Monatsh Chem (2012) 143:437–442
DOI 10.1007/s00706-011-0614-3

ORIGINAL PAPER

Synthesis and electronic absorption studies of novel (trifluoromethyl)phenoxy-substituted phthalocyanines

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Received: 19 July 2010 / Accepted: 5 August 2011 / Published online: 3 September 2011

Abstract The reaction of 4-[4-(trifluoromethyl)phenoxy]phenol with 4-nitrophthalonitrile in the presence of K_2CO_3 leads to formation of 4-[4-[4-(trifluoromethyl)phenoxy]phenoxy]phthalonitrile. Tetrakis[4-[4-(trifluoromethyl) phenoxy]phenoxy]-substituted metal-free phthalocyanine was achieved by tetramerization of the phthalonitrile in 2-(dimethylamino)ethanol, whereas metallophthalocyanines were prepared in the presence of zinc, cobalt, or copper salts. These compounds show high solubility in weakly and medium polar solvents, in strongly polar solvents (dimethylformamide, dimethylsulfoxide), and in aromatic hydrocarbons (toluene, benzene). The new phthalocyanines were characterized by elemental analyses, ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR, ^{19}F NMR, ultraviolet-visible (UV-Vis), Fourier-transform infrared (FT-IR), and mass spectroscopic methods.

Keywords Aggregation · Metals · Phthalocyanines · Phenoxy · Solubility

Introduction

Phthalocyanines have been investigated in detail for many years with respect to their attractive optical and electrical properties combined with thermal and chemical stability [1, 2]. In addition to their use as blue/green colorants, phthalocyanines have been recently expanding into applied fields such as catalysts [3, 4], photocatalysts [4, 5], sensors [6], optical data storage [7], liquid crystals [8], xerography [9], nonlinear optics [10], solar energy conversion [11], and electrochromism [12, 13].

Most notable among the uses of phthalocyanines is as photosensitizers in photodynamic therapy (PDT) [14–16]. Zinc phthalocyanines in particular are well known for their photosensitizing abilities, while unmetallated phthalocyanine derivatives show very little PDT effect [17, 18]. Also metallophthalocyanine derivatives act as photosensitizers for different reactions including transformation of alkenes and alkanes [19] and degradation of pollutants [20].

The specificity of applications of phthalocyanines can be modified by both changes in the phthalocyanine π-conjugation or changes in the central metals. Unsubstituted phthalocyanines and their metal-ion-containing derivatives are characterized by strong intermolecular cohesion, which results in nonmelting, insoluble solids. Peripheral or nonperipheral attachment of bulky or long-chain groups to the phthalocyanine greatly increases the solubility of these complexes in common organic solvents due to enhanced disaggregation over that observed for other phthalocyanine complexes in solution. Among these, we may cite alkoxy [21–24], aryloxy [25–28], alkylsulfanyl [29, 30], arylsulfanyl [31], and bulky groups [32, 33]. The introduction of amino, pyridyl, or carboxy groups gives water-soluble products [34–36]. Also these substituents offer a useful way of regulating the wavelength of the Q band. Although phthalocyanines carrying electron-donating substituents have frequently been described, those with electron-withdrawing groups have not been extensively studied, especially those containing fluorine atoms. Recently, several workers reported the synthesis and properties of some fluoroalkoxy-substituted phthalocyanines [37–39].

Fluorine compounds are known to enhance the solubility of phthalocyanine in polar, aprotic solvents [40]. Introducing electron-withdrawing fluorine substituents to the

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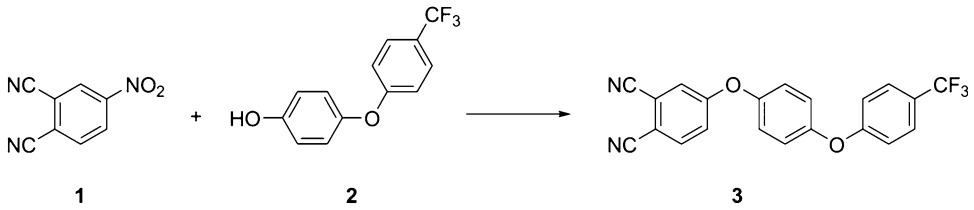
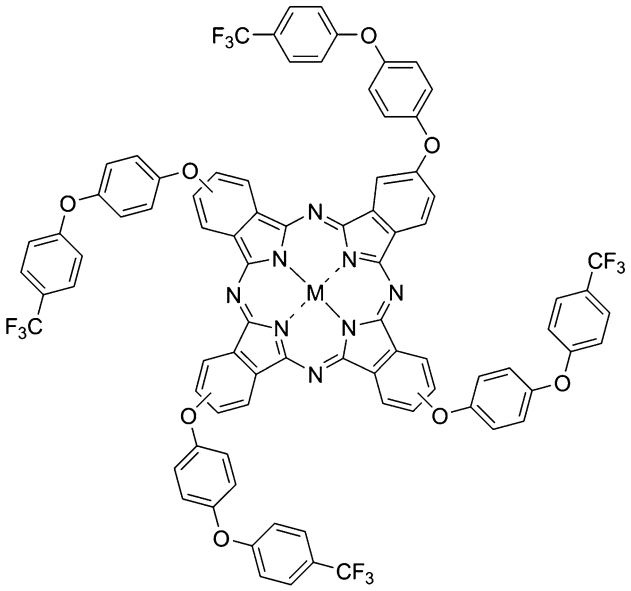
Scheme 1



1 **2** **3**

phthalocyanines shifts the redox processes towards positive potentials [41]. Phthalocyanines are shown to catalyze reactions such as the reduction and/or oxidation of some special species, oxygen, carbon dioxide, and formic acid [42, 43]. Fluorinated phthalocyanines and porphyrin derivatives provide some advantages over nonfluorinated derivatives as photosensitizers [44–47]. The influence of the trifluoromethyl group in biologically active molecules is associated with the increased lipophilicity that this substituent imparts [48].

During the last few years we have focused on the preparation and study of phthalocyanines and related compounds. The introduction of functional groups on the phthalocyanine improves its solubility and enhances electrochemical and optical properties of the phthalocyanines [49–51]. The prime objective of the present work is the synthesis and characterization of new readily soluble phthalocyanines with strong electron-withdrawing substituents. The catalytic efficiency of phthalocyanine complexes depends on their aggregation state and the influence of the medium on stabilization of the catalytically active coordination forms [52]. In this connection, the aggregation behavior of the synthesized complexes was studied by electronic spectroscopy in different solvents and over a wide concentration range.



4 **5** **6** **7**
M= 2H Zn^{2+} Co^{2+} Cu^{2+}

Scheme 2

Results and discussion

A convenient route is to synthesize tetrasubstituted phthalonitriles through reactions between 4-nitrophthalonitrile and donor groups, and the prepared phthalonitriles undergo cyclotetramerization to give the corresponding phthalocyanines [53–55].

Starting from 4-nitrophthalonitrile (**1**) and 4-[4-(trifluoromethyl)phenoxy]phenol (**2**), compound **3** was obtained by a base-promoted nucleophilic aromatic displacement. The reaction was carried out at 30 °C in dry N,N-dimethylformamide (DMF) with K_2CO_3 as the base. The synthetic route is shown in Scheme 1.

Template cyclotetramerization of dinitrile derivative **3** in the presence of anhydrous metal salts [$Zn(CH_3COO)_2$, $CoCl_2$, $CuCl_2$] gave the tetrasubstituted phthalocyanine derivatives as shown in Scheme 2. Metal-free phthalocyanine **4** was obtained directly by refluxing **3** in 2-(dimethylamino)ethanol. Column chromatographic purification, with experimental conditions that may vary from one complex to another, was efficient. The phthalocyanines were isolated by column chromatography on silica gel.

Tetrasubstituted phthalocyanines, synthesized from 3- and 4-substituted phthalonitrile or other *ortho*-disubstituted phenyl derivatives, are obtained as mixtures of four structural isomers with D_{2h}, C_{4h}, C_{2v}, and C_s symmetries, respectively [56]. These isomers are rarely separable, but it was shown to be possible by high-performance liquid chromatography (HPLC) techniques [57]. No attempt was made to separate the isomers of **5**–**7**.

The ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, FT-IR, UV-Vis, and MS spectral data for the newly synthesized compounds were consistent with the assigned formulation. The results are given in the experimental section.

The infrared (IR) spectral results of the metallophthalocyanines **5**–**7** are different from compound **3**, so the sharp peak for the C≡N vibration at 2,233 cm^{-1}, associated with the nitrile group, disappeared after conversion into the phthalocyanines. ^{1}H NMR spectra of **3** in $CDCl_3$ showed only the signal due to the aromatic ring protons at

$\delta = 7.75$–7.07 ppm. ^{19}F NMR spectroscopy is a very useful technique for investigating the fluorinated compound. The ^{19}F NMR spectrum of **3** showed a peak at -64.66 ppm.

The IR spectra of metal-free phthalocyanine **4** show an NH stretching band at 3,287 cm^{-1} due to the inner core imino group. These protons are also very well characterized by the ^{1}H NMR spectrum, which shows a peak at $\delta = -6.08$ ppm as a result of the aromatic 18 π-electron system of the phthalocyanine ring.

^{1}H NMR spectra of ZnPc **5** provided the characteristic chemical shifts for the structure expected. The aromatic protons appeared between 7.55 and 6.98 ppm. The IR spectrum of ZnPc exhibits two bands at 3,111 and 3,063 cm^{-1} assigned to the symmetric and asymmetric stretching vibration of $-CH$ in the aromatic ring, and at two bands 1,407 and 1,251 cm^{-1} assigned to the aromatic C–H bending vibrations.

Phthalocyanines show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300–400 nm (B-band) arising from the deeper π-levels $\rightarrow$ lowest unoccupied molecular orbital (LUMO) transition and the other in the visible region at 600–700 nm (Q band) attributed to the $\pi-\pi^*$ transition from the highest occupied molecular orbital (HOMO) to the LUMO of the phthalocyanine ring [58]. The UV-Vis spectrum of metal-free phthalocyanine in chloroform displayed two characteristic absorption bands in the visible region at 666 and 702 nm.

The UV spectra of ZnPc, CuPc, and CoPc show the typical absorptions of phthalocyanines, mainly the $\pi-\pi^*$ transitions within the heteroaromatic π system. The UV-Vis spectrum of ZnPc **5** in $CHCl_3$ exhibited a typical B-band at 351 nm and a Q band at 680 nm with a weak band at 612 nm. The UV-Vis spectra of CoPc **6** and CuPc **7** were very similar to that of ZnPc, and the data are given in Fig. 1. Cobalt phthalocyanine **6** displays a Q band around 671 nm in chloroform, whereas zinc and copper phthalocyanines show nearly the same values around 680 nm and illustrate $\sim$9 nm bathochromic shifts according to the cobalt phthalocyanine analog. The introduction of CF_3 groups at the *para*-positions of phenoxy groups in phthalocyanines **4**–**7** resulted in very good solubility of these macrocycles in most organic solvents, including acetone. The newly prepared phthalocyanines **4**–**7** displayed high solubility in various organic solvents such as toluene, chloroform, tetrahydrofuran (THF), ethyl acetate, and acetone.

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher-order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, complexed metal ions, and temperature. For phthalocyanines, the aggregation behavior in solution is a good indication of

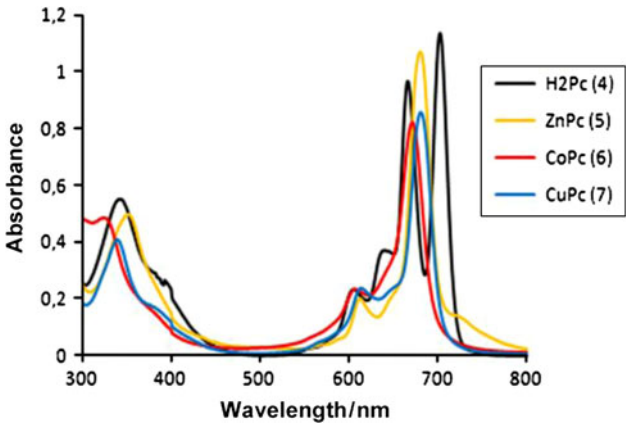


Fig. 1 Electronic spectra of **4**–**7** in chloroform; $c = 6 \times 10^{-6}$ M

interactions between the aromatic macrocycles. Aggregation is easily detected from optical absorption studies. Any increase in concentration results in aggregation of phthalocyanine molecules which is accompanied by a blueshift of the Q band with some decrease in intensity [59]. The aggregation behavior of the phthalocyanine complexes was investigated in different solvents. The optical absorption spectra of compound **4** depend on the solvent type. It has been concluded that aggregation is enhanced by solvent polarity. The tendency to form aggregates increases in the order: tetrahydrofuran < chloroform < dimethylformamide < dichloromethane < ethyl acetate < dimethylsulfoxide for metal-free phthalocyanine **4** (Fig. 2).

In this work, the aggregation behavior of the complexes **4**–**7** was examined in two different concentration ranges in chloroform (Fig. 3, for complex **5** as an example). In the concentration range of 4.00×10^{-6} to 14.00×10^{-6} M, the intensity of absorption of the Q band increased in parallel with the increase in the concentration and there were no new bands (normally blueshifted) due to the aggregated species [1, 36]. This means that the phthalocyanine

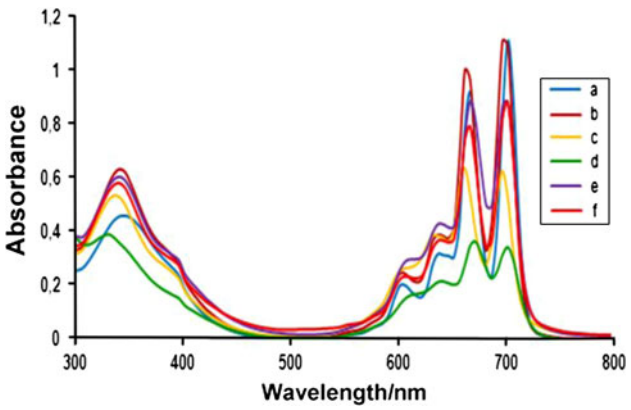


Fig. 2 Electronic spectra of **4** in **a** toluene, **b** tetrahydrofuran, **c** ethyl acetate, **d** dimethylsulfoxide, **e** dimethylformamide, **f** dichloromethane; $c = 6 \times 10^{-6}$ M

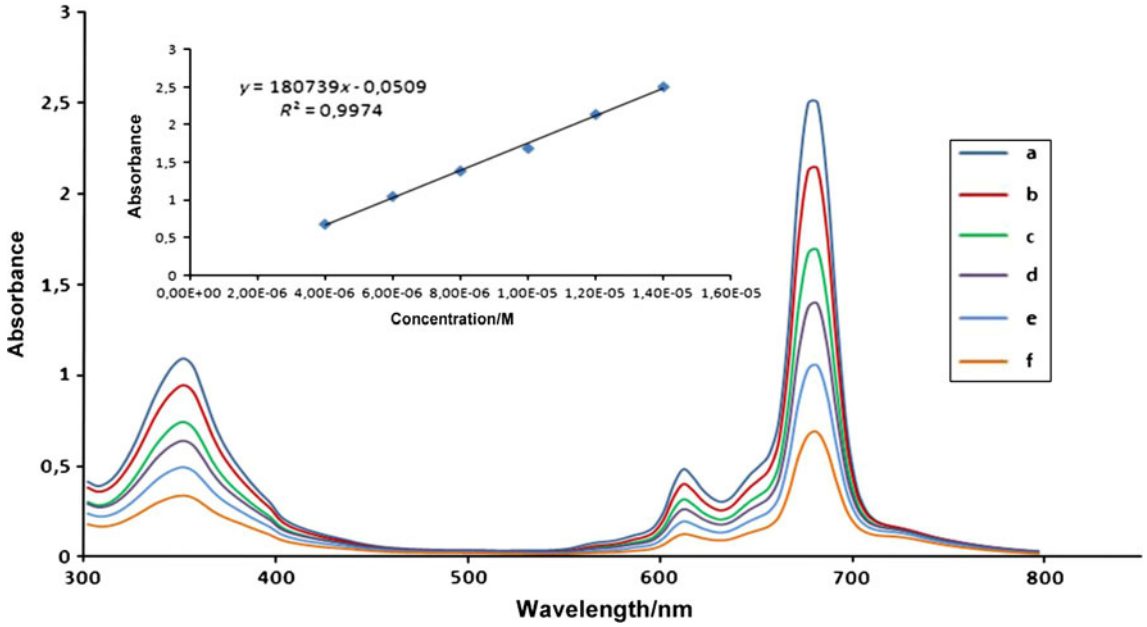


Fig. 3 Aggregation behavior of **5** in chloroform at different concentrations: *a* 14 × 10^{-6} M, *b* 12 × 10^{-6} M, *c* 10 × 10^{-6} M, *d* 8 × 10^{-6} M, *e* 6 × 10^{-6} M, and *f* 4 × 10^{-6} M

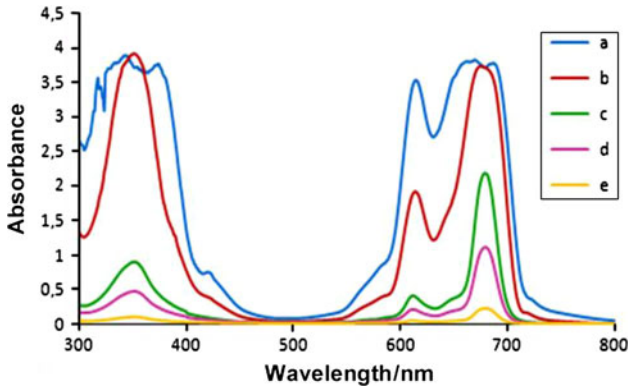


Fig. 4 Electronic spectra of **5** in chloroform: **a** 1 × 10^{-4} M, *b* 5 × 10^{-5} M, *c* 1 × 10^{-5} M, *d* 5 × 10^{-6} M, and *e* 1 × 10^{-6} M

derivatives **4**–**7** did not show aggregation in chloroform in this concentration range and the Beer–Lambert law was obeyed for all of these compounds. The aggregation behavior of the phthalocyanine complex **5** was also investigated for the concentrations ranging from 1.00 × 10^{-6} to 1.00 × 10^{-4} M (Fig. 4). At the lower concentration side (10^{-6} M), the Q band of the phthalocyanine complex **5** is the major band in the long-wavelength region and Q band corresponding to monomeric species appeared around 670–680 nm. When the concentration of the compound was raised to 10^{-4} M, Q band absorptions for monomeric species and aggregated ones become almost equally intense; i.e., the aggregated form of the phthalocyanine molecules has taken the priority at these concentrations.

Conclusions

The main aim of the work is to synthesize new highly soluble phthalocyanine complexes with strong electron-withdrawing substituents on the periphery of the macrocyclic ligand. These novel complexes possessed excellent solubility in various organic solvents such as CH_2Cl_2, THF, DMF, DMSO, toluene, and acetone. Catalytic properties of these novel fluorinated phthalocyanines will be investigated.

Experimental

IR spectra were recorded on a PerkinElmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer, and electronic spectra on a Scinco Neosys-2000 double-beam UV-Vis spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer using tetramethylsilane (TMS) as internal reference. ^{13}C NMR and ^{19}F NMR spectra were recorded on a Varian Unity Inova-500 MHz NMR spectrometer. Mass spectra were performed on a Varian 711 mass spectrometer. All reagents and solvents were of reagent-grade quality, obtained from commercial suppliers. The homogeneity of the products was tested in each step by thin-layer chromatography (TLC). All solvents were dried and purified as described by Perrin and Armarego [60]. The solvents were stored over molecular sieves. 4-Nitrophthalonitrile [61] was prepared by reported procedures.

4-[4-(Trifluoromethyl)phenoxy]phenoxy]phthalonitrile (**3**, $C_{21}H_{11}F_3N_2O_2$)

4-Nitrophthalonitrile (**1**, 0.5 g, 2.89 mmol) was dissolved in 20 cm^3 dry DMF. To this was added 1.47 g 4-[4-(trifluoromethyl)phenoxy]phenol (**2**, 5.78 mmol). After stirring for 15 min, 1.79 g dry and finely powdered potassium carbonate (13 mmol) was added portionwise over 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 48 h. After 2 days, the reaction mixture was poured into a mixture of ice-water (400 cm^3) and the creamy precipitate that formed was filtered and washed several times with water until the washing became neutral. Finally the white compound was crystallized from petroleum ether. Yield 0.89 g (81%); m.p.: 113 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.75$ (d, 1H, Ar–H), 7.62 (d, 2H, Ar–H), 7.28 (d, 2H, Ar–H), 7.15-7.07 (m, 6H, Ar–H) ppm; ^{13}C NMR (125 MHz, APT, $CDCl_3$): $\delta = 162.61$ (aromatic C–O), 155.57 (aromatic C–O), 149.86 (aromatic C–O), 135.43 (aromatic CH), 127.31 (aromatic CH), 126.09 (aromatic C), 125.13 (C–F), 121.55 (aromatic CH), 121.32 (aromatic CH), 118.43 (aromatic C), 118.27 (aromatic CH), 115.53 (C≡N), 115.49 (C≡N), 109.71 (aromatic C) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): $\delta = -64.66$ (CF_3) ppm; IR: $\bar{\nu} = 3{,}111$ (Ar–H), 2,233 (C≡N), 1,598, 1,501, 1,480, 1,322 (C–F), 1,235 (C–O–C), 1,063, 950, 833 cm^{-1}.

2,9,16,23-Tetrakis[4-[4-(trifluoromethyl)phenoxy]-phenoxy]phthalocyanine (**4**, $C_{84}H_{46}F_{12}N_8O_8$)

Compound **3** (0.30 g, 0.79 mmol) was heated in 1 cm^3 2-(dimethylamino)ethanol (DMAE) at 150 °C for 24 h in a sealed glass tube under nitrogen. After cooling to room temperature, the reaction mixture was diluted with methanol until the crude product completely precipitated. The blue precipitate was centrifuged off and washed with hot methanol and then dried in vacuo. The resulting solid was purified by column chromatography on silica gel using chloroform:cyclohexane (5:1) as eluent. Yield 0.09 g (30%); m.p.: >200 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.65$–6.82 (m, 44H, Ar–H), −6.08 (br s, 2H, NH) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): $\delta = 175.21$ (2C, pyrrole C), 160.64 (2C, pyrrole C), 158.00 (2C, pyrrole C), 154.41 (4C, aromatic C–O), 151.71 (4C, aromatic C–O), 149.98 (8C, aromatic C–O), 137.20 (2C, pyrrole C), 131. 14 (4C, aromatic C), 127.30 (4C, aromatic C), 126.29 (8C, aromatic C), 125.22 (4C, C–F), 124.80 (4C, aromatic C), 123.06 (8C, aromatic C), 121.64 (2C, aromatic C), 121.10 (4C, aromatic C), 118.99 (4C, aromatic C), 117.51 (16C, aromatic C), 110.50 (2C, aromatic C) ppm; IR: $\bar{\nu} = 3{,}287$ (NH), 3,058 (Ar–H), 1,611, 1,494, 1,472, 1,423, 1,321 (C–F), 1,216, 1,189, 1,160, 1,090, 1,063, 1,008, 925, 833, 740 cm^{-1}; UV-Vis ($CHCl_3$, $c = 6{\cdot}10^{-6}$ mol dm^{-3}): λ_{max} (ε) = 341 (91,666), 605 (40,000), 639 (61,666), 666 (161,666), 702 (190,000) nm (mol^{-1} dm^3 cm^{-1}).

2,9,16,23-Tetrakis[4-[4-(trifluoromethyl)phenoxy]-phenoxy]phthalocyaninatozinc(II) (**5**, $C_{84}H_{44}F_{12}N_8O_8Zn$)

Compound **3** (0.20 g, 0.52 mmol) and 0.024 g $Zn(CH_3COO)_2$ (0.13 mmol) were mixed in 1 cm^3 dry 2-(dimethylamino)ethanol in a glass tube. The mixture was sealed and heated at 150–160 °C for 24 h under N_2 to give the desired substituted phthalocyanine. After being cooled, the reaction mixture was poured into 50 cm^3 ice-water mixture and the bluish-green precipitate was separated by filtering and washed several times with hot hexane. Finally the solid was dried and purified by column chromatography on silica gel using THF as eluent. Yield 0.050 g (24%); m.p.: >200 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.55$-6.98 (m, 44H, Ar–H) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): $\delta = 175.44$ (2C, pyrrole C), 160.65 (2C, pyrrole C), 158.13 (2C, pyrrole C), 153.14 (4C, aromatic C–O), 151.62 (4C, aromatic C–O), 149.59 (8C, aromatic C–O), 137.64 (2C, pyrrole C), 130.64 (4C, aromatic C), 127.25 (4C, aromatic C), 126.32 (8C, aromatic C), 125.13 (4C, C–F), 124.83 (4C, aromatic C), 122.00 (8C, aromatic C), 121.50 (2C, aromatic C), 120.93 (4C, aromatic C), 118.93 (4C, aromatic C), 117.48 (16C, aromatic C), 110.65 (2C, aromatic C) ppm; IR: $\bar{\nu} = 3{,}111$–3,063 (Ar–H), 1,612, 1,493, 1,470, 1,407, 1,320 (C–F), 1,251, 1,220, 1,158, 1,061, 946, 830, 748 cm^{-1}; UV-Vis ($CHCl_3$, $c = 6{\cdot}10^{-6}$ mol dm^{-3}): λ_{max} (ε) = 351 (83,333), 612 (33,333), 680 (178,333) nm (mol^{-1} dm^3 cm^{-1}).

2,9,16,23-Tetrakis[4-[4-(trifluoromethyl)phenoxy]-phenoxy]phthalocyaninatocobalt(II) (**6**, $C_{84}H_{44}CoF_{12}N_8O_8$)

A mixture of 0.25 g **3** (0.65 mmol) and 0.021 g anhydrous $CoCl_2$ (0.16 mmol) was refluxed in 1 cm^3 DMAE with stirring for 24 h under N_2. The resulting suspension was cooled to room temperature, and the crude product was precipitated by addition of a mixture of ice-water. It was centrifuged off and washed first with water and then with hot hexane. The blue product was obtained on silica gel with toluene:THF (5:1) as eluent. Yield 0.080 g (31%); m.p.: >200 °C; IR: $\bar{\nu} = 3{,}058$ (Ar–H), 1,611, 1,495, 1,470, 1,408, 1,323 (C–F), 1,190, 1,064, 956, 835, 750 cm^{-1}; UV-Vis ($CHCl_3$, $c = 6{\cdot}10^{-6}$ mol dm^{-3}): λ_{max} (ε) = 324 (80,000), 607 (38,333), 671 (136,666) nm (mol^{-1} dm^3 cm^{-1}).

2,9,16,23-Tetrakis[4-[4-(trifluoromethyl)phenoxy]-phenoxy]phthalocyaninatocopper(II) (**7**, $C_{84}H_{44}CuF_{12}N_8O_8$)

Compound **3** (0.30 g, 0.79 mmol) was dissolved in 2 cm^3 DMAE, and 0.026 g anhydrous $CuCl_2$ (0.20 mmol) was added to this solution. The reaction mixture was stirred at reflux temperature for 24 h. The blue mixture was cooled to room temperature and precipitated with a mixture of ice-water. The precipitate was filtered off and washed first with water and then with hexane. The desired compound was purified by column chromatography on silica gel with dichloromethane:hexane (3:1) as eluent. Yield 0.044 g

(14%); m.p.: >200 °C; IR: $\bar{\nu} = 3{,}058$ (Ar–H), 1,611, 1,495, 1,470, 1,408, 1,323 (C–F), 1,190, 1,064, 956, 835, 750 cm^{-1}; UV-Vis ($CHCl_3$, $c = 6{\cdot}10^{-6}$ mol dm^{-3}): λ_{max} (ε) = 339 (68,333), 613 (40,000), 680 (143,333) nm (mol^{-1} dm^3 cm^{-1}); MS (FAB): $m/z = 1{,}585$ (M + 1).

Acknowledgment This work was supported by the Research Fund of the Technical University of Istanbul and TUBİTAK TBAG: 108T448.

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