

Novel peripherally tetra-substituted octacationic metal-free and metallophthalocyanines: Synthesis, spectroscopic characterization and aggregation behaviours

İrfan Acar^b, Volkan Çakır^a, Zekeriya Bıyıklıoğlu^{a,*}, Halit Kantekin^a

^a Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey

^b Department of Woodworking Industry Engineering, Of Faculty of Technology, Karadeniz Technical University, 61830 Of, Trabzon, Turkey

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ABSTRACT

In this study, new 1,3-bis[3-(diethylamino)phenoxy]propan-2-ol 1 and phthalonitrile derivative 3 bearing 1,3-bis[3-(diethylamino)phenoxy]propan-2-ol substituent at peripheral position have been synthesized. The synthesis, characterization of the tetra-4-(2-[3-(diethylamino)phenoxy]-1-[[3-(diethylamino)phenoxy]methyl]ethoxy) substituted metal-free 4 and metallophthalocyanines 5, 6, 7, (MPcs, M = Ni, Co, Cu) are reported for the first time. These new metal-free and metallophthalocyanines 4–7 were converted into water soluble quaternized products by the reaction with methyl iodide 4a–7a. The metal-free phthalocyanine 4 was prepared from phthalonitrile derivative 3 in n-pentanol with a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7ene (DBU). Metallophthalocyanines 5–7 were prepared by cyclotetramerization of 3 with the corresponding metal salts (NiCl₂, CoCl₂, CuCl₂) in n-pentanol with a catalytic amount of DBU. The aggregation behaviours of the phthalocyanine complexes were studied in different solvents and concentrations. The new compounds have been characterized by using UV–vis, IR, ¹H NMR, ¹³C NMR, MS spectroscopic data and elemental analysis.

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1. Introduction

The physical and chemical properties of phthalocyanines (Pc) have long attracted attention due to their interesting electrical, optical, catalytic and photochemical properties [1]. Phthalocyanines (Pcs) are highly delocalized p-conjugated organic systems and exhibit wide variety of roles in a various high technological areas such as semiconductor devices [2], liquid crystals [3], sensors [4], catalysts [5], non-linear optics [6], photovoltaic solar cells [7], photocatalysis [8–10].

In medicine, phthalocyanines have been found to have applications as phototoxic drugs for photodynamic therapy [11–14]. The mode of operation in PDT is based on visible light excitation of a tumor-localized photosensitizer. After excitation, energy is transferred from the photosensitizer (in its triplet excited state) to ground state oxygen (³O₂), forming singlet state oxygen (¹O₂). High triplet state quantum yields and long triplet life times are required for efficient photosensitization, and these criteria may be fulfilled by the incorporation of diamagnetic metals such as zinc, silicon,

aluminum into the Pc macrocycle [15]. However, their insolubility in common organic solvents causes difficulties for many applications, rendering the syntheses of soluble derivatives an important task. Phthalocyanine derivatives of increased solubility have been obtained using substituents such as crown ether, alkyl, alkoxy, alkylthio chains and bulky groups [16–27]. Peripheral substitution with bulky groups or long alkyl, alkoxy or alkylthio chains leads to phthalocyanine products which are soluble in apolar solvents. Sulfo or quaternary ammonium groups enhance solubility in aqueous media over a wide pH range of aqueous solutions [28–33].

Non-transition metallophthalocyanines are effective for photocatalysis since they produce singlet oxygen in high quantum yields. Water-soluble metallophthalocyanines are required for photodegradation to occur in aqueous media, and they may be formed by substitution of the phthalocyanine ring with negatively or positively charged substituents [34].

The size and the nature of the substituents are not the only criteria for the solubility of the substituted phthalocyanines; the change in symmetry caused by the substituents is also important. Generally, tetra substituted phthalocyanines are more soluble than symmetrically octasubstituted ones due to the formation of four positional isomers in the case of tetra substituted analogues [35]. Metallophthalocyanines are particularly interesting since anionic or cationic groups such as sulfonic, carboxylic, phosphonic or quaternized amino groups render them water soluble [36].

* Corresponding author at: Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey. Tel.: +90 462 377 76 39; fax: +90 462 325 31 96.

E-mail address: zekeriya.61@yahoo.com (Z. Bıyıklıoğlu).

In this paper, we report on the synthesis, characterization and spectroscopic properties of metal-free 4 and metallophthalocyanine complexes 5, 6 and 7 tetra substituted at the peripheral position with a of 1,3-bis[3-(diethylamino)phenoxy]propan-2-ol group. Also, we have synthesized octacationic water-soluble phthalocyanines 4a, 5a, 6a and 7a for the first time. We report on comprehensive investigation of solvent effects on the aggregation behaviours of phthalocyanine derivatives in different solvents.

2. Experimental

2.1. Materials

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. 3-Dimethylaminophenol and 1,3-dibromo-2-propanol were purchased from Aldrich. 4-Nitrophthalonitrile 2 [37] was synthesized and purified according to well known literature. All solvents were dried and purified as described by Perrin and Armarego [38].

2.2. Equipment

The IR spectra were recorded on a Perkin Elmer 1600 FT-IR Spectrophotometer, using KBr pellets. ^1H NMR and ^{13}C NMR were recorded on a Varian Mercury 200 MHz spectrometer in CDCl_3 , and chemical shifts were reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quattro LC/ULTIMA LC-MS/MS spectrometer. The elemental analyses were performed on a Costech ECS 4010 instrument. Optical spectra in the UV-vis region were recorded with a Perkin Elmer Lambda 25 spectrophotometer.

2.3. Synthesis

2.3.1. Synthesis of 1,3-bis[3-(diethylamino)phenoxy]propan-2-ol (1)

3-Dimethylaminophenol (5 g, 30.3 mmol) was added to ethanol (35 ml) and nitrogen gas was bubbled through this mixture for 10 min. NaOH (1.5 g, 37.5 mmol) was then added and dissolved by stirring at 50°C for 1 h. 1,3-Dibromo-2-propanol (3.27 g, 15.1 mmol) in 5 ml ethanol was added dropwise to this solution with stirring for 30 min. The reaction mixture was refluxed under nitrogen for 20 h. After the mixture was cooled, the solvent was removed under vacuum, and resulting crude product was dissolved in chloroform (85 ml). The mixture was washed with 10% NaOH and with water. The organic phase was dried over MgSO_4 , filtered and rotary evaporated. The obtained oily crude product was crystallized from ethanol. Yield: 4.05 g (70%). IR (KBr pellet), $\nu_{\text{max}}/\text{cm}^{-1}$: 3410 (O–H), 3090 (Ar–H), 2970–2872 (Aliph. C–H), 1613, 1573, 1501, 1469, 1374, 1356, 1283, 1215, 1178, 1143, 1057, 987, 823, 753, 688. ^1H NMR. (CDCl_3), (δ :ppm): 7.24 (t, 2H, Ar–H), 6.42 (m, 6H, Ar–H), 4.50 (s, 1H, O–H), 4.26 (s, 4H, $\text{CH}_2\text{--O}$), 3.68 (m, 1H, --CH--), 3.41 (m, 8H, $\text{CH}_2\text{--N}$), 1.27 (t, 12H, --CH_3). ^{13}C NMR. (CDCl_3), (δ :ppm): 160.36, 149.54, 130.36, 105.87, 101.26, 99.33, 72.01, 69.18, 44.76, 13.02. MS (ES^+), (m/z): 387 [$\text{M}+\text{H}$] $^+$. $\text{C}_{23}\text{H}_{34}\text{N}_2\text{O}_3$: calcd. C 71.47, H 8.87, N 7.25%; found: C 71.62, H 9.08, N 7.04.

2.3.2. Synthesis of 4-(2-[3-(diethylamino)phenoxy]-1-[[3-(diethylamino)phenoxy]methyl]ethoxy]phthalonitrile (3)

4-Nitrophthalonitrile (2) (1.2 g, 6.94 mmol) was dissolved in 21 ml dry DMF under N_2 atmosphere, and of 1,3-bis[3-(diethylamino)phenoxy]propan-2-ol (1) (2.67 g, 6.94 mmol) was added to mixture. After stirring for 30 min at 60°C , finely ground anhydrous K_2CO_3 (3.83 g, 27.76 mmol) was added portion wise

within 2 h. The reaction mixture was stirred under N_2 at 60°C for 4 days. At the end of this time, the reaction mixture was poured into ice-water (170 g) and stirred at room temperature for 2 h to yield a crude product. Aqueous phase was extracted with chloroform (3×40 ml). The combined extracts were dried over anhydrous sodium sulfate. Finally, pure product (2) was obtained by column chromatography which is placed aluminium oxide using only CHCl_3 as solvent system. Yield: 3 g (84%). IR (KBr pellet), $\nu_{\text{max}}/\text{cm}^{-1}$: 3079 (Ar–H), 2971–2872 (Aliph. C–H), 2231 ($\text{C}\equiv\text{N}$), 1614, 1574, 1505, 1455, 1374, 1357, 1284, 1251, 1214, 1178, 1143, 1096, 1076, 1024, 987, 826, 750, 687. ^1H NMR. (CDCl_3), (δ :ppm): 7.68 (d, 1H, Ar–H), 7.52 (s, 1H, Ar–H), 7.39 (d, 1H, Ar–H), 7.21 (t, 2H, Ar–H), 6.40 (m, 6H, Ar–H), 4.25 (s, 4H, $\text{CH}_2\text{--O}$), 3.64 (m, 1H, --CH--), 3.43 (m, 8H, $\text{CH}_2\text{--N}$), 1.26 (t, 12H, --CH_3). ^{13}C NMR. (CDCl_3), (δ :ppm): 162.89, 160.15, 149.48, 135.38, 130.34, 121.50, 121.09, 117.44, 115.98, 115.52, 107.82, 106.06, 105.65, 99.02, 76.79, 69.43, 44.62, 12.86. MS (ES^+), (m/z): 513 [$\text{M}+\text{H}$] $^+$. $\text{C}_{31}\text{H}_{36}\text{N}_4\text{O}_3$: calcd. C 72.63, H 7.08, N 10.93%; found: C 72.86, H 7.32, N 10.48.

2.3.3. Synthesis of metal-free phthalocyanine (4)

A mixture of 4-(2-[3-(diethylamino)phenoxy]-1-[[3-(diethylamino)phenoxy]methyl]ethoxy]phthalonitrile 3 (0.25 g, 0.487 mmol) and catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 2.5 ml of dry n-pentanol was heated and stirred at 160°C in a sealed glass tube for 12 h under N_2 . After cooling to room temperature the green crude product was precipitated with ethanol, filtered and washed first with ethanol then diethyl ether and then dried in vacuo. Finally, pure metal-free phthalocyanine was obtained by column chromatography which is placed aluminium oxide using $\text{CHCl}_3:\text{CH}_3\text{OH}$ (99:1) as solvent system. Yield: 94 mg (37%). IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3291 (N–H), 3071 (Ar–H), 2967–2868 (Aliph. C–H), 1611, 1573, 1499, 1467, 1355, 1275, 1213, 1141, 1095, 1018, 824, 746. ^1H NMR. (CDCl_3), (δ :ppm): 7.70 (s, 4H, Ar–H), 7.53 (m, 4H, Ar–H), 7.36 (m, 4H, Ar–H), 7.23 (m, 8H, Ar–H), 6.51 (m, 24H, Ar–H), 4.69 (m, 16H, $\text{CH}_2\text{--O}$), 3.72 (m, 4H, --CH--), 3.26 (m, 32H, $\text{CH}_2\text{--N}$), 1.26 (m, 48H, --CH_3), --3.60 (s, br, 2H, NH). UV-vis (chloroform): λ_{max} , nm (log ϵ): 705 (4.85), 669 (4.81), 641 (4.54), 609 (4.36), 340 (4.75), 259 (5.00). MS (ES^+), (m/z): 2053 [$\text{M}+\text{H}$] $^+$. $\text{C}_{124}\text{H}_{146}\text{N}_{16}\text{O}_{12}$: calcd. C 72.56, H 7.17, N 10.92%; found: C 72.90, H 7.01, N 11.18.

2.3.4. General procedures of metallophthalocyanine derivatives (5–7)

A mixture of 4-(2-[3-(diethylamino)phenoxy]-1-[[3-(diethylamino)phenoxy]methyl]ethoxy]phthalonitrile 3 (0.25 g, 0.48 mmol), anhydrous metal salts [NiCl_2 (32 mg), CoCl_2 (30 mg), CuCl_2 (31 mg)] and catalytic amount of DBU in 2.5 ml of dry n-pentanol was heated and stirred at 160°C in a sealed glass tube for 12 h under N_2 . After cooling to room temperature, the reaction mixture was precipitated by the addition of ethanol and green precipitate was filtered off. The obtained green product was filtered off, washed with ethanol and diethyl ether and then dried in vacuo. Purification of the solid products were accomplished by column chromatography which is placed aluminium oxide using $\text{CHCl}_3:\text{CH}_3\text{OH}$ (99:1) as solvent system.

2.3.5. Synthesis of nickel(II) phthalocyanine (5)

Yield: 149 mg (58%). IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3082 (Ar–H), 2926–2851 (Aliph. C–H), 1610, 1569, 1499, 1468, 1410, 1374, 1354, 1274, 1213, 1140, 1094, 1061, 982, 823, 751. ^1H NMR. (CDCl_3), (δ :ppm): 7.73 (s, 4H, Ar–H), 7.54 (m, 4H, Ar–H), 7.39 (m, 4H, Ar–H), 7.25 (m, 8H, Ar–H), 6.56 (m, 24H, Ar–H), 4.70 (m, 16H, $\text{CH}_2\text{--O}$), 3.73 (m, 4H, --CH--), 3.28 (m, 32H, $\text{CH}_2\text{--N}$), 1.27 (m, 48H, --CH_3). UV-vis (chloroform): λ_{max} , nm (log ϵ): 675 (4.85), 609 (4.34), 298 (4.87),

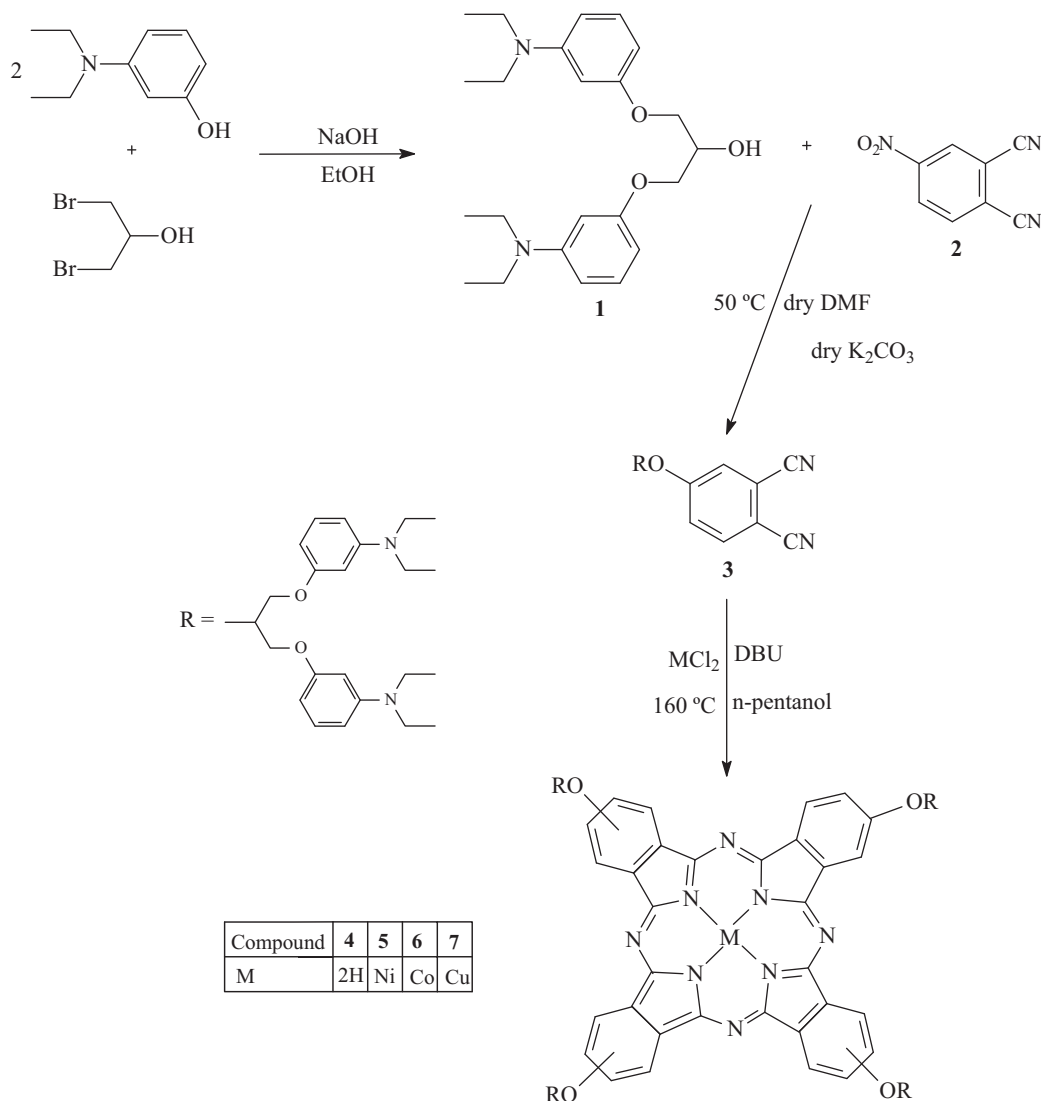


Fig. 1. The synthesis of the metal-free and metallophthalocyanines 4–7.

261 (5.05). MS (ES^+), (m/z): 2178 $[\text{M}+3\text{Na}]^+$. $\text{C}_{124}\text{H}_{144}\text{N}_{16}\text{O}_{12}\text{Ni}$: calcd. C 70.61, H 6.88, N 10.62%; found: C 70.95, H 7.12, N 10.18.

2.3.6. Synthesis of cobalt(II) phthalocyanine (6)

Yield: 127 mg (61%). IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3076 (Ar–H), 2966–2868 (Aliph. C–H), 1610, 1574, 1499, 1473, 1369, 1355, 1275, 1214, 1140, 1094, 1023, 965, 823, 752. UV–vis (chloroform): λ_{max} , nm (log ϵ): 677 (4.66), 611 (4.17), 259 (5.03). MS (ES^+), (m/z): 2132 $[\text{M}+\text{Na}]^+$. $\text{C}_{124}\text{H}_{144}\text{N}_{16}\text{O}_{12}\text{Co}$: calcd. C 70.60, H 6.88, N 10.62%; found: C 71.16, H 7.21, N 10.23.

2.3.7. Synthesis of copper(II) phthalocyanine (7)

Yield: 80 mg (39%). IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3087 (Ar–H), 2967–2868 (Aliph. C–H), 1609, 1575, 1499, 1472, 1397, 1374, 1355, 1275, 1214, 1140, 1094, 1023, 968, 824, 748, 687. UV–vis (chloroform): λ_{max} , nm (log ϵ): 683 (4.93), 615 (4.41), 338 (4.72). MS (ES^+), (m/z): 2137 $[\text{M}+\text{Na}]^+$. $\text{C}_{124}\text{H}_{144}\text{N}_{16}\text{O}_{12}\text{Cu}$: calcd. C 70.45, H 6.87, N 10.60%; found: C 70.77, H 7.11, N 10.32.

2.3.8. General procedures for quaternized phthalocyanine derivatives (4a, 5a, 6a, 7a)

A mixture of metal-free phthalocyanine 4 (50 mg, 0.024 mmol), nickel(II) phthalocyanine 5 (50 mg, 0.023 mmol), cobalt(II)

phthalocyanine 6 (50 mg, 0.023 mmol), copper(II) phthalocyanine 7 (50 mg, 0.023 mmol), (11 g, 0.08 mol) of methyl iodide in 5 mL chloroform was stirred at room temperature for 2 days. The green precipitate was filtered off, washed with chloroform, acetone, diethyl ether. Finally, quaternized phthalocyanine derivatives were dried in vacuo.

2.3.9. Synthesis of quaternized metal-free phthalocyanine (4a)

Yield: 56 mg (73%). IR (KBr pellet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3010 (Ar–H), 2923–2862 (Aliph. C–H), 1607, 1476, 1454, 1388, 1234, 1171, 1095, 1010, 869, 746, 690. UV–vis (DMF): λ_{max} , nm (log ϵ): 704 (4.71), 672 (4.71), 642 (4.45), 613 (4.30), 338 (4.69). MS (ES^+), (m/z): 3142 $[\text{M}-3\text{CH}_3-\text{H}]^+$. $\text{C}_{132}\text{H}_{170}\text{N}_{16}\text{O}_{12}$: calcd. C 72.96, H 7.89, N 10.31%; found: C 73.40, H 8.21, N 10.08.

2.3.10. Synthesis of quaternized nickel(II) phthalocyanine (5a)

Yield: 59 mg (77%). IR (KBr pellet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3014 (Ar–H), 2924–2856 (Aliph. C–H), 1602, 1455, 1390, 1238, 1092, 1018, 870, 752, 687. UV–vis (DMF): λ_{max} , nm (log ϵ): 675 (4.78), 609 (4.27), 329 (4.52). MS (ES^+), (m/z): 2932 $[\text{M}-2\text{I}-4\text{CH}_3+2\text{H}]^+$. $\text{C}_{132}\text{H}_{168}\text{N}_{16}\text{O}_{12}\text{Ni}$: calcd. C 71.11, H 7.60, N 10.05%; found: C 71.36, H 7.94, N 9.78.

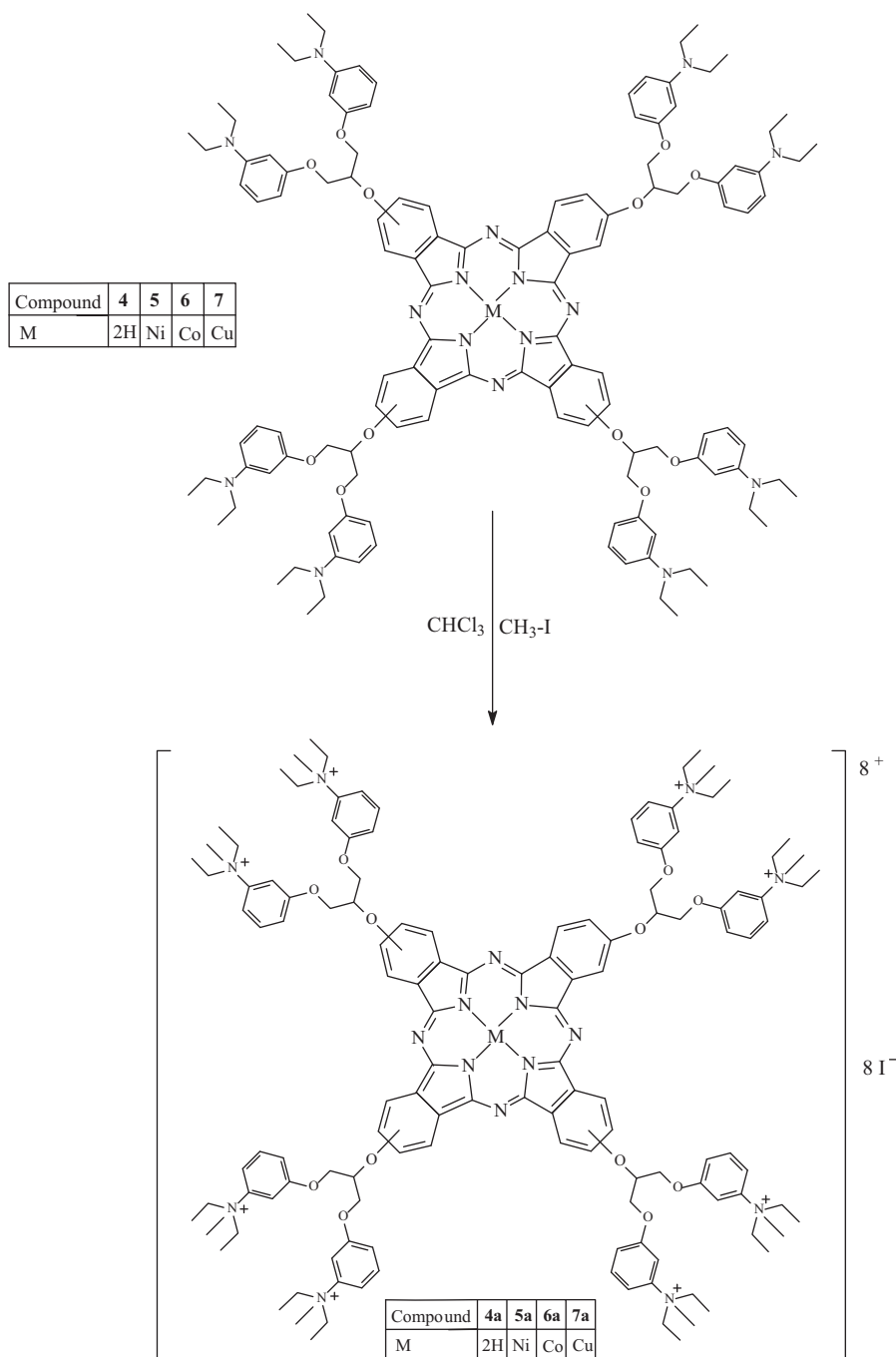


Fig. 2. The synthesis of water soluble octacationic metal-free and metallophthalocyanines.

2.3.11. Synthesis of quaternized cobalt(II) phthalocyanine (6a)

Yield: 48 mg (62%). IR (KBr pellet) $\nu_{\max}/\text{cm}^{-1}$: 3020 (Ar–H), 2974–2852 (Aliph. C–H), 1607, 1522, 1453, 1407, 1329, 1233, 1094, 1059, 871, 780, 752, 690. UV–vis (DMF): λ_{\max} , nm (log ϵ): 668 (4.64), 605 (4.20), 327 (4.61). MS (ES⁺), (m/z): 3230 [M–CH₃]⁺. C₁₃₂H₁₆₈N₁₆O₁₂Co: calcd. C 71.10, H 7.59, N 10.05%; found: C 71.35, H 7.81, N 9.82.

2.3.12. Synthesis of quaternized copper(II) phthalocyanine (7a)

Yield: 58 mg (75%). IR (KBr pellet) $\nu_{\max}/\text{cm}^{-1}$: 3012 (Ar–H), 2978–2843 (Aliph. C–H), 1606, 1455, 1400, 1337, 1231, 1118, 1093, 1051, 961, 871, 747, 686. UV–vis (DMF): λ_{\max} , nm (log ϵ): 680 (5.04), 612 (4.43), 345 (4.74). MS (ES⁺), (m/z): 3213 [M–3CH₃–H]⁺.

C₁₃₂H₁₆₈N₁₆O₁₂Cu: calcd. C 70.95, H 7.58, N 10.03%; found: C 71.24, H 7.27, N 9.78.

3. Results and discussion

3.1. Syntheses and characterization

The synthetic procedures, as outlined in Figs. 1 and 2. The first step in the synthetic procedure was to obtain 1,3-bis[3-(diethylamino)phenoxy]propan-2-ol 1. 1,3-Bis[3-(diethylamino)phenoxy]propan-2-ol 1 was synthesized by treating 3-dimethylaminophenol with 1,3-bromo-2-propanol in ethanol at reflux temperature using NaOH

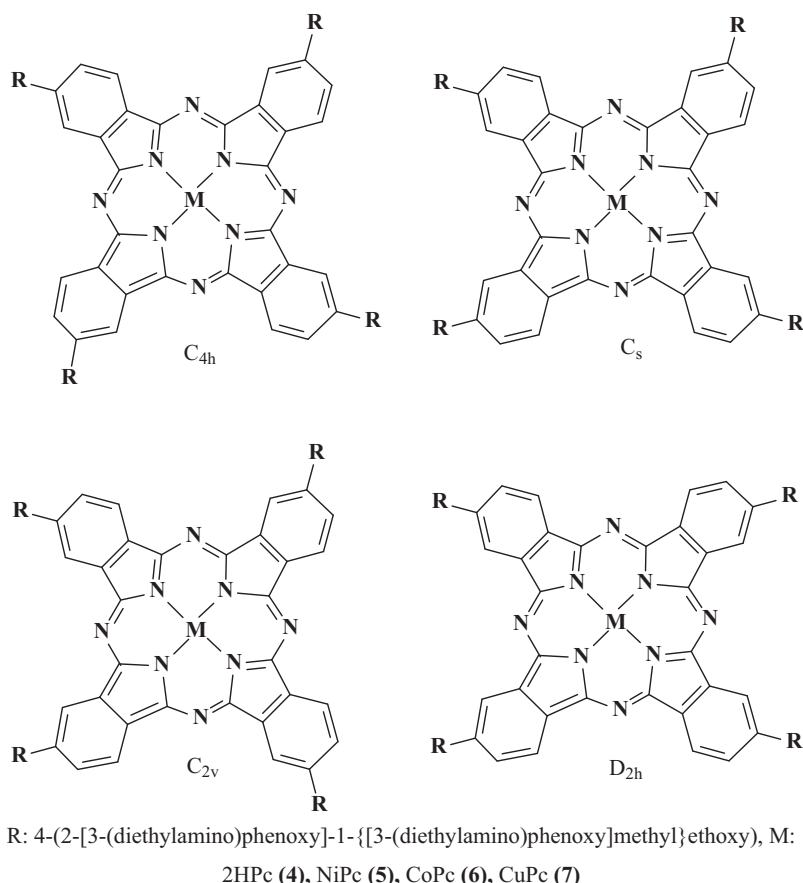


Fig. 3. Isomers of phthalocyanines 4–7.

as the base. Then, 4-(2-[3-(diethylamino)phenoxy]-1-[[3-(diethylamino)phenoxy]methyl]ethoxy)phthalonitrile **3** was synthesized by heating 1,3-bis[3-(diethylamino)phenoxy]propan-2-ol **1** and 4-nitrophthalonitrile **2** in the presence of K_2CO_3 as the base in dry DMF at 50 °C for 96 h. The electron-withdrawing

capability of dinitrile functionalities makes 4-nitrophthalonitrile susceptible to nucleophilic attack. The base catalyzed nucleophilic substitution of the nitro group was performed in dry DMF at 50 °C under inert nitrogen atmosphere. The self-condensation of the dicyano compound **3** in a high-boiling solvent in the

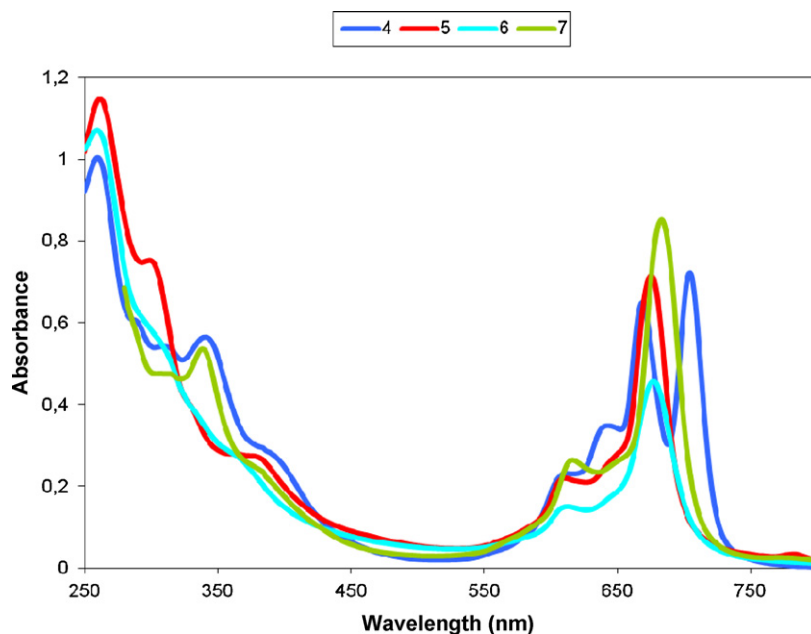


Fig. 4. UV–vis spectrum of 4, 5, 6 and 7 in $CHCl_3$.

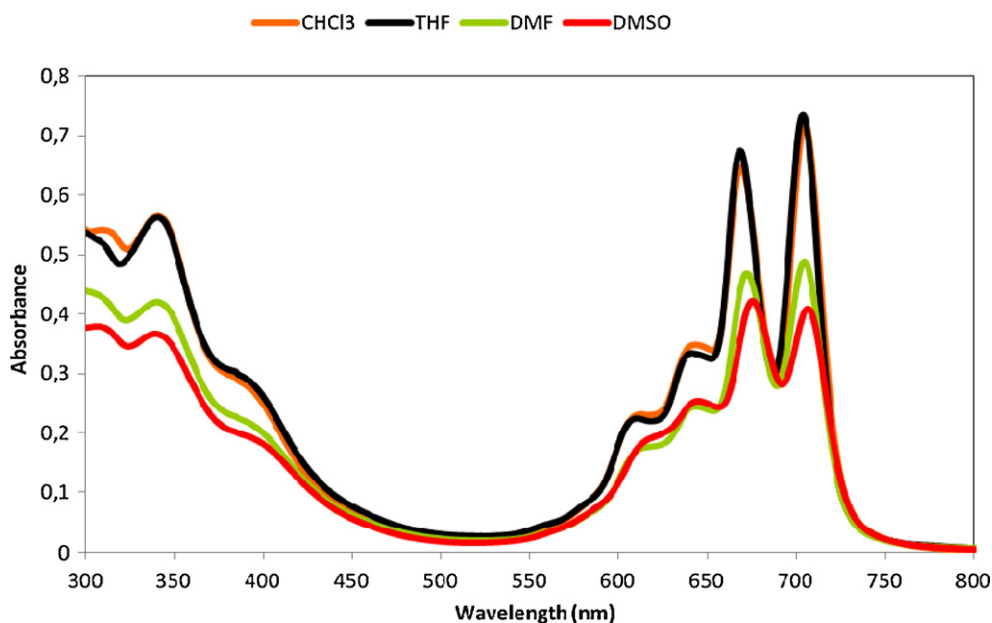


Fig. 5. UV-vis spectrum of metal-free phthalocyanine 4 in different solvents (concentration = $10 \times 10^{-6} \text{ mol dm}^{-3}$).

presence of a few drops 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) as a strong base at reflux temperature under a nitrogen atmosphere afforded the metal-free phthalocyanine 4. Conversion of 3 into metallophthalocyanine derivatives 5, 6 and 7 were accomplished through the usual cyclotetramerization reactions in the presence of metal salts (NiCl_2 , CoCl_2 , CuCl_2) and n-pentanol as solvent. The dark green products are extremely soluble in polar and apolar solvents such as CHCl_3 , THF, DMF and DMSO. However, the complex 5 is not soluble in DMSO, although others are soluble. The 4-(2-[3-(diethylamino)phenoxy]-1-[[3-(diethylamino)phenoxy]methyl]ethoxy) substituents on the complex are suitable for conversion into quaternary ammonium groups and this can increase the products' solubility in water.

So, quaternization of the metal-free and metallophthalocyanine complexes were achieved by reaction with excess methyl iodide as quaternization agent in CHCl_3 at room temperature. After reaction with methyl iodide, quaternized complexes 4a, 5a, 6a and 7a are very soluble in water and DMF, but insoluble in chloroform. All new compounds were characterized by the ways of UV-vis, IR, ^1H NMR, ^{13}C NMR, MS spectral data and elemental analysis, all of which were compatible with the proposed structures. The four probable phthalocyanine isomers can be obtained with molecular symmetries (D_{2h} , C_s , C_{2v} , C_{4v}). Up to now, the successful separation of these four isomers with common column chromatography or by recrystallization has not been reported [39]. In this study, synthesized tetra-substituted phthalocyanine compounds are

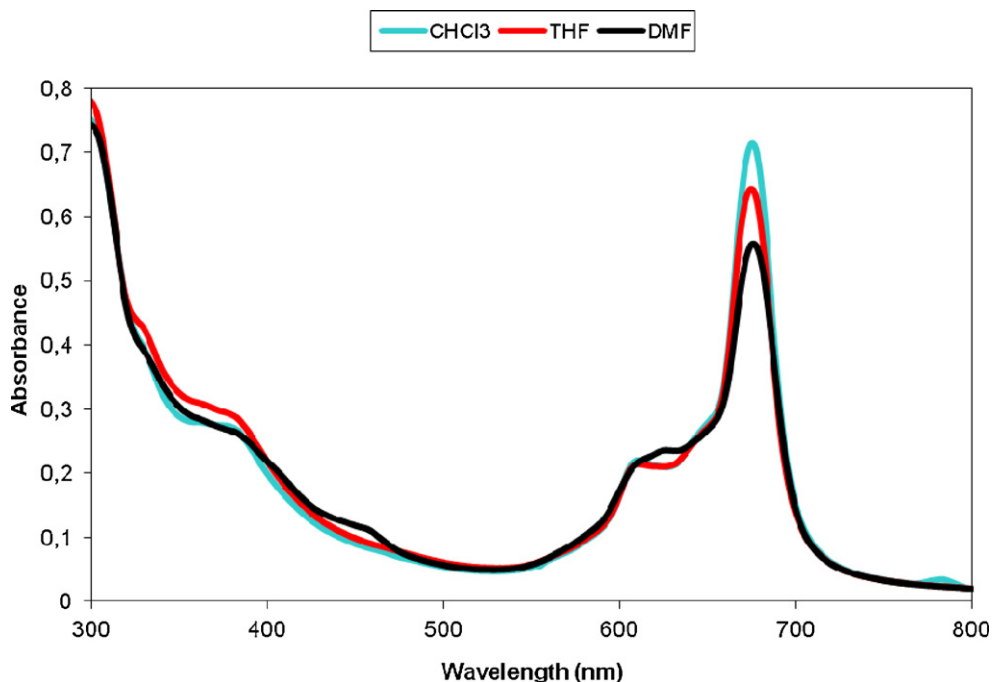


Fig. 6. UV-vis spectrum of nickel phthalocyanine 5 in different solvents (concentration = $10 \times 10^{-6} \text{ mol dm}^{-3}$).

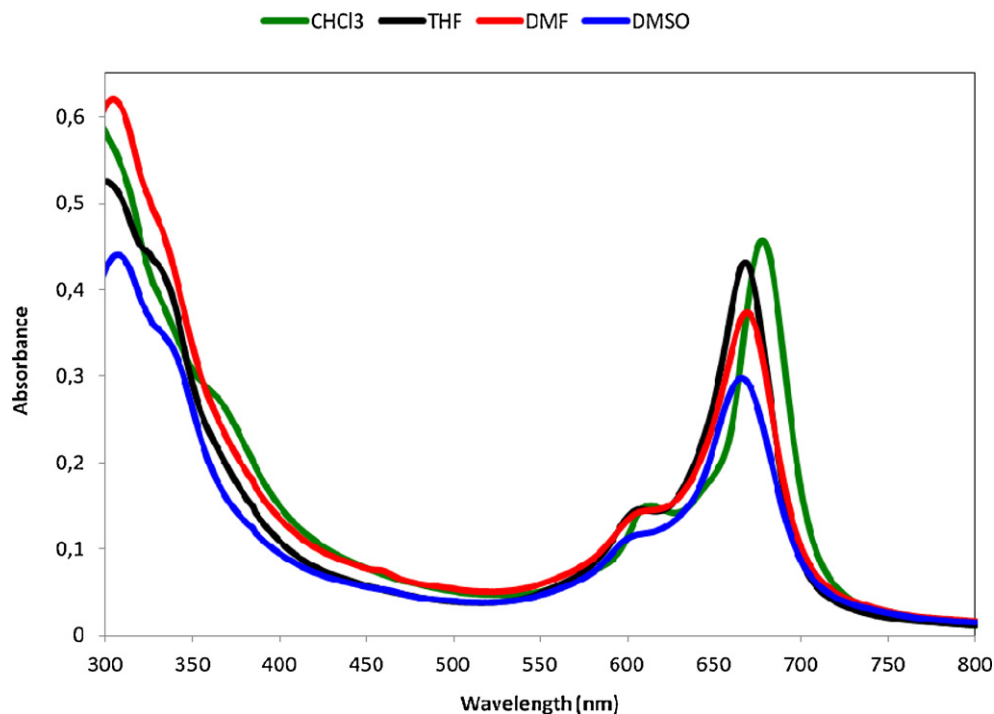


Fig. 7. UV-vis spectrum of cobalt phthalocyanine 6 in different solvents (concentration = 10×10^{-6} mol dm⁻³).

obtained as isomeric mixture as expected (Fig. 3). No attempt was made to separate the isomers of 4–7 and 4a–7a.

In the IR spectra, the formation of compound 1 was clearly confirmed by the disappearance of the aromatic OH vibration frequency at 3410 cm⁻¹, and appearance of the aliphatic OH vibration frequency at 2970–2872 cm⁻¹, respectively. In the ¹H NMR spectrum of 1, aromatic OH signal disappeared as expected and appeared new signal at δ = 4.50 ppm belonging to aliphatic OH

group of 1. Moreover, ¹H NMR spectrum of 1 showed aromatic protons between 7.24 and 6.42 ppm integrating for a total of 8 protons. In the NMR spectra of 1, the aliphatic protons for CH₂–O groups appeared at 4.26 ppm as singlet integrating for 4 protons, for –CH– group appeared at 3.68 ppm as multiplet integrating 1 proton, for CH₂–N groups appeared at 3.41 ppm as multiplet integrating for 8 protons, for –CH₃ groups appeared at 1.27 ppm as triplet integrating 12 protons, respectively. In the ¹³C NMR spectrum of 1

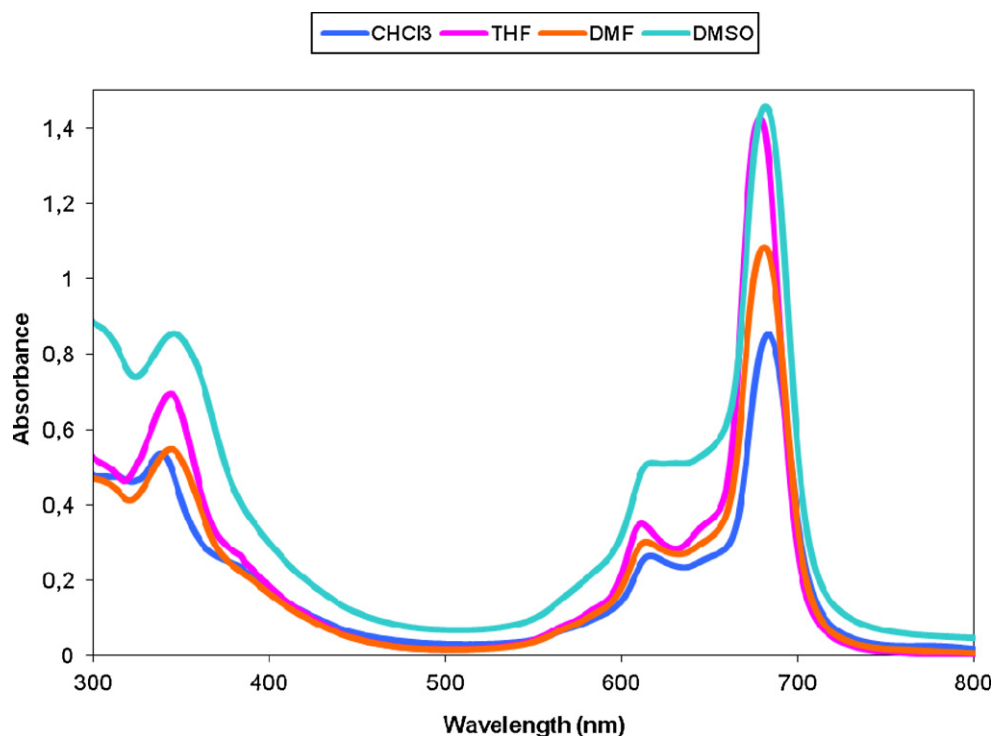


Fig. 8. UV-vis spectrum of copper phthalocyanine 7 in different solvents (concentration = 10×10^{-6} mol dm⁻³).

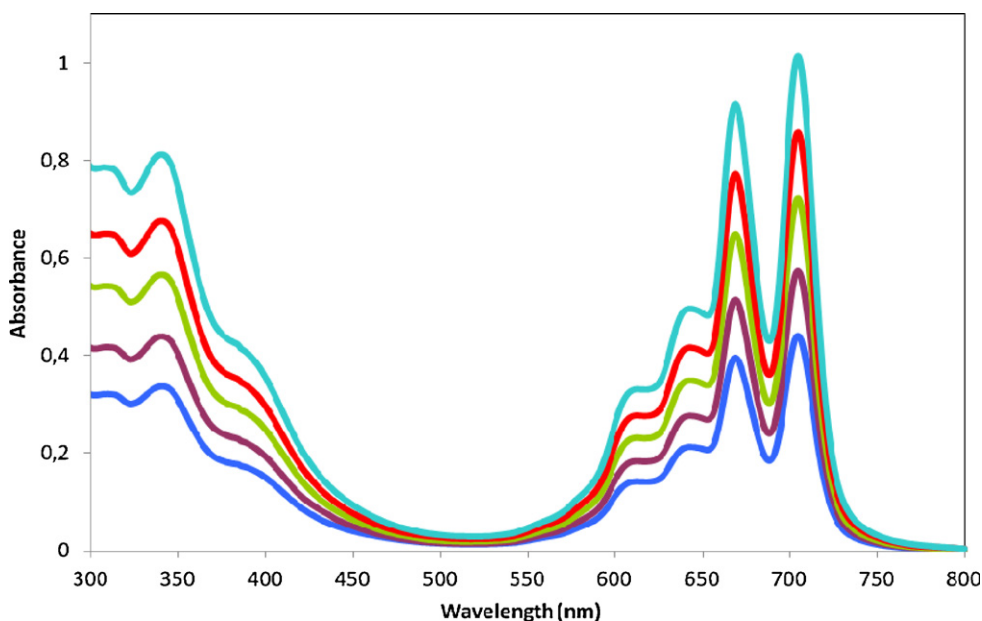


Fig. 9. Absorption spectra of metal-free phthalocyanine in CHCl_3 at different concentrations: 14×10^{-6} , 12×10^{-6} , 10×10^{-6} , 8×10^{-6} , 6×10^{-6} mol dm^{-3} .

shows signals for the new $-\text{CH}-\text{OH}$, $-\text{CH}_2-\text{O}$, $-\text{CH}_2-\text{N}$, $-\text{CH}_3$ carbon atoms at $\delta = 72.01, 69.18, 44.76, 13.02$ ppm, respectively, clearly suggesting compound formation has occurred. These NMR spectral data accordance with the expected structure. The ESI-mass spectrum of compound 1 shows a peak at $m/z = 387$ $[\text{M}+\text{H}]^+$.

In the IR spectra, the formation of compound 3 was clearly confirmed by the disappearance of the OH and NO_2 band at 3410 and $1538\text{--}1355$ cm^{-1} and appearance of the $\text{C}\equiv\text{N}$ band at 2231 cm^{-1} . In the ^1H NMR spectrum of 3, OH group of compound 1 disappeared as expected. In the ^1H NMR spectrum of 3, the doublet, singlet, doublet belonging to new aromatic protons appeared at $\delta = 7.68, 7.52, 7.39$ ppm, respectively, clearly suggesting compound formation has occurred. In the ^{13}C NMR spectrum of 3 have signals for the nitrile carbon atoms $\delta = 115.98$ and 115.52 ppm. The MS spectrum

of compound 3, which shows a peak at $m/z = 513$ $[\text{M}+\text{H}]^+$ support the proposed formula for this compound.

The sharp peak for the $(\text{C}\equiv\text{N})$ vibrations of phthalonitrile 3 at 2231 cm^{-1} disappeared after conversion into metal-free, nickel(II), cobalt(II), copper(II) phthalocyanines, indicative of metal-free and metallophthalocyanine formation. Phthalocyanines 4–7 also have very similar IR absorptions with the exception of the metal-free 4 showing an NH stretching band peak at 3291 cm^{-1} due to the inner core. The NH proton of metal-free phthalocyanine was also identified in the ^1H NMR spectrum with a broad peak at $\delta = -3.60$ ppm, presenting the typical shielding of inner core protons, which is common feature of the ^1H NMR spectra of metal-free phthalocyanines. ^1H NMR spectrum of 4 showed aromatic protons between $7.70\text{--}6.51$ ppm integrating for a total of 44 protons. In the NMR

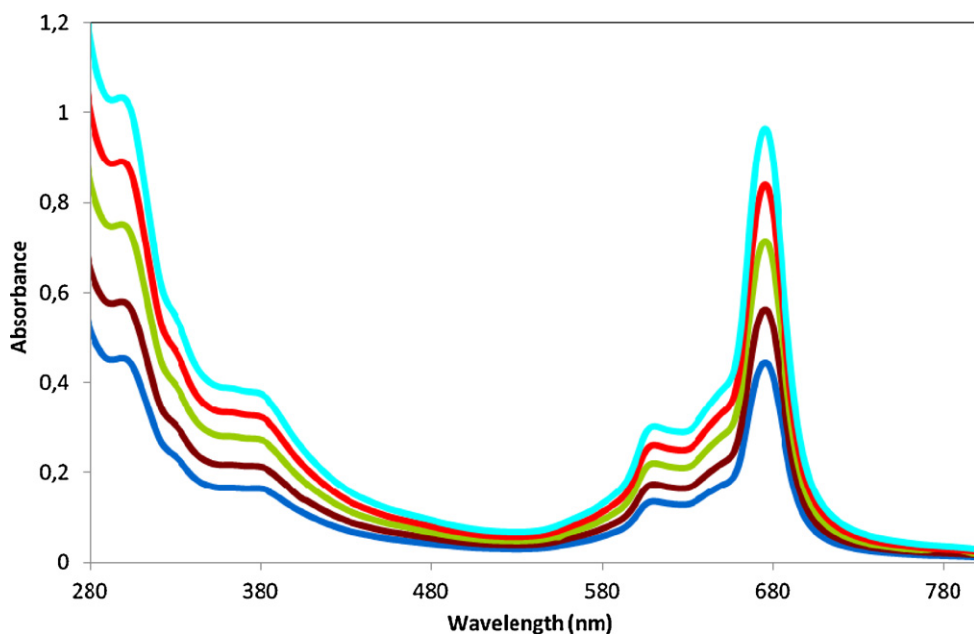


Fig. 10. Absorption spectra of nickel phthalocyanine 5 in CHCl_3 at different concentrations: 14×10^{-6} , 12×10^{-6} , 10×10^{-6} , 8×10^{-6} , 6×10^{-6} mol dm^{-3} .

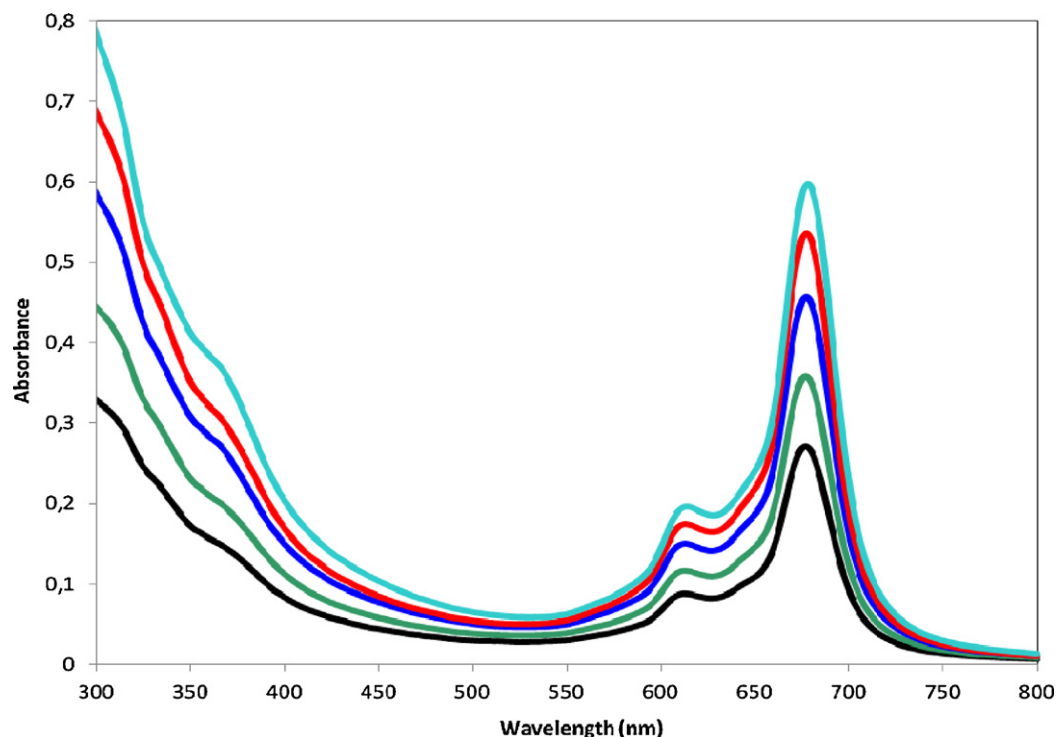


Fig. 11. Absorption spectra of cobalt phthalocyanine 6 in CHCl_3 at different concentrations: 14×10^{-6} , 12×10^{-6} , 10×10^{-6} , 8×10^{-6} , $6 \times 10^{-6} \text{ mol dm}^{-3}$.

spectra of 4, the aliphatic protons for $\text{CH}_2\text{—O}$ groups appeared at 4.69 ppm as multiplet integrating for 16 protons, for —CH— group appeared at 3.72 ppm as multiplet integrating 4 proton, for $\text{CH}_2\text{—N}$ groups appeared at 3.261 ppm as multiplet integrating for 32 protons, for —CH_3 groups appeared at 1.26 ppm as multiplet integrating 48 protons, respectively, clearly suggesting compound formation has occurred. In the mass spectra of compound 4, the presence of the characteristic molecular ion peak at $m/z = 2053$

$[\text{M}+\text{H}]^+$ confirmed the proposed structure. The ^1H NMR spectra of tetra-substituted phthalocyanine derivative 5 confirm our proposed structures and the chemical shifts are almost the same and somewhat broader than the corresponding signals in the dinitrile compound 3. The ^1H NMR spectra of metallophthalocyanines 6 and 7 could not be taken due to the paramagnetic cobalt(II) and copper(II) centers. In the mass spectrum of Ni, Co, Cu phthalocyanines, the presence of molecular ion peaks at $m/z = 2178 [\text{M}+3\text{Na}]^+$,

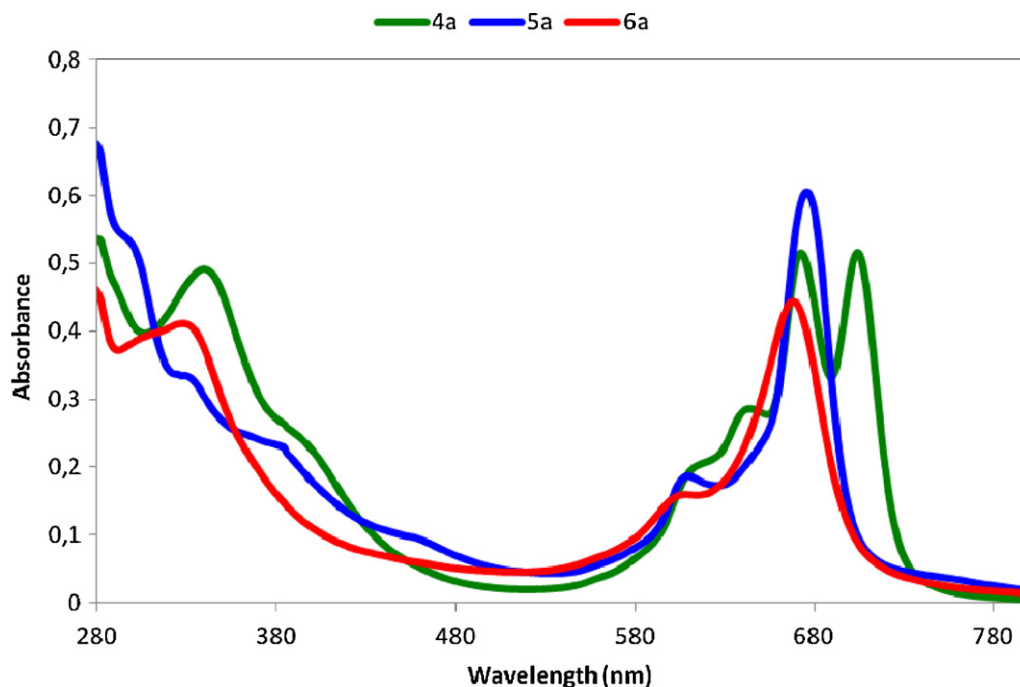


Fig. 12. UV-vis spectrum of quaternized phthalocyanines 4a, 5a and 6a in DMF (concentration = $10 \times 10^{-6} \text{ mol dm}^{-3}$).

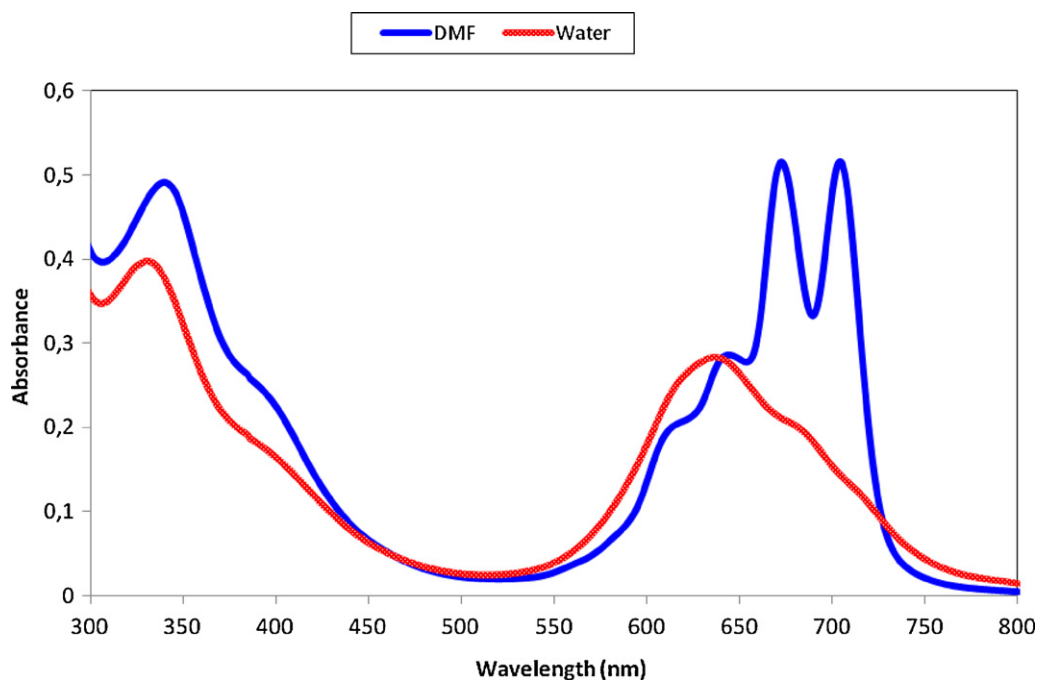


Fig. 13. UV-vis spectrum of quaternized metal-free phthalocyanine 4a in DMF and water (concentration = $10 \times 10^{-6} \text{ mol dm}^{-3}$).

2132 $[\text{M}+\text{Na}]^+$, 2137 $[\text{M}+\text{Na}]^+$ respectively, confirmed the proposed structures.

Quaternized metal-free 4a and metallophthalocyanines 5a, 6a and 7a are very soluble in water as expected. Water soluble metal-free and metallophthalocyanines (4a, 5a, 6a and 7a) were obtained from the reaction of corresponding phthalocyanines (4, 5, 6 and 7) with methyl iodide in chloroform. No major changes in the IR spectra were found after quaternization. The MS spectrum of compound 4a, 5a, 6a and 7a, which show a peak at $m/z = 3142$ $[\text{M}-3\text{CH}_3-\text{H}]^+$, 2932 $[\text{M}-2\text{I}-4\text{CH}_3+2\text{H}]^+$, 3230 $[\text{M}-\text{CH}_3]^+$, and 3213 $[\text{M}-3\text{CH}_3-\text{H}]^+$,

respectively, support the proposed formula for these compound. The elemental analyses for compound 1, 3, 4–7, 4a–7a gave satisfactory results that were close to calculated values.

The UV-vis spectra are especially fruitful to establish the structure of the phthalocyanines. The UV-vis spectra of the phthalocyanine complexes exhibit typical electronic spectra with two strong absorption regions, one of them is in the visible region at 600–700 nm (Q band) and the other one is in the UV region at about 300–500 nm (B band), both correlate to $\pi \rightarrow \pi^*$ transitions [40–42]. The ground state electronic spectra of the compounds showed

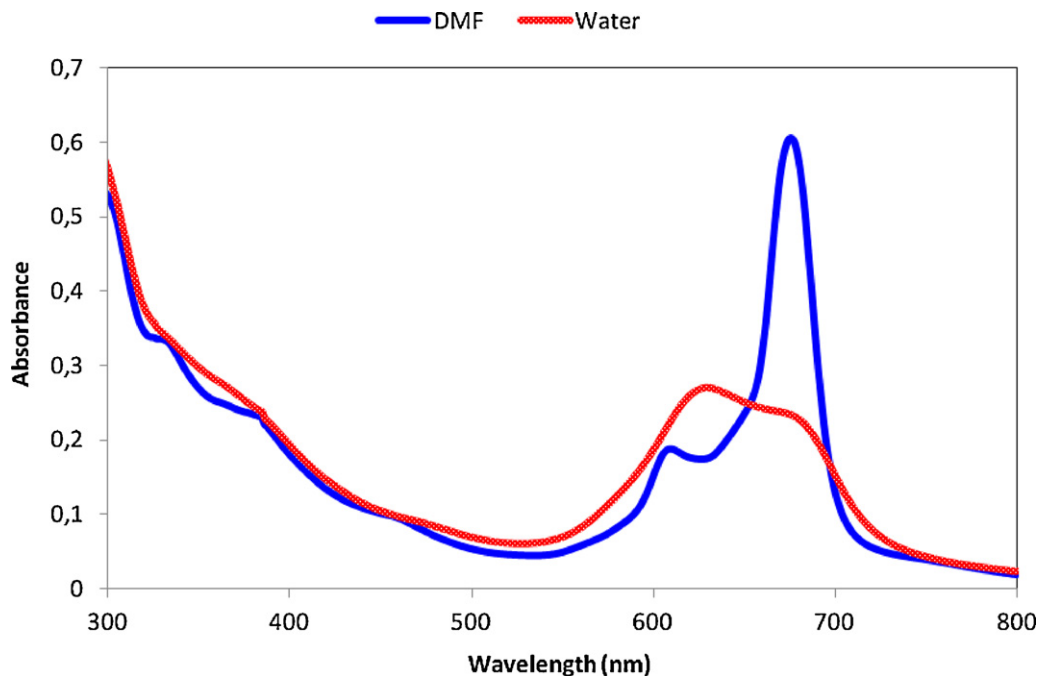


Fig. 14. UV-vis spectrum of quaternized nickel(II) phthalocyanine 5a in DMF and water (concentration = $10 \times 10^{-6} \text{ mol dm}^{-3}$).

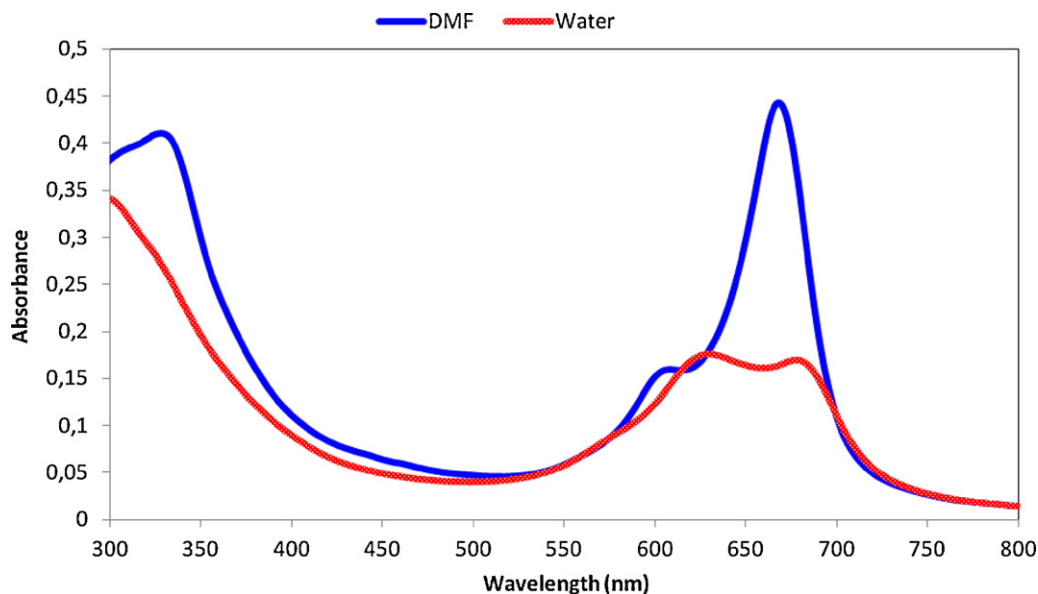


Fig. 15. UV-vis spectrum of quaternized cobalt(II) phthalocyanine 6a in DMF and water (concentration = $10 \times 10^{-6} \text{ mol dm}^{-3}$).

characteristic absorptions in the Q band region at 705/669 nm for compound 4, 675 nm for compound 5, 677 for compound 6, 683 nm for compound 7 in CHCl_3 . B band absorptions of the metal-free and metallophthalocyanines 4–7 were observed at (340, 259), (298, 261), 259, 338 nm, respectively (Fig. 4).

3.2. Aggregation behaviours

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 [43–45]. In this study, the aggregation behaviour of the metal-free 4 and metallophthalocyanine complexes 5, 6 and 7 are investigated in different solvents (chloroform, THF, DMF and DMSO) (Fig. 5

for metal-free Pc, Fig. 6 for complex 5, Fig. 7 for complex 6 and Fig. 8 for complex 7). While metal-free phthalocyanine 4 showed aggregation in DMF and DMSO, the complex 5 showed aggregation in DMF, the complex 6 showed aggregation in DMF and DMSO, the complex 7 showed aggregation in DMSO as judged by a blue shift of the Q band [46,47]. The complex 5 is not soluble in DMSO. Also, metal-free phthalocyanine 4, nickel phthalocyanine 5 and cobalt phthalocyanine 6 did not show aggregation in chloroform and THF, but complex 7 did not show aggregation in chloroform, THF and DMF.

The aggregation behaviour of the metal-free 4 and metallophthalocyanines 5, 6 and 7 were also investigated at different concentrations in chloroform. In chloroform, as the concentration was increased, the intensity of absorption of the Q band also increased and there were no new bands (normally blue shifted) due

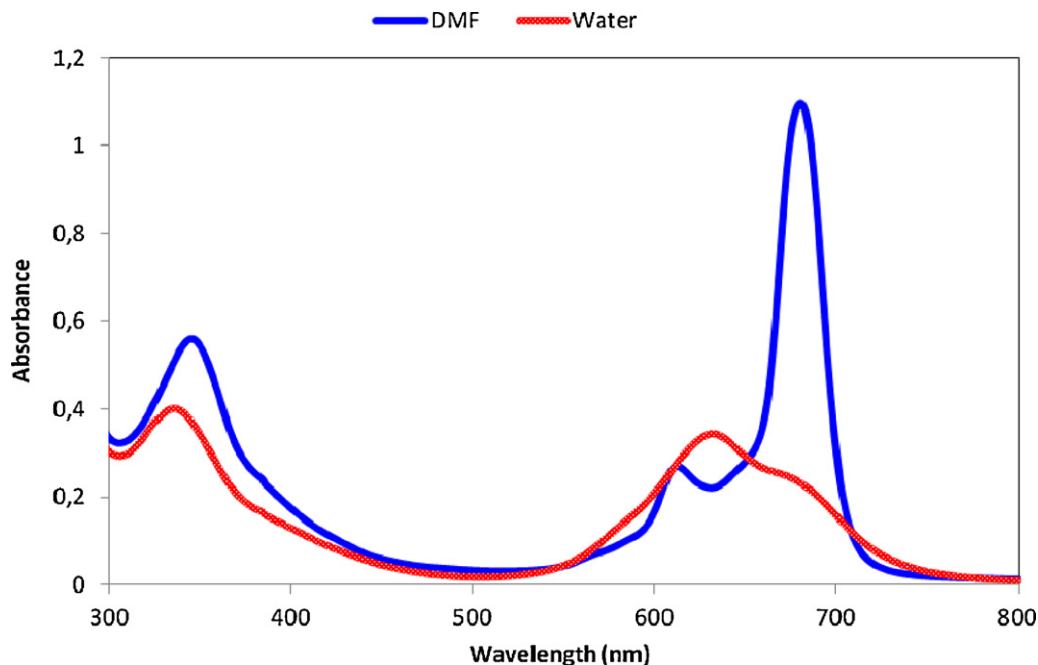


Fig. 16. UV-vis spectrum of quaternized copper(II) phthalocyanine 7a in DMF and water (concentration = $10 \times 10^{-6} \text{ mol dm}^{-3}$).

to the aggregated species for all phthalocyanines (Fig. 9 for metal-free Pc, Fig. 10 for complex 5, Fig. 11 for complex 6). Beer–Lambert law was obeyed for all of the compounds in the concentrations ranging from 14×10^{-6} to 6×10^{-6} mol dm $^{-3}$.

The ground state electronic spectra of the quaternized metal-free 4a and metallophthalocyanines 5a, 6a showed characteristic absorptions in the Q band region at 704/672 nm for 4a, 675 nm for 5a, 668 nm for 6a in DMF (Fig. 12). B band region was observed around 327–338 nm in DMF. The shoulder of quaternized metal-free 4a, nickel(II) 5a and cobalt(II) 6a phthalocyanines registered at 642/613, 609, 605 nm, respectively. However, the electronic spectra of the quaternized metal-free 4a, nickel(II) 5a, cobalt(II) 6a and copper(II)phthalocyanines 7a in water showed some differences from those in DMF as a result of solvent effect. Typical spectra of 4a, 5a, 6a and 7a in DMF and water are shown in Figs. 13–16, respectively. In the electronic spectra of the quaternized metal-free 4a, nickel(II) 5a, cobalt(II) 6a and copper(II)phthalocyanines 7a typical appearance of a new bands around 636, 627, 628 and 638 nm at the blue side of the main Q band absorption in water suggests clearly the presence of aggregated species.

4. Conclusion

In conclusion, novel 1,3-bis[3-(diethylamino)phenoxy]propan-2-ol 1, 4-(2-[3-(diethylamino)phenoxy]-1-[[3-(diethylamino)phenoxy]methyl]ethoxy]phthalonitrile 3, metal-free and metallophthalocyanines 4–7 and its quaternized derivatives 4a–7a have been synthesized and characterized for the first time in this study. This work has also presented a comprehensive investigation of solvent effects on the aggregation of these metal-free and metallophthalocyanines. The aggregation behaviours are studied for all phthalocyanines in chloroform, tetrahydrofuran, dimethylformamide and dimethylsulfoxide. While metal-free, nickel(II) and cobalt(II) phthalocyanines were found to be monomeric in chloroform and THF, copper(II) phthalocyanine was found to be monomeric in chloroform, THF and DMF. In addition, metal-free and cobalt(II) phthalocyanines showed aggregation in DMF and DMSO, nickel(II) phthalocyanine showed aggregation in only DMF and copper(II) phthalocyanine showed aggregation in only DMSO. We have also studied the aggregation behaviour of these new metal-free and metallophthalocyanines 4–7 in different concentration in chloroform. No aggregation was demonstrated in chloroform from concentration between 14×10^{-6} and 6×10^{-6} mol dm $^{-3}$. Quaternized derivatives 4a, 5a, 6a and 7a exhibited excellent solubility in water, but they showed aggregation in this solvent.

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