New approach to the synthesis of phthalocyanines containing strong accepting and donating groups

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The mixed condensation of 3,6-didecyloxyphthalodinitrile and 4-nitrophthalimide in the presence of copper acetate, urea and ammonium molybdate gives new unsymmetrical phthalocyanines containing both alkoxy and nitro groups.

Asymmetrically substituted phthalocyanines (Pcs) are of paramount importance because of their possible applications in nonlinear optics,[1–3] as liquid crystals,[4–5] *etc.* Phthalocyanines containing strong electron-donating and electron-accepting moieties, which can induce strong polarization of the electron system of the macrocycle, are of special interest. The syntheses of such compounds were described in many publications.[6–10]

Peripherally functionalised Pcs like $\mathrm{M[PcA}_n\mathrm{B}_{4-n}]$, where $n = 1$–4, can be synthesised using a statistical condensation method. However, this way is ineffective if the starting phthalodinitriles are very different in reactivity. Dinitriles containing acceptor groups are rapidly tetramerised to form a symmetrical Pc. On the other hand, less reactive components do not undergo condensation of this kind. We used less reactive 4-nitrophthalimide **1** instead of 4-nitrophthalonitrile as a reagent for synthesising asymmetrically substituted Pcs.

Previously,[11] we found that traditional mixed condensation of 4-nitro- and 3,6-didecyloxyphthalonitriles does not give asymmetrically substituted Pcs, and only tetranitrophthalocyanine was obtained in this case.

On the other hand, the statistical condensation of **1** and 3,6-didecyloxyphthalodinitrile **2** in the molar ratio 9:1 in the presence of urea, catalytic quantities of ammonium molybdate and copper(II) acetate gave a mixture of unsymmetrical Pcs with overall yield 20%. The $\mathrm{Cu^{II}}$-templated condensation takes place at 180 °C. The symmetrically octasubstituted copper Pc does not form under these conditions.

The asymmetrically substituted Pcs obtained can be separated by extraction with $\mathrm{CCl_4}$. The mixture was precipitated from DMF, and compounds **3**–**5** were isolated by column chromatography. The yields of **3**–**5** are 4, 2 and 7%, respectively. The yield of copper 4-tetranitrophthalocyanine, which is insoluble in common organic solvents, is 68%. The structures of **3**–**5** were confirmed by ^{1}H and ^{13}C NMR and UV-VIS spectroscopy and mass spectrometry.† All compounds gave satisfactory elemental analyses. These substances are readily soluble in most organic solvents (benzene, $\mathrm{CHCl_3}$, $\mathrm{CCl_4}$ and toluene), but they are only slightly soluble in DMF and acetone. UV-VIS (Figure 1) and ^{1}H NMR spectroscopy showed that compound **5** is not associated in dilute solutions.

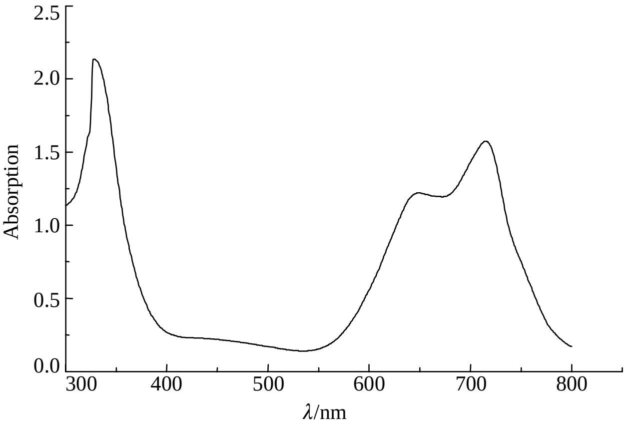
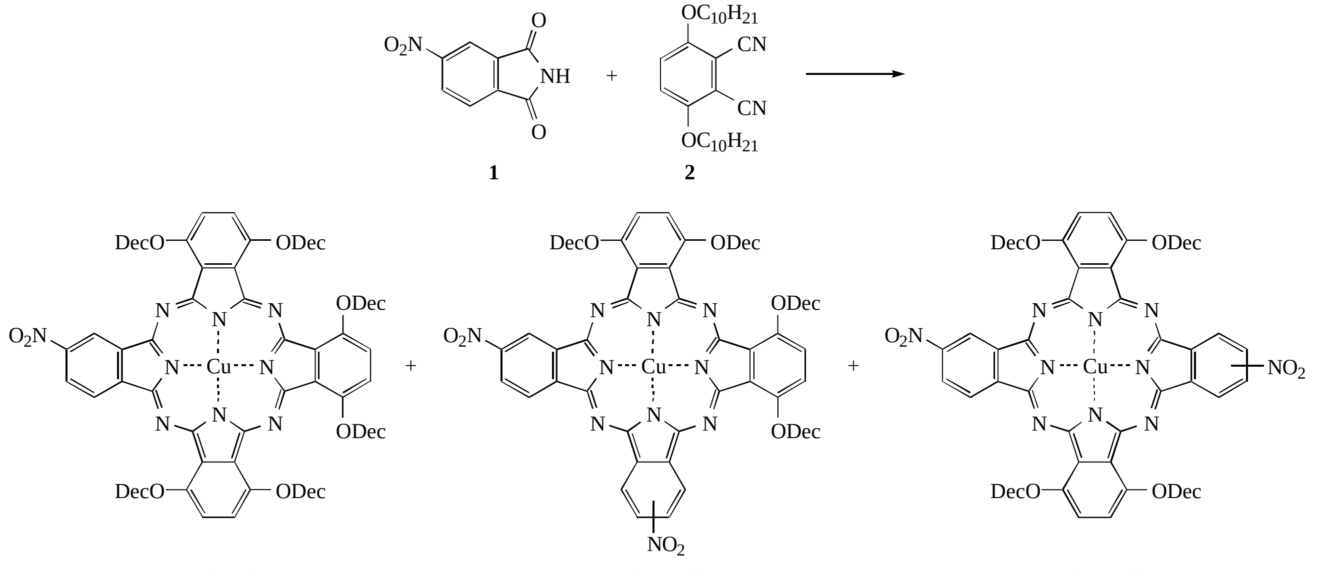


Figure 1 UV-VIS spectrum of **5** in a $\mathrm{CHCl_3}$ solution.

Compounds **3**–**4** possess significant dipole moments and are strongly associated in dilute solutions. The ^{1}H NMR studies of **3** and **4** in isotropic solutions evidenced aggregation phenomena. Line broadening was observed even at a concentration of 1×10^{-3} mol dm^{-3} in $\mathrm{CDCl_3}$, whereas in more dilute solutions (1×10^{-4} mol dm^{-3}) the ^{1}H NMR peaks became narrower. The presence of a broad band at 660–650 nm in the UV-VIS spectra suggests the aggregation of **3** or **4** in chloroform solutions.



1 **2**

3 ($\mathrm{A_3B}$) **4** (AABB) **5** (ABAB)

These facts show that dipole–dipole interaction is the main reason for association in these solutions.

Preliminary data indicate that nitro substitution in phthalocyanine derivatives with four (**5**) or six (**3**) alkoxy groups in non-peripheral positions results in both thermotropic and lyotropic (with a number of organic solvents) mesomorphism.

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Referenses

1 G. de la Torre, P. Vazques, F. Agullo-Lopez and T. Torres, *J. Mater. Chem*., 1998, **8**, 1671.

2 B. Cabezon, F. Fernandez-Lazaro, M. V. Martinez-Diaz, S. Rodrigez-Morgade, A. Sastre and T. Torres, *Synth. Met.*, 1995, **71**, 2289.

3 S. G. Liu, Y. Q. Liu, Y. Xu, D. B. Zhu, A. C. Yu and X. S. Zhao, *Langmuir*, 1998, **14**, 690.

4 Z. Aladib, G. J. Clarkson, N. B. McKeown, K. E. Treacher, H. F. Glecson and A. S. Stennet, *J. Mater. Chem*., 1998, **11**, 2371.

5 G. S. Clarkson, N. B. McKeown and K. E. Treacher, *J. Chem. Soc., Perkin Trans*. *2*, 1995, **14**, 1817.

6 B. Hauschel, R. Jung and M. Hanack, *Eur. J. Inorg. Chem*., 1999, **4**, 693.

7 G. de la Torre, M. V. Martinez-Diaz, P. R. Ashon and T. Torres, *J. Org. Chem*., 1998, **63**, 8888.

8 E. M. Maya, P. Vazquec and T. Torres, *Chem. Eur. J*., 1999, **5**, 2004.

9 E. M. Maya, C. Garsia, E. M. Garsia-Frutos, P. Vazquez and T. Torres, *J. Org. Chem.*, 2000, **65**, 2733.

10 N. Kobayashi, M. Togashi, T. Osa, K. Ishii, S. Yamauchi and H. Hiho, *J. Am. Chem. Soc*., 1996, **118**, 1073.

11 S. Makhsud, A. Cook and N. B. McKeown, *Chem. Commun*., 1999, 419.

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[†] *Phthalocyanines* **3**–**5**. 3,6-Didecyloxyphthalonitrile (1 g, 0.00227 mol), 4-nitrophthalimide (3.9 g, 0.0204 mol), $Cu(MeCOO)_2 \cdot 2H_2O$ (0.59 g, 0.0027 mol), urea (2 g) and ammonium molybdate (0.01 g) were heated at 190 °C. After 2 h, the products were extracted with CCl_4, the solvent was evaporated, and the precipitate was crystallised from DMF. The residue was dissolved in benzene and chromatographed on Al_2O_3 (Reakhim). The blue zone was washed away from the column. Evaporation of the eluate gave a blue powder, a mixture of compounds **3** and **4**. Compound **5** was eluted using benzene–acetone (10:1). Evaporation of the eluate afforded a viscous blue precipitate of **5** (83 mg, 7%). ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 8.94 (s, 2H), 8.35–8.26 (dd, 4H), 7.65 (d, 2H), 7.09 (d, 2H), 4.13–3.88 (m, 4H), 1.90–1.76 (m, 4H), 1.29 (s, 64H), 0.88 (t, 12H). ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ: 165.12, 163.72, 151.08, 139.50, 135.37, 132.46, 131.55, 121.63, 120.15, 114.48, 68.41, 68.20, 31.93, 29.72, 29.66, 25.99, 22.71, 14.13. UV-VIS (λ_{CHCl_3}/nm): 330.1, 452.6, 650.5, 714.8. MS, *m*/*z* (EI): 1201 $(M - 2NO_2 + 2)^+$ (100%), 1200 $(M - 2NO_2 + 1)^+$ (68%), 1199 $(M - 2NO_2)^+$ (80%), 1058 $(M - 2NO_2 - C_{10}H_{21})^+$ (22%), 917 $(M - 2NO_2 - 2C_{10}H_{21})^+$ (23%). Found (%): C, 70.6; H, 8.9; N, 8.0. Calc. for $C_{92}H_{135}N_9O_8Cu$ (%): C, 70.9; H, 8.7; N, 8.1.

A mixture of **3** and **4** was dissolved in benzene and chromatographed on silica gel (L5/40). A blue zone was washed away from the column. After evaporation, compound **4** (28 mg, 2%) was isolated as a viscous blue precipitate. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.56–0.87 (br. t, 72H), 0.07–(–0.03) (br. t, 12H). MS, *m*/*z* (FAB): 1291 $(M + H^+)$. UV-VIS (λ_{CHCl_3}/nm): 273.5, 335.5, 653.0 (br), 764.0 (sh). Found (%): N, 10.6. Calc. for $C_{72}H_{94}N_{10}O_8Cu$ (%): N, 10.8.

The use of benzene–CH_2Cl_2 (5:1) as an eluent gave compound **3** (57 mg, 4%) as a viscous blue precipitate (after evaporation). ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.27–2.07 (br. t, 84H), 1.67–1.47 (br. t, 24H), 0.09–(–0.1) (br. t, 18H). UV-VIS (λ_{CHCl_3}/nm): 332.0, 435.0 (br), 656.5 (br). MS, *m*/*z* (FAB): 1559 $(M + H^+)$. Found (%): C, 66.7; H, 7.6; N, 10.6. Calc. for $C_{72}H_{94}N_{10}O_8Cu$ (%): C, 67.0; H, 7.3; N, 10.8.