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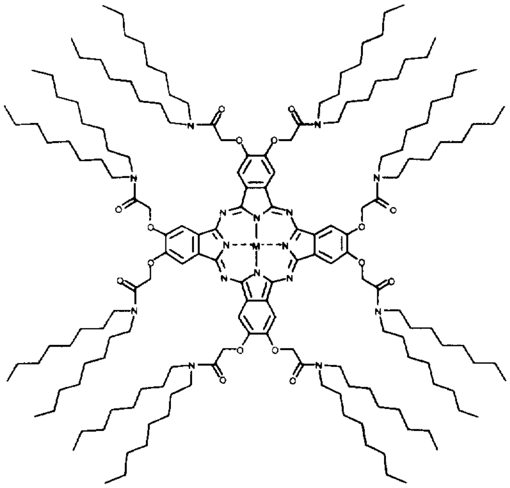
Synthesis and Different Aggregation Properties in Solution of Alkyl- and Dialkyl Amide Surrounded Phthalocyanines

José A. Duro, Gema de la Torre and Tomás Torres*

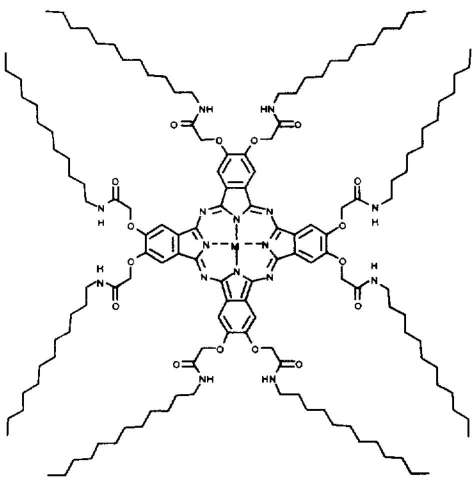
Departamento de Química (C-I), Facultad de Ciencias, Universidad Autónoma de Madrid,
Cantoblanco, 28049-MADRID, Spain

Abstract: The synthesis of dodecylaminocarbonylmethoxy substituted phthalocyanines **5-7** and their precursors is described. It is demonstrated that aggregation in solution of dioctylaminocarbonylmethoxyphthalocyanines **1-4** is induced by the presence of cations whilst hydrogen bonding is the only determinant force in the aggregation of **5-7**.

Since their discovery in the early 20's, phthalocyanines have been the object of numerous investigations related to their interesting physical properties. In this way, extraordinary semi-, metallic- and photoconducting behaviours have been demonstrated.[1] These properties have supramolecular character and drastically depend on the grade of organization of the three dimensional structures these compounds give rise to.[1] By following the studies we had started on dioctylaminocarbonylmethoxy substituted phthalocyaninate copper **1**,[2] we have recently synthesized the corresponding nickel **2**,[3] cobalt **3**,[4] and free **4**[3] phthalocyanines. Our interest in these structures and related compounds **5-7** as well as in certain phthalocyanine analogues is concerned with their capability to self-organize into the liquid-crystal state[3] and in Langmuir-Blodgett films[5], and the possibility of modulating the aggregation in solution by adding cations.[1,6]



1 M = Cu
2 M = Ni
3 M = Co
4 M = 2H



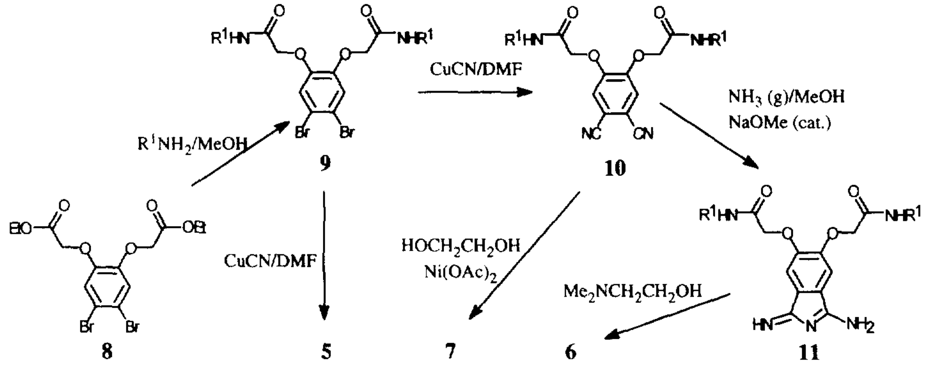
5 M = Cu
6 M = Ni
7 M = 2H

The mesomorphic properties of compounds **1-4** have been studied by us and will be reported elsewhere.[3] Aggregation properties of these and the related compounds **5-7** will be described here.

It is worth pointing out that the expected induced aggregation properties of compounds **1-4** have to be attributed to the OCH_2CONR_2 groups.[2] Since monoalkylamides offer the additional possibility of hydrogen bonding, the soluble dodecylaminocarbonylmethoxy analogues **5-7** were also studied. Although the arrangement of the donor centers responsible for cation coordination is in essence common in both types of phthalocyanines, we demonstrate here that phthalocyanines **5-7** bearing monoalkylamides surrounding the aromatic core show a different behaviour than that of **1-4**, thus indicating the important role of hydrogen bonding.

Synthesis. The synthesis of phthalocyanines **1-4** has been already described.[2-4] Phthalocyanines **5-7** were prepared by the methods shown in Scheme 1: the diester **8**[3] was condensed with dodecylamine (R^1-NH_2) in refluxing MeOH to give the amide **9**[7] (R^1 = dodecyl) in quantitative yield. The synthesis of the 4,5-dicyano derivative **10**[7] (R^1 = dodecyl) was carried out by the Rosenmund von Braun reaction, with an excess of CuCN in boiling DMF. The conversion into 1,3-diiminoisoindoline **11**[7] (R^1 = dodecyl) was achieved by bubbling NH_3 into a solution of **10** in dry MeOH in the presence of catalytic amounts of NaOMe.

In this way, phthalocyaninate copper **5**[7] was prepared by reaction of the dibromo compound **9** with an excess of CuCN in boiling DMF. Trituration with sulfuric acid and water afforded the pure product. Nickel compound **6**[7] was synthesized by self-condensation of the 4,5-dicyano **10** in boiling ethylenglycol in the presence of $Ni(AcO)_2$, and purified by flash cromatography. The metal-free derivative **7**[7] was obtained by refluxing diiminoisoindoline **11** in dimethylaminoethanol and purified by flash chromatography followed by recrystallization in DMF.



Scheme 1

Aggregation properties. The aggregation properties of nickel and cobalt phthalocyanines **2** and **3** are quite similar to those already described for the copper one **1**.[2] In chloroform solution (10^{-3} to 10^{-5} M), compounds exist mainly as monomeric species. In both cases, typical Q-bands at 667 and 669 nm respectively are present in the UV-visible spectra of the metallomacrocycles. The free ligand **4** behaves in a very similar way. In this case, as usual, two bands at 661 and 698 nm are present in the low energy region. The addition of alkali metal ions (Na^+, K^+, Rb^+, Cs^+, iodide as counterion) or ammonium iodide, dissolved in a negligible amount of methanol to chloroform solutions of compounds **2-4**, gives rise to drastic changes in the UV-visible spectra. In Fig. 1 the electronic spectra of **2** and **4** at different concentrations of K^+ and Na^+, respectively, are depicted. On increasing the concentration of the salt, new bands at 640 and 634 nm respectively, shifted to the blue with respect to the

Q-band, are developed. These bands are less intense but broader than the original ones, as expected for dimer or oligomer formation.[8] In the B-band region (ca. 350 nm) only small changes in wavelength and intensity are noticed. A similar effect was observed by adding the other cations to solutions of **2** and **4**. The same behaviour was noticed for cobalt phthalocyanine **3**. In this case, upon addition of the above mentioned metallic salts a new band appears at 631 nm. However, as previously described for phthalocyaninate copper **1**, the behaviour of phthalocyanines **2-4** in the presence of Li^+ is different, very probably due to its small size and, as a matter of fact, aggregation is not clearly achieved with this cation. So, it seems clear that there exists a cooperative effect in the case of Na^+, K^+, Rb^+, Cs^+, and NH_4^+ to promote aggregation , but not with Li^+.

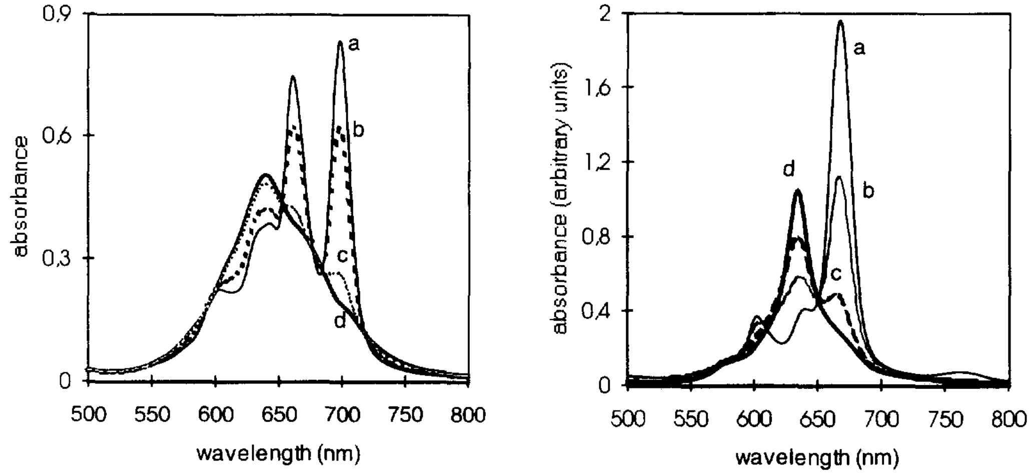


Fig. 1: Lower energy region of the UV-visible spectra of phthalocyanines (ca. 10^{-5} M) in the presence of increasing amounts of cations (a>b>c>d; range: 10^{-6}-10^{-5} M). left: Metal-free phthalocyanine **4** in the presence of Na^+; right: Nickel phthalocyanine **2** in the presence of K^+.

As mentioned above, phthalocyanines **5-7** show in solution a quite different behaviour from that of **1-4**. Firstly, at 10^{-5} M metal free phthalocyanine **7** is monomeric in chloroform, showing in the UV-visible spectrum two bands at 672 and 708 nm. However, copper **5** and nickel **6** complexes are aggregated species at this concentration as demonstrated by the lower intensity of the respective Q-band and the presence of a broad band in the range 600-700 nm. This differential behaviour between the metal and free macrocycles is certainly remarkable and points out the influence of the central metal in phthalocyanine organization. Similar effects have been noticed for certain mesophases of free and metal porphyrins[9] and phthalocyanines.[10]

Taking into account the above described results it is possible to postulate an equilibrium between the monomeric and the aggregated species in **5-7** modulated by the inter- and the intramolecular nature of the hydrogen bonds. This equilibrium is shifted to the aggregated species in **5** and **6** where intermolecular bonds must be predominant by the additional favourable metal-metal interactions. In phthalocyanine **7**, where these interactions can't take place, intramolecular hydrogen bonding seems to be the most favourable one and monomeric species prevail.[11]

On the other hand, surprisingly, the addition of cations to solutions of monoalkylamide phthalocyanines neither induces the aggregation in the case of **7** nor produces additional effects over the spectra of **5** and **6**, thus indicating that the coordinative centers of these compounds are basically implicated in the stronger hydrogen bonds. This fact was further confirmed by ^{1}H-NMR experiments carried out on phthalocyanines **4** and **7**, at higher concentrations (ca. 10^{-3} M), by addition of cations. In the case of **7**, the presence of potassium iodide, for instance, does not produce any changes in the spectrum opposite to the effects noticed in phthalocyanine **4** where the signals become sharper and aliphatic protons are spread out. Similar changes in ^{1}H-NMR spectra of phthalocyanines have been described by other authors.[12]

In summary, the alkylaminocarbonylmethoxy moiety has been established to be an effective subunit for achieving self-organization. This is determined either by cooperative effect of the alkoxycarbonyl functions in the case of **1-4** or by hydrogen bonding interactions as the main force in the case of **5-7**.

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7. **9**: Yield 98%; mp 126-127°C. ^{1}H-NMR ($CDCl_3$): δ 7.14 (s, 2H, arom.), 6.5 (m, 2H, NH), 4.51 (s, 4H, CH_2O), 3.3 (m, 4H, CH_2N), 1.5 (m, 4H, $C\mathit{H}_2CH_2N$), 1.2 (bs, 36H, CH_2), 0.9 (m, 6H, CH_3) ppm. IR (KBr): ν 3440, 2910, 2810, 1670, 1520, 1480, 1440, 1250-1190, 1050, 930, 880, 860 cm^{-1}. FAB-MS (NOBA): m/z 719 ($M+H^+$). Elemental analysis for $C_{34}H_{58}N_2O_4$: Calc.: C, 56.82; H, 8.13; N, 3.89%. Found: C, 56.86; H, 8.27; N, 3.75%.

   10: Yield 27%; m.p. 192-193°C. ^{1}H-NMR ($CDCl_3$): δ 7.21 (s, 2H, arom.), 6.4 (m, 2H, NH), 4.63 (s, 4H, CH_2O), 3.4 (m, 4H, CH_2N), 1.6 (m, 4H, $C\mathit{H}_2CH_2N$), 1.2 (bs, 36H, CH_2), 0.9 (m, 6H, CH_3) ppm. IR (KBr): ν 3390-3300, 2910, 2830, 2220, 1660, 1590, 1550-1520, 1470, 1370, 1300, 1230, 1100, 910, 720 cm^{-1}. FAB-MS (NOBA): m/z 611 ($M+H^+$). Elemental analysis for $C_{36}H_{58}N_4O_4$: Calc.: C, 70.78; H, 9.57; N, 9.17%. Found: C, 70.12; H, 9.88; N, 8.85%.

   11: Yield 95%. ^{1}H-NMR (TFAA-d_1): δ 8.22 (s, 2H, arom.), 5.09 (s, 4H, CH_2O), 3.6 (m, 4H, CH_2N), 1.7 (m, 4H, $C\mathit{H}_2CH_2N$), 1.3 (m, 36H, CH_2), 0.9 (m, 6H, CH_3) ppm. IR (KBr): ν 3300, 2900, 2830, 1660, 1540, 1465, 1425, 1290, 1200, 1150, 1060 cm^{-1}. FAB-MS (NOBA): m/z 628 ($M+H^+$).

   5: Yield 28%, m.p.> 250°C. IR (KBr): ν 3400-3300, 2910, 2840, 1660, 1610, 1550-1530, 1460, 1410, 1280-1200, 890, 740 cm^{-1}. Elemental analysis for $C_{144}H_{232}CuN_{16}O_{16}\cdot 5\,H_2O$: Calc.: C, 66.60; H, 9.39; N, 8.63%. Found: C, 66.47; H, 9.14; N, 8.78%.

   6: Yield 30%, m.p. > 250°C. ^{1}H-NMR ($CDCl_3$): δ 8.1 (bs, 8H, arom.), 4.7 (m, 16H, CH_2O), 3.5 (m, 16H, CH_2N), 1.7 (m, 16H, $C\mathit{H}_2CH_2N$), 1.3 (m, 144H, CH_2), 0.9 (m, 24H, CH_3) ppm. IR (KBr): ν 3400-3200, 2900, 2830, 1650, 1600, 1535, 1460, 1425, 1340, 1270-1250, 1200, 1100, 840, 720 cm^{-1}. Elemental analysis for $C_{144}H_{232}N_{16}NiO_{16}\cdot 5H_2O$: Calc.: C, 66.72; H, 9.41; N, 8.64%. Found: C, 66.69; H, 9.04; N, 8.67%.

   7: Yield 22%, m.p. > 250°C. ^{1}H-NMR ($CDCl_3$): δ 8.3 (bs, 8H, arom.), 5.0 (m, 16H, CH_2O), 4.4 (m, 16H, CH_2N), 1.6 (m, 16H, $C\mathit{H}_2CH_2N$), 1.3 (m, 144H, CH_2), 0.9 (m, 24H, CH_3) ppm. IR (KBr): ν 3550-3270, 2960, 2840, 1690, 1610, 1470, 1390, 1330, 1285-1260, 1100, 1020, 885, 750 cm^{-1}. Elemental analysis for $C_{144}H_{234}N_{16}O_{16}$: Calc.: C, 70.72; H, 9.64; N, 9.16%. Found: C, 69.75; H, 9.16; N, 9.68%.
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