Dyes and Pigments 80 (2009) 93–97

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The microwave-assisted synthesis and characterization of novel metal-free and metallophthalocyanines peripherally fused to four 13-membered diazadithia macrocycles

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A R T I C L E I N F O

Article history:
Received 4 February 2008
Received in revised form 21 May 2008
Accepted 23 May 2008
Available online 3 June 2008

Keywords:
Phthalocyanine
Metallophthalocyanine
Macrocyclic compound
Mixed-donor macrocyclic
Tosylation
Macrocyclization

A B S T R A C T

The novel tetrasubstituted metal-free phthalocyanine and metallophthalocyanines **7**, bearing four 13-membered diazadithia macrocycle moieties at peripheral positions were synthesized by cyclotetramerization of the corresponding phthalonitrile derivative in a multi-step reaction sequence. The metal-free phthalocyanine was synthesized by microwave irradiation of the corresponding dicyano compound in 2-(dimethylamino)ethanol for 10 min. Metallophthalocyanines were obtained from the respective dicyano derivative and corresponding anhydrous metal salts $NiCl_2$ and $ZnCl_2$, $CoCl_2$, $CuCl_2$, respectively, by microwave irradiation in 2-(dimethylamino)ethanol at 175 °C, 350 W for 10 min. The new compounds were characterized by a combination of IR, ^{1}H NMR, ^{13}C NMR, UV–vis, elemental analysis and MS spectral data.

1. Introduction

Phthalocyanines, aromatic macrocycles constituted of four isoindole subunits bound through aza-bridges, have been widely studied in the last few years due to their unusual physical properties [1–3]. Metal phthalocyanines and their peripherally substituted derivatives were found to be of great technological and commercial interest as dyes and printing inks [4]. Recently, intensive research work was initiated in this field to develop the substituted metal phthalocyanine derivatives as catalysts [5], photoconductors [6], photosenstizers [7], photovoltaic materials [8], and semiconductors [9]. Recently, metal phthalocyanines attracted a great deal of interest in medicine in photodynamic therapy [10–12] and as electronic carpets with deodorizer properties for indoor air [13]. Photodynamic therapy (PDT) is used in the treatment of cancer and consists of the administration of a photosensitizing chemical followed by activation of the chemical by light. Some of the drugs currently being investigated for use with PDT include porphyrins, chlorins, phthalocyanines, and purpurins [14]. It is well known that microwave (MW) irradiation can accelerate a great number of chemical processes, and, in particular, the reaction time and energy input are supposed to be mostly reduced in the reactions that are run for a long time at high temperatures under conventional conditions [15]. On the other hand, the most successful examples of microwave applications are necessarily found to be related to the use of solvent-free systems, in which microwaves interact directly with reagents and, therefore, can more efficiently drive chemical reactions [16,17]. The acceleration of reactions by microwaves results from material–microwave interactions leading to thermal and non-thermal effects [18–20]. The thermal heating phenomenon associated with microwave irradiation in the organic synthesis is mainly due to dipolar and interfacial polarization, although conduction losses can also be important at higher temperatures; when a molecule is irradiated with microwaves, it rotates to align itself with the applied field and consequently the molecule continually attempts to realign itself with changing field and energy is absorbed. The non-thermal effects associated with microwave irradiation may be mainly due to the increase of probability of molecular impacts, the decrease of activation energy and the intervention of localized microscopic high temperatures.

We have previously described the synthesis of phthalocyanines containing four 27-membered diazaheptathia macrocyclic moieties on peripheral positions [21]. In the present paper, we have

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doi:10.1016/j.dyepig.2008.05.006

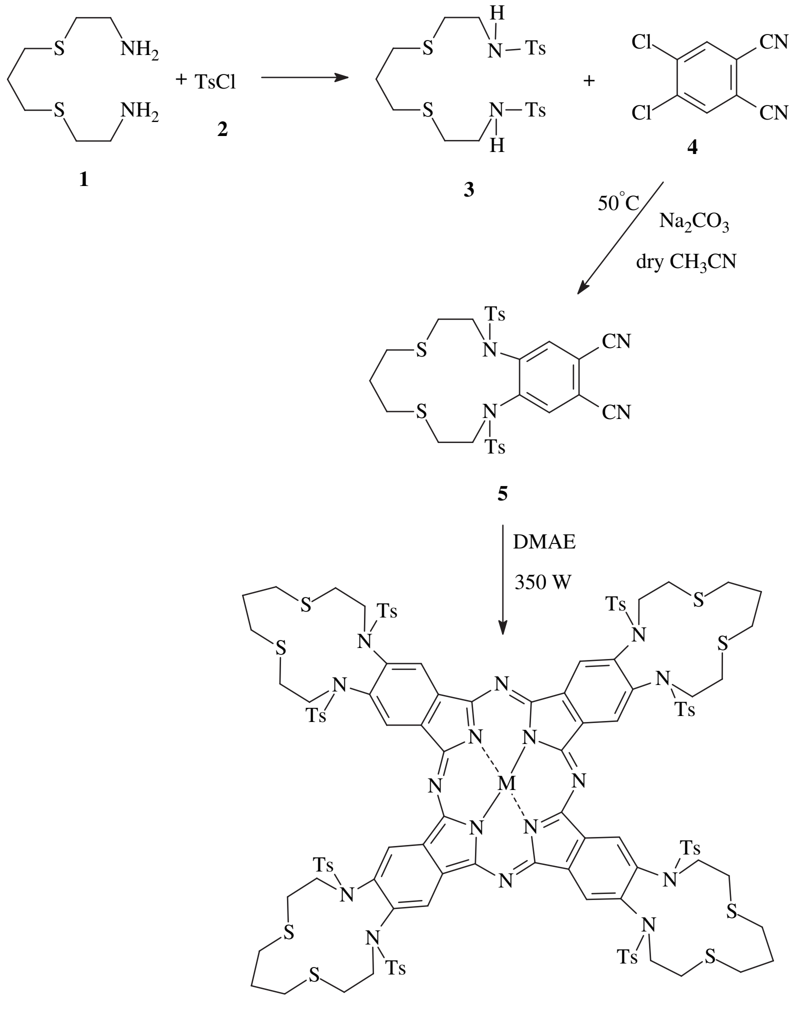
discussed the synthesis, characterization and structural investigation of novel symmetrical phthalocyanine and its zinc(II), copper(II), cobalt(II), and nickel(II) derivatives.

2. Experimental

All reactions were carried out under a dry nitrogen atmosphere using Standard Schlenk techniques. The IR spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer, using potassium bromide pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in DMSO-d_6 or $CDCl_3$, and chemical shifts (δ) are reported relative to Me_4Si as internal standard. Mass spectra were measured on a Varian 711 and VG Zapspec spectrometer. Elemental analysis and metal contents of these compounds were determined by a LECO Elemental Analyser (CHNS O932) and Unicam 929 AA spectrophotometer. UV–vis absorption spectra were measured by a Unicam UV–visible spectrometer. Melting points were measured on an electrothermal apparatus. Domestic oven was used for all the syntheses of phthalocyanines (Scheme 1).

2.1. *N,N′-(2,2′-(Propane-1,3-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(4-methylbenzene sulfonamide) (**3**)*

Compound **1** (0.5 g, 2.6 mmol) was dissolved in pyridine (20 ml) under nitrogen and a solution Ts–Cl **2** (1.3 g, 6.5 mmol) in pyridine (5 ml) was added dropwise over a period of 1 h at −10 °C. Stirring and cooling of the reaction mixture was continued for 3 h at −10 °C, then the mixture was stirred at room temperature overnight. The solution was poured slowly on ice (100 g) and diluted with water (100 ml) and then extracted with chloroform (3 × 50 ml). The combined organic layers were dried over anhydrous sodium sulfate and filtered and then concentrated. Yield: 0.980 g (78%). Anal. Calcd for $C_{21}H_{30}N_2O_4S_4$ (%): C, 50.17; H, 6.01; N, 5.57; S, 25.51. Found: C, 50.37; H, 6.13; N, 5.55; S, 25.48. IR (NaCl disk): 3272, 2922–2852, 1730, 1596, 1458, 1288, 1150, 1089, 812. ^{1}H NMR ($CDCl_3$): $\delta = 7.76$ (d, 4H, Ar–H), 7.31 (d, 4H, Ar–H,), 5.36 (t, 2H, NH,) 3.07 (t, 4H, N–CH_2), 2.59 (m, 8H, S–CH_2), 2.41 (s, 6H, CH_3), 1.24 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): $\delta = 143.59$(Ar–C), 129.80 (Ar–CH), 127.07 (Ar–CH), 42.04 (N–CH_2), 30.16 (S–CH_2), 21.57 (CH_3). MS; $m/z = 541$ $[M + K]^+$.



Compound	6	7	8	9	10
M	2H	Zn(II)	Cu(II)	Co(II)	Ni(II)

Scheme 1. The synthesis of the metal-free phthalocyanine and metallophthalocyanines.

2.2. *1,11-Ditosyl-2,3,5,6,7,9,10,11-octahydro-1*H*-benzo[*e*][1,4,7,10]dithiadiazacyclotridecine-13,14-dicarbonitrile (**5**)*

Compound **3** (0.930 g, 1.85 mmol) was dissolved in acetonitrile (110 ml), finely ground anhydrous Na_2CO_3 (0.589 g, 5.56 mmol) was added and the mixture stirred for 2 h at 50 °C. A solution of 1,2-dichloro-4,5-dicyanobenzene **4** (0.364 g,1 .85 mmol) in dry acetonitrile (90 ml) was added dropwise over 4 h. After stirring for 3 days at 85 °C, the reaction mixture was poured into ice-water and stirred for 2 h. The mixture was evaporated until 20 ml under reduced pressure. The residue was extracted with chloroform (2×100 ml). The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure to give an orange crude product. The product was crystallized from ethanol. Yield: 0.900 g (76%). Anal. Calcd for $C_{29}N_4O_4S_4H_{30}$ (%): C, 55.52; H, 4.79; N, 8.93; S, 20.42. Found: C, 55.71; H, 4.82; N, 8.85; S, 20.32. IR (NaCl disk): 2925–2854, 2236, 1730, 1597, 1537, 1465, 1328, 1224, 1159, 1090, 815. ^1H NMR ($CDCl_3$): 7.72 (m, 2H, Ar–H), 7.38 (m, 8H, Ar–H), 4.78 (t, 4H, N–CH_2), 2.89 (t, 4H, S–CH_2), 2.82 (t, 4H, S–CH_2), 2.43 (s, 6H, CH_3), 1.57 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): $\delta = 143.92$ (Ar–C), 135.19 (Ar–C), 131.32 (Ar–CH), 130.70 (Ar–C), 129.02 (Ar–CH), 113.87 (Ar–C), 127.29 (Ar–CH), 115.28 (C≡N), 68.38 (N–CH_2), 32.14 (S–CH_2), 30.25 (S–CH_2), 29.58 (CH_2), 21.77 (CH_3). MS; $m/z = 663$ $[M + 2H_2O + 1]^+$.

2.3. *Metal-free phthalocyanine (**6**)*

Compound **5** (0.2 g, 0.32 mmol) and 2-(dimethylamino)ethanol (2 ml) were irradiated in a microwave oven at 175 °C, 350 W for 10 min. After cooling to room temperature the reaction mixture was refluxed with ethanol to precipitate the product which was filtered off. The dark green product was washed with hot EtOH–MeOH and dried in vacuo. The solid product was chromatographed on silica gel with chloroform/methanol (9:1) as eluents. Yield: 0.072 g (36%), mp 258–261 °C. Anal. Calcd for $C_{116}H_{122}N_{16}O_{16}S_{16}$ (%): C, 55.57; H, 4.87; N, 8.93; S, 20.42. Found: C, 55.54; H, 4.68; N, 8.96; S, 20.30. IR (KBr pellets): 3351, 2923–2851, 1713, 1597, 1327, 1156, 1089, 813. ^1H NMR ($CDCl_3$): $\delta = 7.39$ (m, 8H, Ar–H), 7.34 (m, 32H, Ar–H), 4.86 (t, 16H, N–CH_2), 2.94 (t, 16H, S–CH_2), 2.87 (t, 16H, S–CH_2), 2.42 (s, 24H, CH_3), 1.78 (m, 8H, CH_2). UV–vis [(in chloroform) λ_{max}(nm)10^{-5} ε (mol^{-1} cm^{-1})]: 704 (4.78), 644 (4.72), 350 (5.12), 293 (5.28). MS; $m/z = 2508$ $[M + 1]^+$.

2.4. *Zinc(II) phthalocyanine (**7**)*

Compound **5** (0.150 g, 0.24 mmol), anhydrous $ZnCl_2$ (0.0081 g, 0.06 mmol) and 2-(dimethylamino)ethanol (2 ml) were irradiated in a microwave oven at 175 °C, 350 W for 10 min. After cooling to room temperature the reaction mixture was refluxed with ethanol to precipitate the product which was filtered off. The dark green product was washed with hot EtOH–MeOH and dried in vacuo. The solid product was chromatographed on silica gel with chloroform/methanol (9:1) as eluents. Yield: 0.048 g (31%), mp >300 °C. Anal. Calcd for $C_{116}H_{120}N_{16}O_{16}S_{16}Zn$ (%): C, 54.2; H, 4.67; N, 8.71; S, 19.91. Found: C, 54.27; H, 4.56; N, 8.85; S, 20.63. IR (KBr pellets): 2925–2852, 1600, 1409, 1328, 1159, 1086, 813, 744. ^1H NMR ($CDCl_3$): $\delta = 7.68$ (m, 8H, Ar–H), 7.35 (m, 32H, Ar–H), 4.82 (t, 16H, N–CH_2), 2.96 (t, 16H, S–CH_2), 2.88 (t, 16H, S–CH_2), 2.47 (s, 24H, CH_3), 1.61 (m, 8H, CH_2). UV–vis [(in chloroform) λ_{max}(nm)10^{-5} ε (mol^{-1} cm^{-1})]: 689 (5.23), 635 (4.86), 353 (5.19), 290 (5.22). MS; $m/z = 2571$ $[M + 1]^+$.

2.5. *Copper(II) phthalocyanine (**8**)*

Compound **5** (0.150 g, 0.24 mmol), anhydrous $CuCl_2$ (0.008 g, 0.06 mmol) and 2-(dimethylamino)ethanol (2 ml) were irradiated in a microwave oven at 175 °C, 350 W for 10 min. After cooling to room temperature the reaction mixture was refluxed with ethanol to precipitate the product which was filtered off. The dark green product was washed with hot EtOH–MeOH and dried in vacuo. The solid product was chromatographed on silica gel with chloroform/methanol (9:1) as eluents. Yield: 0.043 g (28%), mp >300 °C. Anal. Calcd for $C_{116}H_{120}N_{16}O_{16}S_{16}Cu$ (%): C, 54.24; H, 4.68; N, 8.72; S, 19.93. Found: C, 54.35; H, 4.52; N, 8.79; S, 19.97. IR (KBr pellets): 2923–2855, 1599, 1414, 1327, 1159, 1085, 816. UV–vis [(in chloroform) λ_{max}(nm)10^{-5} ε (mol^{-1} cm^{-1})]: 692 (4.96), 626 (4.86), 380 (4.9), 293 (5.21). MS; $m/z = 2568$ $[M]^+$.

2.6. *Cobalt(II) phthalocyanine (**9**)*

Compound **5** (0.15 g, 0.24 mmol), anhydrous $CoCl_2$ (0.0077 g, 0.06 mmol) and 2-(dimethylamino)ethanol (2 ml) were irradiated in a microwave oven at 175 °C, 350 W for 10 min. After cooling to room temperature the reaction mixture was refluxed with ethanol to precipitate the product which was filtered off. The dark green product was washed with hot EtOH–MeOH and dried in vacuo. The solid product was chromatographed on silica gel with chloroform/methanol (9:1) as eluents. Yield: 0.052 g (34%), mp >300 °C. Anal. Calcd for $C_{116}H_{122}N_{16}O_{16}S_{16}Co$ (%): C, 54.33; H, 4.68; N, 8.74; S, 19.97. Found: C, 54.30; H, 4.59; N, 8.85; S, 19.95. IR (KBr pellets): 2925–2854, 1596, 1462, 1344, 1158, 1090, 960, 812. ^1H NMR ($CDCl_3$): $\delta = 7.64$ (m, 8H, Ar–H), 7.33 (m, 32H, Ar–H), 3.70 (t, 16H, N–CH_2), 2.42 (t, 16H, S–CH_2), 2.17 (t, 16H, S–CH_2), 2.00 (s, 24H, CH_3), 1.64 (m, 8H, CH_2). UV–vis [(in chloroform) λ_{max}(nm)10^{-5} ε (mol^{-1} cm^{-1})]: 683 (5.17), 626 (4.99), 290 (5.26). MS; $m/z = 2565$ $[M + 1]^+$.

2.7. *Nickel(II) phthalocyanine (**10**)*

Compound **5** (0.2 g, 0.32 mmol), anhydrous $NiCl_2$ (0.01 g, 0.08 mmol) and 2-(dimethylamino)ethanol (2 ml) were irradiated in a microwave oven at 175 °C, 350 W for 10 min. After cooling to room temperature the reaction mixture was refluxed with ethanol to precipitate the product which was filtered off. The dark green product was washed with hot EtOH–MeOH and dried in vacuo. The solid product was chromatographed on silica gel with chloroform/methanol (9:1) as eluents. Yield: 0.053 g (26%), mp >300 °C. Anal. Calcd for $C_{116}H_{122}N_{16}O_{16}S_{16}Ni$ (%): C, 54.3; H, 4.68; N, 8.74; S, 19.97. Found: C, 54.27; H, 4.74; N, 8.74; S, 20.00. IR (KBr pellets): 2922–2853, 1596, 1403, 1347, 1158, 1089, 813. ^1H NMR ($CDCl_3$): $\delta = 7.70$ (m, 8H, Ar–H), 7.31 (m, 32H, Ar–H), 4.82 (t, 16H, N–CH_2), 2.95 (t, 16H, S–CH_2), 2.87 (m, 16H, S–CH_2), 2.41 (s, 24H, CH_3), 1.76 (m, 8H, CH_2). UV–vis [(in chloroform) λ_{max}(nm)10^{-5} ε (mol^{-1} cm^{-1})]: 692 (5.15), 620 (4.9), 296 (5.26). MS; $m/z = 2563$ $[M]^+$.

3. Results and discussion

The amine groups of 2,2′-(propane-1,3-diylbis(sulfanediyl)) diethanamine **1** [22] were then tosylated in pyridine at −10 °C with *p*-toluenesulfonylchloride **2** to protect amino groups and to make use of the high reactivity of tosylamides in cyclization reactions. In the IR spectra of **1** the intense absorption bands at 3365–3291 cm^{-1} for **1** corresponding to the –NH_2 groups, disappear after the conversion to the tosylamido compounds. In the IR spectrum of **3**, the intense absorption band at 3272 cm^{-1} corresponds to the N–H stretching vibration. FAB mass spectrum and elemental analysis also confirm the formation of **3**.

As in the case of most other phthalocyanines containing macrocyclic moieties, a convenient method for similar compounds is to start with the dibromo or dicyano derivatives of the corresponding macrocyclic units. For this aim, **3** was reacted with 1,2-dichloro-4,5-dicyanobenzene **4** [23] in dry acetonitrile containing finely ground anhydrous Na_2CO_3 as a template agent at reflux temperature in a Schlenk system under a nitrogen atmosphere to give **5** in 76% yield. On the other hand, tosylation of aza groups, which are used as protective groups of aza functions in the cyclotetramerization, is also effective in the cyclization. Analytical and spectroscopic data of **5** clearly confirm the success of the cyclization reaction. Comparison of the IR spectral data clearly indicated the formation of compound **5** by the disappearance of the C–Cl band of 1,2-dichloro-4,5-dicyanobenzene at 684 $\mathrm{cm^{-1}}$ and of NH band of compound **3** at 3272 $\mathrm{cm^{-1}}$, and the appearance of a new absorption at 2236 $\mathrm{cm^{-1}}$ ($C\equiv N$). The spectrum of **5** also indicates the presence of alkyl, CN, and SO_2 groups by the intense stretching bands at 2925–2854 (C–H), 2236 ($C\equiv N$) and 1328–1159 $\mathrm{cm^{-1}}$ (SO_2). The ^{1}H NMR spectrum of a $CDCl_3$ solution of **5** was well resolved and showed that the formation of this macrocycle was accomplished. The chemical shifts belonging to the deuterium exchangeable NH groups at $\delta = 5.36$ ppm disappear after the condensation reaction between **3** and **4**. The ^{13}C NMR spectrum of **5** shows the presence of nitrile carbon atoms at $\delta = 115.28$ ppm which indicates the completion of conversion of **3** to **5**. FAB mass spectrum and elemental analysis also confirm the formation of compound **5**.

Starting from the dicyano derivatives, many chemical routes may be used to form the corresponding metal-free phthalocyanine. Metal-free phthalocyanine **6** was synthesized by microwave irradiation of the corresponding dicyano compound **5** in 2-(dimethylamino)ethanol for 10 min. The IR spectrum of metal-free phthalocyanine **6** shows the 3351 $\mathrm{cm^{-1}}$ (NH) vibrations. The disappearance of the $C\equiv N$ stretching vibration on the IR spectra of **5** suggested the formation of compound **6**. The ^{1}H NMR spectra of this compound the inner core protons of Pc–2H could not be observed due to strong aggregation of molecules [24]. The mass spectrum of this compound at $m/z = 2507$ $[\mathrm{M}]^+$ supports the proposed formula for this structure. The elemental analysis confirms the desired compound **6**.

The metallophthalocyanines **7**, **8**, **9**, **10** were synthesized in moderate yield 31%, 28%, 34%, 26%, respectively. The metallophthalocyanines **7**, **8**, **9** and **10** were obtained from dicyano derivative **5** and corresponding anhydrous metal salts $NiCl_2$ and $ZnCl_2$, $CoCl_2$, $CuCl_2$, respectively, by microwave irradiation in 2-(dimethylamino)ethanol at 175 °C, 350 W for 10 min. In the IR spectra of **7**, **8**, **9** and **10** compounds, disappearence of $C\equiv N$ vibration for compound **5** confirm the formation of these compounds. The NMR characteristics of these compounds were similar to those of the precursor dicyano compound **5** and the metal-free phthalocyanine **6**. In the mass spectrum of compounds **7**, **8**, **9** and **10** the presence of molecular ion peaks at $m/z = 2571$ $[\mathrm{M}+1]^+$, $m/z = 2568$ $[\mathrm{M}]^+$, $m/z = 2565$ $[\mathrm{M}+1]^+$, $m/z = 2563$ $[\mathrm{M}]^+$, respectively, confirmed the proposed structures. The elemental analysis confirms the desired compounds **7**, **8**, **9**, **10**.

Phthalocyanines **7**, **8**, **9** and **10** show typical electronic spectra with two different strong absorption regions. The first, in the UV region at around 340 nm called the Soret (or B) band [25], arising from the deeper π levels → LUMO transition between an a_{2u} and the same e_g orbitals and extending to the blue of the visible spectrum, and is generally much less intense. The second, in the visible region at 600–700 nm called the Q-band, is attributed to the $\pi \rightarrow \pi^*$ transition from the HOMO to the LUMO of the Pc^{2-} ring [26,27]. The purity and depth of colour of phthalocyanines arise from an isolated Q-band at the far-red end of the visible spectrum [28]. The electronic absorption spectrum of the metal free in chloroform at room temperature is shown in Fig. 1. The metal-free phthalocyanine **6** showed that the Q-band appeared as an intense peak at 704 nm with a shoulder at around 644 nm, corresponding to monomeric and aggregated forms in chloroform, and B-band regions in chloroform appeared as an intense peak at 350 nm with a shoulder at around 293 nm.

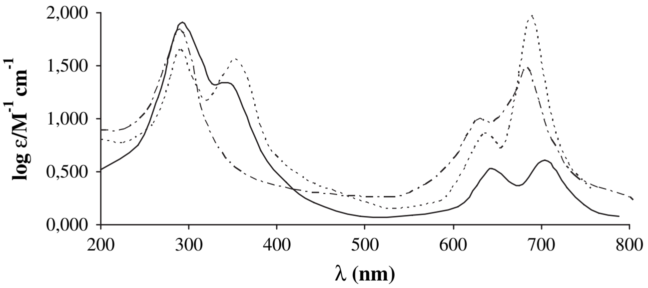


Fig. 1. UV–vis spectra of H_2Pc(–), ZnPc(…) and CoPc(-.-.-.) complexes.

The UV–vis absorption spectra of metallophthalocyanines **7**, **9** (Fig. 1) **8**, **10** in chloroform show intense Q absorption at $\lambda_{\max} = 689$, 692, 683 and 692 nm, with a weaker absorptions at 635, 626, 626 and 620 nm, respectively. The single Q-bands in metallo derivatives **7**, **8**, **9** and **10** are characteristic. This result is typical of metal complexes of substituted and unsubstituted metallophthalocyanines with D_{4h} symmetry [29]. Soret region B-band absorptions of zinc(II) phthalocyanine **7**, copper(II) phthalocyanine **8**, cobalt(II) phthalocyanine **9**, nickel(II) phthalocyanine **10**, were observed at $\lambda = 290$, 293, 290 and 296 nm. Zinc(II) phthalocyanine **7** and copper(II) phthalocyanine **8** show weaker absorptions at 353 and 380 nm as expected, respectively.

Acknowledgements

This work was supported by The Scientific Technological Research Council of Turkey (TÜBİTAK Project no: 107T429).

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