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Microwave-assisted synthesis and characterization of differently substituted phthalocyanines containing 3,5-dimethoxyphenol and octanethiol moieties

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Abstract

New differently substituted metal-free and metal (Cu, Zn) phthalocyanines are described. One group (**1**, **2**, **3**) contains peripheral 3,5-dimethoxyphenoxy and chloro substituents and the other group (**4**, **5**, **6**) contains 3,5-dimethoxyphenoxy and octanethiol substituents. All products were synthesized by both classical and microwave-assisted methods. Structures were confirmed by elemental analysis, ^{1}H NMR, ^{13}C NMR, UV/vis and FTIR spectroscopies. The crystal structure of starting material **I** was also determined using a single crystal diffraction technique. All of the complexes were only slightly soluble in polar solvents such as $CHCl_3$, DMF and DMSO.

Keywords: Phthalocyanines; Complexes; X-ray diffraction; Microwave-assisted

1. Introduction

Since their first synthesis early in this century, phthalocyanines have established themselves as blue and green dyestuffs par excellence. Phthalocyanines are an important industrial commodity used primarily in inks, coloring for plastics and metal surfaces and dyestuffs for jeans and other clothing [1]. The importance of phthalocyanines in many fields, including electrochromic display devices [2,3], photodynamic reagents for cancer therapy [4] and other medical applications [1], optical computer read/write discs [5], laser dyes, new red-sensitive photocopying applications [1,2] and liquid crystal color display applications is increasing rapidly as a result of the synthesis of new compounds [6]. The specificity of their applications can be modified by both changes to the phthalocyanine large and flat π-conjugation system and/or changes in the central metals [7,8]. Another important aim of research into the chemistry of phthalocyanines is to enhance their solubility in various solvents. Phthalocyanines can be obtained by the classical template reactions of diverse precursors such as phthalonitrile, cyano-benzamide, phthalamide and phthalic acid with metal salts in high-boiling nonaqueous solvents at elevated temperatures [9,10]. Microwave processing has attracted potential interest as an alternative to classical thermal processing because of the inherent advantages of microwave heating, which is selective, direct, rapid, internal and controllable [11–13].

We have previously synthesized novel phthalocyanines carrying macrocyclic substituents (*e.g.* aza [14,15], oxa [16], oxa thia [17,18], oxadithiadiaza macrocyles [19] and triazoles [20]) which are capable of binding to transition metal cations.

The present work introduces the preparation and characterization of the differently substituted phthalocyanines (see Scheme 1). One group of them (**1**, **2**, **3**) has peripheral 3,5-dimethoxyphenoxy and chloro substituents and the other

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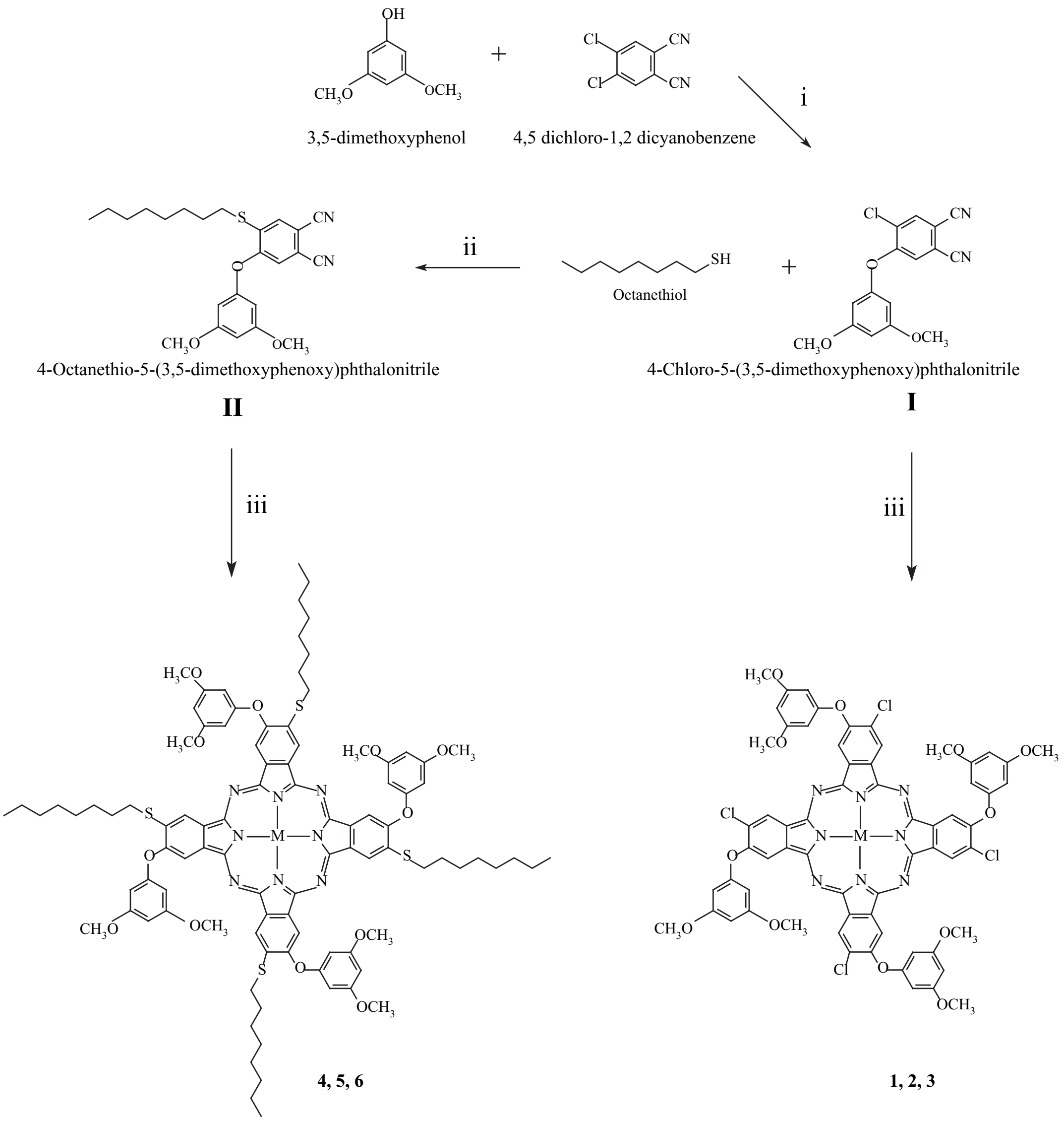

i) DMSO, Na_2CO_3, r tor MW 350 W, DMSO, 8 min
ii) DMF, K_2CO_3, 60 °C or MW 350 W, DMF, K_2CO_3, 8 min
iii) Classical or microwave-assisted synthesis method

Compound	1	2	3	4	5	6
M	2H	Cu	Zn	2H	Cu	Zn

Scheme 1. Synthesis of ligands and complexes.

group (**4**, **5**, **6**) has 3,5-dimethoxyphenoxy and octanethiol ones.

2. Results and discussion

4,5-Dichloro-1,2-dicyanobenzene was recently used to prepare 4,5-disubstituted phthalonitrile derivatives through base catalysed nucleophilic aromatic displacement [21–23]. First, 4-chloro-5-(3,5-dimethoxyphenoxy)phthalonitrile (**I**) was synthesized by treating 3,5-dimethoxyphenol with 4,5-dichloro-1,2-dicyanobenzene in DMSO at room temperature using Na_2CO_3 as the base for the nucleophilic substitution [21–23]. Then, 4-octanethio-5-(3,5-dimethoxyphenoxy)phthalonitrile (**II**) was synthesized by heating octanethiol and compound **I** in DMF at 60 °C for 48 h. K_2CO_3 was used as the base to avoid steric hindrance of the bulky groups. Compounds **I** and **II** were also obtained by microwave irradiation of the same starting materials at 350 W for 8 min. The yields using microwave irradiation were in all cases higher than with that of the classical method. According to these studies, displacement of one chloro atom might be a consequence of steric hindrance of the bulky groups, the acidic capacities of the displacement groups and the strength of the bases used in these reactions [24–27]. The design strategy for functional phthalonitriles substituted by the same or different substituents is based on mainly the size and the strength of the base, and the Lewis acidity of the aromatic phenol and aliphatic thiol used during the reaction. The approach described here allows us to prepare a wide number of novel phthalocyanines having mixed substituents on the periphery.

Metal-free phthalocyanines **1** and **4** were synthesized by heating the corresponding dicyano compounds in dimethylaminoethanol (DMAE) at 180 °C for 24 h. The metallophthalocyanines **2**, **3**, **5**, and **6** were prepared from the corresponding dicyano derivatives and the corresponding metal salts (Cu and Zn) in high-boiling solvents (*e.g.* quinoline or DMAE).

Metal-free phthalocyanines **1** and **4** were also synthesized by microwave irradiation of the corresponding dicyano compounds in DBU for 8 min and the metallophthalocyanines **2**, **3**, **5**, and **6** were also prepared by microwave irradiation from the corresponding dicyano derivatives and metal salts in DMAE. Characterization of the products involved a combination of methods, including elemental analysis, FTIR, UV/vis, ^{1}H and ^{13}C NMR spectroscopies. X-ray crystallography was also used for compound **I**. Elemental analyses of the starting materials and the phthalocyanines show good agreement with the calculated values.

The formation of compound **I** was clearly indicated by the appearance in its FTIR spectrum of the OCH_3 band at 2944 cm^{-1} and the CN band at 2235 cm^{-1}. In its ^{1}H NMR spectrum the aromatic protons appear as five singlets at 7.9, 7.8, 7.1, 6.4 and 6.2 ppm and the OCH_3 aliphatic protons as a singlet at 3.8 ppm. The ^{13}C NMR of compound **I** in $CDCl_3$ gave signals at 134.1 ppm (C–Cl), 114.4 ppm (CN) and 55.6 ppm (OCH_3).

The FTIR spectrum of the phthalocyanines clearly indicates the cyclotetramerization of the phthalonitrile derivatives with the disappearance of the CN peak at 2235 cm^{-1}. The FTIR spectrum of metal-free phthalocyanine **1** shows the 3390 (NH), 3081 (Ar–CH) and 742 cm^{-1} (C–Cl) vibrations. In the ^{1}H NMR spectra of compound **1**, the aromatic protons appear as a multiplet at 6.5–6.2 and aliphatic protons as a singlet at 3.8 ppm. A common feature of the spectra of metal-free phthalocyanines is the broad absorption probably caused by the aggregation of the phthalocyanines [28–30]. ^{13}C NMR data could not be obtained for this compound due to its poor solubility in polar solvents such as $CHCl_3$, DMF and DMSO.

The FTIR spectrum of compound **2** indicates an Ar–CH band at 3091 cm^{-1} and a C–Cl band at 741 cm^{-1}. ^{1}H NMR measurements were precluded, due to its paramagnetic nature. The FTIR bands of compound **3** were very similar to those of compound **2**. In the ^{1}H NMR spectrum of compound **3**, the aromatic protons appear as a multiplet at 6.3–6.2. ^{1}H NMR values for the aromatic protons of the phthalocyanines are comparable to those for the aromatic protons of the starting material compound **I**. The aliphatic protons appear as a singlet at 3.7 ppm.

The FTIR spectrum of compound **II** clearly indicates the presence of the octyl group (CH_2, CH_3) at 2956–2921 cm^{-1} and Ar–S band at 584 cm^{-1}, and the disappearance of the C–Cl band at 742 cm^{-1}. In the ^{1}H NMR spectra of compound **II** in $CDCl_3$, the aromatic protons appear as five singlets at 7.8, 7.4, 7.1, 6.4 and 6.2 ppm, the methoxy protons as a singlet at 3.8 ppm, the octyl $-CH_2-$ protons as a multiplet at 1.8–1.5 ppm, the $S-CH_2$ protons as a triplet at 3.2–3.0 ppm and the octyl CH_3- protons as a triplet at 1.0–0.8 ppm. The ^{13}C NMR spectrum of compound **II** in $CDCl_3$ indicated the presence of nitrile carbon atoms at 114.4 ppm, a methoxy carbon atom at 55.6 ppm and octyl carbon atoms at 32.7, 31.7, 29.1, 29.0, 28.8, 28.0, 22.6, and 14.0 ppm.

The FTIR spectrum of compound **4** displays an NH band at 3417 cm^{-1}, CH_2 and CH_3 bands at 2924–2857 cm^{-1} and an Ar–S band at 590 cm^{-1}. In the ^{1}H NMR spectrum of compound **4**, the aromatic protons appear as a multiplet at 6.6–6.4 ppm, the octyl $-CH_2-$ protons as a multiplet at 1.8–1.4 ppm, the methoxy protons as a singlet at 3.8 ppm, the $S-CH_2$ protons as a triplet at 3.2–3.0 and the octyl CH_3- protons as a triplet at 1.1–0.8 ppm.

The FTIR spectrum of compound **5** shows an Ar–CH band at 3096 cm^{-1}, octyl $-CH_2-$ and CH_3- bands at 2923–2852 cm^{-1} and an Ar–S band 586 cm^{-1}.

The IR spectra bands of compound **6** were very similar to those of **5**. In its ^{1}H NMR spectrum the aromatic protons appear as a multiplet at 6.4–6.0 ppm and the octyl $-CH_2-$ protons as a multiplet at 1.8–1.4 ppm, the methoxy OCH_3 protons as a singlet at 3.7 ppm, the $S-CH_2$ protons as a triplet at 3.1–2.9 ppm and the octyl CH_3- protons as a triplet 1.0–0.8 ppm.

The best indication for the phthalocyanine systems is their UV/vis spectra in solution. The newly synthesized phthalocyanines showed typical electronic spectra with two strong absorption regions, one of them in UV region at about 340 nm (B band) and the other in the visible region at about 699 nm (Q band). This band was not split to two bands due to the aggregation of phthalocyanines in organic solvents.

2.1. Crystal structure of 4-chloro-5-(3,5-dimethoxyphenoxy)phthalonitrile (*I*) [31]

A single crystal of compound **I** was obtained from ethanol at room temperature *via* slow evaporation. The title compound, $C_{16}H_{11}N_2O_3Cl$, contains two benzene rings (Fig. 1). The two benzene rings are planar and molecule of the title compound displays the characteristic features of phthalonitrile derivatives. The C8–N1 and C7–N2 bonds display triple bond character and these bond lengths [C8–N1 = 1.140(2) Å and C7–N2 = 1.137(2) Å] are close to the values reported in literature [32–34]. There is a hydrogen bond between the C2–H2–N1 atoms. The packing diagram of compound **1** can be seen in Fig. 2.

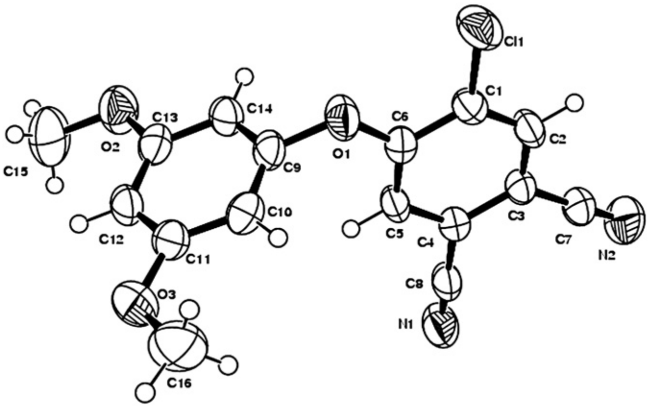

Fig. 1. Crystal structure of compound **I**.

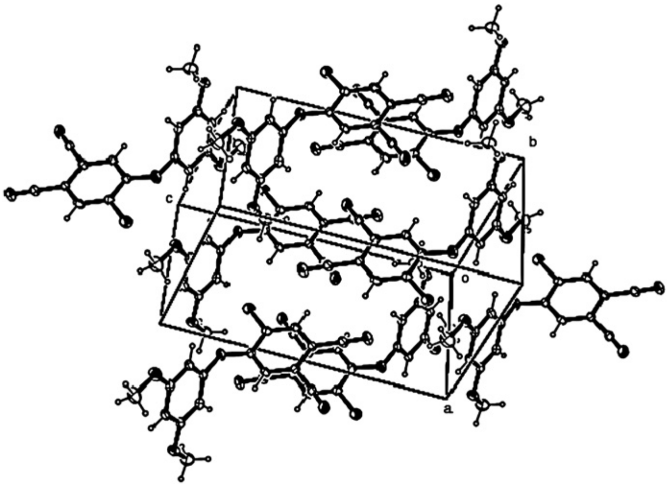

Fig. 2. The packing diagram of compound **I**.

3. Conclusion

In conclusion, the synthesis of phthalocyanines under microwave irradiation reduces reaction times and enhances yields in comparison with the classical method.

4. Experimental

4.1. General

4,5-Dichloro-1,2-dicyanobenzene was prepared by a reported procedure [23]. 3,5-Dimethoxyphenol and octanethiol were purchased from the Merck Chemical Company. FTIR spectra were recorded on a Jasco FT-IR/430 Fourier transform infrared spectrometer as KBr pellets. UV/vis spectra were recorded on a Mattson Unicam UV/vis spectrometer. ^{1}H NMR and ^{13}C NMR studies were done on a Bruker AC-200 or FT-200 FT-NMR spectrometer. Elemental analyses were performed by the Instrumental Analyses Laboratory of the TÜBİTAK Gebze Research Center. X-ray studies were performed on a Stoe IPDS-II diffractometer.

*4.1.1. 4-Chloro-5-(3,5-dimethoxyphenoxy)phthalonitrile (**I**)*

4.1.1.1. Method A. 3,5-Dimethoxyphenol (6 g, 38.9 mmol) and 4,5-dichlorophthalonitrile (7.76 g, 38.9 mmol) were dissolved in dry dimethylsulfoxide (DMSO, 100 mL) under nitrogen. After stirring for 30 min, finely ground anhydrous Na_2CO_3 (6.19 g, 58.3 mmol) was added portionwise over 2 h with efficient stirring. The reaction mixture was stirred under N_2 at room temperature for 48 h, and then poured into ice water (500 mL). The product was filtered off, washed with 10% NaOH solution to remove unreacted phenol and then with water until the filtrate became neutral. Recrystallization from ethanol gave a white product. This compound is soluble in ethanol, chloroform, ethyl acetate, DMSO and *N*,*N*-dimethylformamide (DMF). Yield: 7.5 g, 61%; m.p. 148 °C; FTIR ν_{max}/cm^{-1}: 3085 (Ar–CH), 2944 (OCH_3), 2235 (CN), 1621, 1575, 1424, 1384, 1309, 1276, 1128 and 739 (C–Cl); ^{1}H NMR ($CDCl_3$): δ 7.9 (1H, s, Ar), 7.8 (1H, s, Ar), 7.1 (1H, s, Ar), 6.4 (1H, s, Ar), 6.2 (1H, s, Ar) and 3.8 (6H, s, OCH_3) ppm; ^{13}C NMR ($CDCl_3$): δ 162.3, 157.8, 154.8, 134.1 (C–Cl), 129.4, 114.4 (CN), 114.2, 113.5, 111.0, 109.6, 98.8, 98.4, 98.3, 96.0 and 55.6 (OCH_3) ppm. Anal. Calcd. for $C_{16}H_{11}O_3N_2Cl$: C, 61.06; H, 3.52; N, 8.9. Found: C, 60.98; H, 3.55; N, 8.86; crystal data: $C_{16}H_{11}N_2O_3Cl$, MW: 314.72, triclinic, $a = 7.5599(10)$, $b = 7.7749(12)$, $c = 13.5966$ Å, $U = 750.64(19)$ A^3, $T = 293$ K, space group $P1$, $Z = 2$, μ(Mo Kα) = not measured, $R_{int} = 0.0560$. The final $wR(F_2)$ was 0.0767.

4.1.1.2. Method B (microwave-assisted method). 3,5-Dimethoxyphenol (6 g, 38.9 mmol), 4,5-dichlorophthalonitrile (7.76 g, 38.9 mmol) and anhydrous Na_2CO_3 (6.19 g, 58.3 mmol) were finely ground and the resulting powder was suspended in dry DMSO (15 mL) in a 50 mL round bottom flask. This mixture was irradiated by a microwave oven at 350 W for 8 min [35]. The above purification methods were also applied to this material. Yield: 9.83 g, 80%.

*4.1.2. Metal-free phthalocyanine (**1**)*

4.1.2.1. Method A. A mixture of compound **I** (1 g, 3.1 mmol) and *N*,*N*-dimethylaminoethanol (15 mL) was heated to 180 °C under N_2 and held at this temperature for 24 h. After cooling to room temperature the reaction mixture was treated with ethanol to precipitate the product which was then filtered off. The green product was washed with hot ethanol (3 × 50 mL) and hot water (100 mL). This compound is only slightly soluble in CH_2Cl_2, $CHCl_3$, DMF and DMSO. Yield: 0.75 g, 73%; m.p. > 200 °C (dec); FTIR ν_{max}/cm^{-1}: 3390 (NH), 3081 (Ar–CH), 2836, 1766, 1704(C=N), 1594, 1425, 1378, 1328, 1153, 1126 and 742 (C–Cl); ^{1}H NMR ($CDCl_3$): δ 6.5–6.2 (20H, m, Ar) and 3.8 (24H, s, OCH_3) ppm; UV/vis λ_{max} ($CHCl_3$)/nm 229, 291, 340, 666 (shoulder) and 699. Anal. Calcd. for $C_{64}H_{46}O_{12}N_8Cl_4$: C, 60.96; H, 3.67; N, 8.88. Found: C, 60.86; H, 3.59; N, 8.82.

4.1.2.2. Method B (microwave-assisted synthesis method for metal-free phthalocyanines). A mixture of compound **I** (1 g, 3.1 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 2 mL) was irradiated in a microwave oven at 350 W for 8 min. Above purification methods were applied to this material. Yield: 0.77 g, 75%.

*4.1.3. Copper(II) phthalocyanine (**2**)*

4.1.3.1. Method A. A mixture of compound **I** (0.8 g, 2.5 mmol), anhydrous CuCl (0.06 g, 0.625 mmol) and *N*,*N*-dimethylaminoethanol (15 mL) was heated at 150 °C under N_2 and held at this temperature for 24 h. After cooling to room temperature, the reaction mixture was treated with ethanol to precipate the product which was then filtered off. The green product was washed with hot ethanol (3 × 50 mL) and hot water (100 mL). This compound is poorly soluble in CH_2Cl_2,

$CHCl_3$, DMF and DMSO. Yield: 0.73 g, 73%; m.p. > 200 °C (dec); FTIR ν_{max}/cm^{-1}: 3091 (Ar–CH), 2834, 1698 (C=N), 1594, 1455, 1428, 1257, 1181, 1153, 1128 and 741 (C–Cl); UV/vis λ_{max} ($CHCl_3$)/nm 230, 338, 624 and 679. Anal. Calcd. for $C_{64}H_{44}O_{12}N_8Cl_4Cu$: C, 58.12; H, 3.35; N, 8.47. Found: C, 58.2; H, 3.4; N, 3.36.

4.1.3.2. Method B (microwave-assisted synthesis method). A mixture of compound **I** (0.8 g, 2.5 mmol), anhydrous CuCl (0.06 g, 0.625 mmol) and *N*,*N*-dimethylaminoethanol (3 mL) was irradiated in a microwave oven at 350 W for 8 min. Above purification methods were applied to this material. Yield: 0.80 g, 80%.

4.1.4. Zinc(II) phthalocyanine (***3***)

4.1.4.1. Method A. A mixture of compound **I** (1 g, 3.1 mmol), anhydrous zinc acetate (0.14 g, 0.77 mmol) and dry quinoline (15 mL) was heated and stirred at 180–190 °C for 24 h under N_2. After cooling to room temperature the green product was filtered off and then washed with hot ethanol (3 × 50 mL) and hot water (100 mL). This compound is only slightly soluble in CH_2Cl_2, $CHCl_3$, DMF and DMSO. Yield: 0.31 g, 29%; m.p. > 200 °C (dec); FTIR ν_{max}/cm^{-1}: 3094 (Ar–CH), 2834, 1592, 1457, 1423, 1290, 1240, 1106 and 742 (C–Cl); ^1H NMR ($CDCl_3$): δ 6.3–6.2 (20H, m, Ar) and 3.7 (24H, s, OCH_3) ppm; UV/vis λ_{max} ($CHCl_3$)/nm 287, 344, 630 and 679. Anal. Calcd. for $C_{64}H_{44}O_{12}N_8Cl_4Zn$: C, 58.04; H, 3.34; N, 3.46. Found: C, 57.95; H, 3.39; N, 3.52.

4.1.4.2. Method B (microwave-assisted synthesis method). A mixture of compound **I** (1 g, 3.1 mmol), anhydrous zinc acetate (0.14 g, 0.77 mmol) and *N*,*N*-dimethylaminoethanol (3 mL) was irradiated by a microwave oven at 350 W for 8 min. The above purification methods were applied to this material. Yield: 0.90 g, 85%.

4.1.5. 4-Octanethio-5-(3,5-dimethoxyphenoxy) phthalonitrile (***II***)

4.1.5.1. Method A. Octanethiol (2.09 g, 14.33 mmol) and K_2CO_3 (2.63 g, 19.05 mmol) were dissolved in dry DMF (50 mL) under N_2. After stirring for 1 h at 60 °C, solution of compound **I** (3 g, 9.55 mmol) in dry DMF (20 mL) was added dropwise into the above mixture over 2 h with efficient stirring. The reaction mixture was stirred under N_2 at 60 °C for 48 h and then poured into ice water (200 mL). The product was filtered off. Recrystallization from ethanol gave a light yellow product. This compound is soluble in common organic solvents such as ethanol, ethyl acetate, $CHCl_3$, DMF and DMSO. Yield: 2.6 g, 64%; m.p. 51 °C; FTIR ν_{max}/cm^{-1}: 3077 (Ar–CH), 2956, 2921 (CH_3), 2229 (CN), 1617, 1600, 1560, 1459, 1384, 1276, 1130, 1051, 881 and 584 (Ar–S); ^1H NMR ($CDCl_3$): δ 7.8 (1H, s, Ar), 7.4 (1H, s, Ar), 7.1 (1H, s, Ar), 6.4 (1H, s, Ar), 6.2 (1H, s, Ar), 3.8 (6H, s, OCH_3), 3.2–3.0 (2H, t, S–CH_2), 1.8–1.5 (12H, m, CH_2) and 1.0–0.8 (3H, t, CH_3) ppm; ^{13}C NMR ($CDCl_3$): δ 162.3, 157.8, 154.8, 135.8, 135.4, 129.4, 126.0, 114.4 (CN), 114.2, 111.0, 109.6, 98.4, 98.4, 96.0, 55.6 (OCH_3), 32.7 (S–CH_2), 31.7, 29.05, 28.8, 28.0, 22.6 and 14.06 (CH_3) ppm. Anal. Calcd. for $C_{24}H_{28}O_3N_2S$: C, 67.89; H, 6.64; N, 6.59. Found: C, 67.82; H, 6.6; N, 6.55.

4.1.5.2. Method B (microwave-assisted synthesis method). A mixture of compound **I** (3 g, 9.55 mmol), octanethiol (2.09 g, 14.33 mmol) and K_2CO_3 (2.63 g, 19.05 mmol) in DMF (20 mL) was also irradiated by a microwave oven at 350 W for 8 min. The above purification methods were also applied to this material. Yield: 3.25 g, 80%.

4.1.6. Metal-free phthalocyanine (***4***)

4.1.6.1. Method A. A mixture of compound **II** (0.7 g, 1.61 mmol) and *N*,*N*-dimethylaminoethanol (15 mL) was heated to 180 °C under N_2 and held at this temperature for 24 h. After cooling to room temperature the reaction mixture was treated with ethanol to precipitate the product which was then filtered off. The green product was washed with hot ethanol (3 × 50 mL) and hot water (100 mL). This compound is only slightly soluble in CH_2Cl_2, $CHCl_3$, DMF and DMSO. Yield: 0.18 g, 20%; m.p. > 150 °C (dec); FTIR ν_{max}/cm^{-1}: 3417 (NH), 2924–2857 (CH_2), 1454, 1424, 1376, 1149, 1065, 943 and 590 (Ar–S); ^1H NMR ($CDCl_3$): δ 6.6–6.4 (20H, m, Ar), 3.8 (24H, s, OCH_3), 3.2–3.0 (8H, t, S–CH_2), 1.8–1.4 (48H, m, CH_2) and 1.1–0.8 (12H, t, CH_3); UV/vis λ_{max} ($CHCl_3$)/nm 232, 340, and 699. Anal. Calcd. for $C_{96}H_{114}O_{12}N_8S_4$: C, 67.81; H, 6.75; N, 6.59. Found: C, 67.72; H, 6.80; N, 6.56.

4.1.6.2. Method B (microwave-assisted synthesis method). A mixture of compound **II** (0.7 g, 1.61 mmol) and DBU (2 mL) was irradiated in a microwave oven at 350 W for 8 min. The above purification methods were applied to this material. Yield: 0.67 g, 75%.

4.1.7. Copper(II) phthalocyanine (***5***)

4.1.7.1. Method A. A mixture of compound **II** (0.7 g, 1.6 mmol) anhydrous CuCl (0.053 g, 0.4 mmol) and *N*,*N*-dimethylaminoethanol (15 mL) was heated at 150 °C and held at this temperature for 24 h. After cooling to room temperature the reaction mixture was treated with ethanol to precipitate the product and was then filtered. The green product was washed with hot ethanol (3 × 50 mL) and hot water (100 mL). This compound is slightly soluble in CH_2Cl_2, $CHCl_3$, DMF and DMSO. Yield: 0.3 g, 41%; m.p. > 200 °C (dec); FTIR ν_{max}/cm^{-1}: 3096 (Ar–CH), 2923–2852 (CH_2), 1710, 1594, 1430, 1230, 1236, 1205, 1128 and 586 (Ar–S); UV/vis λ_{max} ($CHCl_3$)/nm 226, 290, 696. Anal. Calcd. for $C_{96}H_{112}O_{12}N_8S_4Cu$: C, 65.44; H, 6.4; N, 6.36. Found: C, 65.4; H, 6.33; N, 6.42.

4.1.7.2. Method B (microwave-assisted synthesis method). A mixture of compound **II** (0.7 g, 1.6 mmol), anhydrous CuCl (0.053 g, 0.4 mmol) and *N*,*N*-dimethylaminoethanol (3 mL) was irradiated in a microwave oven at 350 W for 8 min. The product was purified as described above. Yield: 0.54 g, 75%.

*4.1.8. Zinc(II) phthalocyanine (**6**)*

4.1.8.1. Method A. A mixture of compound **II** (0.7 g, 1.6 mmol), anhydrous zinc acetate (0.06 g, 0.04 mmol) and dry quinoline (15 mL) was heated and stirred at 180–190 °C for 24 h under N_2. After cooling to room temperature the green mixture was diluted with ethanol (50 mL) and treated with a 5% solution of HCl (10 mL) to precipitate the product which was then filtered off. The product was washed with 10% NaOH solution (20 mL) and water until the filtrate became neutral. The green product was washed with hot ethanol (3 × 50 mL) and hot water (100 mL). This compound is only slightly soluble in CH_2Cl_2, $CHCl_3$, DMF and DMSO. Yield: 0.15 g, 18%; m.p. > 200 °C (dec); FTIR ν_{max}/cm^{-1}: 3131 (Ar–CH), 2923, 2853 (CH_2), 1592, 1521, 1473, 1423, 1375, 1240, 1153, 1128 and 590 (Ar–S); ^{1}H NMR ($CDCl_3$): δ 6.4–6.0 (20H, m, Ar), 3.7 (24H, s, OCH_3), 3.1–2.9 (8H, t, S–CH_2), 1.8–1.4 (48H, m, CH_2) and 1.0–0.8 (12H, t, CH_3) ppm; UV/vis λ_{max} ($CHCl_3$)/nm 231, 340 and 698. Anal. Calcd. for $C_{96}H_{112}O_{12}N_8S_4Zn$: C, 65.37; H, 6.4; N, 6.35. Found: C, 65.43; H, 6.32; N, 6.4.

4.1.8.2. Method B (microwave-assisted synthesis method). A mixture of compound **II** (0.8 g, 1.5 mmol), anhydrous zinc acetate (0.06 g, 0.04 mmol) and *N*,*N*-dimethylaminoethanol (3 mL) was irradiated in a microwave oven at 350 W for 8 min. The product was purified as described above. Yield: 0.66 g, 80%.

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