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Highly soluble phthalocyanines with hexadeca *tert*-butyl substituents

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ABSTRACT

A phthalonitrile derivative bearing 2,4-di-*tert*-butylphenoxy substituents at peripheral positions was synthesized; subsequent cyclotetramerization in DMF and hexanol furnished the desired zinc (II), magnesium (II), copper (II) and nickel (II) phthalocyanines. These metallo-phthalocyanines were highly soluble in solvents such as dichloromethane, chloroform, acetone, ethyl acetate, tetrahydrofuran, diethyl ether, *n*-hexane and DMF. The structures of the compounds were confirmed by elemental analyses, IR, ^{1}H NMR, ^{13}C NMR, electronic spectra and mass spectroscopic methods.

1. Introduction

Although many phthalocyanines are insoluble in common organic solvents, their solubility can be improved by the incorporation of substituents, such as alkyl or alkoxy groups of different chain lengths [1–3], or branched systems at peripheral positions [4–8]. Apart from their traditional use as industrial dyes and pigments, these compounds have been extensively studied as advanced materials for various applications [9–11]. Thus, phthalocyanines can be tuned to suit desired technological applications. The solubility of phthalocyanines is very important for the investigation of their chemical and physical characteristics [12]. Solubility of phthalocyanines in polar solvents and water [13–15] is mainly achieved by introduction of polar or ionic groups (e.g. $-SO_3^-$, $-NR_3^+$, $-COO^-$, etc.) on the peripheral positions [16–18]. In the case of soluble products in apolar organic solvents, these substituents are long alkyl or alkoxy chains, bulky substituents or macrocyclic groups such as crown ether [4,19]. 4,5-Disubstituted phthalonitrile and zinc phthalocyanine have been synthesized and photochemical properties have been reported [20].

We have demonstrated that four 2,4-di-*tert*-butylphenoxy substituents result with extremely soluble phthalocyanines in apolar solvents [6].

In this study, the synthesis and characterization of soluble metallo-phthalocyanines (Zn, Mg, Cu, Ni) carrying at two positions 2,4-di-*tert*-butylphenoxy substituents on the periphery are reported. These phthalocyanines display good solubility in common organic solvents such as acetone, ethyl acetate, dichloromethane, chloroform, tetrahydrofuran, diethyl ether, dimethyl formamide, toluene, and *n*-hexane.

2. Experimental

Electronic spectra on a Perkin Elmer Lambda 25 UV–Vis and Unicam spectrophotometers. Routine IR spectra were recorded on a Mattson 1000 FTIR spectrometer in KBr pellets. ^{1}H NMR spectra were recorded on a Bruker 200 MHz spectrometer with tetramethylsilane as internal standard. Mass spectra were recorded on a Bruker Daltonics Autoflex III MALDI–TOF–MS. Elemental analyses results were found in good agreement with calculated values. 4,5-Dichloro-1,2-dicyanobenzene and 4,5-disubstituted phthalonitrile were synthesized according to published procedures [20,21]. All other reagents and solvents were of reagent-grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [22] the solvents were stored over molecular sieves (4 Å).

2.1. 4,5-Disubstituted phthalonitrile (**1**)

The 4,5-dichloro-1,2-dicyanobenzene (1.97 g, 0.01 mol) was dissolved in dimethyl sulfoxide (DMSO) (20 cm^3) under nitrogen and 2,4-di-*tert*-butylphenol (4.53 g, 0.02 mol) was added. After stirring for 15 min at 70 °C, finely ground anhydrous potassium carbonate (8 × 20 mmol,) was added in portions during 2 h with

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efficient stirring. The reaction mixture was stirred under nitrogen at 50–60 °C for 24 h. Then the mixture was poured into 200 ml ice–water, and precipitate was filtered off, washed with water and dried. The residue was recrystallized from ethanol–ethyl acetate.

The yield was 4.43 g (82.6%). mp 272 °C. Calcd for $C_{36}H_{44}N_2O_2$: C, 80.56; H, 8.26; N, 5.22%. Found: C, 80.61; H, 8.22; N, 5.19%. IR spectrum (cm^{-1}): 3114, 2955, 2868, 2227, 1746, 1603, 1585, 1505, 1493, 1394, 1363, 1293, 1253, 1211, 1086, 881, 836, 648, 531, 494. ^1H NMR ($CDCl_3$): $\delta = 7.49–7.24$ (6H, m, Ar–H), 7.16 (1H, s, Ar–H), 6.82 (1H, d, Ar–H), 1.36 (36H, d, CH_3). ^{13}C NMR ($CDCl_3$): $\delta = 152.4, 150.4, 148.4, 140.8, 125.1, 124.6, 121.4, 120.3, 115.3, 109.4, 77.6, 77.0, 76.3, 34.9, 34.8, 31.4, 30.3$.

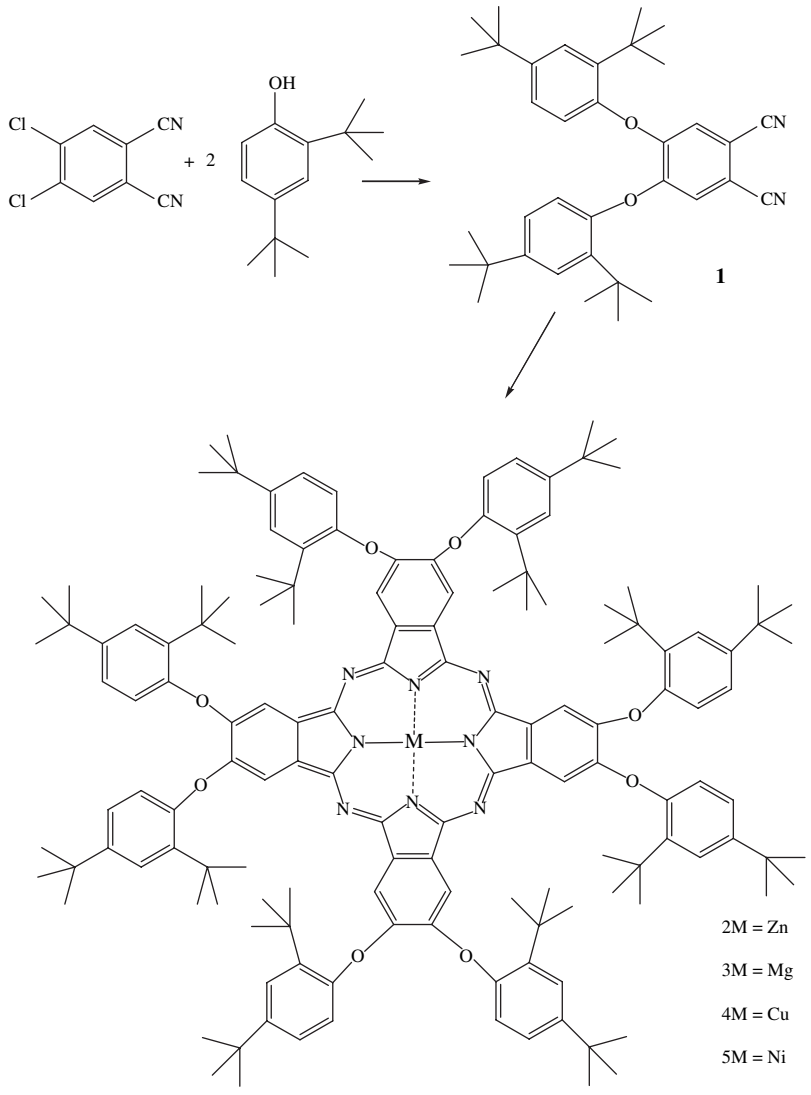
2.2. Phthalocyaninato zinc (II) (**2**)

Compound **1** (0.268 g, 0.5 mmol), anhydrous $ZnCl_2$ (0.017 g) and 1.2 ml of dry dimethyl formamide (DMF) were placed in a standard Schlenk tube in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.05 ml) under nitrogen atmosphere and held at reflux temperature for 6 h. After cooling to room temperature, the reaction mixture was precipitated by adding it drop-wise into water. The dark green product was filtered off, washed with water and ethanol. Further purified chloroform ($CHCl_3$) was added in order to dissolve the crude product, which was then precipitated with ethanol. The dark green product was filtered off, washed with ethanol and dried. The product is soluble in dichloromethane (CH_2Cl_2), $CHCl_3$, acetone, ethyl acetate, tetrahydrofuran (THF), diethyl ether, toluene, *n*-hexane, and DMF.

The yield was 0.111 g (40%). Calcd for $C_{144}H_{176}N_8O_8Zn$: C, 78.18; H, 8.02; N, 5.06%. Found C, 78.23; H, 8.00; N, 5.09%. IR spectrum (cm^{-1}): 2958, 2862, 1722, 1662, 1604, 1586, 1492, 1451, 1396, 1362, 1273, 1220, 1124, 1086, 1027, 908, 882, 831, 746. UV–vis ($CHCl_3$) λ_{max}/nm (log ε): 680 (5.38), 651 (4.54) 613 (4.59), 368 (4.88). ^1H NMR ($CDCl_3$): $\delta = 7.49–7.15$ (Ar–H), 1.56–1.21 (aliphatic CH_3 protons). MALDI–TOF–MS *m*/*z*: 2212 $[M]^+$.

2.3. Phthalocyaninato magnesium (II) (**3**)

Compound **1** (0.268 g, 0.5 mmol), anhydrous $MgCl_2 2H_2O$ (0.029 g) and 1 ml of 1-hexanol were placed in a standard Schlenk tube in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.05 ml) under nitrogen atmosphere and held at 160 °C for 4 h. After cooling to room temperature, the reaction mixture was precipitated by adding it drop-wise into ethanol. The dark green product was filtered off, washed with ethanol. Further purified $CHCl_3$ was added in order to dissolve the crude product, which was then precipitated



Scheme 1.

Table 1
UV–vis data for the phthalocyanines

Compound	Solvent	λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1})
2	$CHCl_3$	680 (5.38), 651 (4.54), 613 (4.59), 368 (4.88)
3	$CHCl_3$	681 (5.10), 650 (4.25), 614 (4.30), 365 (4.68)
4	$CHCl_3$	680 (5.28), 651 (4.51), 612 (4.54), 350 (4.76)
5	$CHCl_3$	765 (4.53), 676 (5.12), 608 (4.57), 304 (5.03)

with ethanol. The dark green product was filtered off, washed with ethanol and dried. The product is soluble in CH_2Cl_2, $CHCl_3$, THF, acetone, ethyl acetate, diethyl ether, toluene, *n*-hexane, and DMF.

The yield was 0.105 g (39%). Calcd for $C_{144}H_{176}N_8O_8Mg$: C, 79.65; H, 8.17; N, 5.16%. Found C, 79.71; H, 8.14; N, 5.15%. IR spectrum (cm^{-1}): 2960, 2868, 1720, 1665, 1604, 1493, 1448, 1397, 1360, 1270, 1215, 1196, 1119, 1085, 1026, 905, 883, 817, 735. UV–vis ($CHCl_3$) λ_{max}/nm (log ε): 681 (5.10), 650 (4.25), 614 (4.30), 365 (4.68). ^{1}H NMR ($CDCl_3$): $\delta = 7.26$–7.25 (Ar–H), 1.46–1.21 (aliphatic CH_3 protons). MALDI–TOF–MS *m*/*z*: 2171 [M]$^+$.

2.4. Phthalocyaninato copper (II) (**4**)

Compound **1** (0.268 g, 0.5 mmol), anhydrous $CuCl_2$ (0.0168 g) and 1.5 ml of 1-hexanol were placed in a standard Schlenk tube in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.05 ml) under nitrogen atmosphere and held at 160 °C for 17 h. After cooling to room temperature, the reaction mixture was precipitated by adding it drop-wise into water. The dark green product was filtered off, washed with ethanol. Further purified $CHCl_3$ was added in order to dissolve the crude product, which was then precipitated with ethanol. The dark green product was filtered off, washed with ethanol and methanol dried. The product is soluble in CH_2Cl_2, $CHCl_3$, THF, acetone, ethyl acetate, diethyl ether, toluene, *n*-hexane, and DMF.

The yield was 0.099 g (36%). Calcd for $C_{144}H_{176}N_8O_8Cu$: C, 78.24; H, 8.03; N, 5.07%. Found C, 78.21; H, 7.99; N, 5.09%. IR spectrum (cm^{-1}): 2959, 2868, 1602, 1493, 1454, 1409, 1360, 1272, 1215, 1197, 1122, 1087, 1037, 908, 887, 850, 814, 751. UV–vis ($CHCl_3$) λ_{max}/nm (log ε): 680 (5.28), 651 (4.51), 612 (4.54) 350 (4.76).

2.5. Phthalocyaninato nickel (II) (**5**)

Compound **1** (0.268 g, 0.5 mmol), anhydrous $NiCl_2$ (0.017 g) and 2 ml of 1-hexanol were placed in a standard Schlenk tube in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.05 ml) under nitrogen atmosphere and held at 160 °C for 24 h. After cooling to room temperature, the reaction mixture was precipitated by adding it drop-wise into ethanol. The dark green product was filtered off, washed with ethanol. Further purified $CHCl_3$ was added in order to dissolve the crude product, which was then precipitated with ethanol. The dark green product was filtered off, washed with ethanol and methanol dried. The product is soluble in CH_2Cl_2, $CHCl_3$, THF, acetone, ethyl acetate, diethyl ether, toluene, *n*-hexane, and DMF.

The yield was 0.097 g (35%). Calcd for $C_{144}H_{176}N_8O_8Ni$: C, 78.41; H, 8.04; N, 5.08%. Found C, 78.37; H, 8.06; N, 5.05%. IR spectrum (cm^{-1}): 2957, 2868, 1604, 1489, 1417, 1396, 1273, 1215, 1193, 1122, 1087, 1087, 1048, 908, 888, 858, 817, 743. UV–vis ($CHCl_3$) λ_{max}/nm (log ε): 765 (4.53), 676 (5.12), 608 (4.57), 304 (5.03).

3. Results and discussion

The synthesis of 4,5-disubstituted phthalonitrile is based on the reaction of 2,4-di-*tert*-butylphenol with 4,5-dichloro-1,2-dicyanobenzene (in DMSO and in the presence of dry K_2CO_3 as base, at 50–60 °C in 24 h). 4,5-disubstituted phthalonitrile was obtained in higher yield than reported in Ref. [20]. The metallophthalocyanines **2**–**5** were prepared from the corresponding 4,5-disubstituted phthalonitrile and corresponding metal salts (Zn [20], Mg, Cu, Ni) in DMF and 1-hexanol at 153–160 °C for 4–24 h (Scheme 1).

Characterization of the products involved a combination of methods, including elemental analysis, UV–vis, mass spectra were used for compounds **2** and **3**, ^{1}H and ^{13}C NMR spectroscopies. Elemental analyses of the starting materials and the phthalocyanines show good agreement with the calculated values.

The formation of 4,5-disubstituted phthalonitrile **1** was clearly indicated by the appearance in its FTIR spectrum of the CH_3 bands at 2955, 2868 cm^{-1} and the CN band at 2227 cm^{-1}. In its ^{1}H NMR spectrum the aromatic protons appear at 7.49–7.24, 7.16, 6.82 ppm

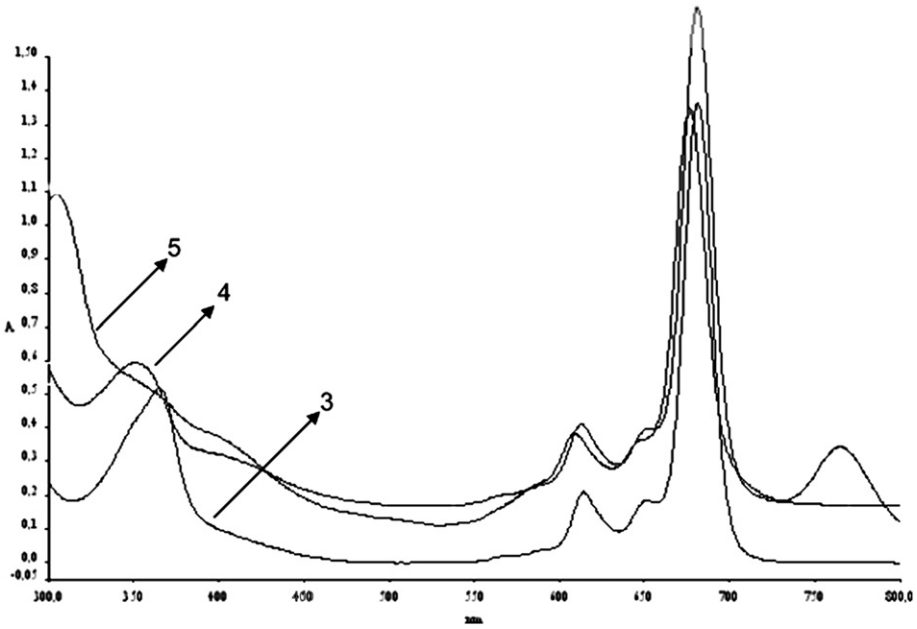


Fig. 1. Electronic spectra of **3**–**5** in chloroform.

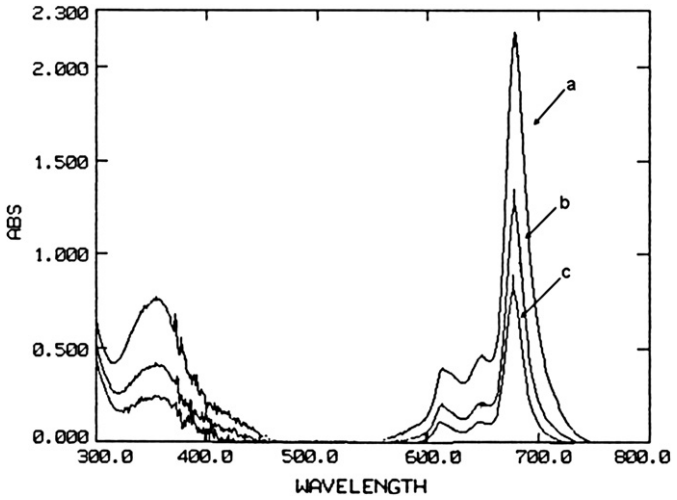


Fig. 2. Electronic spectra of **2** in hexane in a concentration range of a (10^{-3} M), b (10^{-4} M), and c (10^{-6} M).

and the CH_3 aliphatic protons at 1.36. The ^{13}C NMR of compound **1** in $CDCl_3$ gave signals at 152.4–120.3 ppm (aromatics), at 115.3 ppm (CN), and 34.9–30.3 ppm (CH_3).

The FTIR spectrum on the phthalocyanines clearly indicates the cyclotetramerizations of the 4,5-disubstituted phthalonitrile with the disappearance of the CN peak at 2227 cm^{-1} [14,15]. In the ^1H NMR spectrum of compound **2** in $CDCl_3$ aromatic protons appear at 7.49–7.15 ppm (Ar–H) and aliphatic protons at 1.56–1.21 (CH_3) groups. In the ^1H NMR spectrum of compound **3** in $CDCl_3$ aromatic protons appear at 7.26–7.25 ppm (Ar–H) and aliphatic protons at 1.46–1.21 (CH_3) groups.

The best indication for the phthalocyanine systems is their UV–vis spectra in solutions. The synthesized metal phthalocyanines (**2**–**5**) showed typical electronic spectra with two strong absorption regions at B band and the other in the visible region at Q band (Table 1). The UV–vis spectra of compounds **3–5** recorded in chloroform show the typical metallo-phthalocyanine complexes (Fig. 1). The Q band was attributed to the $\pi \rightarrow \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. Other bands (B) in UV region were observed due to transition from the deeper π levels to the LUMO.

Table 2
Solubility of compounds in various solvents

Solvents	2	3	4	5
Acetone	++	++	++	++
Ethyl acetate	++	++	++	++
Chloroform	++	++	++	++
Toluene	++	++	++	++
Dichloromethane	++	++	++	++
Tetrahydrofuran	+	+	+	+
Diethyl ether	+	+	+	+
Dimethyl formamide	+	+	+	+
n-Hexane	+	+	+	+
Dimethyl sulfoxide	−	−	−	−
Methanol	−	−	−	−

++: Solubility in the range of 0.101–0.212 mol l^{-1} at 20 °C; +: solubility in the range of 0.043–0.076 mol l^{-1} at 20 °C; and −: insoluble at 20 °C.

The consequence of the substitution with eight di-*tert*-butylphenoxy groups has been clearly observed by the extremely high solubility of the Pcs **2–5** in organic solvents varying solubility such as acetone, ethyl acetate, dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), tetrahydrofuran (THF), diethyl ether, dimethyl formamide (DMF), toluene, and *n*-hexane.

UV–vis spectra of zinc Pc (**2**) were measured in hexane in a concentration range of 10^{-3}–10^{-6} M and it was observed that no appreciable aggregation was taking place even up to this relatively high concentration value of 10^{-3} M (Fig. 2).

In addition to these apparent results for the structures, the MALDI–TOF–MS measurements of the compounds **2** and **3** gave the characteristic molecular ion peaks at *m*/*z*: 2212 $[M]^+$ and *m*/*z*: 2171 $[M]^+$, respectively, by which the proposed structures were

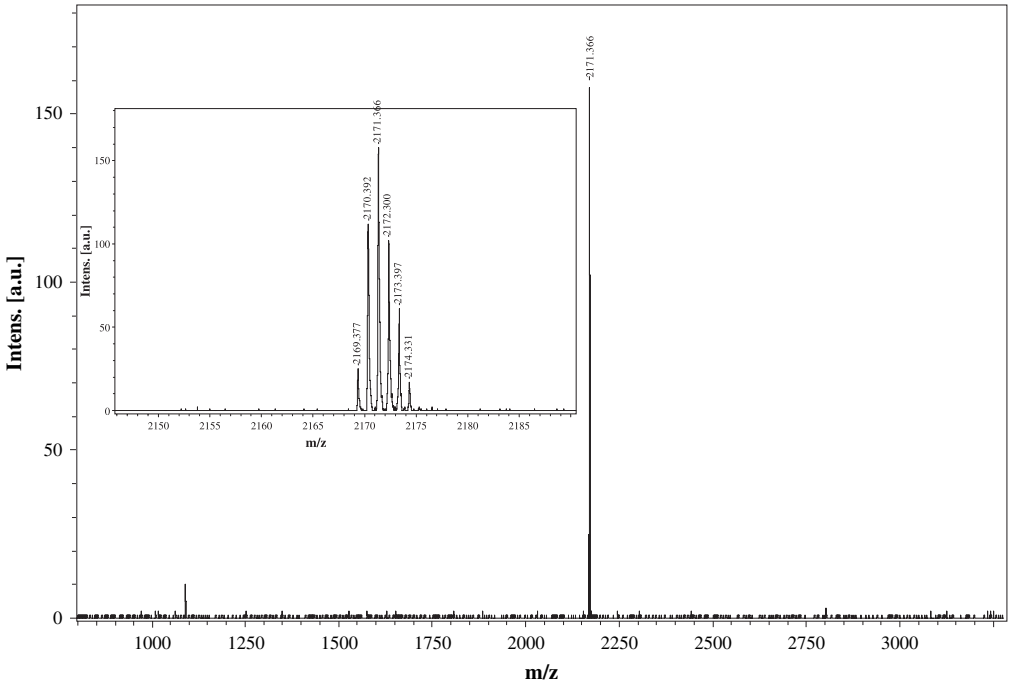


Fig. 3. Mass spectra of **3**.

confirmed. MALDI–TOF–MS is an excellent tool for thoroughly investigating this kind of compounds (Fig. 3).

4. Conclusion

Soluble zinc (II) [20], magnesium (II), copper (II) and nickel (II) phthalocyanines with eight 2,4-di-*tert*-butylphenoxy substituents were synthesized, separated and characterized. Through the introduction of butylphenoxy groups into peripherical positions of phthalocyanines, the solubility in organic solvents increased (Table 2). With the current coating technology in the fabrication of optical disks, a good solubility of phthalocyanine in alcohols and other organic solvents is becoming more important [23]. Solvent soluble macrocycles are of interest to the energy research community because of their potential application in the preparation of sensor, electrode coating, catalysts and oxygen transporting agents [24]. In conclusion the Pcs reported in this work can be considered as efficient candidates for solution studies requiring monomeric form of these materials as in the case of photosensitizers used in photodynamic therapy.

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