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The synthesis and spectral properties of novel phthalocyanines with pendant bulky units

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Abstract

Novel phthalocyanines with biphenyl substituents and ester groups that are readily soluble in organic solvents were synthesized from a phthalonitrile derivative obtained by displacement of the −CH proton in 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxymethyl)benzene with 4-(chloromethyl)biphenyl, followed by cyclotetramerization in the presence of metal salts {$CuCl_2$, $Pb(CH_3COO)_2 \cdot 3H_2O$, $CoCl_2$ and $Zn(CH_3COO)_2$}. Transesterification of malonyl esters occurred during the cyclotetramerization of dinitrile with $CuCl_2$, $Pb(CH_3COO)_2 \cdot 3H_2O$ in 1-pentanol in the presence of DBU. The structures of the newly synthesized molecules were verified using elemental analysis, ^{1}H NMR, FT-IR, MicroTOF mass and UV−vis spectral data.

Keywords: Phthalocyanine; Phthalonitrile; Copper; Cobalt; Lead; Zinc; Aggregation

1. Introduction

Various substituted phthalocyanines (Pcs) have been developed for use as commercial dyes and pigments over the last few decades [1]. Recently, increasing investigation of metal-containing Pcs has resulted in potential for new applications beyond the traditional areas. Since they exhibit high thermal and chemical stability, well-defined optical absorption, semiconducting and photoconducting properties, and self organizing abilities to form columnar mesophases, Langmuir−Blodgett (LB) multilayers, or aggregates in solution, Pcs have been employed as subunits for the construction of functional materials [2,3].

Peripherally unsubstituted Pcs are insoluble in common organic solvents. The introduction of bulky or long chain groups, e.g. alkyl, alkoxy or alkylthio, in the peripheral positions of the macrocycle drastically increases their solubility in organic solvents extending potential fields of their technology [4−12]. Besides solubility, the spectral and electrochemical properties of Pcs are also strongly influenced by peripheral substituents on the macrocycle [2]. Furthermore, the tendency of Pcs to self-aggregate through coplanar association of the phthalocyanine rings to form dimer and higher order leads to insolubility [13], and reduces efficiency in their use in PDT [14].

For many years, aromatic compounds based on biphenyls were overemphasized as the most important core unit for liquid crystals, partly because of their easier synthesis and the link between highly polarizable π-electron systems and mesogenity. With this context, in this present paper, we have focused on preparation of new phthalocyanines carrying mesogenic biphenyl units [15]. Previously in our studies, we have synthesized different phthalocyanines bearing bulky malonic esters [16−18], sulfanyls [19], carboxylates, and quaternized amino groups [20] as peripheral substituents. As a continuance of these studies herein we have tried to incorporate biphenyl groups between two ester moieties in the phthalocyanine precursor [16]. Thus, starting with this new dinitrile, we have afforded the synthesis and characterization of metallophthalocyanines substituted with four chloro and four

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biphenyl-malonic ester bulky groups peripherally that are anticipated for hindering aggregation [21–23].

2. Experimental

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer and electronic spectra on a Unicam UV2 spectrophotometer. ^{1}H NMR spectra were recorded on Bruker 250 MHz using TMS as internal standard. Mass spectra were measured on a Bruker Daltonics MicrOTOF mass spectrometer. All starting materials were purchased from major suppliers and used without any further purification. The homogeneity of the products was tested in each step by TLC. Dimethylformamide was dried over 4 Å sieves and 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxymethyl)benzene (**2**) [16] was prepared from 1,2-dichloro-4,5-dicyanobenzene (**1**) [24] according to the procedures described in the literature.

*2.1. Potassium salt of 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxymethyl)benzene (**3**)*

Compound **2** (1 g, 3.12 mmol) was dissolved by heating in 25 ml of ethanol. The solution of 0.25 g of potassium hydroxide in 20 ml of ethanol was added, and the yellow precipitate was filtered off and washed with cold ethanol. The yield was 0.91 g (81.2%). M.p. 148 °C. IR ν_{max} (cm^{-1}): 2983–2896 (CH, aliphatic), 2236 (C≡N), 1660 (C=O). $C_{15}H_{12}N_2O_4ClK$.

*2.2. 1-Chloro-3,4-dicyano-6-(1,1-dicarbethoxy-2-(4-biphenyl)-ethyl)benzene (**4**)*

To a solution of 0.81 g (2.26 mmol) of potassium salt of 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxymethyl)benzene (**3**) in 70 ml of acetonitrile was added 1.372 g (6.77 mmol) 4-(chloromethyl)biphenyl under N_2 atmosphere. The mixture was refluxed for 5 days and filtered. The solvent was removed and the residue was recrystallized from 50 ml of ethanol. After recrystallization we obtained 0.862 g (78.4%) of colorless substance melting at 161 °C. The compound was soluble in $CHCl_3$, CH_2Cl_2, THF, and acetone. IR ν_{max} (cm^{-1}): 3118 (CH, aromatic), 3052–3030 (CH, aromatic), 2980–2938 (CH, aliphatic), 2239 (C≡N), 1734 (C=O), 1175 (C–O–C). ^{1}H NMR ($CDCl_3$) δ: 7.80–6.85 (m, 11H, Ar–H), 4.32–4.22 (q, 4H, CH_2), 3.78 (s, 2H, CH_2), 1.30–1.24 (t, 6H, CH_3). MS (*m*/*z*): 487.2 [M$^+$]. Calculated for $C_{28}H_{23}N_2O_4Cl$: C 69.06; H 4.76; N 5.75%. Found: C 68.91; H 4.85; N 5.53%.

*2.3. 2,9(10),16(17),23(24)-Tetra-(1,1-(dicarbpentoxy)-2-(4-biphenyl)-ethyl)-3,(9)10,(16)17,(23)24-tetrachlorophthalocyaninato copper(II) (**5**)*

A mixture of **4** (0.1 g, 0.20 mmol), anhydrous $CuCl_2$ (7.8 mg, 0.058 mmol), 10 μl 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 1 ml of 1-pentanol was heated at 140 °C with stirring under N_2 atmosphere for 24 h. After cooling to room temperature the mixture was treated with MeOH (10 ml) in order to precipitate the product. The resulting dark green solid was centrifuged off and the crude product was passed through a silica gel column using first MeOH and then THF as the eluents. Yield: 80 mg (68%); m.p. > 200 °C. IR ν_{max} (cm^{-1}): 3025 (CH, aromatic), 2955–2868 (CH, aliphatic), 1728 (C=O), 1185 (C–O–C). Calculated for $C_{136}H_{140}Cl_4N_8O_{16}Cu$: C 69.57; H 6.01; N 4.77%. Found: C 69.51; H 5.78; N 4.85%. UV–vis λ_{max} (nm) (log ε) in $CHCl_3$: 344 (4.89), 684 (5.34).

*2.4. 2,9(10),16(17),23(24)-Tetra-(1,1-(dicarbpentoxy)-2-(4-biphenyl)-ethyl)-3,(9)10,(16)17,(23)24-tetrachlorophthalocyaninato lead(II) (**6**)*

A mixture of **4** (0.1 g, 0.20 mmol), $Pb(CH_3COO)_2 \cdot 3H_2O$ (22.2 mg, 0.058 mmol) and 10 μl DBU in 1 ml of 1-pentanol was heated at 140 °C under N_2 for 24 h. After cooling, crude product was precipitated by addition of MeOH (10 ml). The precipitate was filtered off, washed with MeOH and then dried *in vacuo*. Further purification by flash column chromatography on silica (SiO_2) by eluting with THF gave pale green solid. Yield: 55 mg (44%); m.p. > 200 °C. IR ν_{max} (cm^{-1}): 3025 (CH, aromatic), 2955–2862 (CH, aliphatic), 1726 (C=O), 1180 (C–O–C). ^{1}H NMR ($CDCl_3$) δ: 9.54–7.03 (br, 44H, aromatic H), 4.42–4.18 (m, 16H, CH_2), 3.84–3.48 (br, 8H, CH_2), 1.48–0.63 (m, 72H, CH_2 and CH_3). Calculated for $C_{136}H_{140}Cl_4N_8O_{16}Pb$: C 65.56; H 5.66; N 4.50%. Found: C 65.47; H 5.58; N 4.55%. UV–vis λ_{max} (nm) (log ε) in $CHCl_3$: 357 (4.77), 723 (5.31).

*2.5. 2,9(10),16(17),23(24)-Tetra-(1,1-(dicarbethoxy)-2-(4-biphenyl)-ethyl)-3,(9)10,(16)17,(23)24-tetrachlorophthalocyaninato cobalt(II) (**7**)*

To a mixture of **4** (0.1 g, 0.20 mmol) and anhydrous $CoCl_2$ (7.6 mg, 0.058 mmol) was added 1 ml of 1-pentanol. The reaction mixture was stirred at 140 °C under N_2 for 24 h. The resulting suspension was cooled to room temperature and the crude product was purified by column chromatography with silica gel using first MeOH and then THF as eluents. Yield: 57 mg (56.8%); m.p. > 200 °C. IR ν_{max} (cm^{-1}): 3030 (CH, aromatic), 2978–2930 (CH, aliphatic), 1729 (C=O), 1186 (C–O–C). MS (*m*/*z*): 2006.51 [M$^+$]. Calculated for $C_{112}H_{92}Cl_4N_8O_{16}Co$: C 67.03; H 4.62; N 5.58%. Found: C 66.94; H 4.58; N 5.61%. UV–vis λ_{max} (nm) (log ε) in $CHCl_3$: 332 (5.01), 673 (5.38).

*2.6. 2,9(10),16(17),23(24)-Tetra-(1,1-(dicarbethoxy)-2-(4-biphenyl)-ethyl)-3,(9)10,(16)17,(23)24-tetrachlorophthalocyaninato zinc(II) (**8**)*

Compound **4** (0.1 g, 0.20 mmol) and anhydrous $Zn(CH_3COO)_2$ (10.7 mg, 0.058 mmol) were dissolved in 1 ml of 1-pentanol under N_2. The reaction mixture was stirred at 140 °C for 24 h. It was allowed to cool to room temperature and the green reaction mixture was purified by silica gel column chromatography, using first MeOH and then THF as the eluting solvents to give the desired metallophthalocyanine. Yield: 67 mg (66.5%); m.p. > 200 °C. IR ν_{max} (cm^{-1}): 3025

(CH, aromatic), 2979–2935 (CH, aliphatic), 1734 (C=O), 1187 (C–O–C). ^{1}H NMR ($CDCl_3$) δ: 9.34–7.08 (br, 44H, aromatic H), 4.40–4.22 (m, 16H, CH_2), 3.81–3.28 (br, 8H, CH_2), 1.42–1.14 (m, 24H, CH_3). MS (*m*/*z*): 2013.5 [M^+]. Calculated for $C_{112}H_{92}Cl_4N_8O_{16}Zn$: C 66.82; H 4.61; N 5.57%. Found: C 66.89; H 4.54; N 5.63%. UV–vis λ_{max} (nm) (log ε) in $CHCl_3$: 354 (4.92), 682 (5.49).

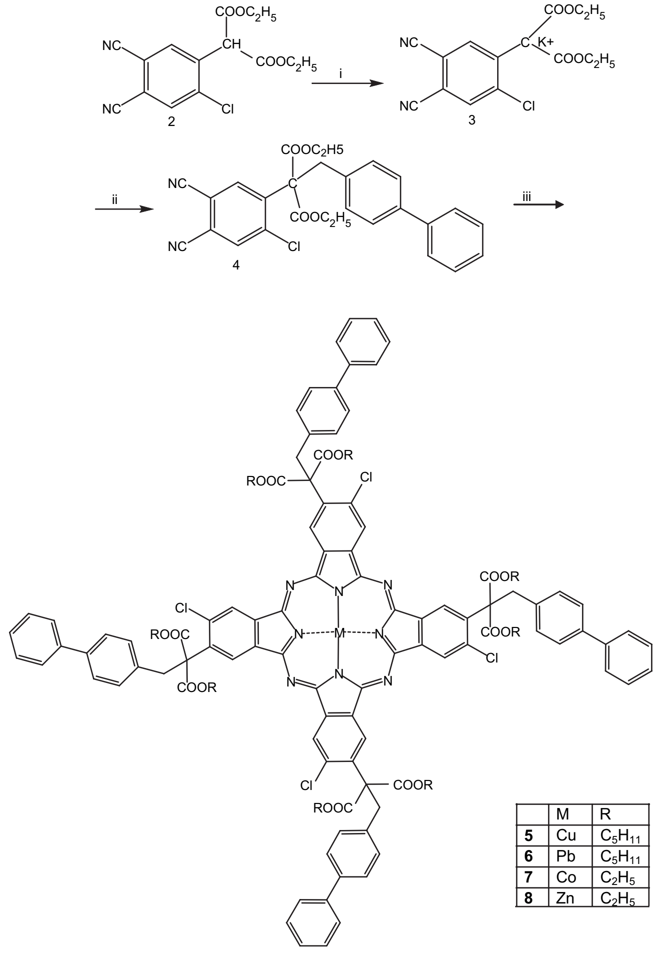
3. Results and discussion

3.1. Synthesis and characterization

For the synthesis of aimed starting compound, treatment of compound **3** with a strong base and addition of 4-(chloromethyl)biphenyl were carried out. We used the ratio of 1:3 compound **3** and 4-(chloromethyl)biphenyl because of the steric hindrance of the chloro group on phthalonitrile (**3**) with long reaction time. Resulting new phthalonitrile named 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxy-2-(4-biphenyl)-ethyl)benzene (**4**) has been converted into phthalocyanines through the cyclotetramerization reactions in 1-pentanol as a high boiling solvent. Transesterification of the malonyl group occurred when the cyclotetramerization was carried out in the presence of DBU in the case of the metal salts $Pb(CH_3COO)_2 \cdot 3H_2O$ and $CuCl_2$. Since no N-base was required for $CoCl_2$ and $Zn(CH_3COO)_2$ salts no transesterification took place [16,17]. The synthetic pathway and the structures of target molecules are shown in Scheme 1.

Conversion of new dinitrile compound to the aimed phthalocyanine derivatives accomplished relatively high yields in 55–68% range. ZnPc and CoPc derivatives were particularly obtained in high yields directly from dinitrile (**4**) and related metal salts in 1-pentanol without any reductant. The newly synthesized four phthalocyanines were purified by column chromatography on silica gel using methanol and THF as the eluents. Due to the presence of two different substituents on -4 and -5 positions of the phthalonitrile (**4**), phthalocyanines obtained from this precursor are naturally a mixture of four constitutional isomers [25]. Our attempts to separate these isomers with column chromatography and HPLC methods using different solvents are not successful. These new phthalocyanines (**5**–**8**) show high solubility in most organic solvents such as dichloromethane, chloroform, ethyl acetate, acetonitrile, acetone, and tetrahydrofuran.

All new compounds were identified through several spectroscopic techniques such as ^{1}H NMR, FT-IR, UV–vis, FAB-MS and elemental analysis. The spectroscopic data of desired products were in accordance with the assigned structures. IR spectrum of **3** indicated the alkyl, nitrile and carbonyl groups by the intense stretching bands at 2983–2896 cm^{-1}, 2236 cm^{-1} and 1660 cm^{-1}, respectively. Addition of 4-(chloromethyl)biphenyl to this compound gave the stretching band at 3118–3030 cm^{-1} indicating aromatic –CH groups additionally, aliphatic groups at 2980–2938 cm^{-1}, C≡N groups at 2239 cm^{-1} and ester groups at 1734 cm^{-1} (C=O), 1175 cm^{-1} (C–O–C) by the intense bands. IR spectra of phthalocyanines (**5**–**8**) exhibit these similar vibrations of the substituent groups around similar frequencies and the only difference being the disappearance of the C≡N band at 2236 cm^{-1} which proves the cyclotetramerization of dinitrile.



	M	R
5	Cu	C_5H_{11}
6	Pb	C_5H_{11}
7	Co	C_2H_5
8	Zn	C_2H_5

Scheme 1. Synthesis of Pcs. (i) KOH, ethanol; (ii) acetonitrile, 4-(chloromethyl)biphenyl, 5 days, reflux; (iii) metal salts and/or DBU, pentanol, 24 h, 140 °C. (One of the four constitutional isomers is shown for simplicity.)

In the ^{1}H NMR spectrum of compound **4**, the aromatic protons are observed as multiplet at 7.80–6.85 ppm, aliphatic CH_2 protons at 4.32–4.22 ppm and 3.78 ppm as quartet and singlet, respectively, and aliphatic CH_3 protons as triplet at 1.30–1.24 ppm. In the case of zinc and lead phthalocyanines, ^{1}H NMR spectra confirm our proposed structures and chemical shifts are almost the same and somewhat broader than the corresponding signals in the dinitrile compound **4**. Furthermore, in the MS spectrum, we observed the molecular ion peaks at *m*/*z* 487.2 for **4**, at *m*/*z* 2006.51 for **7** and at *m*/*z* 2013.5 for **8** which confirm the proposed structures.

Electronic spectra are especially useful to identify the structure of the phthalocyanines. The typical Q and B bands, corresponding to the transitions π–π^* ($a_{1u} \rightarrow e_g$ or HOMO–LUMO) (at approximate wavelength range $660 < \lambda < 720$ nm) and a_{2u}–LUMO (at approximate wavelength range $300 < \lambda < 450$ nm), respectively, allow an easy spectral identification of a phthalocyanine. The existence of a range for the transition energies of the Q and B bands is due to their dependence on the nature of ring substituents, the symmetry of the molecule as determined by the nature

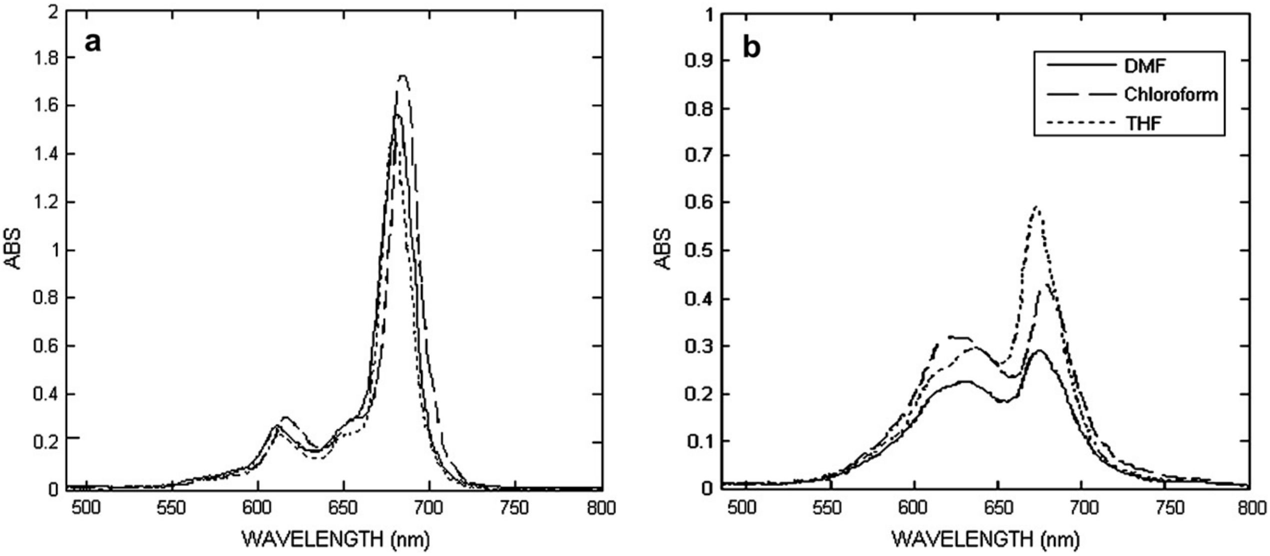


Fig. 1. UV–vis spectra of **5** (a) and **9** (b) in various solvents of different polarity (10^{-6} M).

of the central atom, the positions of the peripheral substituents, and the molecular environment of the Pc macroring [1]. The electronic spectra of all phthalocyanines (**5–8**) taken in chloroform displayed sharp Q bands around 673–723 nm and nearly no shoulder on the higher energy side related to aggregated species. The UV–vis spectra of CuPc (**5**) in solvents of different polarity (tetrahydrofuran, chloroform, dimethylformamide) show almost no shoulder on the higher energy side indicating the lack of any aggregated species as observed in Fig. 1(a). When compared with the UV–vis spectrum of a similar copper phthalocyanine with H instead of biphenylmethyl moiety (**9**), which was reported recently [16], it can be seen that peaks corresponding to aggregated species around 624–637 nm increase in the case of **9** in parallel with the polarity of the solvents (tetrahydrofuran < chloroform < dimethylformamide) (Fig. 1(b)). These results are attributed to the displacement of bulky 4-(chloromethyl)biphenyl with acidic proton (−CH) in malonyl unit. Lead phthalocyanine displays a Q band shifted to the red region when compared with the other divalent metal-containing analogues in the electronic spectrum [16,18–20]. All UV–vis spectra of phthalocyanines (**5–8**) show that bulky methylbiphenyl substituent on the periphery prevent the aggregation.

4. Conclusion

In this work we have demonstrated that biphenylmethyl rigid groups can be introduced by substituting the acidic CH proton of malonic ester moiety on phthalonitriles and the phthalocyanines derived from this precursor do not show any tendency for aggregation independent of the polarity of the solvents used.

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