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The synthesis of some phthalocyanines derived from bulky substituted phthalonitriles

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ABSTRACT

Phthalocyanine precursors were prepared by displacement of the –CH proton in 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxymethyl) benzene with 1-(chloromethyl)-2-methyl benzene and 1-(chloromethyl)-4-methyl benzene. Metallo-phthalocyanines were obtained by cyclotetramerization in the presence of template metal salts {$Zn(CH_3COO)_2$, $CoCl_2$, $CuCl_2$, and $Pb(CH_3COO)_2\cdot 3H_2O$} that possessed substituents to enhance the solubility of the macrocycle and reduce its propensity to aggregate in solution. The structures of the newly synthesized molecules were proposed according to elemental analysis and ^1H NMR, FT-IR, Micro-TOF mass, MALDI-TOF mass and UV–vis spectral data.

1. Introduction

Phthalocyanines have been investigated in different fields such as non-linear optics, sensors, optical data storage, photodynamic cancer therapy, solar energy conversion and electrochromism [1–5]. Recently, there has been a substantial effort to synthesize novel Pc derivatives which possess enhanced attributes relative to the substituents on the macrocycle such as solubility in common organic solvents, absorbency in the near-IR, liquid crystallinity, redox behavior, and the ability to produce well-ordered thin films [6].

Phthalocyanines show a propensity to aggregate through coplanar association of the Pc rings in solution to form the dimer and higher oligomeric species owing to the extended π system [7,8], a characteristic that may negatively impact their solubility in many solvents, non-linear optical properties, also dramatically affect their photochemical properties [9]. Peripheral substitution is used for enhancing the solubility of phthalocyanine compounds in aqueous and organic media and for changing the aggregation behavior [10–13].

Generally, tetra-substituted Pcs are more soluble than symmetrically octasubstituted ones due to the formation of four positional isomers in the case of tetra-substituted analogues [14]. A useful and less studied synthetic route to soluble octasubstituted Pcs involves the reaction between 1,2-dichloro-4,5-dicyanobenzene (**1**) and a suitable oxygen or sulfur nucleophile followed by the cyclotetramerization of the resultant phthalonitrile derivative with two different substituents in the 4- and 5-positions [15–19]. In this sense, in our recent works, we have synthesized new phthalonitrile compound bearing two different groups on periphery for the first time using acidic nature of the CH_2 group among two ester moieties in the diethylmalonate [20,21]. In addition, we investigated the reactivity of the remaining chloro group in newly synthesized phthalonitrile to obtain other sophisticated differently substituted phthalonitriles such as bearing bulky diethylmalonate and alkylsulfanyl [22] or dimethylaminoethylsulfanyl groups [23] at 4- and 5-positions. Besides, recently we have incorporated bulky biphenyl moiety between two ester groups in diethylmalonyl unit [24]. The aim of the present work was to extend this synthetic methodology to provide phthalonitrile precursors derived from 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxymethyl)benzene (**2**) and 1-(chloromethyl)-2-methylbenzene (**4a**) and 1-(chloromethyl)-4-methylbenzene (**4b**). It was anticipated that this would result in Pcs containing four chloro and four *o*-methylbenzyl and *p*-methylbenzyl malonic ester bulky groups placed at peripheral positions where they can enhance solubility and hinder aggregation.

2. Experimental

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer. UV–vis was recorded

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on a Unicam UV2 spectrophotometer. ^{1}H NMR spectra were measured on Bruker 250 MHz using TMS as internal standard. Mass spectra were measured on a Bruker Daltonics Micro-TOF and MALDI-TOF 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. Silicagel (60 Merck) was used in the separation and purification of compounds by column chromatography. Dimethylformamide (DMF) was dried over 4-Å sieves and 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxymethyl)benzene (**2**) [20] and potassium salt of 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxymethyl)benzene (**3**) [24] was prepared from 1,2-dichloro-4,5-dicyanobenzene (**1**) [25] according to procedures described in the literature.

*2.1. 1-Chloro-3,4-dicyano-6-(1,1-dicarbethoxy-2-(2-methylbenzyl)-ethyl)benzene (**5a**)*

A total of 1 g (2.78 mmol) of potassium salt of 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxymethyl)benzene (**3**) and 1-(chloromethyl)-2-methylbenzene (**4a**) (8.36 mmol, 1.103 ml) were stirred in 60 ml of acetonitrile under a nitrogen atmosphere for 24 h at 85 °C. The mixture was cooled to room temperature and filtered off. Evaporation of solvent under reduced pressure yielded the oily product. Reprecipitation from methanol–water mixture gave colorless substance as powder. Purification by column chromatography (silicagel, first hexane then dichloromethane eluant) afforded pure new phthalonitrile compound (0.65 g, 54.89% yield), m.p. >84 °C. The compound was soluble in $CHCl_3$, CH_2Cl_2, THF, and acetone. IR, γ_{max} (cm^{-1}): 3120 (CH, aromatic), 3081–3042 (CH, aromatic), 2981–2935 (CH, aliphatic), 2235 (C≡N), 1734 (C=O), 1175 (C–O–C), 726 (*ortho*-disubstituted benzene). ^{1}H NMR ($CDCl_3$) δ: 7.77–7.76 (s, 2H, Ar-H), 7.22–6.78 (m, 4H, Ar-H), 4.32–4.17 (m, 4H, CH_2), 3.78 (s, 2H, CH_2), 2.16 (s, 3H, CH_3), 1.31–1.19 (t, 6H, CH_3). MS: (*m*/*z*): 447.2 $[M+Na]^+$. Calculated for $C_{23}H_{21}ClN_2O_4$: C, 65.02; H, 4.98; N, 6.59%. Found: C 64.89; H 5.04; N 6.64%.

*2.2. 1-Chloro-3,4-dicyano-6-(1,1-dicarbethoxy-2-(4-methylbenzyl)-ethyl)benzene (**5b**)*

A total of 1 g (2.78 mmol) of potassium salt of 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxymethyl)benzene (**3**) and 1-(chloromethyl)-4-methylbenzene (**4b**) (8.36 mmol, 1.103 ml) were stirred in 60 ml of acetonitrile under a nitrogen atmosphere for 24 h at 85 °C. The mixture was cooled to room temperature and filtered. Evaporation of solvent under reduced pressure yielded the oily product. Recrystallization from methanol gave phthalonitrile compound as colorless (0.80 g, 67.56% yield), m.p. >122 °C. The compound was soluble in $CHCl_3$, CH_2Cl_2, THF, and acetone. IR, γ_{max} (cm^{-1}): 3114 (CH, aromatic), 3081 (CH, aromatic), 2981–2901 (CH, aliphatic), 2239 (C≡N), 1737 (C=O), 1174 (C–O–C), 813 (*para*-disubstituted benzene). ^{1}H NMR ($CDCl_3$) δ: 7.77 (s, H, Ar-H), 7.63 (s, H, Ar-H), 6.92–6.89 (d, 2H, Ar-H), 6.65–6.62 (d, 2H, Ar-H), 4.34–4.21 (m, 4H, CH_2), 3.69 (s, 2H, CH_2), 2.25 (s, 3H, CH_3), 1.29–1.23 (t, 6H, CH_3). MS: (*m*/*z*): 447.2 $[M+Na]^+$. Calculated for $C_{23}H_{21}ClN_2O_4$: C, 65.02; H, 4.98; N, 6.59%. Found: C 64.92; H 5.06; N 6.69%.

*2.3. Preparation of phthalocyanines (**6**(**a**, **b**)–**9**(**a**, **b**))*

Phthalonitrile compound **5a** or **b** (0.1 g, 0.23 mmol) was dissolved in 1 ml of *n*-pentanol, and the mixture was heated to 100 °C under nitrogen atmosphere and metal salt (0.078 mmol; 0.0143 g $Zn(CH_3COO)_2$, 0.0101 g $CoCl_2$, 0.0105 g $CuCl_2$ or 0.0278 g $Pb(CH_3COO)_2\cdot 3H_2O$) subsequently added into the solution. After heating 145 °C for 24 h in a sealed tube, the mixture was cooled and precipitation by adding methanol afforded, filtered off and crude product obtained. Compound **6a** and **b** were purified by reprecipitation from hexane then centrifuged and washed several times with hexane and petroleum ether. In the case of purification with column chromatography on silicagel metal-free analogues were obtained. Purification of (**7**(**a**, **b**)–**9**(**a**, **b**)) was accomplished by column chromatography using silicagel (dichloromethane: methanol (100:12.5) for **7a** and **b**, tetrahydrofuran: hexane (100:10) for **8a** and **b**, methanol: tetrahydrofuran (100:10) for **9a**, first methanol then tetrahydrofuran for compound **9b** as eluant).

*2.3.1. 2,9,16,23-Tetra-(1,1-(dicarbethoxy)-2-(2-methylbenzyl))-ethyl 3,10,17,24-Tetra chloro-phthalocyaninato zinc (II), Zn o-MBPc (**6a**)*

^{1}H NMR ($CDCl_3$) δ: 9.35 (br, 8H, Ar-H), 7.80–6.97 (br, 16H, Ar-H), 4.22 (br, 16H, CH_2), 3.82 (s, 8H, CH_2), 1.97–1.91 (br, 12H, CH_3), 1.23–1.20 (t, 24H, CH_3). Yield: 40 mg (28.7%); m.p. >200 °C. IR, γ_{max} (cm^{-1}): 3047 (CH, aromatic), 2978–2873 (CH, aliphatic), 1728 (C=O), 1175 (C–O–C), 745 (*ortho*-disubstituted benzene). MS (MALDI-TOF): *m*/*z* = 1764 [M$^+$], Calculated for $C_{92}H_{84}Cl_4N_8O_{16}Zn$: C, 62.61; H, 4.80; N, 6.35%. Found: C 62.64; H 4.85; N 6.28%.

*2.3.2. 2,9,16,23-Tetra-(1,1-(dicarbethoxy)-2-(4-methylbenzyl))-ethyl 3,10,17,24-Tetra chloro-phthalocyaninato zinc (II), Zn p-MBPc (**6b**)*

^{1}H NMR ($CDCl_3$) δ: 9.35 (br, 8H, Ar-H), 7.81–6.76 (br, 16H, Ar-H), 4.42–4.21 (m, 16H, CH_2), 3.74 (s, 8H, CH_2), 2.19–2.06 (br, 12H, CH_3), 1.37–1.21 (t, 24H, CH_3). Yield: 46 mg (33.4%); m.p. >200 °C. IR, γ_{max} (cm^{-1}): 3042 (CH, aromatic), 2978–2929 (CH, aliphatic), 1731 (C=O), 1182 (C–O–C), 811 (*para*-disubstituted benzene). MS (MALDI-TOF): *m*/*z* = 1764 [M$^+$], Calculated for $C_{92}H_{84}Cl_4N_8O_{16}Zn$: C, 62.61; H, 4.80; N, 6.35%. Found: C 62.63; H 4.84; N 6.30%.

*2.3.3. 2,9,16,23-Tetra-(1,1-(dicarbethoxy)-2-(2-methylbenzyl))-ethyl 3,10,17,24-Tetra chloro-phthalocyaninato cobalt (II), Co o-MBPc (**7a**)*

Yield: 13 mg (9.4%); m.p. >200 °C. IR, γ_{max} (cm^{-1}): 3047 (CH, aromatic), 2978–2901 (CH, aliphatic), 1732 (C=O), 1185 (C–O–C), 755 (*ortho*-disubstituted benzene). MS (MALDI-TOF): *m*/*z* = 1758 [M$^+$], Calculated for $C_{92}H_{84}Cl_4CoN_8O_{16}$: C, 62.84; H, 4.81; N, 6.37%. Found: C 62.87; H 4.84; N 6.31%.

*2.3.4. 2,9,16,23-Tetra-(1,1-(dicarbethoxy)-2-(4-methylbenzyl))-ethyl 3,10,17,24-tetra chloro-phthalocyaninato cobalt (II), Co p-MBPc (**7b**)*

Yield: 15 mg (10.9%); m.p. >200 °C. IR, γ_{max} (cm^{-1}): 3047 (CH, aromatic), 2977–2901 (CH, aliphatic), 1728 (C=O), 1184 (C–O–C), 811 (*para*-disubstituted benzene). MS (MALDI-TOF): *m*/*z* = 1758 [M$^+$], Calculated for $C_{92}H_{84}Cl_4CoN_8O_{16}$: C, 62.84; H, 4.81; N, 6.37%. Found: C 62.89; H 4.85; N 6.33%.

*2.3.5. 2,9,16,23-Tetra-(1,1-(dicarbethoxy)-2-(2-methylbenzyl))-ethyl 3,10,17,24-tetra chloro-phthalocyaninato copper (II), Cu o-MBPc (**8a**)*

Yield: 12 mg (8.5%); m.p. >200 °C. IR, γ_{max} (cm^{-1}): 3047 (CH, aromatic), 2978–2890 (CH, aliphatic), 1731 (C=O), 1185 (C–O–C), 754 (*ortho*-disubstituted benzene). MS (MALDI-TOF): *m*/*z* = 1763 [M$^+$], Calculated for $C_{92}H_{84}Cl_4CuN_8O_{16}$: C, 62.67; H, 4.80; N, 6.36%. Found: C 62.72; H 4.83; N 6.29%.

*2.3.6. 2,9,16,23-Tetra-(1,1-(dicarbethoxy)-2-(4-methylbenzyl))-ethyl 3,10,17,24-Tetra chloro-phthalocyaninato copper (II), Cu p-MBPc (**8b**)*

Yield: 16 mg (11.7%); m.p. >200 °C. IR, γ_{max} (cm^{-1}): 3042 (CH, aromatic), 2977–2901 (CH, aliphatic), 1731 (C=O), 1184 (C–O–C), 811 (*para*-disubstituted benzene). MS (MALDI-TOF): *m*/*z* = 1763

[M^+], Calculated for $C_{92}H_{84}Cl_4CuN_8O_{16}$: C, 62.67; H, 4.80; N, 6.36%. Found: C 62.74; H 4.84; N 6.31%.

2.3.7. 2,9,16,23-Tetra-(1,1-(dicarbethoxy)-2-(2-methylbenzyl))-ethyl 3,10,17,24-Tetra chloro-phthalocyaninato lead (II), Pb o-*MBPc (**9a**)*

^{1}H NMR ($CDCl_3$) δ: 9.41–9.23 (br, 8H, Ar-H), 7.08–6.82 (br, 16H, Ar-H), 4.41–4.17 (br, 16H, CH_2), 3.84 (s, 8H, CH_2), 2.02–1.99 (br, 12H, CH_3), 1.38–1.24 (t, 24H, CH_3). Yield: 50 mg (33.4%); m.p. >200 °C. IR, γ_{max} (cm^{-1}): 3042 (CH, aromatic), 2957–2873 (CH, aliphatic), 1728 (C=O), 1186 (C–O–C), 742 (*ortho*-disubstituted benzene). MS (MALDI-TOF): $m/z = 1907$ [M^+], Calculated for $C_{92}H_{84}Cl_4N_8O_{16}Pb$: C, 57.95; H, 4.44; N, 5.88%. Found: C 57.99; H 4.48; N 5.82%.

2.3.8. 2,9,16,23-Tetra-(1,1-(dicarbethoxy)-2-(4-methylbenzyl))-ethyl 3,10,17,24-Tetra chloro-phthalocyaninato lead (II), Pb p-*MBPc (**9b**)*

^{1}H NMR ($CDCl_3$) δ: 9.41–9.26 (br, 8H, Ar-H), 7.02–6.82 (br, 16H, Ar-H), 4.41–4.12 (br, 16H, CH_2), 3.76 (s, 8H, CH_2), 2.25–1.99 (br, 12H, CH_3), 1.41–1.24 (t, 24H, CH_3). Yield: 37 mg (24.8%); m.p. >200 °C. IR, γ_{max} (cm^{-1}): 3047 (CH, aromatic), 2955–2873 (CH, aliphatic), 1731 (C=O), 1182 (C–O–C), 810 (*para*-disubstituted benzene). MS (MALDI-TOF): $m/z = 1907$ [M^+], Calculated for $C_{92}H_{84}Cl_4N_8O_{16}Pb$: C, 57.95; H, 4.44; N, 5.88%. Found: C 58.01; H 4.49; N 5.80%.

3. Result and discussion

3.1. Synthesis and characterization

The syntheses of 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxy-2-(2-methylbenzyl)-ethyl)benzene (**5a**) or 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxy-2-(4-methylbenzyl)-ethyl)benzene (**5b**) were achieved by treatment of compound **3** with 1-(chloromethyl)-2-methylbenzene (**4a**) or 1-(chloromethyl)-4-methylbenzene (**4b**), in acetonitrile at 85 °C, in an inert nitrogen atmosphere (Fig. 1). Unfortunately, metal-free phthalocyanine analogues were obtained owing to cyclotetramerizations of phthalonitriles in the presence of DBU as N-base. Therefore, cyclotetramerizations for all metallo-phthalocyanines were accomplished in *n*-pentanol without the aid of any N-base. Octakis metallo-phthalocyanines which are substituted with four chloro and four *o*-methylbenzyl or *p*-methylbenzyl malonic ester at periphery were obtained by cyclotetramerisation of 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxy-2-(2-methylbenzyl)-ethyl)benzene (**5a**) or 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxy-2-(4-methylbenzyl)-ethyl)benzene (**5b**) in *n*-pentanol in the presence of related metal salts ($Zn(CH_3COO)_2$, $CoCl_2$, $CuCl_2$ and $Pb(CH_3COO)_23H_2O$) (Fig. 1). Satisfactory yields were acquired for the synthesis of compounds **5a** and **b** and for all the metallo-phthalocyanines (**6**(**a**, **b**)–**9**(**a**, **b**)). Due to the

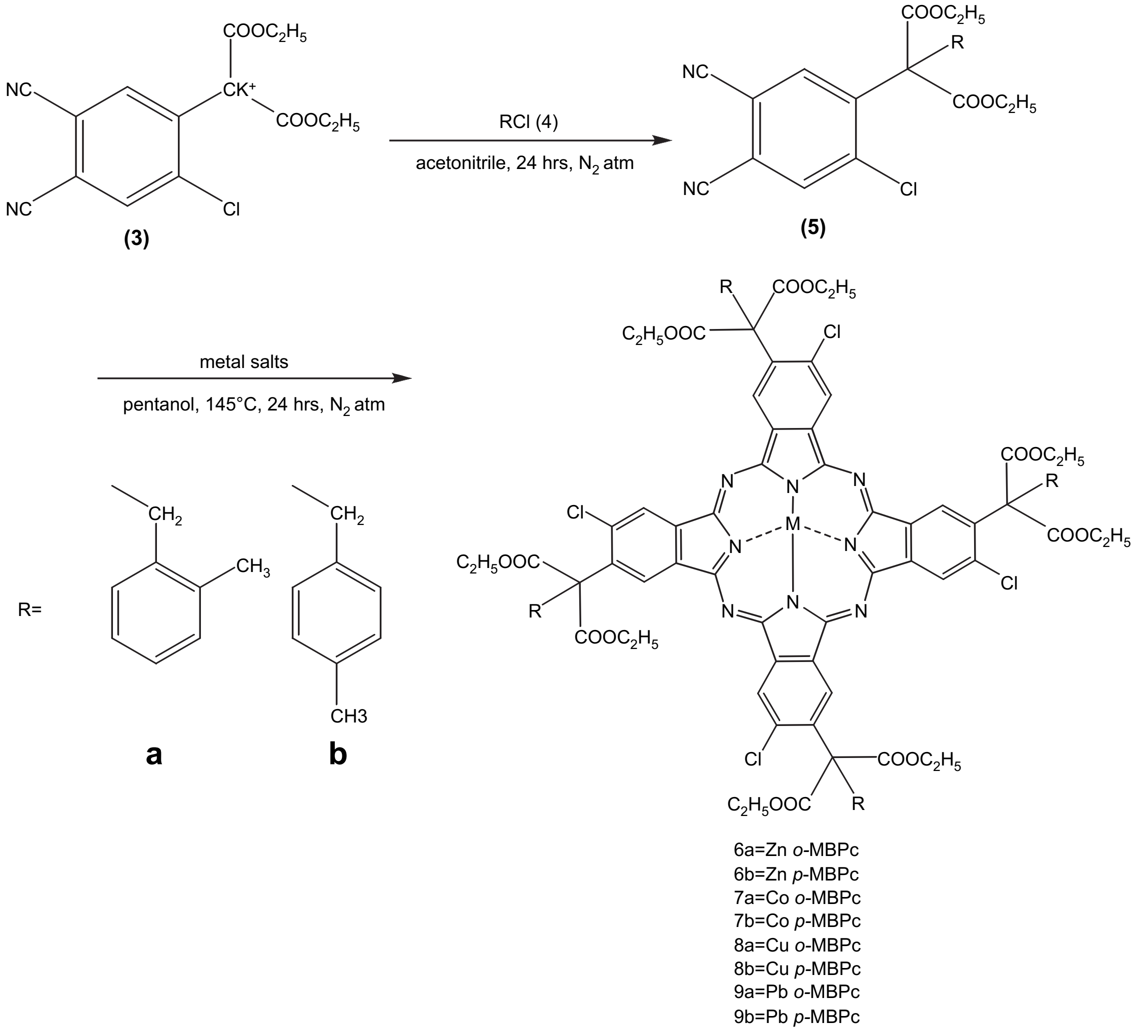

Fig. 1. Synthetic route for phthalonitrile and phthalocyanine compounds.

Table 1
UV–vis spectral data of the phthalocyanines (**6**(**a**, **b**)–**9**(**a**, **b**))

Compound	Solvent	Q band (nm)	B band (nm)
6a, **b**	Toluene	683, 683	354, 353
	THF	678, 678	353, 353
	$CHCl_3$	682, 682	353, 353
	DMF	680, 680	351, 353
	DMSO	682, 682	354, 354
7a, **b**	Toluene	674, 674	334, 335
	THF	667, 667	335, 334
	$CHCl_3$	673, 673	332, 333
	DMF	668, 667	335, 335
	DMSO	666, 666	338, 338
8a, **b**	Toluene	683, 683	351, 351
	THF	678, 677	352, 351
	$CHCl_3$	683, 683	345, 345
	DMF	678, 678	352, 352
	DMSO	679, 679	353, 351
9a, **b**	Toluene	720, 720	355, 355
	THF	712, 712	351, 352
	$CHCl_3$	722, 722	355, 355
	DMF	709, 709	349, 350
	DMSO	710, 710	350, 350

presence of two different substituents on 4- and 5-positions of phthalonitriles **5a** and **b**, phthalocyanines are naturally a mixture of positional isomers [14]. The compounds prepared in this study show good solubility in a number of organic solvents, such as ethylacetate, acetone, chloroform, dichloromethane, tetrahydrofuran, toluene, DMF and DMSO.

For all compounds spectroscopic analyses (UV–vis, IR, and ^{1}H NMR), MALDI-TOF and Micro-TOF mass spectroscopies and elemental analyses gave spectra consistent with the proposed structures.

The CN band in the IR spectrum of **5a** was observed, as expected, at 2235 cm^{-1} and 2239 cm^{-1} for **5b**. Besides, the bands indicating *ortho* or *para*-disubstituted benzene appeared at 726 cm^{-1} and 813 cm^{-1} for compounds **5a** and **b**, respectively. In the ^{1}H NMR spectrum of **5a**, the aromatic protons of *o*-methylbenzyl group appeared as a multiplet between 7.22 ppm and 6.78 ppm and CH_2 and CH_3 protons at 3.78 ppm and 2.16 ppm as singlet, respectively. The aromatic protons of phenyl and CH_2–CH_3 protons of malonyl groups were observed at 7.77–7.76 ppm as singlet, 4.32–4.17 ppm as multiplet and 1.31–1.19 ppm as triplet, respectively. For compound **5b**, aromatic protons were observed at 7.77 ppm and 7.63 ppm as a singlet belonging to phenyl and 6.92–6.89 ppm and 6.65–6.62 ppm as doublet belonging to *p*-methylbenzyl group. CH_2 and CH_3 protons of *p*-methylbenzyl unit were observed at 3.69 ppm and 2.25 ppm as a singlet, CH_2 and CH_3 protons of malonyl unit at 4.34–4.21 ppm as a multiplet and 1.29–1.23 ppm as a triplet, respectively.

In the case of phthalocyanines (**6**(**a**, **b**)–**9**(**a**, **b**)), the disappearance of the CN bands in the IR spectra evidenced the cyclotetramerization of dinitriles **5a** and **b**. Only the Zn *o*-MBPc (**6a**), Zn

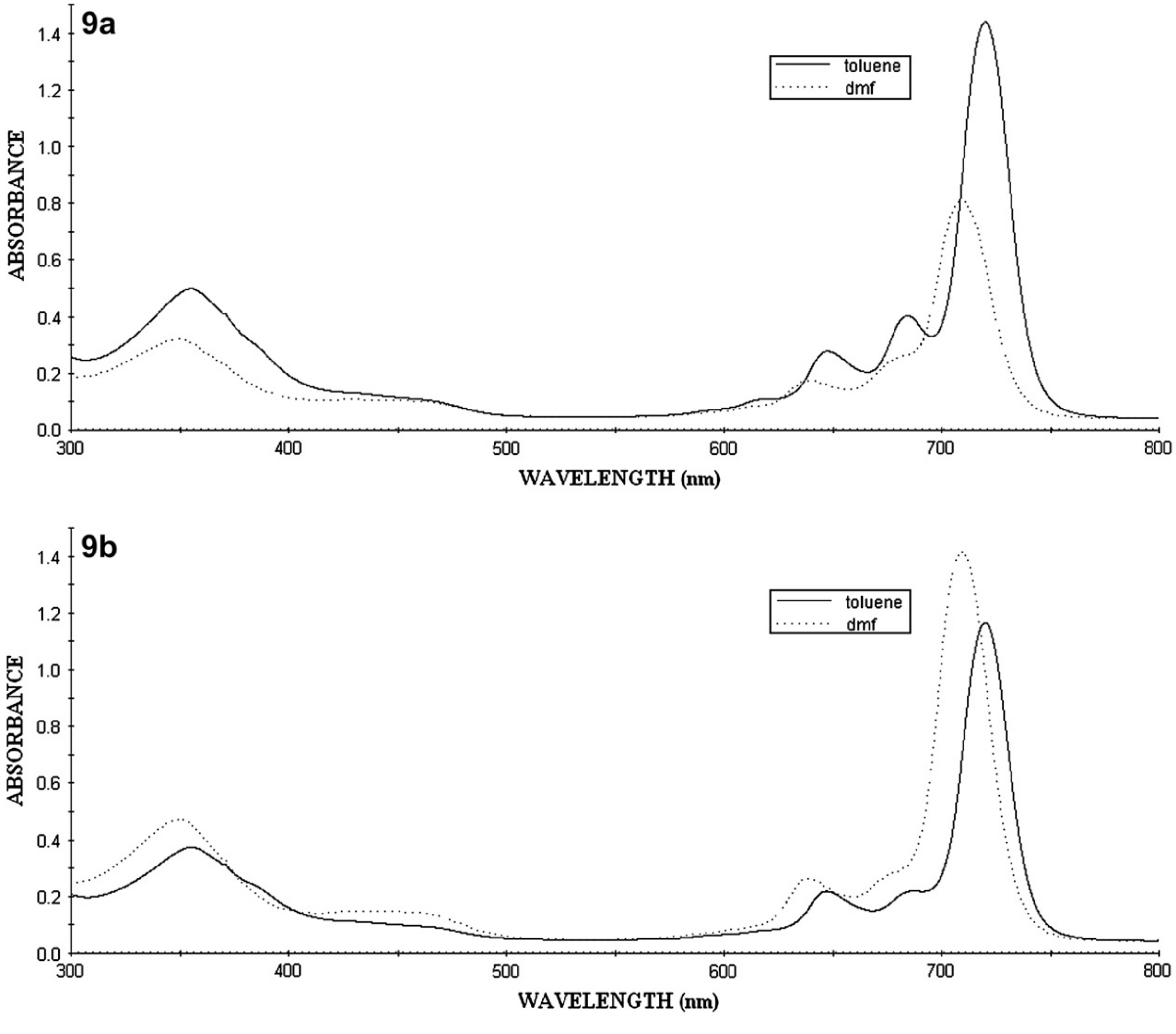

Fig. 2. Absorption spectra of the compounds **9a** and **b** in toluene and dmf. Concentration = 5.2×10^{-6} mol dm^{-3}.

p-MBPc (**6b**), Pb *o*-MBPc (**9a**) and Pb *p*-MBPc (**9b**) derivatives were employed for ^{1}H NMR analysis since the central metals are diamagnetic. The ^{1}H NMR spectra of zinc and lead phthalocyanines, confirm our proposed structures and chemical shifts are almost the same and somewhat broader than the corresponding signals in the dinitrile compounds **5a** and **b.** Micro-TOF spectra of **5a** and **b** and MALDI-TOF spectra of phthalocyanines (**6**(**a**, **b**)–**9**(**a**, **b**)) gave expected masses as shown in Section 2.

3.2. Spectral properties

The Pc system is characterized by strong absorption bands in the UV region (the Soret band) and in the visible region (the Q-band); low intensity bands in the visible region to shorter wavelength of the Q-band are vibronic in origin [26].

In the present work, the effects of peripheral substituents and metal atoms on spectroscopic and aggregation properties of phthalocyanine derivatives (**6**(**a**, **b**)–**9**(**a**, **b**)) were investigated in different solvents (toluene, THF, $CHCl_3$, DMF, and DMSO).

Q-Band absorption data obtained for representative compounds in toluene, THF, $CHCl_3$, DMF, and DMSO are summarized in Table 1. The variations in λ_{max} in Table 1 reveal how, substituent, central ion and solvent provide a means of tuning the wavelength of the Q-band absorption. Cobalt phthalocyanines (**7a**, **b**) display Q bands around 666–674 nm in different solvents whereas copper (**8a**, **b**) and zinc phthalocyanines (**6a**, **b**) have nearly the same values around 678–683 nm and illustrate ∼9–12 nm bathochromic shifts according to cobalt phthalocyanine (**7a**, **b**) analogues. It can be seen that in Table 1, lead phthalocyanines (**9a**, **b**) have the largest bathochromic shifts compared to cobalt phthalocyanines (**7a**, **b**) around 41–49 nm, copper phthalocyanines (**8a**, **b**) around 31–39 nm and zinc phthalocyanines (**6a**, **b**) around 28–40 nm, respectively.

Comparison of the λ_{max} of *ortho*-methylbenzyl malonic ester-substituted phthalocyanines (**6a**–**9a**) with *para*-methylbenzyl maloni cester-substituted phthalocyanines (**6b**–**9b**) in different solvents such as toluene, THF, $CHCl_3$, DMF and DMSO illustrates no sensitivity of the Q band to substituent (Table 1).

The term solvatochromism is used to describe the pronounced change in position (and sometimes intensity) of the UV–vis absorption band that accompanies a change in the polarity of the medium. A hypsochromic (or blue) shift with increasing solvent polarity is usually named negative solvatochromism, while the positive solvathochromism corresponds to a bathochromic (or red) shift [27]. Solvatochromic effect of metallo-phthalocyanines (**6**(**a**, **b**)–**9**(**a**, **b**)) was studied in toluene and DMF with different polarities. The spectra of compounds (**6**(**a**, **b**)–**8**(**a**, **b**)) show a small change of the maximum of the Q band from 683, 674 and 683 nm in toluene to 680, 668, 678 nm in DMF, respectively. In the case of lead phthalocyanines (**9a**, **b**) was found relatively large negative solvatochromism from 720 nm in toluene to 709 nm in DMF (Fig. 2). These results can be interpreted in terms of a simple dipole–dipole

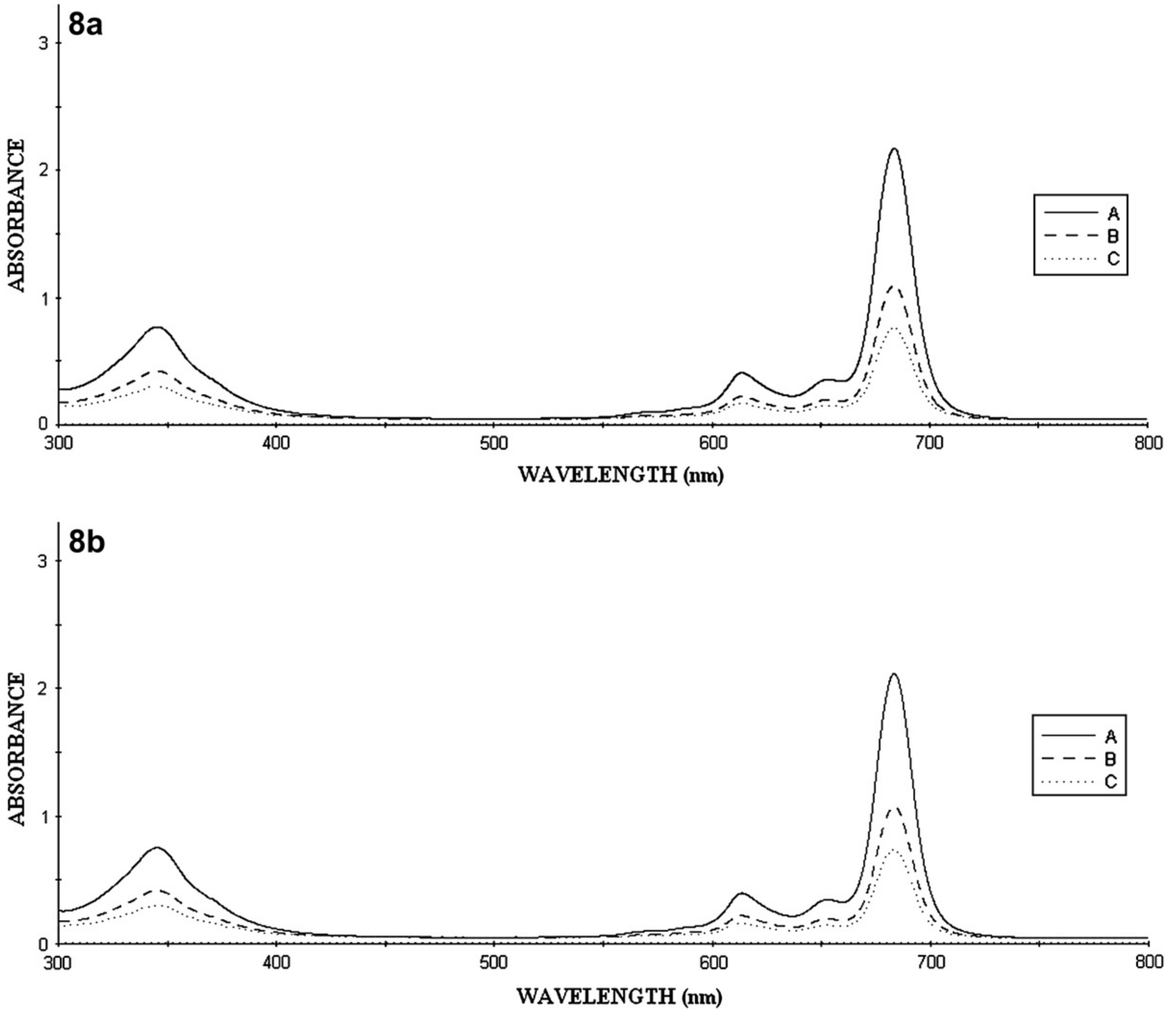

Fig. 3. Absorption spectra of the compounds **8a** and **b** in $CHCl_3$ at different concentrations. 11.2×10^{-6} (A), 5.6×10^{-6} (B), 3.7×10^{-6} (C) mol dm^{-3}.

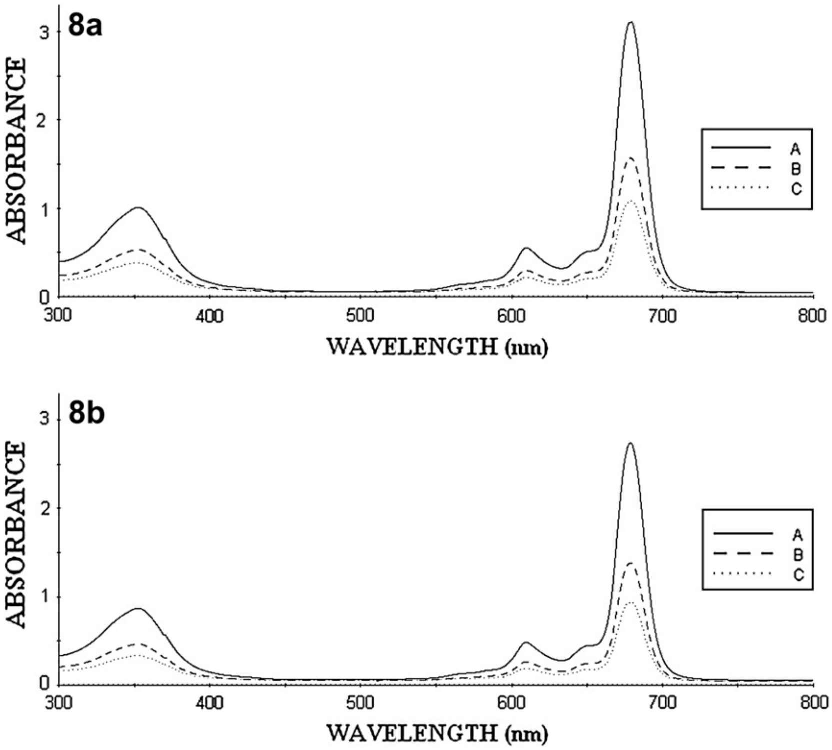

Fig. 4. Absorption spectra of the compounds **8a** and **b** in DMF at different concentrations. 11.2×10^{-6} (A), 5.6×10^{-6} (B), 3.7×10^{-6} (C) mol dm^{-3}.

interaction between Pc and solvent molecules unless effects of any solvent-induced chemical reaction are significant [28].

The electronic spectra of all phthalocyanines (**6**(**a**, **b**)–**9**(**a**, **b**)) were studied in five solvents with different polarities (toluene < THF < chloroform < DMF < DMSO) and displayed single (narrow) Q bands around 666–722 nm which depict monomeric nature of these complexes in these solvents (Table 1).

In our recent works, in the case of copper phthalocyanine derivative bearing four chloro and four diethylmalonyl moieties at periphery [20] showed aggregation behavior in solvents with different polarities (tetrahydrofuran, chloroform, dimethylformamide). In order to hinder the aggregation, methylbiphenyl rigid group was introduced into two diethylmalonyl units instead of H in phthalocyanine precursor thus it was demonstrated that bulky methylbiphenyl substituents at periphery prevent the aggregation of its phthalocyanine derivatives independent of the solvent polarity [24]. Here, aggregation behavior of copper phthalocyanines (**8a**, **b**) which are substituted with four chloro and four *ortho*-methyl or *para*-methylbenzyl malonic ester bulky groups was examined at different concentrations (11.2×10^{-6}, 5.6×10^{-6}, 3.7×10^{-6} mol dm^{-3}) in $CHCl_3$ (Fig. 3) and in DMF (Fig. 4). In $CHCl_3$ and DMF, as the concentration was increased from 3.7×10^{-6} to 11.2×10^{-6} mol dm^{-3}, the intensity of absorption of the Q band also increased and there were no new bands (normally blue shifted) due to the aggregated species for the copper phthalocyanines (**8a**, **b**) (Figs. 3 and 4). This can be explained by the fact that incorporation of bulky *ortho*-methylbenzyl and *para*-methylbenzyl groups into two diethylmalonyl units results in non-aggregated species like rigid methylbiphenyl unit.

4. Conclusion

As shown above, *ortho*-methylbenzyl and *para*-methylbenzyl groups can be displaced with –CH proton of 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxymethyl)benzene (**2**) thus, achieved hindering aggregation of phthalocyanine derivatives of these precursors. Future studies may be aimed at achieving incorporation of several units into diethylmalonyl groups of phthalonitrile (**2**) for tuning of optical property and aggregation behavior of new phthalocyanine compounds derived from these phthalonitriles.

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