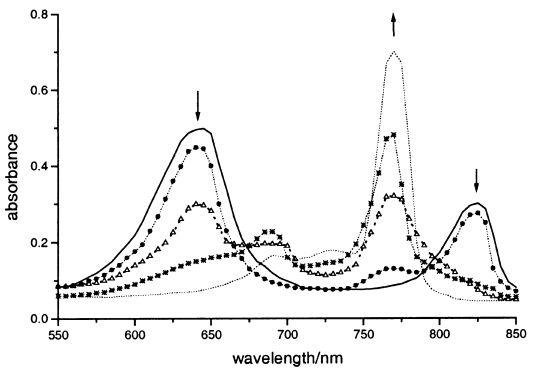


Fig. 5. Electronic spectral changes for 2.5% (–), 7.5% (•), 15% (Δ), 25% (*) and 50% (...) solutions of compound **2f** in chloroform.

In accordance with molecular exciton theory [22], the blue-shifted peak at 642 nm and the red-shifted peak at 822 nm would arise from plane-to-plane aggregation and head-to-tail aggregation, respectively. The lower steric hindrance associated with the asymmetrical compound makes head-to-tail aggregation possible, a behavior seldom observed in symmetrical Pcs.

A two-step aggregation mechanism involving monomer (A) and its two aggregate states (P_m: plane-to-plane aggregate and H_n: head-to-tail aggregate) is denoted by Eqs. (1) and (2).

$$m\mathrm{A} \xrightarrow{k_1} \mathrm{P}_m \tag{1}$$

$$n\mathrm{A} \xrightarrow{k_2} \mathrm{H}_n \tag{2}$$

where k_1 and k_2 are rate constants, m is the plane-to-plane aggregation number, and n is the head-to-tail aggregation number. The rates of aggregate formation are determined by Eqs. (3) and (4).

$$\frac{\mathrm{d}[\mathrm{P}_m]}{\mathrm{d}t} = k_1[\mathrm{A}]^m \tag{3}$$

$$\frac{\mathrm{d}[\mathrm{H}_n]}{\mathrm{d}t} = k_2[\mathrm{A}]^n \tag{4}$$

where [A], [P_m], and [H_n] are concentrations of the monomer, plane-to-plane and head-to-tail aggregates at moment t, respectively. The concentrations can be measured by Beer's law (cell length = 1 cm). It is reasonable to assume that the absorbances at 642, 769 and 822 nm arise from plane-to-plane aggregate, monomer, and head-to-tail aggregate. With this in mind, Eqs. (5) and (6) were obtained from Eqs. (3) and (4):

$$\frac{\mathrm{d}(ABS)_\mathrm{p}}{\mathrm{d}t} = (k_1\varepsilon_\mathrm{p}/\varepsilon_\mathrm{A}^m)(ABS)_\mathrm{A}^m = R_1(ABS)_\mathrm{A}^m \tag{5}$$

$$\frac{d(ABS)_H}{dt} = (k_2\varepsilon_H/\varepsilon_A^n)(ABS)_A^n = R_2(ABS)_A^n \quad (6)$$

where $(ABS)_X$, ε_X ($X =$ A, P, H) are the absorbances and extinction coefficients at the absorption maxima, $R_1 = (k_1\varepsilon_P/\varepsilon_A^m)$ and $R_2 = (k_2\varepsilon_H/\varepsilon_A^n)$, and both were constant at a given temperature. This led to the approximations shown in Eq. (7), and to Eqs. (8) and (9) from Eqs. (5)–(7).

$$\frac{d(ABS)_X}{dt} = \frac{\Delta(ABS)_X}{\Delta t} \quad (X = P, H) \quad (7)$$

$$\frac{\Delta(ABS)_P}{\Delta t} = R_1(ABS)_A^m \quad (8)$$

$$\frac{\Delta(ABS)_H}{\Delta t} = R_2(ABS)_A^n \quad (9)$$

Therefore, Eqs. (8) and (9) can be rewritten as Eqs. (10) and (11) below.

$$\log\left[\frac{\Delta(ABS)_P}{\Delta t}\right] = \log\ R_1 + m\ \log(ABS)_A \quad (10)$$

$$\log\left[\frac{\Delta(ABS)_H}{\Delta t}\right] = \log\ R_2 + n\ \log(ABS)_A \quad (11)$$

Plots of $\log[\Delta(ABS)_P/\Delta t]$ vs. $\log(ABS)_A$ and $\log[\Delta(ABS)_H/\Delta t]$ vs. $\log(ABS)_A$ could then be generated, the slopes of which represent the corresponding aggregation numbers. In this paper, two plots with good linearity were obtained at concentrations between 2×10^{-6} and 1×10^{-4} mol dm^{-3}. Fig. 6 shows the plots representing plane-to-plane and head-to-tail aggregation at a concentration of 5.22×10^{-5} mol dm^{-3} at room temperature. For plane-to-plane aggregation, the aggregation number was 1.72, and for head-to-tail aggregate, the aggregation number was 2.07. The existence of two aggregation numbers that are close to 2 suggests that the asymmetrical compound prefers to form plane-to-plane and head-to-tail dimers, simultaneously.

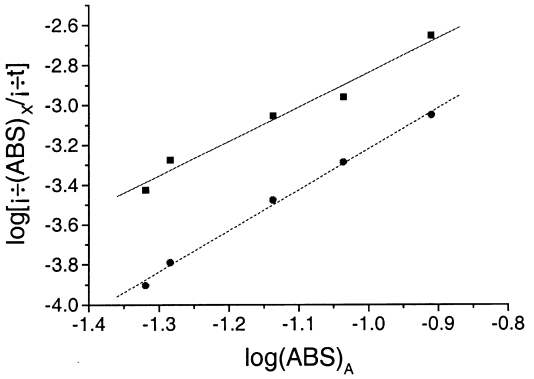


Fig. 6. Plots of Eq. (10) (–) and Eq. (11) (- - -) for chloroform solutions of compound **2f**.

3. Experimental

Elemental analyses were measured by the ST-02.G.L method, MALDI-TOF-MS data were obtained on BIFLEX III instrument, IR spectra were measured in KBr on a Perkin–Elmer 983G instrument and UV/Vis spectra were recorded on a Hewlett Packard 8451A instrument. Substituted 2,3-dicyanonaphthalenes were prepared by a published method [18], and the solvents employed were further purified by distillation.

3.1. Tetracyanonaphthalocyanines (*2a–c*)

To a solution of lithium (2 g) in *n*-pentanol (50 ml) was added 2,3,6-tricyanonaphthalene (1.0 g, 4.92 mmol) under reflux. After 2 h, acetic acid (20 ml) was added, and refluxing was continued for 1 h. After removal of solvents under reduced pressure, the blue residue was diluted with benzene (350 ml) and the resultant blue solid was filtered, and then extracted with methanol and chloroform, successively. Compound **2a** was then washed with water and dried to give a 60% yield.

By conducting the initial step of the above procedure in the presence of $ZnCl_2$ or $CoCl_2$ (i.e. before adding acetic acid), compounds **2b–c** were obtained.

3.2. Tetracarboxynaphthalocyaninatozinc (*2i*)

Compound **2i** (0.25 g, 0.25 mmol) was obtained from hydrolysis of **2b** (0.55 g, 0.57 mmol) in sulfuric

acid (50%, 40 ml) at 80–90°C for 5–6 h. The resultant mixture was diluted with water (1000 ml) and filtered. The solid was dissolved in aq. NaOH (0.2 M, 50 ml) and after removal of insoluble substances by filtration, the product was precipitated from the filtrate by acidifying with hydrochloric acid (2 M, 30 ml). The precipitate was washed with water and dried to give a 45% yield.

3.3. Tetra-nitronaphthalocyaninatozinc (**2d**)

A mixture of 6-nitro-2,3-dicyanonaphthalene (2 g, 9.04 mmol), zinc chloride (2 g), urea (15 g), and ammonium molybdate (0.2 g) in nitrobenzene (35 ml) was stirred under reflux for 12 h. After removal of the solvent at reduced pressure, the residue was washed with water, dried, and extracted with chloroform and methanol, successively. The blue residue left after extraction weighed 0.75 g (35%).

3.4. Tri-t-butyl naphthalocyanine (**2e**)

3.4.1. Ring-expansion method

Phenyl-(2,11,20)-tri-*t*-butyl subnaphthalocyanin atoboron was prepared according to the literature [19]. The product (0.1 g, 0.13 mmol) was stirred with 1,3-diiminobenzoisoindole (1.5 g, 7.68 mmol) in a mixture of DMSO (15 ml) and trichlorobenzene (15 ml) at 90∼100°C. After removal of the solvents under reduced pressure, the resultant dark-blue mixture was separated by column chromatography using chloroform-cyclohexane (2:3) as the eluent. The chromatography gave the greenish colored starting material (R_f = 0.61) and the blue product (R_f = 0.30, yield = 10%).

3.4.2. Mixed condensation method

A mixture of **1e** and 2,3-dicyanonaphthalene in a 3:1 molar ratio was heated at 280°C under a nitrogen atmosphere for 5 h. The resultant mixture was initially separated by column chromatography using $CHCl_3$ as eluent, and a blue band was collected. This impure blue component was then further chromatographed using CH_2Cl_2–cyclohexane (2:3), giving two components. The band with R_f = 0.27 was chromatographed using cyclohexane as the eluent, with the band at R_f = 0.15 providing compound **2e**.

3.5. Asymmetrical derivatives (**2f–h**)

The procedure employed was the same as that reported above for the synthesis of **2e**, using the mixed condensation method and the appropriate 2,3-dicyanonaphthalene precursors. Thus were obtained **2f** (R_f = 0.17, yield = 2.5%), **2g** (R_f = 0.12, yield = 5.5%), and **2h** (R_f = 0.09, yield = 1%).

4. Conclusions

When several new naphthalocyanines, including soluble asymmetrical derivatives, were prepared using the conventional condensation method and from substituted subnaphthalocyanine, ring-expansion was the better method for two reasons, namely, ease of purification and higher yield. The majority of these compounds had Q-bands above 750 nm. Substituents at peripheral sites had little influence on the Q-band position, but the nature of the central metal atoms significantly affected the Q-bands. In addition, the asymmetrical dye tri-*t*-butyl naphthalocyaninatozinc formed a mixture of plane-to-plane and head-to-tail aggregated dimers in chloroform. The observed aggregation behavior was prevented by ether, alcohol and amines.

Acknowledgements

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