Synthesis and Aggregation Properties in Solution of a New Octasubstituted Copper Phthalocyanine: {2,3,9,10,16,17,23,24-Octakis-[(dioctylaminocarbonyl)methoxy]phthalocyaninato}copper(II)

José Antonio Duro and Tomás Torres*

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

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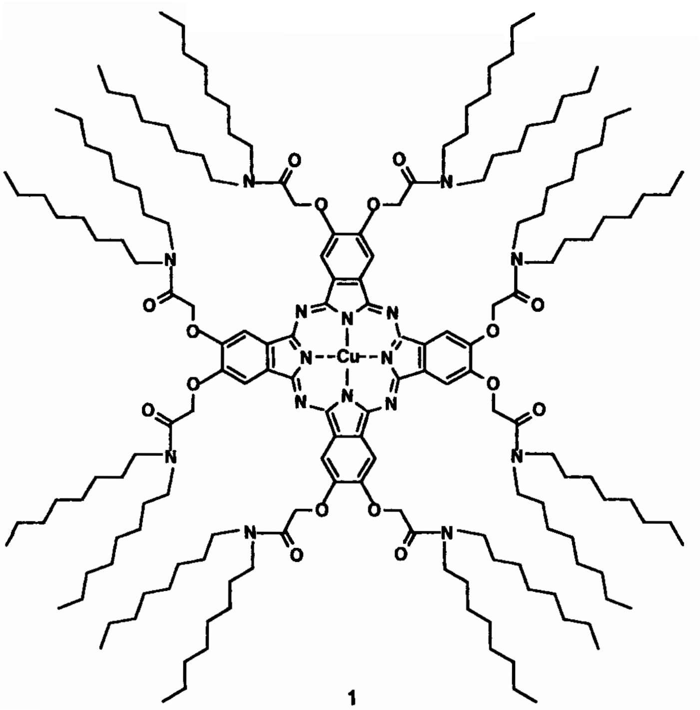
The synthesis of the octasubstituted phthalocyanine **1**, highly soluble in organic solvents, is described. Its aggregation properties in different solvents and in the presence of alkaline, alkaline earth, and ammonium salts are studied.

In recent years an increasing recognition of the important role of phthalocyanines in the construction of low-dimensional organic conductors has stimulated synthetic interest in these compounds[1]. Unsubstituted phthalocyanines show limitations in the spontaneous arrangement and organization of their molecular units in suitable crystal structures because they usually exhibit polymorphism in the solid state. In order to enable a higher organization degree, Hanack and coworkers have developed structure-enforced polymeric assemblies based on this moiety[2]. On the other hand, the extremely poor solubility of unsubstituted phthalocyanines in common organic solvents often precludes successful deposition onto solid substrates as ordered Langmuir-Blodgett (LB) films. Peripheral substitution of these metallomacrocycles with long alkyl, alkoxy chains, or crown ether moieties enhances their solubility drastically. Some of these compounds have been shown to form self-organized systems as discotic mesophases[3]. In organic solvents some specially substituted phthalocyanines as the so-called "crowned" phthalocyanines tend to form aggregates[4]. Aggregation phenomena are also induced in these compounds by alkali metal ions which are sandwiched between two crown ether rings[4].



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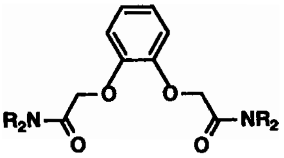
In this paper, the synthesis and aggregation properties of an octasubstituted phthalocyanine **1**, highly soluble in organic solvents, are described.

Results and Discussion

The reaction of *o*-phenylenedioxydiacetyl dichloride[5] with dioctylamine affords the diamide **2**, which is brominated in the presence of a catalyst to give the *o*-dibromo derivative **3**. Treatment of **3** with CuCN gives **1** in 31% yield after recrystallization. Phthalocyanine **1** has been identified by IR, FAB mass spectrometry, UV/Vis spectrophotometry, and elemental analysis. Compound **1** is very soluble in apolar organic solvents such as *n*-hexane but only partially soluble in polar ones (DMF, acetonitrile).



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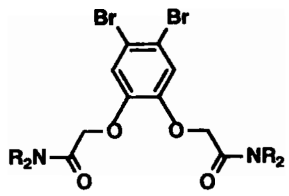
R: $(CH_2)_7CH_3$



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Electronic absorption spectra of phthalocyanine **1** in different solvents are depicted in Figure 1. The observed solvent dependence of the absorption spectra does not differ markedly from that in "crowned" phthalocyanines. Thus, the spectrum in chloroform (a), analogous to that obtained in pyridine (not represented), is typical of a monomeric (Q band at 676 nm) species[4] in solution and in polar protic solvents such as ethanol (b), methanol, and *n*-butanol, dimeric or oligomeric (band at 637 nm) species[4] prevail. However, in *n*-hexane (d) the Q band has almost disappeared and the band centered at 637 nm appears now as a broad maximum between 600 and 640 nm attributable to

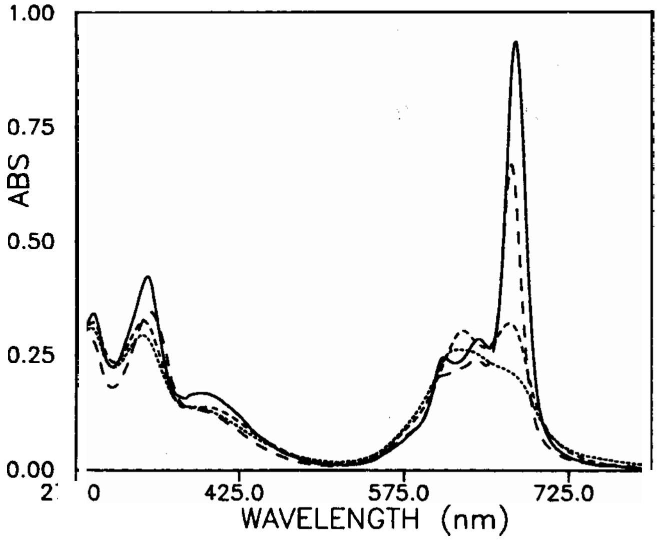

Figure 1. Electronic spectra of **1** in a) chloroform (——), b) ethanol (— — —), c) THF (— — — —), and d) *n*-hexane (······)

trimeric and larger species in agreement with literature data[6].

Diamides structurally analogous to **2** have been shown to act as alkaline and alkaline earth ionophores[5,7]. In agreement with this fact, the addition of alkaline, alkaline earth, and ammonium salts to solutions of phthalocyanine **1** in chloroform/methanol (15:1) gives rise to important changes in the UV/Vis spectrum, thus resembling the behavior of the above mentioned "crowned" phthalocyanines[4]. As in the referred case, on increasing the concentration of the salt, the absorption band at 676 nm attributable to the monomer decreases in intensity, whereas the one due to oligomeric aggregates at 637 nm increases. In Figure 2 the electronic spectra of **1** at different concentrations of potassium nitrate are depicted. Similar qualitative and quantitative results have been obtained with sodium, rubidium, calcium, and ammonium nitrates due to the capability of the amide chains to accomodate cations of different size. In the case of lithium nitrate a much higher concentration of salt is needed to detect the presence of oligomeric species, thus indicating the lower aptitude of this cation to induce aggregation.

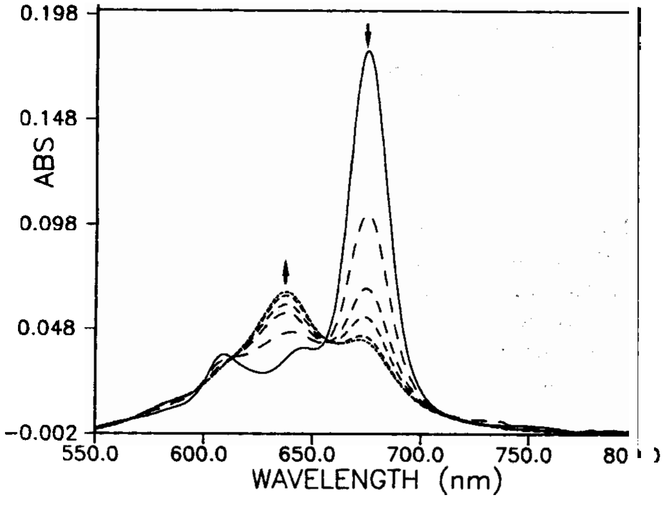

Figure 2. Electronic spectra of **1** [$9.4 \cdot 10^{-7}$ M in chloroform/MeOH (15:1)] in the presence of increasing concentrations of KNO_3 (from 10^{-6} to 10^{-5} M)

On the other hand, the effect anions exert on the aggregation of phthalocyanine **1** is not pronounced as deduced from the experiments carried out at different concentrations of sodium thiocyanate, perchlorate, and iodide as represented in Figure 3. Therefore, it must be assumed that aggregation phenomena are mainly determined by the cation.

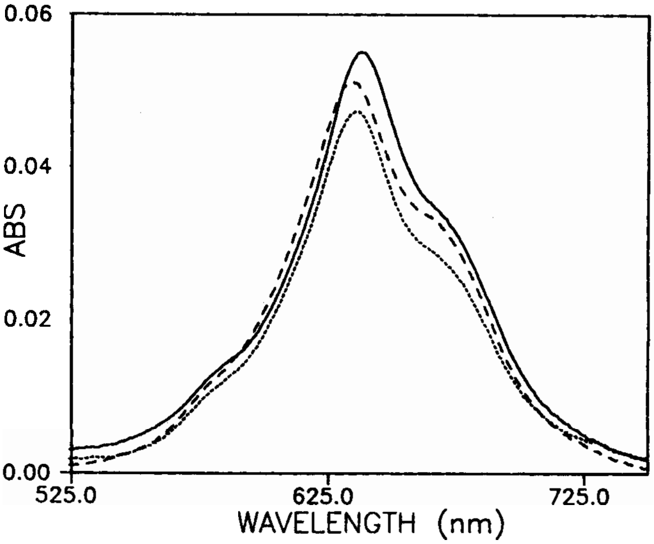

Figure 3. Electronic spectra of **1** ($9.4 \cdot 10^{-7}$ M) in the presence of different salts ($6.0 \cdot 10^{-6}$ M): a) sodium iodide (——), b) perchlorate (······), and c) thiocyanate (— — —)

As in the aggregation model proposed by Nolte[4a], and Kobayashi and Lever[4b] for phthalocyanines containing crown ether subunits, the nucleophilic centers of the eight amide chains of **1** can act cooperatively in cation coordination to promote sandwich-like aggregation in solution, leading to cofacial dimers.

The mesogenic properties of **1** and related compounds will be reported in due course.

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Experimental

IR: Philips PU 9716. – ^{1}H NMR and off resonance-decoupled ^{13}C NMR: Bruker WM 200 SY. – UV/Vis: Perkin Elmer lambda 6. – MS (EI and FAB): VG Autospec and MAT 900 (Finnigan MAT, GmbH, Bremen).

N,N,N',N'-Tetraoctyl-1,2-phenylenedioxydiacetamide (**2**): *o*-Phenylenedioxydiacetyl dichloride was prepared according to a slight modification of the described method[5]. Thus, 5.60 g (24.8 mmol) of *o*-phenylenedioxydiacetic acid was suspended in 30 ml of thionyl chloride, and 3–4 drops of pyridine was added. The reaction mixture was stirred at reflux temp. until the solid was completely dissolved (usually 2–3 h). The solvent was removed in vacuo and the residue used without purification in the next step. The crude product was dissolved in 35 ml of toluene and a solution of 14.5 g (60.0 mmol) of dioctylamine and 10.0 ml (7.26 g, 71.7 mmol) of triethylamine in 35 mnl of toluene was carefully added to the solution.

The mixture was kept with stirring overnight at room temp. After usual workup **2** was purified by flash chromatography [silica gel; hexane/ethyl acetate (5:2)] giving a colorless oil; yield: 10.59 g (63%). – IR (Nujol): $\tilde{\nu}$ = 1660 cm^{-1} (C=O), 1200–1260 (C–O–C), 1060–1130 (C–O–C). – ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 6.9 Hz, 12H, CH_3), 1.25 (s, 40H, CH_2), 1.52 (m, 8H, CH_2CH_2N), 3.30 (m, 8H, CH_2N), 4.74 (s, 4H, CH_2CO), 6.91 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6, 26.9, 27.4, 28.9, 29.2, 29.3, 31.8 (CH_2), 46.0, 47.2 (CH_2N), 68.1 (CH_2O), 115.2 (aromatic C-3,6), 122.3 (aromatic C-4,5), 148.2 (C–O), 167.6 (C=O). – MS (70 eV), *m/z* (%): 672 (6) [M^+], 404 (100) [M^+ – $OCN((CH_2)_7CH_3)_2$].

$C_{42}H_{76}N_2O_4$ (673.1)
Calcd. C 74.95 H 11.38 N 4.16
Found C 74.92 H 11.26 N 4.16

N,N,N',N'-Tetraoctyl-1,2-(4,5-dibromophenylenedioxy)diacetamide (**3**): To a solution of 1.72 g (2.55 mmol) of the diamide **2** in 10 ml of dichloromethane containing catalytic amounts of powdered iron and iodine was added dropwise a solution of 1.00 g (6.26 mmol) of bromine in 10 ml of dichloromethane. The mixture was stirred at room temp. for 48 h, then diluted with 50 ml of hexane and washed with a 15% solution of sodium hydrogen sulfite (2 × 50 ml). The solvent was removed in vacuo and the residue purified by flash chromatography [silica gel, toluene/acetone (20:1)] giving 2.00 g (94%) of a colorless oil. – IR (Nujol): $\tilde{\nu}$ = 1660 cm^{-1} (C=O), 1200–1250 (C–O–C), 1060 (C–O–C). – ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 6.2 Hz, 6H, CH_3), 0.88 (t, *J* = 6.2 Hz, 6H, CH_3), 1.26 (s, 40H, CH_2), 1.53 (m, 8H, CH_2CH_2N), 3.28 (m, 8H, CH_2N), 4.74 (s, 4H, CH_2O), 7.12 (s, 2H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6, 26.9, 27.4, 28.9, 29.2, 29.3, 31.7 (CH_2), 47.0, 49.5 (CH_2N), 67.8 (CH_2O), 116.0 (CBr), 119.6 (aromatic CH), 148.0 (C–O), 166.4 (C=O). – MS (FAB, *m*-nitrobenzyl alcohol), *m/z* (%): 830 (64), 832 (100), 834 (56) [M + 1^+], 560 (11), 562 (20), 564 (10) [M^+ – $OCN((CH_2)_7CH_3)_2$].

$C_{42}H_{74}Br_2N_2O_4$ (830.9)
Calcd. C 60.71 H 8.98 N 3.37
Found C 61.01 H 8.78 N 3.13

{2,3,9,10,16,17,23,24-Octakis[(dioctylaminocarbonyl)methoxy]-phthalocyaninato}copper(II) (**1**): To 1.10 g (1.32 mmol) of **3** were added 1.5 ml of DMF, 0.31 g (3.46 mmol) of CuCN, and 2 drops of pyridine. The mixture was heated with magnetic stirring at reflux temp. for 10 h. After cooling, it was dissolved in hexane/NH_4OH (30%) (1:1). The hexane layer was washed with NH_4OH until no blue color developed in the aqueous phase, subsequently with water. After removal of the solvent in vacuo the residue was washed with ethanol/hydrochloric acid (37%) (10:1.5), filtered, and recrystallized from ethanol/hydrochloric acid (37%) to give a dark green solid. The product was completely dried as a melt at 130°C/3 · 10^{-2} Torr. Yield: 0.31 g (31%) of **1**, m.p. 100–102°C. – IR (Nujol): $\tilde{\nu}$ = 1660 cm^{-1} (C=O), 1200–1280 (C–O–C), 1070–1110 (C–O–C). – UV ($CHCl_3$): λ_{max} (lg ε) = 292 nm (4.615), 340 (4.683), 392 (4.110), 609 (4.304), 644–646 (sh), 676 (5.124). – MS (FAB, *m*-nitrobenzyl alcohol), *m/z* (%): 2953.4 (49), 2954.4 (65), 2955.4 (73), 2956.4 (66), 2957.4 (52), 2958.4 (36), 2959.4 (20) [M^+, M + 1^+], 2976.4, 2977.4 [M + Na^+].

$C_{176}H_{296}CuN_{16}O_{16}$ (2955.9)
Calcd. C 71.51 H 10.09 N 7.58
Found C 71.22 H 9.93 N 7.79

UV/Vis Experiments and Measurements: Spectra of **1** in different solvents (chloroform, pyridine, *n*-butanol, ethanol, hexane, tetrahydrofuran), were recorded at 5.1 · 10^{-6} M. Experiments in the presence of salts were performed by the addition of 1 ml of methanolic solutions containing variable concentrations (typically between 10^{-5} and 10^{-4} M) of the slats [$NaNO_3$, KNO_3, $RbNO_3$, $Ca(NO_3)_2$ · 4 H_2O, NH_4NO_3, NaI, $NaClO_4$, NaSCN] to 15 ml of a 1.0 · 10^{-6} M solution of **1** in chloroform (final concentration of **1**: 9.4 · 10^{-7} M). When necessary (e.g. potassium and rubidium nitrates) some drops of DMF were added in order to dissolve the nitrates in 100 ml of the methanolic solution. Spectra with $LiNO_3$ were recorded in the concentration range between 10^{-5} and 10^{-2} M.

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