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Synthesis, characterisation and aggregation properties of novel metal-free and metallophthalocyanines containing four 21-membered oxatetrathiadiaza macrocycles

Halil Zeki Gök*, Berna Farsak

Department of Chemistry, Faculty of Arts and Sciences, Osmaniye Korkut Ata University, 80000 Osmaniye, Turkey

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ABSTRACT

The synthesis of novel metal-free phthalocyanine **4** and metallophthalocyanines **5**, **6**, **7** (MPcs, M = Ni, Zn, Co) containing four 21-membered oxatetrathiadiaza macrocycles at the peripheral positions was achieved by cyclotetramerisation of a novel 6,16-dioxo-5,6,7,9,10,12,13,15,16,17-decahydrotribenzo [h,k,n] [1,4,10,13,19,7,16]oxatetrathiadiazacyclohenicosine-24,25-dicarbonitrile. The aggregation behaviours of phthalocyanines **4**, **5**, **6** and **7** were investigated at different concentrations in dimethylformamide. No aggregation behaviour was observed in dimethylformamide at concentrations between 10×10^{-6} and 1×10^{-6} mol dm$^{-3.}$ The aggregation properties of all phthalocyanines were also investigated in different solvents. All new compounds were characterised by a combination of elemental analysis and ^{1}H NMR, ^{13}C NMR, IR, UV–Vis and MS spectral data.

1. Introduction

Phthalocyanines are an important class of compounds with many potential applications due to their high thermal and chemical stability [1]. Because of these properties, phthalocyanines have been extensively studied and are used in a wide variety of areas, for instance, in photodynamic therapy as photosensitisers [2]; as chemical sensors [3], green and blue pigments [4], corrosion inhibitors [5], and semiconductors; and in biomedicine, catalysis, electronics [6,7], and non-linear optics [8]. Because of their potential applications, tens of thousands of tons of phthalocyanines (Pc's) are produced per year worldwide [9].

The optical and electrochemical properties of phthalocyanines can be significantly altered by incorporating substituents at the peripheral and nonperipheral positions. The first introduction of crown ether into a phthalocyanine was reported in 1986 [10] and the ability of this molecule to bind alkali metal cations was investigated [11]. The design and synthesis of phthalocyanine-bearing macrocycles has found potential applications in biochemistry and materials science [12]. A goal of research on the chemistry of phthalocyanines is to achieve control over the structure of synthetic molecules and enhance their solubility in various solvents. Particularly, the attachment of a macrocycle containing nitrogen and sulphur donor atoms to phthalocyanines increases their selectivity towards alkaline-earth and soft transition metal cations. Complexation of phthalocyanines with metal ions has an influence on their photophysical properties [13,14]. To enhance the coordination properties of these macrocycles, different parameters have been modified such as the ring size, the nature of substituents, and the type of donor atoms present [15–19]. Macrocycles that contain sulphur and nitrogen atoms as donor atoms have high complexabilities with some transition metal ions [20]. A challenge in the synthesis of thiol-derivatised phthalocyanines is the time-consuming, tedious purification process and use of toxic chemicals. Therefore, phthalocyanines containing sulphur donors are the least reported class of phthalocyanines in literature [21].

We have previously described the synthesis of metal-free and metal-containing phthalocyanines that contain four 27-membered dioxadiazapentathia and diazaheptathia macrocycles [22,23]. The objective of this research is to describe a simple strategy for the synthesis of metal-free and metallophthalocyanines containing four 21-membered macrocycles with oxygen, nitrogen and sulphur donor atoms.

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* Corresponding author. Tel.: +90 328 827 1000x2539; fax: +90 328 825 0097.
E-mail addresses: zekigok@osmaniye.edu.tr, zek_i@yahoo.com (H.Z. Gök).

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2. Experimental

2.1. Materials and equipment

4,5-Bis(2′-aminophenylsulfanyl)-1,2-dicyanobenzene **1** was prepared according to the literature [24]. All reagents and solvents were reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [25]. Melting points were determined with an electrothermal apparatus and are reported uncorrected. FTIR spectra were measured on a Perkin Elmer Spectrum 65 spectrometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer using $CDCl_3$ and DMSO-d_6 (99.9%). Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS and a Bruker Daltonics MALDI-TOF spectrometer. Optical spectra were recorded in the UV–Vis region with a PG-T80 + spectrophotometer using 1 cm path length cuvettes at room temperature. Elemental analyses were obtained with a LECO Elemental Analyser (CHNS 0932) spectrophotometer. The homogeneity of the products was tested at each step using TLC.

2.2. Synthesis

2.2.1. *N,N′-(2,2′-(4,5-Dicyano-1,2-phenylene)bis(sulfanediyl)bis(2,1-phenylene))bis(2-chloroacet-amide) (**2**, Fig. 1)*

Chloroacetic anhydride (4.176 g, 36.97 mmol) in CH_2Cl_2 (65 ml) was added dropwise through a dropping funnel to a stirred solution of 4,5-bis(2′-aminophenylsulfanyl)-1,2-dicyanobenzene **1** (4.61 g, 12.32 mmol) in CH_2Cl_2 (260 ml) at 0–5 °C over a 1.5 h period. The reaction was monitored by thin layer chromatography using ethyl acetate–hexane (4:6) as the solvent system. The mixture was stirred overnight under a nitrogen atmosphere at room temperature. At the end of this period, saturated aqueous $NaHCO_3$ was added to neutralise the reaction mixture. The organic layer was separated and washed twice with a 100 ml portion of saturated aqueous $NaHCO_3$ and then twice with water. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to give the crude product. The crude product was crystallised from acetonitrile to give 5.65 g (87%). Mp 221–222 °C. Anal. calcd. for $C_{24}H_{16}Cl_2N_4O_2S_2$: C, 54.65; H, 3.06; N, 10.62%. Found: C, 53.89; H, 2.99; N, 10.55%. IR (KBr disc) ν_{max}/cm^{-1}: 3336 (NH), 3080 (CH_{Ar}), 2230 (C$\equiv$N), 1697 (C=O), 1584, 1565, 1525, 1437, 1348, 1304, 1219, 1161, 1105, 1035, 918, 757, 632, 528, 501. ^{1}H NMR ($CDCl_3$) δ: 9.27 (s, 2H, NH), 8.65 (d, J = 8.31 Hz, 2H, ArH), 7.70 (t, J = 8.31 Hz, 2H, ArH), 7.66 (d, J = 7.82 Hz, 2H, ArH), 7.38 (t, J = 7.82 Hz, 2H, ArH), 6.92 (s, 2H, ArH), 4.21 (s, 4H, O=CCH_2Cl). ^{13}C NMR ($CDCl_3$) δ: 163.80 (C=O), 141.75, 139.38, 137.21, 133.36, 129.48, 126.46, 121.61, 116.14 (ArC), 114.79 (C$\equiv$N), 113.16, 43.26 (O=CCH_2Cl). MS (LC-MS/MS) m/z: 527 $[M + H]^+$, 549 $[M + Na]^+$.

2.2.2. *6,16-Dioxo-5,6,7,9,10,12,13,15,16,17-decahydrotribenzo[h,k,n][1,4,10,13,19,7,16]oxatetrathiadiazacyclohenicosine-24,25-dicarbonitrile (**3**, Fig. 1)*

A two-necked round-bottom flask containing a solution of 2-mercaptoethylether (1.05 g, 7.59 mmol) and anhydrous sodium carbonate (3.22 g, 30.36 mmol) in dry dimethylformamide (400 ml) was placed under a nitrogen atmosphere in an ice bath and cooled to 0–5 °C. A solution of **2** (4 g, 7.59 mmol) in dry dimethylformamide (300 ml) was added to the above solution using a dropping funnel with stirring and under dry inert gas over 1.5 h at 0–5 °C. After addition was complete, the reaction mixture was stirred for another 16 h at 0–5 °C. The reaction was monitored by thin layer chromatography [hexane–ethyl acetate (6:4)]. When the reaction was complete, the mixture was filtered and the filtrate was evaporated to dryness under reduced pressure. The yellowish oil was dissolved in CH_2Cl_2. The organic layer was washed twice with 100 ml portions of a 5% Na_2CO_3 solution and then twice with water. The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to give a crude product that was purified by silica gel chromatography. The elution was carried out with hexane–ethyl acetate (6:4). The product was obtained as white solid. The yield was 2.7 g (60%). Mp 213–215 °C. Anal. calcd. for $C_{28}H_{24}N_4O_3S_4$: C, 56.73; H, 4.08; N, 9.45%. Found: C, 56.42; H, 4.13; N, 9.40. IR (KBr disc) ν_{max}/cm^{-1}: 3251 (NH), 3067 (CH_{Ar}), 2919, 2860 (CH_3), 2227 (C$\equiv$N), 1691 (C=O), 1577, 1455, 1435, 1346, 1295, 1103, 1033, 917, 763, 667, 529. ^{1}H NMR ($CDCl_3$) δ: 9.68 (s, 2H, NH), 8.73 (d, J = 8.31 Hz, 2H, ArH), 7.69 (t, J = 7.82 Hz, 2H, ArH), 7.61 (d, J = 7.58 Hz, 2H, ArH), 7.33 (t, J = 7.58 Hz, 2H, ArH), 6.87 (s, 2H, ArH), 3.80 (t, J = 5.13 Hz, 4H, OCH_2), 3,52 (s, 4H, O=CCH_2Cl), 2.80 (t, J = 5.13 Hz, 4H, SCH_2). ^{13}C NMR ($CDCl_3$) δ: 167.22 (C=O), 142.16, 140.60, 137.14, 133.39, 128.99, 126.06, 121.58 (ArC), 115.31 (C$\equiv$N), 114.89, 112.79 (ArC), 71.19 (OCH_2), 38.15 (O=CCH_2S), 33.10 (SCH_2). MS (LC-MS/MS) m/z: 593 $[M + H]^+$, 615 $[M + Na]^+$.

2.2.3. *Metal-free phthalocyanine (**4**, Fig. 1)*

A mixture of **3** (0.4 g, 0.674 mmol) and a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dry *n*-pentanol (1.5 ml) were placed under a nitrogen atmosphere in a standard Schlenk tube. The reaction mixture was heated and stirred under nitrogen at 145 °C for 24 h. After cooling to room temperature, the mixture was diluted with ethanol (10 ml) until the product precipitated. The precipitated crude product was filtered. The crude product was refluxed with ethanol (25 ml) in a Soxhlet extractor for 4 h. The product was then filtered and washed with ethanol, diethyl ether, CH_2Cl_2 and dried under vacuum. Finally, pure metal-free phthalocyanine was obtained by silica gel column chromatography using dichloromethane:methanol as the solvent system. This product was soluble in DMF, DMSO and THF. The yield was 0.085 g (21%). Mp >300 °C. Anal. calcd. for $C_{112}H_{98}N_{16}O_{12}S_{16}$: C, 56.68; H, 4.16; N, 9.44%. Found: C, 56.42; H, 4.21; N, 8.92. IR (KBr disc) ν_{max}/cm^{-1}: 3386 (NH), 3290(NH), 3051 (CH_{Ar}), 2918 (CH_3), 1658 (C=O), 1607, 1576, 1508, 1473, 1439, 1379, 1304, 1262, 1107, 1025, 877, 740, 677. ^{1}H NMR (DMSO-d_6) δ: 9.92 (s, 8H, NH), 9.07 (m, 8H, ArH), 7.39–6.85 (m, 32H, ArH), 3.54 (br, 16H, OCH_2), 3.45 (s, 16H, O=C–CH_2), 2.89–2.74 (m, 16H, SCH_2), −3.28 (br, s, 2H, NH). UV–Vis (DMF): λ_{max}, nm (log ε): 324 (5.23), 364 (5.21), 743 (5.06). MS (MALDI-TOF) m/z: 2371 $[M + H]^+$.

2.2.4. *Nickel(II) phthalocyanine (**5**, Fig. 2)*

A mixture of **3** (0.3 g, 0.506 mmol), anhydrous $NiCl_2$ (0.020 g, 0.153 mmol) and quinoline (2 ml) was heated and stirred at 190 °C for 7 h in a Schlenk tube under nitrogen. After cooling to room temperature, the product was precipitated by adding ethanol (10 ml) and filtered off. The crude product was refluxed with ethanol (25 ml) in a Soxhlet extractor for 4 h. The green product was then filtered and washed with ethyl acetate, acetone, and diethyl ether. Finally, pure nickel(II) phthalocyanine was obtained by silica gel column chromatography using dichloromethane:methanol as the solvent system. The product was dried under vacuum over P_2O_5. The yield was 0.100 g (33%). Mp >300 °C. Anal. calcd. for $C_{112}H_{96}N_{16}O_{12}S_{16}Ni$: C, 55.36; H, 3.98; N, 9.22%. Found: C, 54.78; H, 4.36; N, 9.31. IR (KBr disc) ν_{max}/cm^{-1}: 3275 (NH), 3058 (CH_{Ar}), 2914 (CH_3), 2856, 1686 (C=O), 1578, 1513, 1434, 1410, 1380, 1296, 1116, 961, 754. ^{1}H NMR (DMSO-d_6): δ 10.02 (s, 8H, NH), 8.59 (m, 8H, ArH), 8.02-6.99 (m, 32H, ArH), 3.58 (br, 16H, OCH_2), 3.48 (s, 16H, O=C–CH_2), 2.77 (m, 16H, SCH_2). UV–Vis (DMF): λ_{max}, nm (log ε): 322 (4.97), 416 (4.47), 634 (4.49), 707 (5.17). MS (MALDI-TOF) m/z: 2427 $[M + H]^+$.

2.2.5. *Zinc(II) phthalocyanine (**6**, Fig. 2)*

A mixture of **3** (0.3 g, 0.506 mmol), anhydrous $Zn(CH_3CO_2)_2$ (0.028 g, 0.153 mmol) and quinoline (2 ml) was heated and stirred at

190 °C for 7 h in a Schlenk tube under nitrogen. After cooling to room temperature, the product was precipitated by adding ethanol (10 ml) and filtered off. The crude product was refluxed with ethanol (25 ml) in a Soxhlet extractor for 4 h. The green product was then filtered and washed with ethyl acetate, acetone, and diethyl ether. Finally, pure zinc(II) phthalocyanine was obtained by silica gel column chromatography using dichloromethane:methanol as the solvent system. The product was then dried under vacuum over P_2O_5. The yield was 0.138 g (46%). Mp >300 °C. Anal. calcd. for $C_{112}H_{96}N_{16}O_{12}S_{16}Zn$: C, 55.21; H, 3.97; N, 9.20%. Found: C, 55.90; H, 4.40; N, 8.40. IR (KBr disc) ν_{max}/cm^{-1}: 3280 (NH), 3055 (CH_{Ar}), 2914 (CH_3), 2856, 1680 (C═O), 1578, 1512, 1434, 1400, 1370, 1297, 1109, 938, 755. ^{1}H NMR (DMSO-d_6): δ 10.07 (s, 8H, NH), 8.68 (m, 8H, ArH), 8.06–6.89 (m, 32H, ArH), 3.64 (br, 16H, OCH_2), 3.48 (s, 16H, O═C–CH_2), 2.82 (m, 16H, SCH_2). UV–Vis (DMF): λ_{max}, nm (log ε): 372 (5.15), 637 (4.80), 711 (5.44). MS (MALDI-TOF) *m/z*: 2433 [M + H]$^+$, 2455 [M + Na]$^+$.

2.2.6. Cobalt(II) phthalocyanine (**7**, Fig. 2)

A mixture of **3** (0.3 g, 0.506 mmol), anhydrous $Co(CH_3CO_2)_2$ (0.027 g, 0.153 mmol) and quinoline (2 ml) were placed in a Schlenk tube under nitrogen atmosphere and held at 190 °C for 7 h. After cooling to room temperature, the product was precipitated by adding ethanol (10 ml) and filtered off. The crude product was refluxed with ethanol (25 ml) in a Soxhlet extractor for 4 h. The green product was then filtered and washed with ethyl acetate, acetone, and diethyl ether. Finally, pure cobalt(II) phthalocyanine was obtained by silica gel column chromatography using dichloromethane:methanol as the solvent system. The green solid was then dried under vacuum over P_2O_5. The yield was 0.197 g (65.6%). Mp >300 °C. Anal. calcd. for $C_{112}H_{96}N_{16}O_{12}S_{16}Co$: C, 55.36; H, 3.98; N, 9.22%. Found: C, 54.91; H, 3.41; N, 8.62. IR (KBr disc) ν_{max}/cm^{-1}: 3292(NH), 3058 (CH_{Ar}), 2918 (CH_3), 2865, 1683 (C═O), 1578, 1514, 1435, 1408, 1379, 1297, 1115, 958, 755. UV–Vis (DMF): λ_{max}, nm (log ε): 338 (5.17), 629 (4.70), 694 (5.17). MS (MALDI-TOF) *m/z*: 2428 [M + H]$^+$, 2522 [M+4Na]$^+$.

3. Result and discussion

3.1. Synthesis and characterisation

The scheme for the preparation of the target metal-free **4** and metallophthalocyanines **5**, **6** and **7** is shown in Figs. 1 and 2. The structures of novel compounds were characterised by a combination of elemental analysis and ^{1}H NMR, ^{13}C NMR, IR, UV–Vis and MS spectral data. 4,5-bis(2′-aminophenylsulfanyl)-1,2-dicyanobenzene **1** was synthesised as described in the reported procedure [24].

N,N′-(2,2′-(4,5-Dicyano-1,2-phenylene)bis(sulfanediyl)bis(2,1-phenylene))bis(2-chloroacet-amide) **2** was synthesised by acylating **1** with acetyl chloride. The precursor compound for the synthesis of the macrocycle contains the amide moieties, which increases the reactivity of the chloro-substituted carbon towards nucleophilic substitution [26]. In the IR spectrum of **2**, the presence of an intense C≡N stretching band at 2230 cm^{-1}, the disappearance of the strong NH_2 stretching vibrations at 3450–3350 cm^{-1} [24],

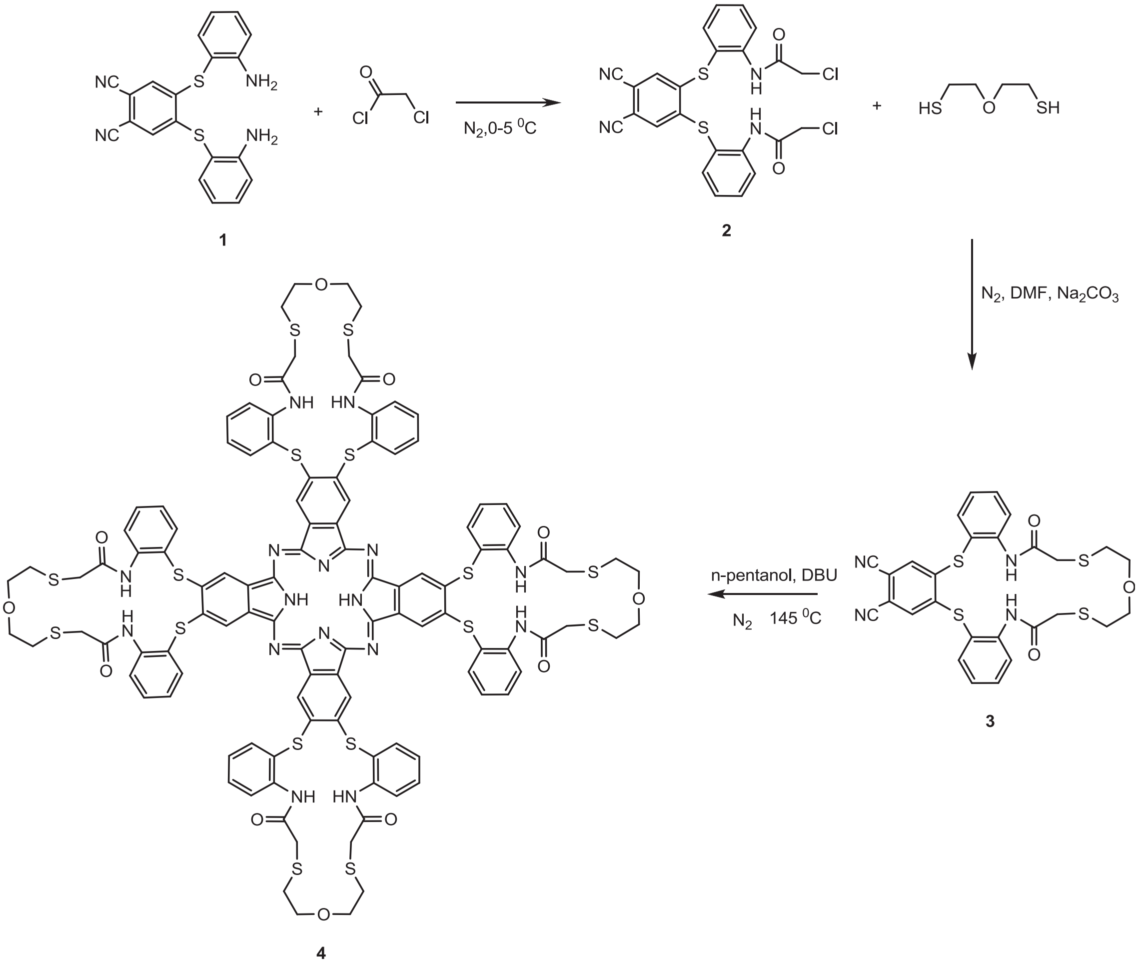
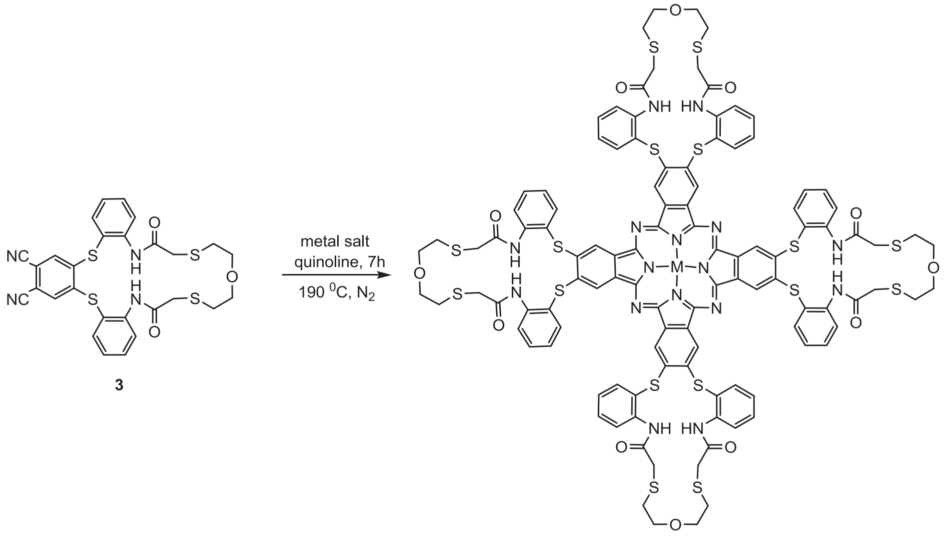


Fig. 1. Synthesis of metal-free phthalocyanine **4**.



Compound	5	6	7
M	Ni	Zn	Co

Fig. 2. Synthesis of metallophthalocyanines **5**, **6** and **7**.

the appearance of an NH stretching vibration at 3336 cm^{-1} and the sharp C=O vibration at 1697 cm^{-1} confirmed the formation of compound **2**. The ^{1}H NMR spectrum of **2** indicates the presence of a new singlet at $\delta = 4.21$ ppm due to the methylene protons of the amide moiety. The resonance of the NH proton shifted downfield on transformation from compound **1** to compound **2**, appearing at $\delta = 9.27$ ppm as a singlet in the spectrum of **2**. In the ^{13}C NMR spectrum of **2**, the peak at 114.79 ppm arises from the unsaturated carbon atoms of C≡N groups. The appearance of new peaks at $\delta = 163.80$ and 43.26 ppm, which were assigned to the C=O and $-CH_2Cl$ groups of the amide moiety and the other peaks at 141.75, 139.38, 137.21, 133.36, 129.48, 126.46, 121.61, 116.14, and 113.16 ppm (ArC) due to the aromatic carbons agree with the proposed structure. The molecular ion peak at $m/z = 527$ $[M + H]^+$ in the LC-MS/MS mass spectra of **2** also confirms the proposed structure.

The macrocyclisation was performed by adding a solution of **2** in dry dimethylformamide through dropping funnels to a stirring a solution of 2-mercaptoethylether in dry dimethylformamide containing anhydrous sodium carbonate as the base at 0–5 °C for 1.5 h under a nitrogen atmosphere. This procedure afforded macrocycle 6,16-dioxo-5,6,7,9,10,12,13,15,16,17-decahydrotribenzo[h,k,n][1,4,10,13,19,7,16]oxatetrathiadiazacyclohenicosine-24,25-dicarbonitrile **3** in 60% yield. The IR spectrum of **3** is very similar to that of **2**, but with small shifts in wavenumbers. An intense NH stretching vibration was observed at 3251 cm^{-1} in the spectrum of **3**. The ^{1}H NMR spectrum of **3** was collected in $CDCl_3$. Two new triplet signals were observed at $\delta = 3.80$ and 2.80 ppm due to the OCH_2 and SCH_2 protons of 2-mercaptoethylether, respectively, which supports the formation of the macrocycle. The ^{13}C NMR spectrum of **3** also supports this structure, with two new signals at $\delta = 71.19$ ppm for the OCH_2 carbon and 33.10 ppm for the SCH_2 carbon. The molecular ion peak at $m/z = 593$ $[M + H]^+$ in the LC-MS/MS mass spectra of **3** also confirms the proposed structure.

The cyclotetramerisation of phthalonitrile derivative **3** to the metal-free phthalocyanine **4** was accomplished in dry *n*-pentanol at reflux temperature for 24 h under a nitrogen atmosphere. In the

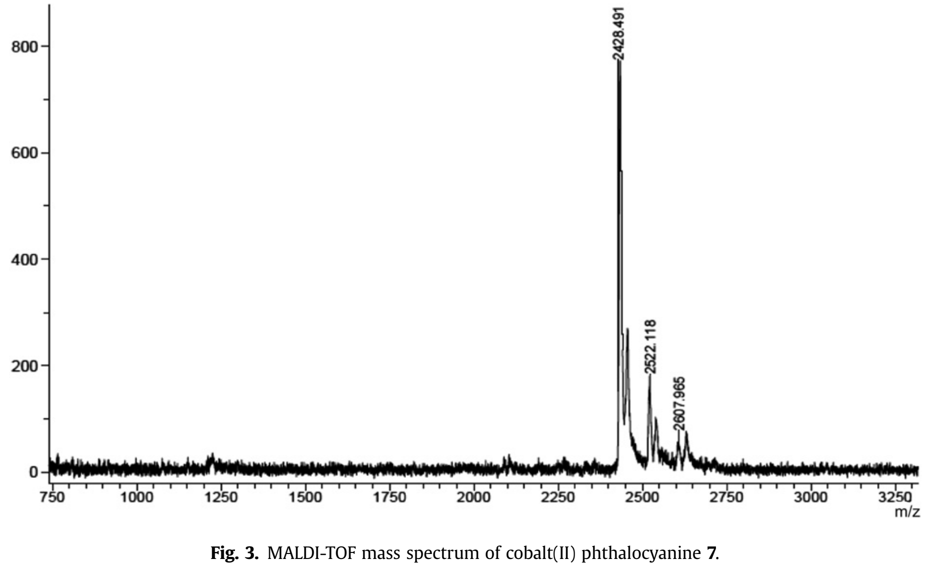


Fig. 3. MALDI-TOF mass spectrum of cobalt(II) phthalocyanine **7**.

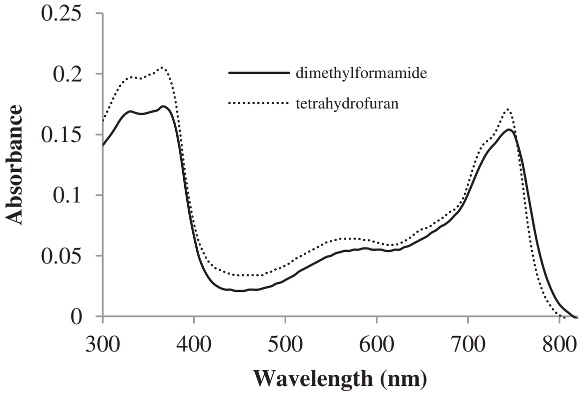


Fig. 4. UV–Vis spectrum of metal-free phthalocyanine **4** in DMF and THF.

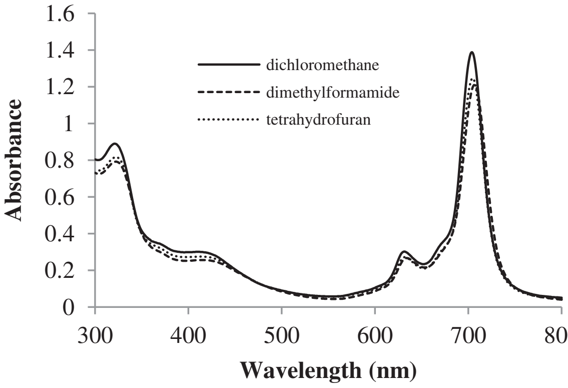


Fig. 6. UV–Vis spectra of nickel(II) phthalocyanine **5** in different solvents (concentration = 8×10^{-6} mol dm^{-3}).

^{1}H NMR spectrum of **4**, the typical shielding of the inner core protons was observed, with a broad signal at $\delta = -3.28$ ppm [27]. Characteristic absorbance signals due to the aromatic and aliphatic protons in the macrocyclic and the phthalocyanine moieties of the proposed structure were observed. The disappearance of the C≡N stretching vibration in the IR spectrum of **3** suggested the formation of compound **4**. In addition to the elemental analysis results, the mass spectrum was acquired. The MALDI-TOF mass spectrum of metal-free phthalocyanine **4** contained a molecular ion peak at $m/z = 2371$ [M + H]$^+$.

Metallophthalocyanines **5**, **6** and **7** were synthesised in moderate yield. Metallophthalocyanines **5**, **6** and **7** were obtained from dicyano derivative **3** and the corresponding anhydrous metal salts, $NiCl_2$, $Zn(CH_3CO_2)_2$, $Co(CH_3CO_2)_2$, respectively, in a Schlenk system in quinoline at 190 °C for 7 h. The intense vibrations observed at 3275, 3280 and 3292 cm^{-1} in the IR spectra of metallophthalocyanines **5**, **6** and **7** indicate the presence of NH groups in the macrocyclic ring, respectively. The disappearance of the strong C≡N stretching vibration of **3** is further evidence for the formation of metallophthalocyanines **5**, **6** and **7**. The rest of the IR spectra of the metallophthalocyanines are very similar to that of metal-free phthalocyanine **4**. The ^{1}H NMR spectra of metallophthalocyanines **5** and **6** are almost identical to that of metal-free phthalocyanine **4**. The ^{1}H NMR spectra of cobalt(II) phthalocyanine **7** could not be acquired due to the paramagnetic cobalt(II) centre. It should also be mentioned that, in the ^{1}H NMR spectra of metal-free phthalocyanine **4** and metallophthalocyanines **5** and **6**, broad signals were observed due to the aggregation of the planar phthalocyanine molecules at the considerably high concentration used for NMR measurements [28]. These signals are in agreement with the other structural information. In the mass spectra of **5**, **6** and **7**, the presence of molecular ion peaks at $m/z = 2427$ [M + H]$^+$, 2433 [M + H]$^+$ and 2428 [M + H]$^+$ (Fig. 3 for compound **7**), respectively, confirmed the proposed structures.

3.2. Absorption and aggregation properties

In general, phthalocyanines show typical electronic spectra with two strong absorption regions, one in the UV region at approximately 300–500 nm due to the B band and the other in the visible region at 600–700 nm due to the Q band [29]. Fig. 4 shows the electronic absorption spectra of metal-free phthalocyanine **4** in DMF and THF. Metal-free phthalocyanines are known to show a pair of sharp Q band absorptions in the visible region at 600–800 nm. The resolution of the split of the Q band decreases with increasing wavelength [30,31] and the presence of aggregated phthalocyanine species in solution [32,33]. In the case of UV–Vis spectrum of metal-free phthalocyanine **4** recorded in DMF, the Q band was observed without splitting at 743 nm. The large red shift or presence of aggregated species must have resulted in an unsplit Q band [31,34,35]. An unclear Q band split was barely observed as a broad absorption in the 600–800 nm with an absorption max at 741 nm and a shoulder at 717 nm in the UV–Vis spectra of metal-free phthalocyanine **4** recorded in THF (Fig. 4). The presence of strong absorption bands in **4** in the near UV region at $\lambda_{max} = 324$ and 364 nm are Soret region B bands, which have been ascribed to the deeper $\pi-\pi^*$ levels of LUMO transitions [36].

The UV–Vis absorption spectra of metallophthalocyanines **5**, **6** and **7** in DMF are shown in Fig. 5. Nickel phthalocyanine **5** shows characteristic absorptions in the Q band region at approximately 707 nm without splitting, with weaker absorptions at 634 nm and

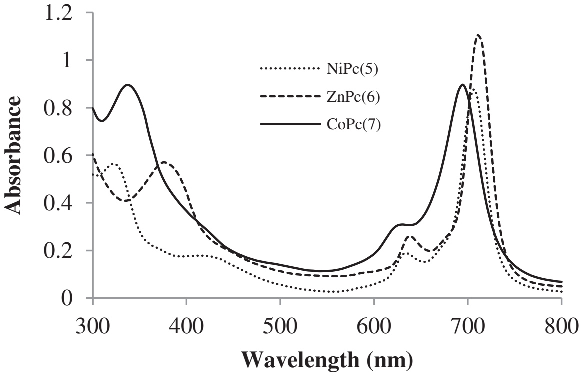


Fig. 5. UV–Vis spectra of metallophthalocyanines **5**, **6** and **7** in DMF.

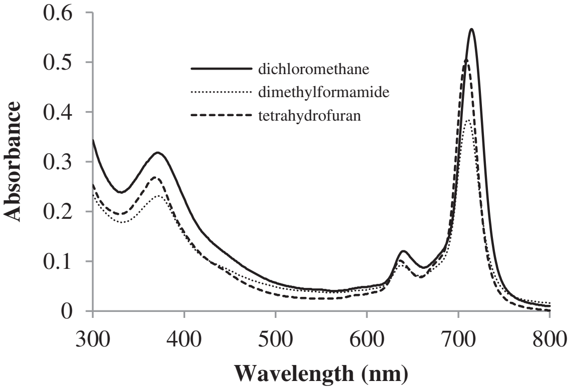


Fig. 7. UV–Vis spectra of zinc(II) phthalocyanine **6** in different solvents (concentration = 6×10^{-6} mol dm^{-3}).

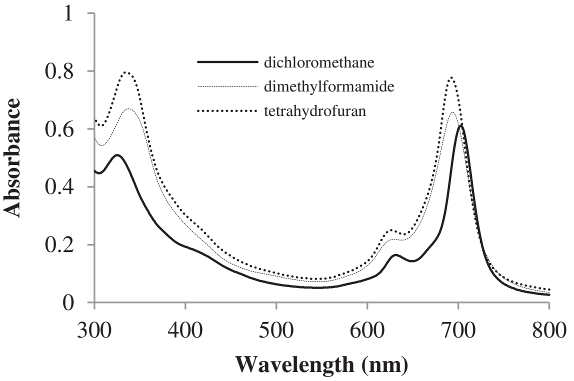


Fig. 8. UV–Vis spectra of cobalt(II) phthalocyanine **7** in different solvents (concentration = 8×10^{-6} mol dm^{-3}).

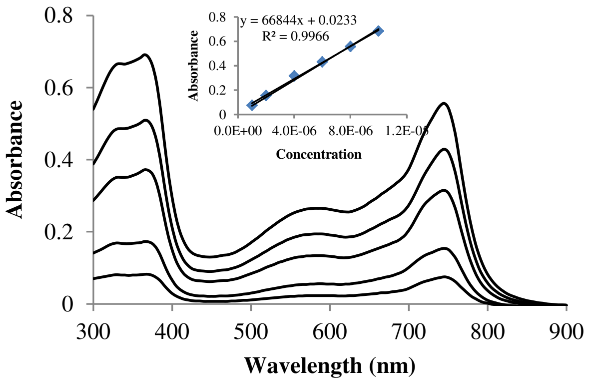


Fig. 9. Aggregation properties of metal-free phthalocyanine **4** in DMF at different concentrations 10×10^{-6}, 8×10^{-6}, 6×10^{-6}, 4×10^{-6}, 2×10^{-6}, 1×10^{-6} mol dm^{-3}. Inset: Beer–Lambert plot.

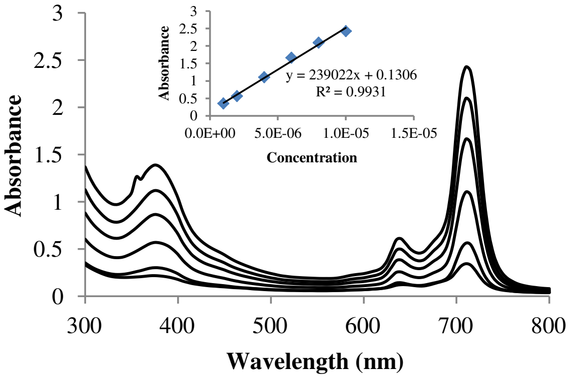


Fig. 11. Aggregation properties of zinc(II) phthalocyanine **6** in DMF at different concentrations 10×10^{-6}, 8×10^{-6}, 6×10^{-6}, 4×10^{-6}, 2×10^{-6}, 1×10^{-6} mol dm^{-3}. Inset: Beer–Lambert plot.

in the B band region at approximately 322 nm. Zinc phthalocyanine **6** and cobalt phthalocyanine **7** exhibit the characteristic absorption in the Q band region at approximately 711 and 694 nm without splitting with weaker absorptions at 637 and 629 nm and in the B band region at approximately 372 and 338 nm, respectively. An intense Q band absorption is typical of metal complexes of substituted and unsubstituted metallophthalocyanines with D_{4h} symmetry [37]. The UV–Vis spectra of metallophthalocyanines **5**, **6** and **7**, displayed a similar-shaped Q band, but with a small shift in the wavelength (Fig. 5). This can be attributed to the molecular structure of metallophthalocyanines, which share a macrocycle peripherally substituted on the phthalocyanine ring, but have different central metal ions such as nickel, zinc and cobalt for **5**, **6** and **7**. This structural similarity leads to the similar shapes of their Q-bands [38]. In general, a red shift in the Q band was observed with increasing size of the central metal [38] and number of electrons in the d-orbitals [39]. The order of the Q band positions is ZnPc > NiPc > CoPc. The saturated d-orbitals on the zinc atom of metallophthalocyanine **6** can be expected to destabilise the HOMO more than the unfilled d-orbitals on the nickel and cobalt atoms of metallophthalocyanines **5** and **7**. The greater destabilisation resulting from zinc will result in a smaller HOMO–LUMO separation, causing the largest red-shift in its spectrum.

The appearance of a broadening and/or splitting of the Q band in the UV–Vis spectra in the presence of dimers and higher order complexes of phthalocyanines are referred to as aggregation [31,34,35]. In this study, the aggregation behaviours of phthalocyanine complexes **5**, **6** and **7** were investigated in different solvents (DMF, THF, CH_2Cl_2), while metal-free phthalocyanine **4** could only be investigated in DMF and THF because of its poor solubility in CH_2Cl_2. (Fig. 6 for complex **5**, Fig. 7 for complex **6** and Fig. 8 for complex **7**). All synthesised metallophthalocyanine complexes did not show aggregation in DMF, THF or CH_2Cl_2.

The aggregation behaviours of metal-free **4** and metallophthalocyanine **5**, **6** and **7** were also investigated at different concentrations in DMF. The Beer–Lambert law was obeyed for metal-free **4** and metallophthalocyanines **5**, **6** and **7** in DMF from concentrations between 10×10^{-6} and 1×10^{-6} mol dm^{-3}. As the

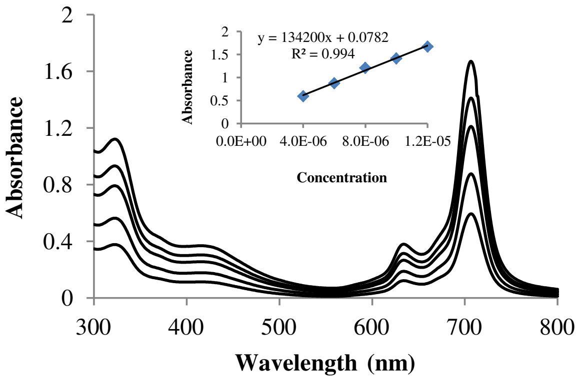


Fig. 10. Aggregation properties of nickel(II) phthalocyanine **5** in DMF at different concentrations 12×10^{-6}, 10×10^{-6}, 8×10^{-6}, 6×10^{-6}, 4×10^{-6} mol dm^{-3}. Inset: Beer–Lambert plot.

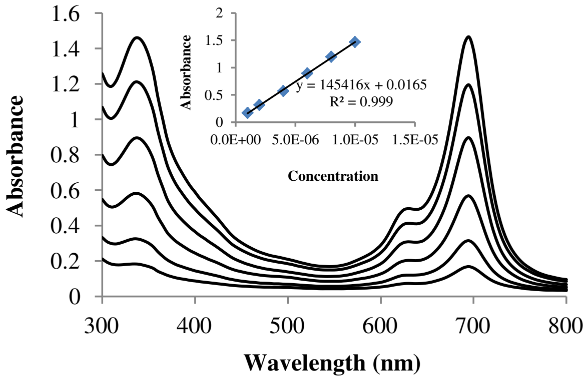


Fig. 12. Aggregation properties of cobalt(II) phthalocyanine **7** in DMF at different concentrations 10×10^{-6}, 8×10^{-6}, 6×10^{-6}, 4×10^{-6}, 2×10^{-6}, 1×10^{-6} mol dm^{-3}. Inset: Beer–Lambert plot.

concentration increased, the intensity of the absorption of the Q band also increased, and there were no new bands shifted to the higher energy region due to the presence of aggregated species for all phthalocyanines (Fig. 9 for metal-free Pc **4**, Fig. 10 for NiPc **5**, Fig. 11 for ZnPc **6** and Fig. 12 for CoPc **7**).

4. Conclusion

In the present work, the syntheses and spectral and aggregation properties of novel metal-free **4** and metallophthalocyanines **5**, **6** and **7** are reported. The octasubstituted phthalocyanines were purified by flash silica gel column chromatography and characterised by a combination of elemental analysis and ^{1}H NMR, IR, UV–Vis and MS spectral data, all of which were in agreement with the proposed structures. The solvent and concentration effects on the aggregation properties of the phthalocyanines were determined. All metallophthalocyanines were found to exist in monomeric form in DMF, THF and CH_2Cl_2. The metal-free and metallophthalocyanines demonstrated no aggregation behaviour in DMF from concentrations between 10×10^{-6} and 1×10^{-6} mol dm^{-3}.

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