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Synthetic Studies of Substituted 2,3-Naphthalocyanines

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Abstract: A series of di- and tetra-substituted 2,3-dicyanonaphthalenes were prepared which were converted into the respective 2,3-naphthalocyaninato zinc complexes. The synthetic pathways to and the spectroscopic properties of these novel compounds are described. © 1997 Elsevier Science Ltd.

INTRODUCTION

2,3-Naphthalocyanine contains a phthalocyanine core onto which four linearly annelated benzene rings are attached. Having a more extended π-electron-delocalized system, this compound and its derivatives absorb strongly in the near-infrared region and exhibit enhanced electrical conductivity as compared with phthalocyanines.[1,2] Due to their intriguing physical properties, these dyes are prospective materials for electronic and optical devices such as semiconductors,[3] electrochromic displays,[4] optical storage media,[5] and optical limiters,[6] and can also be used as photosensitizers in photodynamic cancer therapy.[7] Most of the efforts have been devoted to exploring the chemistry and applications of unsubstituted 2,3-naphthalocyanine and its metal complexes. Most of these compounds have poor solubility in common organic solvents which greatly limits their applications. The chemistry and properties of substituted analogs have only been reported sporadically.[8] A substantial barrier to the development in these aspects is the shortage of convenient synthetic routes to the precursors 2,3-dicyanonaphthalene derivatives. During the course of this investigation, Hanack *et al.*[9] and Cook *et al.*[10] have reported the synthesis of several substituted 2,3-dicyanonaphthalenes and the corresponding metal-free and metallo-naphthalocyanines. Here we wish to report the results of our independent study on this area.

RESULTS AND DISCUSSION

The synthetic route used to prepare 1,4- and 5,8-disubstituted 2,3-dicyanonaphthalenes is shown in Scheme 1, which is based on the pathways to iptycenes reported by Hart *et al.*.[11] Treatment of **1-3** with 1.5 equiv. of n-BuLi and furan or 2,5-dihexylfuran gave the corresponding epoxides **4-7** in moderate yields. As compounds **1** and **2** are only sparingly soluble in hexane, the reactions were carried out in toluene at room temperature that is different from the literature procedures which employ a hexane / toluene mixture and low temperature.[11,12] Deoxygenation of **4-7** was accomplished by using $TiCl_4$ and zinc leading to the dibromonaphthalenes **8-11**. Compound **11** was described previously but no characterizing data was given.[13] By using the Rosenmund-von Braun reaction, these dibromides were converted into the corresponding alkylated dinitriles **12-15**.

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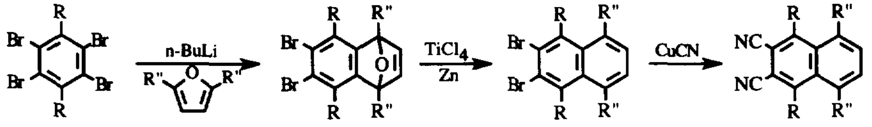
Scheme 1



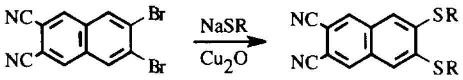
1 R = H
2 R = CH_3
3 R = n-C_6H_{13}

4-7 **8-11** **12-15**

4, 8, 12 R = H, R" = n-C_6H_{13}
5, 9, 13 R = CH_3, R" = H
6, 10, 14 R = CH_3, R" = n-C_6H_{13}
7, 11, 15 R = n-C_6H_{13}, R" = H

Since 3,4-disubstituted furans are not readily accessible although a substantial progress has been made recently,[14] we employed a different strategy to 6,7-disubstituted 2,3-dicyanonaphthalenes. Compound **16**, which can be prepared from *o*-xylene in three steps,[15] underwent aromatic nucleophilic substitution with thiolate ions RS^- (R = C_3H_7, C_6H_5) (Scheme 2). The use of copper(I) oxide promoted the reactions and greatly improved the reaction yields.[16] Reaction of **16** with alkoxide ions under similar conditions, however, did not lead to the substituted products. A number of unidentified products were obtained instead.

Scheme 2

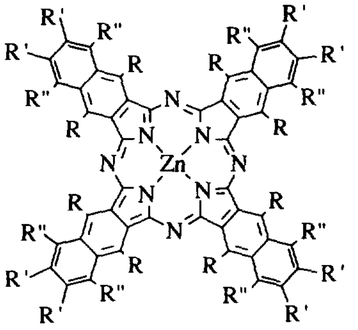


16

17 R = C_3H_7
18 R = C_6H_5

Treatment of the dinitriles **12-15**, **17-18** with zinc acetate and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 1-hexanol produced the corresponding 2,3-naphthalocyaninato zinc(II) complexes **19-24** in moderate yields. Purifications of these compounds were performed by column chromatography and / or Soxhlet extraction. Because of the high tendency of aggregation, 2,5- and 3,4-substituted naphthalocyanines **19**, **23**, and **24** tended to be stuck in the column and usually eluent having a donor atom such as tetrahydrofuran (THF) was required to disrupt the molecular interactions. The 1,6-substituted analogs **21** and **22** were unstable in the silica gel column. The initially green band turned to red gradually when chloroform was used as eluent. Changing the eluent to hexanes / ethyl acetate mixture slowed down the decomposition that allowed the isolation of preliminary pure products which were characterized with UV-Vis, ^1H NMR, and high resolution mass spectrometry.

The high aggregation tendency of the macrocycles **19**, **23**, and **24** was also revealed by ^1H NMR and UV-Vis spectrometry. The ^1H NMR spectrum of **19** in $CDCl_3$ showed only broad signals due to the aliphatic side chains, while the aromatic signals were not observed. By changing the solvent to THF-d_8, a satisfactory spectrum was obtained in which a broad band at δ 9.60 and a relatively sharp band at δ 7.44 appeared which can be attributed to the H_1 and H_3 aromatic protons, respectively. The ^1H NMR spectra of **23** and **24** in both $CDCl_3$ and THF-d_8 did not show the aromatic signals, while the ^1H NMR spectrum of **22** in $CDCl_3$ exhibited two multiplets at δ 8.70-8.80 and 7.80-7.89 assignable to the AA'BB' system of the aromatic ring. These observations may suggest that the aggregation tendency of these compounds follows the order **23**, **24** > **19** > **22** which may be related to the substitution pattern (3,4- > 2,5- > 1,6-substitution). Compound **20** has poor solubility in common organic solvents and NMR data could not be obtained.



19 R = H, R" = n-C_6H_{13}, R' = H
20 R = CH_3, R" = R' = H
21 R = CH_3, R" = n-C_6H_{13}, R' = H
22 R = n-C_6H_{13}, R" = R' = H
23 R = R" = H, R' = SC_3H_7
24 R = R" = H, R' = SC_6H_5

The UV-Vis spectrum of compound **19** in toluene was found to be concentration dependent (Figure 1). The Q band absorption at 776 nm was unshifted but the molar absorptivity decreased from 2.48 x 10^5 to 3.94 x 10^4 $M^{-1}cm^{-1}$ as the concentration increased from 2.06 x 10^{-7} to 5.51 x 10^{-5} M. Since further spectral change was not observed at concentrations lower than 2.06 x 10^{-7} M, the spectrum recorded in this concentration could be ascribed to the purely monomeric **19**. Assuming that a one step equilibrium between the naphthalocyanine monomer (Nc) and the aggregated species (Nc_n) exists (Eq. 1) and by using the method described by Mataga[17] and Hayashi,[18] the values of the aggregation number (n) and the aggregation constant (K) for **19** were determined to be 1.57 and 2.48 x 10^3, respectively. The former value suggests that compound **19** tends to form dimer in toluene solution that is analogous to other tetrasubstituted naphthalocyanines.[18] The K value

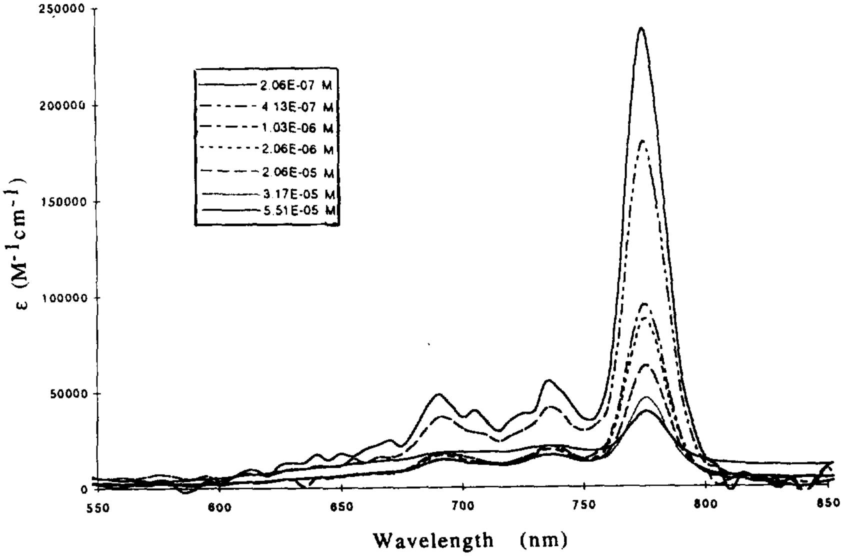


Figure 1. Concentration dependence of UV-Vis spectra of **19** in toluene

for **19** is however considerably smaller than those for other tetrabutyl counterparts (4×10^3 - 3×10^4) under similar conditions. By changing the solvent to THF, the absorption spectrum of **19** was essentially independent of concentration over the range of 5.51×10^{-7} to 1.38×10^{-5} M. This indicates that aggregation of **19** in THF is not significant in these concentrations.

$$n \cdot \mathrm{Nc} \xrightleftharpoons{K} \mathrm{Nc}_n \qquad \text{(Eq. 1)}$$

The UV-Vis spectra of **23** and **24** in toluene and chloroform were measured in different concentrations. Although the molar absorptivity of the Q band increased on dilution, no absorption spectra assignable to the monomeric species could be observed in all cases. Thus the corresponding n and K values could not be determined under these conditions. However, by using THF as solvent, the values for compound **24** ($n = 1.97$, $K = 4.40 \times 10^4$) could be calculated from the spectra recorded over the concentration range of 2.14×10^{-7} to 2.14×10^{-5} M. The propylthio analog **23** appeared to have higher aggregation tendency and the spectrum due to the monomer could not be obtained even in high dilution. The relative aggregation tendency (**23** > **24** > **19**) derived from the UV-Vis spectroscopic studies is thus in accord with the results based on the ^{1}H NMR data.

Table 1 shows a comparison of the Q band absorption maxima of the substituted naphthalocyanines with respect to that of the unsubstituted analog (ZnNc). The data for compound **21** could not be obtained as it is virtually insoluble in dimethyl sulfoxide, which is one of the few solvents that can slightly dissolve ZnNc. It is worth noting that introduction of electron donating substituents induces a bathochromic shift, in particular, when the substituents are attached to the 1,6-positions. The absorption position also depends on the chain length of the substituent (compound **20** *vs.* **22**).

Table 1. λ_{max} of the Q Band of 2,3-Naphthalocyaninato Zinc(II) Complexes in Dimethyl Sulfoxide

Compound	λ_{max} (nm)	$\Delta\lambda_{max}{}^a$ (nm)
ZnNc	770	0
19	811	41
20	800	30
22	816	46
23	791	21
24	785	15

[a] Bathochromic shift with respect to the λ_{max} of unsubstituted (2,3-naphthalocyaninato)zinc(II) (ZnNc) taken from ref. 19

Due to the strong aggregation tendency of 2,3-naphthalocyanines, unambiguous characterization with ^{1}H NMR and UV-Vis spectrometry may not be feasible in some cases. Mass spectroscopic method thus provides an alternative means for identification. The liquid secondary ion mass spectra (LSIMS) for **19-24** were measured with a ultra-high resolution Fourier transform ion cyclotron resonance (FTICR) spectrometer. The molecular ion was detected in all cases with the isotopic distribution in good agreement with the corresponding calculated pattern.

CONCLUSION

We have developed general routes to differently substituted 2,3-dicyanonaphthalenes and their corresponding 2,3-naphthalocyaninato zinc(II) complexes. It can be envisaged that a wide range of naphthalocyanine derivatives can be synthesized by using these strategies which can certainly widen the applications of these novel macrocyclic compounds. Research endeavors along this direction are in progress.

EXPERIMENTAL

General. Hexane, toluene, 1-pentanol, and 1-hexanol were distilled from sodium prior to use. THF was distilled from sodium benzophenone ketyl. *N*, *N*-Dimethylformamide (DMF) was dried over barium oxide and distilled under reduced pressure. Furan was shaken with 5% aqueous KOH, dried with Na_2SO_4, then distilled under nitrogen from sodium. Hexanes used in column chromatography was distilled from anhydrous $CaCl_2$. Column chromatographic purifications were carried out on silica gel (Merck, Kieselgel 60, 70-230 mesh) with the indicated eluents. All other reagents and solvents were of reagent grade and used without further purification. Compounds **1**,[11] **2**,[12] **3**,[20] **5**,[12] **16**,[15] and 2,5-dihexylfuran[21] were prepared by the literature procedures with minor modifications.

Melting points are uncorrected. NMR spectra were recorded on a Bruker WM 250 (^1H, 250 MHz; ^{13}C, 62.9 MHz) or on a Bruker ARX 500 (^1H, 500 MHz; ^{13}C, 125.8 MHz) spectrometer in a $CDCl_3$ solution unless stated otherwise with $Si(CH_3)_4$ as an internal reference ($\delta = 0$). Electron impact (EI) mass spectra were obtained on a VG 7070F spectrometer (70 eV) and LSI spectra were taken on a Bruker APEX 47e FTICR spectrometer with 3-nitrobenzyl alcohol as matrix. UV-Vis absorption spectra were measured on a Hitachi U-3300 spectrophotometer. IR spectra were recorded on a Nicolet 205 spectrometer as KBr pellets. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, and the Microanalytical Department of the Inorganic Chemistry Laboratory, University of Oxford.

Preparation of 6,7-dibromo-1,4-epoxy-1,4-dihexyl-1,4-dihydronaphthalene (4). A mixture of compound **1** (6.00 g, 15 mmol) and 2,5-dihexylfuran (3.80 g, 16 mmol) in toluene (250 mL) was stirred at r.t. under nitrogen, then a solution of n-BuLi (1.6 M in hexanes, 15.0 mL, 24 mmol) in toluene (100 mL) was added dropwise over 3 h. The mixture was stirred for a further 16 h at r.t., then methanol (1 mL) was added. The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was subjected to column chromatography with hexanes / chloroform (5:1) as eluent giving a pale yellow oil (3.36 g, 48%). ^1H NMR (250 MHz) δ 7.30 (s, 2 H, ArH), 6.73 (s, 2 H, C=CH), 2.12-2.20 (m, 4 H, CH_2), 1.50-1.68 (m, 4 H, CH_2), 1.28-1.50 (m, 12 H, CH_2), 0.86-1.00 (m, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (125.8 MHz) δ 154.1, 145.5, 124.1, 120.2, 91.7, 31.7, 29.7, 29.2, 24.6, 22.6, 14.1; MS (EI): an isotopic cluster peaking at *m/z* 470 (M^+, 43%).

Preparation of 6,7-dibromo-1,4-epoxy-1,4-dihexyl-5,8-dimethyl-1,4-dihydronaphthalene (6). According to the procedure described above, compound **2** (8.43 g, 20 mmol), upon treatment with 2,5-dihexylfuran (6.86 g, 29 mmol) and n-BuLi (1.6 M in hexanes, 18.8 mL, 30 mmol), was converted to **6** as a colorless liquid (4.98 g, 50%). Purification was performed with column chromatography with hexane / chloroform (4:1) as eluent. ^1H NMR (250 MHz) δ 6.71 (s, 2 H, C=CH), 2.46 (s, 6 H, CH_3), 2.31-2.36 (m, 4 H, CH_2), 1.31-1.59 (m, 16 H, CH_2), 0.89 (vt, J = 6.5 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (62.9 MHz) δ 150.5, 146.1, 129.8, 126.2, 93.0, 32.1, 31.7, 29.7, 25.0, 22.6, 20.4, 14.0; MS (EI): an isotopic cluster peaking at *m/z* 498 (M^+, 5%); HRLSIMS Calcd. for $C_{24}H_{35}{}^{79}Br_2O$ (MH^+): 497.1056. Found: 497.1164.

Preparation of 6,7-dibromo-1,4-epoxy-5,8-dihexyl-1,4-dihydronaphthalene (7). By using the method described for **4**, compound **3** (5.00 g, 9 mmol) was treated with furan (4.5 mL, 62 mmol) and n-BuLi (1.6 M in hexanes, 8.3 mL, 13 mmol) in hexane (200 mL) to give **7** as a pale yellow oil which crystallized in hexane as white crystals (1.50 g, 36%). M.p. 68-70°C; ^1H NMR (250 MHz) δ 7.02 (s, 2 H, C=CH), 5.75 (s, 2 H, OCH), 2.81 (vt, *J* = 7.7 Hz, 4 H, $ArCH_2$), 1.45-1.58 (m, 4 H, CH_2), 1.32-1.37 (m, 12 H, CH_2), 0.90 (vt, *J*= 6.3 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (125.8 MHz) δ 147.5, 142.7, 134.9, 124.5, 81.8, 34.8, 31.6, 29.8, 29.3, 22.6, 14.0; MS (EI): an isotopic cluster peaking at *m/z* 470 (M^+, 10%); Anal. Calcd. for $C_{22}H_{30}Br_2O$: C, 56.19; H, 6.43. Found: C, 55.99; H, 6.48.

Preparation of 2,3-dibromo-5,8-dihexylnaphthalene (8). To an ice-cold suspension of zinc dust (4.7 g, 71 mmol) in THF (120 mL) was added slowly $TiCl_4$ (5.2 mL, 47 mmol) under nitrogen. The mixture was refluxed for 10 min then cooled in an ice-bath. A solution of **4** (3.4 g, 7 mmol) in THF (50 mL) was then added dropwise. The mixture was refluxed overnight, cooled and then poured into cold 10% HCl (250 mL). The mixture was extracted with dichloromethane (3 x 100 mL) and the combined extracts were washed with water (3 x 50 mL), dried over $CaCl_2$, and evaporated. The residue was purified by chromatography with hexanes as eluent to yield a pale yellow oil which crystallized in hexane as white crystals (2.5 g, 76%). M.p. 48-49°C; ^1H NMR (250 MHz) δ 8.29 (s, 2 H, ArH), 7.24 (s, 2 H, ArH), 2.94 (vt, *J* = 7.8 Hz, 4 H, $ArCH_2$), 1.63-1.72 (m, 4 H, CH_2), 1.30-1.44 (m, 12 H, CH_2), 0.89 (vt, *J* = 6.9 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (125.8 MHz) δ 136.3, 132.3, 129.4, 126.8, 121.4, 32.7, 31.7, 30.6, 29.3, 22.6, 14.1; MS (EI): an isotopic cluster peaking at *m/z* 454 (M^+, 100%); Anal. Calcd. for $C_{22}H_{30}Br_2$: C, 58.17; H, 6.66. Found: C, 58.37; H, 6.83.

Preparation of 2,3-dibromo-1,4-dimethylnaphthalene (9). Compound **5** (4.76 g, 14 mmol) was treated with zinc dust (8.72 g, 133 mmol) and $TiCl_4$ (8.7 mL, 79 mmol) in THF according to the above procedure. The resulting mixture was stirred at r.t. overnight, then worked up as described. The product was purified by chromatography with dichloromethane as eluent (3.80 g, 84%). M.p. 156-160°C; ^1H NMR (250 MHz) δ 8.03-8.07 (m, 2 H, ArH), 7.52-7.57 (m, 2 H, ArH), 2.91 (s, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (62.9 MHz) δ 134.2, 131.9, 126.6, 125.6, 125.3, 21.3; MS (EI): an isotopic cluster peaking at *m/z* 314 (M^+, 64%); Anal. Calcd. for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21. Found: C, 46.16; H, 3.19.

Preparation of 2,3-dibromo-5,8-dihexyl-1,4-dimethylnaphthalene (10). By employing the procedure described above, compound **6** (1.6 g, 3.3 mmol) was treated with zinc dust (2.0 g, 30.6 mmol) and $TiCl_4$ (2.0 mL, 18.2 mmol) to give **10** as a colorless liquid, which was purified by column chromatography with hexanes as eluent (1.1 g, 70%). ^1H NMR (250 MHz) δ 7.20 (s, 2 H, ArH), 2.96 (vt, *J* = 8.0 Hz, 4 H, $ArCH_2$), 2.81 (s, 6 H, $ArCH_3$), 1.47-1.63 (m, 4 H, CH_2), 1.16-1.35 (m, 12 H, CH_2), 0.86 (vt, *J* = 6.8 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (62.9 MHz) δ 137.8, 135.5, 134.1, 127.8, 126.5, 36.9, 32.1, 31.6, 29.5, 27.0, 22.6, 14.0; MS (EI): an isotopic cluster peaking at *m/z* 482 (M^+, 15%); HRLSIMS Calcd. for $C_{24}H_{34}{}^{79}Br_2$ (M^+): 480.1028. Found: 480.0991.

Preparation of 2,3-dibromo-1,4-dihexylnaphthalene (11). By using the procedure described above, compound **7** (2.9 g, 6.2 mmol), upon treatment with zinc dust (3.7 g, 56.6 mmol) and $TiCl_4$ (3.7 mL, 33.4 mmol), was converted to **11**. The crude product was chromatographed with ethyl acetate / hexanes (1:10) as eluent, then recrystallized from hexane giving white crystals (2.4 g, 84%). M.p. 57-58°C; ^1H NMR (250 MHz) δ 8.02-8.06 (m, 2 H, ArH), 7.52-7.56 (m, 2 H, ArH), 3.33 (vt, *J* = 8.1 Hz, 4 H, $ArCH_2$), 1.46-1.70

(m, 8 H, CH_2), 1.35-1.40 (m, 8 H, CH_2), 0.92 (vt, J = 7.0 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (125.8 MHz) δ 139.0, 131.7, 126.5, 125.4, 125.2, 34.9, 31.6, 29.7, 29.4, 22.7, 14.1; MS (EI): an isotopic cluster peaking at *m/z* 454 (M^+, 100%); Anal. Calcd. for $C_{22}H_{30}Br_2$: C, 58.17; H, 6.66. Found: C, 58.39; H, 6.67.

Preparation of 2,3-dicyano-5,8-dihexylnaphthalene (12). Compound **8** (1.10 g, 2.4 mmol) and CuCN (0.65 g, 7.3 mmol) were dissolved in DMF (10 mL) and the mixture was heated at 140°C for 10 h under nitrogen. A 35% ammonia solution (40 mL) was added to the mixture which was then bubbled with air overnight. The precipitate was filtered off and washed with chloroform (3 x 20 mL). The filtrate was extracted with chloroform (3 x 50 mL) and the combined organic portions were dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was recrystallized from hexane to give pale yellow needles (0.40 g, 48%). M.p. 85-87°C; ^1H NMR (250 MHz) δ 8.52 (s, 2 H, ArH), 7.52 (s, 2 H, ArH), 3.03 (vt, J = 7.8 Hz, 4 H, $ArCH_2$), 1.61-1.75 (m, 4 H, CH_2), 1.29-1.50 (m, 12 H, CH_2), 0.89 (vt , J = 6.9 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (125.8 MHz) δ 138.5, 132.8, 132.5, 130.6, 116.4, 109.1, 32.6, 31.6, 31.0, 29.3, 22.6, 14.0; MS (EI): *m/z* 346 (M^+, 14%); Anal. Calcd. for $C_{24}H_{30}N_2$: C, 83.19; H, 8.73; N, 8.08. Found: C, 83.81; H, 8.92; N, 8.25.

Preparation of 2,3-dicyano-1,4-dimethylnaphthalene (13). A mixture of **9** (2.20 g, 7.0 mmol) and CuCN (1.88 g, 21.0 mmol) in DMF (25 mL) was refluxed under nitrogen for 10 h. The mixture was cooled then poured into ammonia solution (35 %, 100 mL) which was bubbled with air for 12 h. The solid residue was collected and extracted with dichloromethane (3 x 250 mL). The combined organic extracts were washed with dilute NaCl solution (300 mL) and dried over $MgSO_4$. The volatiles were removed under reduced pressure to give a residue which was purified by column chromatography with dichloromethane as eluent (0.53 g, 37%). M.p. 243-247°C; ^1H NMR (250 MHz) δ 8.13-8.18 (m, 2 H, ArH), 7.79-7.85 (m, 2 H, ArH), 2.96 (s, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (62.9 MHz) δ 141.9, 132.7, 130.1, 125.9, 116.2, 109.9, 18.1; MS (EI): *m/z* 206 (M^+, 100%); IR: 3076w, 2988w, 2927w, 2222s, 1438m, 1397s, 1196w, 1167w, 1019w, 940w, 869w, 769s, 638w, 599w, 520w cm^{-1}; Anal. Calcd. for $C_{14}H_{10}N_2$: C, 81.53; H, 4.89; N, 13.58. Found: C, 80.88; H, 4.80; N, 13.72.

Preparation of 2,3-dicyano-5,8-dihexyl-1,4-dimethylnaphthalene (14). Compound **10** (1.35 g, 2.8 mmol) was mixed with CuCN (0.75 g, 8.4 mmol) in DMF (10 mL) under nitrogen. The light green suspension was refluxed for 6 h then cooled to r.t.. A 35 % ammonia solution (40 mL) was added to the mixture which was bubbled with air overnight. The suspension was filtered and the filtrate was extracted with chloroform (3 x 50 mL), dried over $CaCl_2$, and rotary evaporated. The crude product was purified by column chromatography with hexanes as eluent yielding a white solid (0.73 g, 70%). M.p. 50-51°C; ^1H NMR (250 MHz) δ 7.46 (s, 2 H, ArH), 3.12 (vt, J = 7.9 Hz, 4 H, $ArCH_2$), 3.01 (s, 6 H, $ArCH_3$), 1.50-1.65 (m, 4 H, CH_2), 1.19-1.43 (m, 12 H, CH_2), 0.90 (vt, J = 6.5 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (62.9 MHz) δ 142.0, 140.1, 135.7, 132.0, 116.6, 110.8, 37.1, 32.4, 31.5, 29.3, 23.3, 22.5, 13.9; MS (EI): *m/z* 374 (M^+, 100%); IR: 2956s, 2922s, 2856s, 2222s, 1578w, 1461m, 1378m, 1178w, 1128w, 1033w, 944w, 844w, 800w, 722w, 667w, 522w cm^{-1}; Anal. Calcd. for $C_{26}H_{34}N_2$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.46; H, 9.21; N, 7.39.

Preparation of 2,3-dicyano-1,4-dihexylnaphthalene (15). A mixture of compound **11** (1.2 g, 2.6 mmol) and CuCN (0.7 g, 7.8 mmol) in DMF (15 mL) was heated at 170°C for 10 h under nitrogen. A 35% ammonia solution (40 mL) was added and the mixture was bubbled with air overnight. The precipitate was filtered off and washed with chloroform (3 x 20 mL) and the filtrate was extracted with chloroform (3 x 50 mL). The combined organic portions were evaporated to give a solid which was recrystallized from hexane to give pale yellow needles (0.4 g, 44%). M.p. 95-96°C; ^{1}H NMR (250 MHz) δ 8.15-8.19 (m, 2 H, ArH), 7.76-7.80 (m, 2 H, ArH), 3.33 (vt, *J*= 8.0 Hz, 4 H, ArCH$_2$), 1.68-1.77 (m, 4 H, CH$_2$), 1.48-1.55 (m, 4 H, CH$_2$), 1.32-1.38 (m, 8 H, CH$_2$), 0.89 (vt, *J* = 7.0 Hz, 6 H, CH$_3$); ^{13}C{^{1}H} NMR (125.8 MHz) δ 146.7, 132.5, 129.8, 125.9, 116.2, 109.8, 32.1, 31.5, 31.0, 29.5, 22.5, 14.0; MS (EI): *m/z* 346 (M$^+$, 100%); Anal. Calcd. for $C_{24}H_{30}N_2$: C, 83.19; H, 8.73; N, 8.08. Found: C, 83.05; H, 8.99; N, 8.31.

Preparation of 2,3-dicyano-6,7-dipropylthionaphthalene (17). To an ice-cold suspension of NaH (60 % dispersion in mineral oil, 0.08 g, 2.0 mmol) in DMF (30 mL) was added slowly 1-propanethiol (0.19 mL, 2.1 mmol). The mixture was stirred for a few min until the evolution of hydrogen gas was completed, then 2,3-dibromo-6,7-dicyanonaphthalene (**16**) (0.34 g, 1.0 mmol) and copper(I) oxide (0.28 g, 2.0 mmol) were added and the mixture was refluxed for 3 h. The cooled mixture was poured into ice then extracted with diethyl ether (3 x 50 mL). The combined organic portions were washed with ammonia solution (35 %, 3 x 30 mL) and water (3 x 30 mL), then dried over K_2CO_3. The volatiles were rotary-evaporated to give a yellow solid which was essentially pure for further reactions (0.29 g, 89%). Analytically pure sample was obtained by recrystallization from chloroform / hexane mixture. M.p. 196-197°C; ^{1}H NMR (250 MHz) δ 8.15 (s, 2 H, ArH), 7.58 (s, 2 H, ArH), 3.07 (t, *J* = 7.3 Hz, 4 H, SCH$_2$), 1.83 (sextet, *J* = 7.3 Hz, 4 H, CH$_2$), 1.12 (t, *J* = 7.3 Hz, 6 H, CH$_3$); ^{13}C{^{1}H} NMR (62.9 MHz) δ 142.7, 134.0, 130.8, 123.2, 116.1, 109.3, 34.9, 21.6, 13.7; MS (EI): *m/z* 326 (M$^+$, 58%); IR: 2962s, 2929s, 2872s, 2220m, 1463m, 1424s, 1386m, 1230m, 1105m, 908m, 750m, 590m cm^{-1}; Anal. Calcd. for $C_{18}H_{18}N_2S_2$: C, 66.22; H, 5.56; N, 8.58; S, 19.64. Found: C, 65.63; H, 5.55; N, 8.46; S, 19.42.

Preparation of 2,3-dicyano-6,7-diphenylthionaphthalene (18). By using the above procedure with thiophenol (0.22 mL, 2.1 mmol) as the starting material and refluxing the mixture overnight, compound **18** was obtained which was purified by column chromatography with chloroform / hexanes (1:1) as eluent (0.33 g, 84 %). M.p. 246-247°C (lit.[16] 256-257°C); ^{1}H NMR (250 MHz) δ 7.95 (s, 2 H, ArH), 7.53-7.59 (m, 4 H, Ph), 7.48-7.51 (m, 6 H, Ph), 7.28 (s, 2 H, ArH); ^{13}C{^{1}H} NMR (62.9 MHz) δ 142.8, 134.5, 134.4, 131.2, 130.6, 130.2, 129.7, 125.9, 115.8, 109.5 ; MS (EI): *m/z* 394 (M$^+$, 100%).

Preparation of (2,5,11,14,20,23,29,32-octahexyl-2,3-naphthalocyaninato)zinc(II) (19). A mixture of compound **12** (250 mg, 0.72 mmol) and Zn(OAc)$_2$·2H$_2$O (50 mg, 0.23 mmol) in 1-hexanol (10 mL) was heated at 90°C, then DBU (0.4 mL) was added and the mixture was refluxed under nitrogen for 3 h. The mixture was cooled then poured into methanol / water (1:1, 50 mL). The precipitate was filtered off and the filtrate was mixed with methanol (50 mL) to give a second crop of green solid. The combined solid was dissolved into hexanes (50 mL) then subjected to chromatography with hexanes / THF (2:1) as eluent giving a green powder which was recrystallized from hexane (124 mg, 47%). ^{1}H NMR (250 MHz, THF-d$_8$, 2.8 x 10^{-3} M) δ 9.60 (br s, 8 H, ArH), 7.44 (br s, 8 H, ArH), 3.52 (br s, 16 H, ArCH$_2$), 2.10-2.22 (m, 16 H, CH$_2$), 1.80-1.92 (m, 16 H, CH$_2$), 1.43-1.66 (m, 32 H, CH$_2$), 1.05 (t, *J* = 6.9 Hz, 24 H, CH$_3$); UV-Vis [THF, λ_{max} nm (log ε)]: 338 (4.82), 684 (4.55), 729 (4.60), 766 (5.34); MS (LSI): an isotopic cluster peaking at *m/z* 1451.09 [Calcd. for M$^+$ 1450.89]; IR: 2922s, 2852m, 1654w, 1579w, 1463m, 1370s, 1120s, 731w cm^{-1}; Anal. Calcd. for $C_{96}H_{120}N_8Zn$: C, 79.44; H, 8.33; N, 7.72. Found: C, 78.68; H, 8.38; N, 7.55.

Preparation of (1,6,10,15,19,24,28,33-octamethyl-2,3-naphthalocyaninato)zinc(II) (20). To a mixture of dinitrile **13** (152 mg, 0.74 mmol) and Zn(OAc)$_2$·2H$_2$O (55 mg, 0.25 mmol) in 1-hexanol (10 mL) at 90°C was added DBU (0.4 mL). The mixture was refluxed under nitrogen for 20 h then poured into a mixture of methanol / acetone (1:1, 50 mL). The precipitate was washed with acetone, methanol, and water, then dried *in vacuo* (90 mg, 55%). The green powder was then Soxhlet extracted with methanol / acetone (1:1). UV-Vis [THF, λ_{max} nm (log ε)]: 331 (5.29), 709 (4.98), 754 (5.12), 791 (5.58); IR: 3073w, 2924m, 2858w, 1705w, 1651w, 1609m, 1521m, 1476m, 1407m, 1381m, 1358m, 1407m, 1328m, 1196m, 1127s, 1014s, 940w, 822w, 751s cm^{-1}; Anal. Calcd. for $C_{58}H_{48}N_8O_2Zn$ (**20**·$2CH_3OH$): C, 72.99; H, 5.07; N, 11.74. Found: C, 72.25; H, 5.04; N, 11.63.

Preparation of (2,5,11,14,20,23,29,32-octahexyl-1,6,10,15,19,24,28,33-octamethyl-2,3-naphthalocyaninato)zinc(II) (21). According to the procedure described for **19**, compound **14** (220 mg, 0.59 mmol) was treated with $Zn(OAc)_2 \cdot 2H_2O$ (40 mg, 0.18 mmol) and DBU (0.4 mL) in refluxing 1-hexanol (10 mL) for 16 h. The crude product was purified by column chromatography with hexanes / ethyl acetate (5:1) as eluent (40 mg, 17%). UV-Vis [hexane, λ_{max} nm (log ε)]: 727 (4.75), 812 (5.35); MS (LSI): an isotopic cluster peaking at *m/z* 1562.92 [Calcd. for M^+ 1563.01].

Preparation of (1,6,10,15,19,24,28,33-octahexyl-2,3-naphthalocyaninato)zinc(II) (22). By using the procedure described for **19**, compound **15** (260 mg, 0.75 mmol) was treated with $Zn(OAc)_2 \cdot 2H_2O$ (55 mg, 0.25 mmol) and DBU (0.4 mL) in refluxing 1-hexanol (10 mL) for 20 h. The crude product was subjected to chromatography with hexanes / ethyl acetate (9:1) as eluent giving a brown powder (45 mg, 17%). ^1H NMR (250 MHz) δ 8.70-8.80 (m, 8 H, ArH), 7.80-7.89 (m, 8 H, ArH), 5.04-5.27 (m, 16 H, $ArCH_2$), 1.94-2.11 (m, 16 H, CH_2), 1.61-1.77 (m, 16 H, CH_2), 1.12-1.35 (m, 16 H, CH_2), 0.85 (quintet, *J* = 7.0 Hz, 16 H, CH_2), 0.71 (t, *J* = 7.0 Hz, 24 H, CH_3); UV-Vis [THF, λ_{max} nm (log ε)]: 722 (4.67), 808 (5.30); MS (LSI): an isotopic cluster peaking at *m/z* 1450.90 [Calcd. for M^+ 1450.89]; IR: 3074w, 2954s, 2924s, 2853s, 1707m, 1649m, 1598m, 1462m, 1356m, 1133m, 1093m, 754m, 727w cm^{-1}.

Preparation of (3,4,12,13,21,22,30,31-octapropylthio-2,3-naphthalocyaninato)zinc(II) (23). According to the procedure described for **19**, dinitrile **17** (250 mg, 0.77 mmol) was treated with $Zn(OAc)_2 \cdot 2H_2O$ (53 mg, 0.24 mmol) and DBU (0.4 mL) in refluxing 1-hexanol (10 mL) for 5 h. The cooled solution was poured into methanol / water (1:1, 50 mL) and the precipitate formed was filtered off which was then washed with methanol, water, and hexanes, and was dried in vacuum (139 mg, 53%). Further purification with column chromatography with THF as eluent gave only 25 mg of deep green solid while most of the material stuck in the column. Alternatively, the green solid was Soxhlet extracted with methanol / acetone (1:1) for 2 days. The extract was discarded and the solid was further extracted with chloroform. After evaporating the chloroform extract, analytically pure **23** was obtained. UV-Vis [THF, 1.94 x 10^{-7} M, λ_{max} nm (log ε)]: 355 (4.83), 693 (4.41), 745 (4.59), 778 (5.17); MS (LSI): an isotopic cluster peaking at *m/z* 1370.22 [Calcd. for M^+ 1370.30]; IR: 2961m, 2928m, 2871w, 1722w, 1626w, 1582m, 1455s, 1410m, 1345m, 1261w, 1144w, 1103s, 1033m, 904w, 803w, 736w, 696w cm^{-1}; Anal. Calcd. for $C_{74}H_{74}Cl_6N_8S_8Zn$ (**23**·$2CHCl_3$): C, 55.20; H, 4.63; N, 6.96. Found: C, 54.91; H, 5.03; N, 6.63.

Preparation of (3,4,12,13,21,22,30,31-octaphenylthio-2,3-naphthalocyaninato)zinc(II) (24). By using the above procedure, dinitrile **18** (250 mg, 0.63 mmol) was converted to **24**, which was purified by column chromatography with THF as eluent (125 mg, 48%). Analytically pure sample was prepared by Soxhlet extraction with methanol / acetone (1:1) followed by chloroform. UV-Vis [THF, λ_{max} nm (log ε)]: 353 (5.16), 694 (4.92), 741 (4.90), 779 (5.67); MS (LSI): an isotopic cluster peaking at *m/z* 1642.09 [Calcd. for M^+ 1642.17]; IR: 3053w, 2912w, 2838w, 1579m, 1476m, 1439m, 1406m, 1370m, 1342s, 1088s, 1024m, 738m, 689m cm^{-1}; Anal. Calcd. for $C_{98}H_{58}Cl_6N_8S_8Zn$ (**24**·$2CHCl_3$): C, 62.54; H, 3.11; N, 5.95. Found: C, 62.74; H, 3.52; N, 5.67.

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