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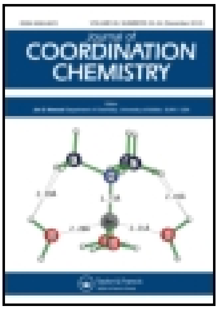

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Tetrakis (2-[2-(2-naphthyloxy)ethoxy]ethoxy) substituted metal-free and metallophthalocyanines and their aggregation behavior

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Metal-free **4** and metallophthalocyanines **5**, **6** and **7** substituted with four {2-[2-(2-naphthyloxy)ethoxy]ethoxy} functional groups at peripheral positions have been prepared. These new phthalocyanine compounds have been characterized by IR, UV-Vis, ^{1}H-NMR spectroscopy, MS spectra data, and elemental analysis. The aggregation behavior of these compounds was investigated in different concentrations of chloroform. The effect of solvents on the absorption spectra was studied in various solvents.

Keywords: Phthalocyanine; Aggregation; Microwave; Phthalonitrile; Nickel; Cobalt

1. Introduction

Phthalocyanines (Pcs) are aromatic macrocyclic, delocalized 18-π electron systems studied for more than 70 years; however, researchers are still interested in this class of compounds [1]. Pc-based materials find many applications in nonlinear optics [2], optical data storage [3], photodynamic cancer therapy [4], sensors [5], catalysis [6], and solar energy conversion [7]. The most important applications are as photosensitizers in photodynamic therapy (PDT); diamagnetic metals such as Zn enhance phototoxicity of Pcs [8–11]. Because of its ability to generate reactive oxygen such as singlet oxygen, Pcs have been used for the treatment of various cancers and viruses [12–14].

A main disadvantage of Pcs is their low solubility in organic solvents or water. To increase solubility Pcs require addition of functional groups on the periphery to enhance the distance between 18-π electron-conjugated Pcs [15–17]. Introducing long chain alkyl or alkoxy groups in peripheral positions of the Pc framework can also increase solubility [18–22]. Tetra-substituted Pcs are more soluble than octa-substituted ones because of their lower degree of order in the solid state.

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Microwave irradiation is used for synthesis of Pcs, increasing reaction yield and decreasing chemical reaction times [23–25]. Aggregation behavior of Pc compounds has been extensively investigated [26, 27]. Aggregate formation among Pcs involves ligand–metal coordination [28, 29], π-stacking [30, 31], hydrogen-bonding, and donor–acceptor [32] interactions. Pcs generate high aggregation due to interactions between their 18 π-electron systems and decrease the solubility of these compounds. It also affects their spectroscopic, photophysical, photochemical, and electrochemical properties. The aim of our ongoing research is to synthesize soluble metal-free and metallophthalocyanine complexes to be used in applications. Recently, we reported that metal-free and metallophthalocyanine (Zn, Co, Ni, and Cu) derivatives functionalized with substituents such as 2-[2-(1-naphthyloxy)ethoxy]ethanol, 2-[2-(2-naphthyloxy)ethoxy]ethanol [33, 34] and 2-[2-(dimethylamino)ethoxy]ethanol [35] in peripheral and non-peripheral positions offered PDT and electrochemical properties. Aggregation of metallophthalocyanines represents the main concern causing efficiency limitation in PDT and related applications. So, in this article, we report the synthesis, characterization, spectroscopic properties, and aggregation behavior of metal-free and metallophthalocyanine complexes in different solvents and concentrations.

2. Experimental

2-[2-(2-Naphthyloxy)ethoxy]ethanol **1** [36], 4-nitrophthalonitrile **2** [37] and 4-{2-[2-(2-naphthyloxy)ethoxy]ethoxy}phthalonitrile **3** [34] were prepared according to the literature. All reagents and solvents were of reagent grade obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [38]. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer using KBr pellets. ^{1}H-NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$ and chemical shifts are reported (δ) relative to Me_4Si as an internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC MS/MS spectrometer. Melting points were measured on an electrothermal apparatus and are uncorrected. 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. Domestic microwave oven was used in the synthesis of the Pcs.

2.1. *Preparation of metal-free Pc (4)*

A standard Schlenk tube was charged with **3** (0.15 g, 0.418 mmol), 2 mL of dry *n*-pentanol and 0.05 mL 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under N_2 and degassed several times. The temperature was gradually increased to 160°C and stirred for 24 h. After cooling to room temperature, the reaction mixture was refluxed with ethanol (15 mL) to precipitate the product, which was washed with hot ethanol and dried in vacuum over P_2O_5. The solid green product was purified by preparative thin layer chromatography (TLC) using chloroform/methanol (100 : 4) solvent system. Yield: 70 mg (47%); m.p.: >300°C. Anal. IR (KBr tablet), ν_{max}/cm^{-1}: 3291 (N–H), 3058 (Ar–H), 2927–2876 (C–H), 1628, 1600, 1524, 1470, 1390, 1357, 1257, 1218, 1183, 1118, 1058, 971, 837, 749. ^{1}H-NMR. ($CDCl_3$), (δ:ppm): 7.72–7.64 (m, 16H, Ar–H), 7.38–7.31

(m, 12H, Ar–H), 7.16–7.09 (m, 12H, Ar–H), 4.23 (m, 16H, CH_2–O), 3.95 (m, 16H, CH_2–O) −5.38 (s, br, 2H, NH). UV-Vis (chloroform): λ_{max}, nm (log ε): 328 (4.54), 607 (3.81), 645 (4.03), 667 (4.40), 704 (4.48). MS (ES^+) (*m*/*z*) 1436 $[M+H]^+$. Calcd for $C_{88}H_{74}N_8O_{12}$ (%): C, 73.62; H, 5.20; N,7.81. Found (%): C, 73.50; H, 5.45; N, 7.67.

2.2. *Preparation of nickel(II) Pc (5)*

4-{2-[2-(2-Naphthyloxy)ethoxy]ethoxy}phthalonitrile **3** (0.15 g, 0.42 mmol) and anhydrous $NiCl_2$ (0.027 g, 0.21 mmol) were ground together and 2-(dimethylamino)ethanol (2.5 mL) was added. The reaction mixture was irradiated in the microwave oven at 175°C, 350 W for 8 min. After cooling to room temperature the reaction mixture was refluxed with ethanol to precipitate the product, which was filtered off and washed with hot ethanol, diethyl ether and dried in vacuum over P_2O_5. The solid product was purified by preparative TLC using chloroform/methanol (100 : 3). Yield: 75 mg (48%); m.p.: > 300°C. IR (KBr tablet), ν_{max}/cm^{-1}: 3058 (Ar–H), 2926–2868 (C–H), 1628, 1613, 1600, 1533, 1485, 1470, 1390, 1354, 1245, 1217, 1183, 1119, 1095, 1057, 970, 840, 750. ^{1}H-NMR ($CDCl_3$), (δ:ppm): 7.71–7.68 (m, 16H, Ar–H), 7.36–7.29 (m, 12H, Ar–H), 7.17–7.12 (m, 12H, Ar–H), 4.28 (m, 16H, CH_2–O), 3.99 (m, 16H, CH_2–O). UV-Vis (chloroform): λ_{max}, nm (log ε): 328 (4.31), 610 (4.05), 674 (4.55). MS (ES^+) (*m*/*z*) 1493 $[M+H]^+$. Calcd for $C_{88}H_{72}N_8O_{12}Ni$ (%): C, 70.83; H, 4.86; N, 7.51. Found (%): C, 70.50; H, 4.45; N, 7.72.

2.3. *Preparation of cobalt(II) Pc (6)*

Complex **3** (0.13 g, 0.36 mmol) and anhydrous $CoCl_2$ (0.024 g, 0.18 mmol) were ground together and 2-(dimethylamino)ethanol (2 mL) was added. The reaction mixture was irradiated in the microwave oven at 175°C, 350 W for 7 min. After cooling to room temperature the reaction mixture was refluxed with ethanol to precipitate the product, which was filtered off and washed with hot ethanol, diethyl ether and dried in vacuum over P_2O_5. The solid product was purified by preparative TLC using chloroform/methanol (100 : 3.5) solvent system. Yield: 50 mg (37%); m.p.: > 300°C. IR (KBr tablet), ν_{max}/cm^{-1}: 3060 (Ar–H), 2926–2851 (C–H), 1624, 1600, 1506, 1467, 1346, 1256, 1243, 1215, 1183, 1119, 1094, 1069, 969, 839, 750. UV-Vis (chloroform): λ_{max}, nm (log ε): 328 (4.51), 613 (4.18), 677 (4.71). MS (ES^+) (*m*/*z*) 1493 $[M+H]^+$. Calcd for $C_{88}H_{72}N_8O_{12}Co$ (%): C, 70.82; H, 4.86; N, 7.51. Found (%): C, 70.55; H, 4.52; N, 7.70.

2.4. *Preparation of copper(II) Pc (7)*

Complex **3** (0.1 g, 0.28 mmol) and anhydrous $CuCl_2$ (0.018 g, 0.14 mmol) were ground together and 2-(dimethylamino)ethanol (2 mL) was added. The reaction mixture was irradiated in a microwave oven at 175°C, 350 W for 8 min. After cooling to room temperature the reaction mixture was refluxed with ethanol to precipitate the product, which was filtered off and washed with hot ethanol and dried in vacuum over P_2O_5. The solid product was purified by preparative TLC using chloroform/methanol (100 : 3) solvent system. Yield: 35 mg (33%); m.p.: > 300°C. IR (KBr tablet), ν_{max}/cm^{-1}: 3054 (Ar–H), 2927–2868 (C–H), 1624, 1599, 1509, 1484, 1469, 1390, 1352, 1258, 1217, 1183, 1119, 1062, 970, 838, 748. UV-Vis (chloroform): λ_{max}, nm ($\log \varepsilon$): 327 (4.69), 614 (4.01), 681 (4.46). MS (ES$^+$) (m/z) 1520 $[M+Na]^+$. Calcd for $C_{88}H_{72}N_8O_{12}Cu$ (%): C, 70.60; H, 4.85; N, 7.48. Found (%): C, 70.41; H, 4.47; N, 7.75.

3. Results and discussion

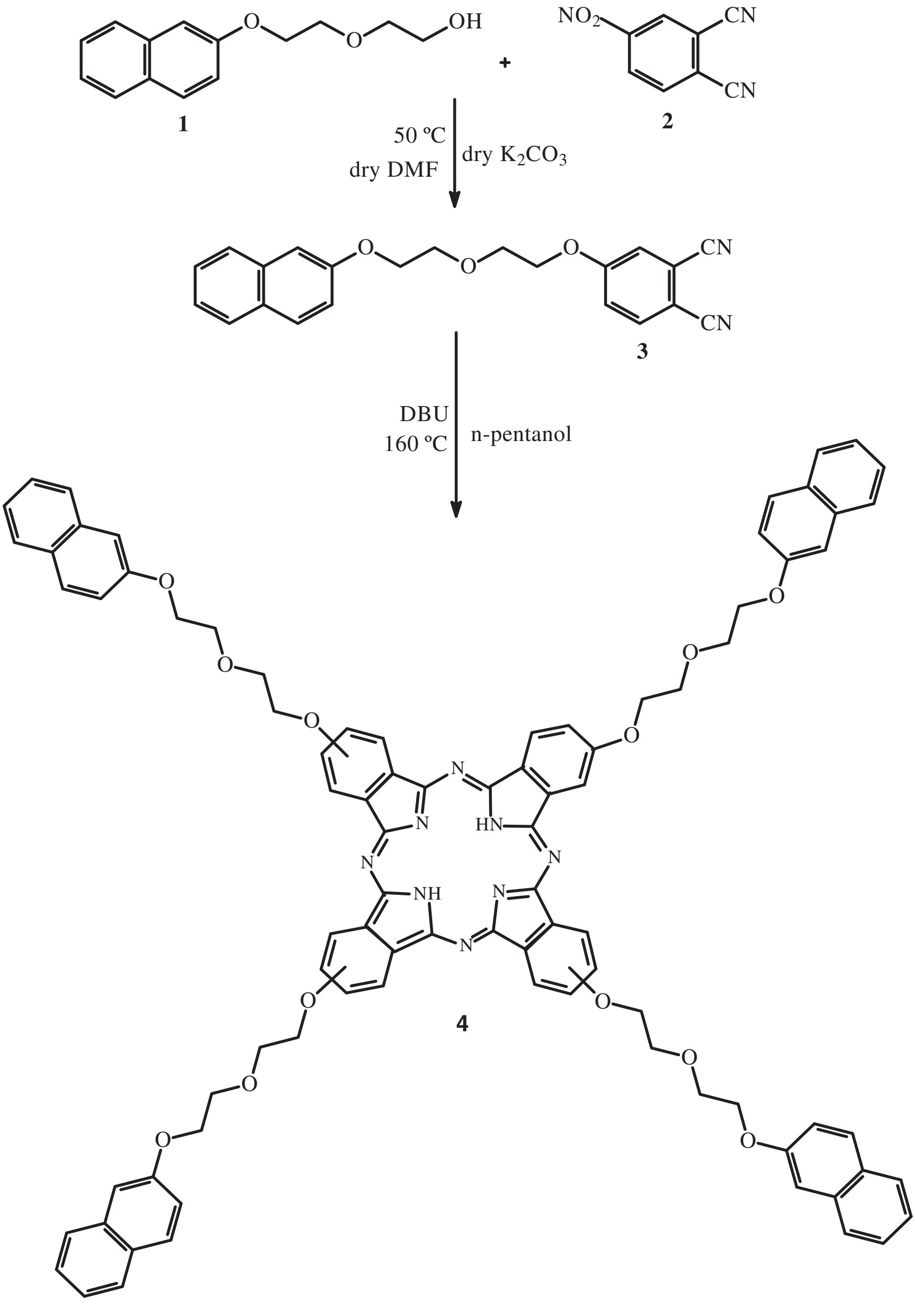
Preparations of metal-free **4** and metallophthalocyanines **5**–**7** are shown in schemes 1 and 2, respectively. The compounds were characterized by a combination of ^{1}H-NMR, IR, UV-Vis, MS spectral data, and elemental analysis.

Metal-free Pc **4** was synthesized in dry *n*-pentanol in the presence of a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at reflux under N_2. The IR spectrum of **4** showed 3291 (N–H) and 3058 (Ar–H) vibrations. Disappearance of the C≡N stretching vibration in the IR spectra of **3** suggested formation of **4**. IR spectra of **4** and **5**–**7** were very similar, except for ν(NH) of the inner Pc core in the metal-free molecule. These protons were very well characterized by the ^{1}H-NMR spectrum which shows a peak at −5.38 ppm, as a result of the 18 π-electron system of the Pc ring. The ^{1}H-NMR spectrum of **4** indicated characteristic aromatic protons at 7.72–7.64 (m, 16H, Ar–H), 7.38–7.31 (m, 12H, Ar–H), and 7.16–7.09 (m, 12H, Ar–H), and aliphatic protons at 4.23 (m, 16H, CH_2–O) and 3.95 (m, 16H, CH_2–O) ppm. The mass spectrum of **4**, which showed a peak at $m/z = 1436$ $[M+H]^+$, supported the proposed formula for this compound.

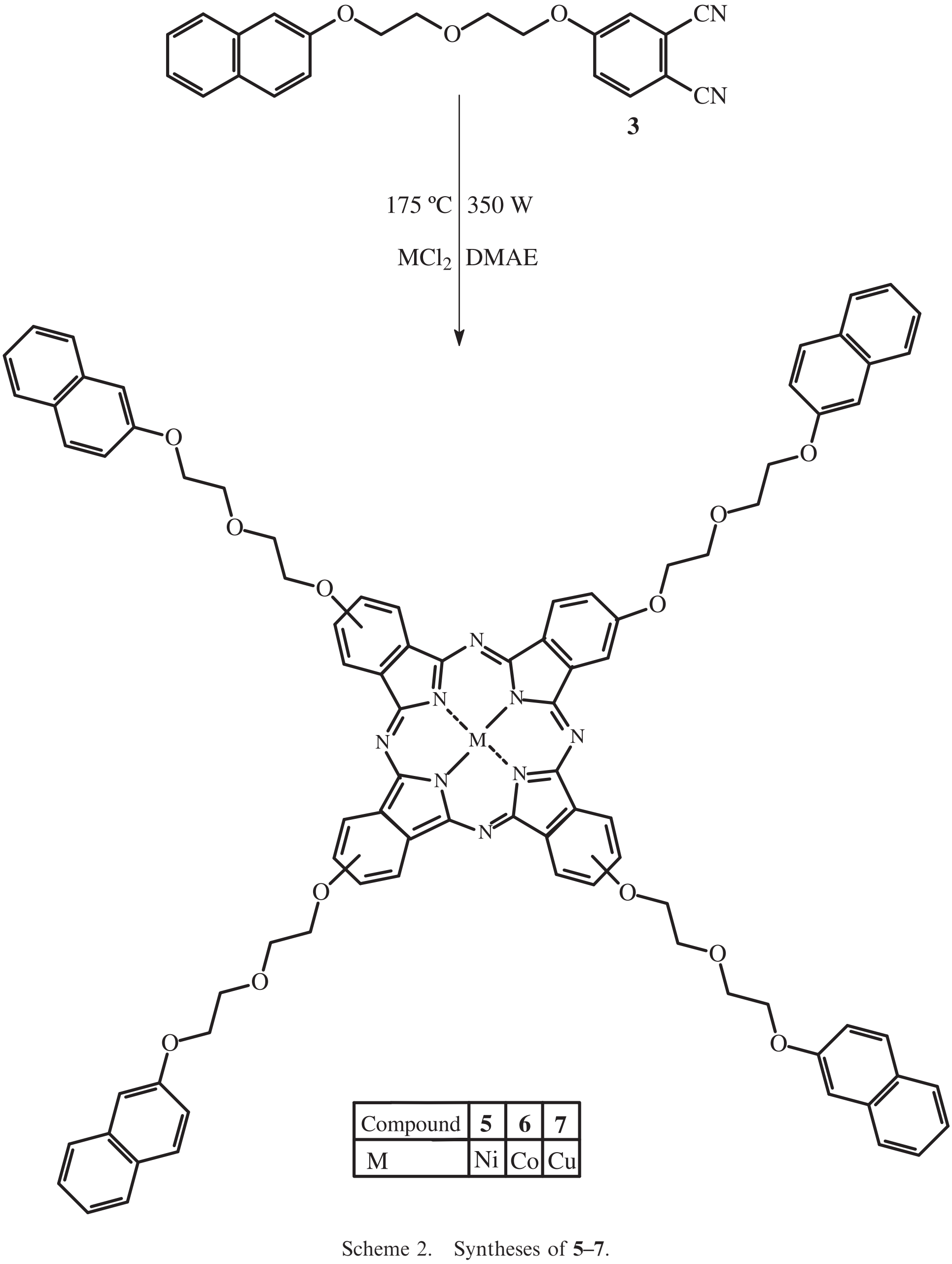
Metallophthalocyanines **5**, **6**, and **7** were synthesized in moderate yield 48%, 37%, and 33%, respectively. The metallophthalocyanines **5**, **6**, and **7** were obtained from dinitrile derivative **3** and the corresponding anhydrous metal salts $NiCl_2$, $CoCl_2$, and $CuCl_2$, respectively, by microwave irradiation in 2-(dimethylamino)ethanol for 8, 7, and 8 min, respectively. In the IR spectra of the metallophthalocyanines **5**, **6**, and **7**, the disappearance of the strong C≡N stretch of **3** was evidence for the formation of **5**, **6**, and **7**. The rest of the IR spectra of the metallophthalocyanines were very similar to those of **4**. The ^{1}H-NMR spectrum of **5** was almost identical to that of **4**. ^{1}H-NMR measurements of the cobalt(II) and copper(II) Pcs**6** and **7** were precluded due to their paramagnetism. In the mass spectra of **5**, **6**, and **7**, the presence of molecular ions at $m/z = 1493$ $[M+H]^+$, 1493 $[M+H]^+$, and 1520 $[M+Na]^+$, respectively, confirmed the proposed structures.

In general, Pcs show electronic spectra with two strong absorptions, one at 300–500 nm related to the B band and the other at 600–800 nm related to the Q band [39]. The split Q bands in **4**, characteristic for metal-free Pcs, were observed at $\lambda_{max} = 704$ and 667 nm (figure 1). These Q band absorptions point to monomeric species with D_{2h} symmetry and to the Pc related to the fully conjugated 18 π-electron system [40–42]. The presence of strong absorption bands in **4** in the near UV region at $\lambda_{max} = 328$ nm also showed Soret region B bands which have been ascribed to the deeper π–π* levels of LUMO transitions.

The UV-Vis absorption spectra of **5**, **6**, and **7** in chloroform (figure 1) showed intense Q absorption at $\lambda_{max} = 674$, 677, and 681 nm, with weaker absorptions at 610, 613, and 614 nm, respectively. The single Q bands in **5**, **6**, and **7** are typical of metal complexes of substituted and unsubstituted metallophthalocyanines with D_{4h} symmetry [43]. Soret region B band absorptions of **5**, **6**, and **7** were observed at $\lambda_{max} = 328$, 328, and 327 nm.



Scheme 1. Synthesis of **4**.



Compound	**5**	**6**	**7**
M	Ni	Co	Cu

Scheme 2. Syntheses of **5**–**7**.

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes, depending on the concentration, nature of the solvent, nature of the substituents, complexed metal ions, and temperature [44–46]. Hence, aggregations of **4**–**7** were investigated in chloroform, THF, and DMSO (figure 2 for **5** as an example; the other spectra are provided in ‘‘Supplementary material’’ section). Complex **4** did not show any aggregation in chloroform and THF

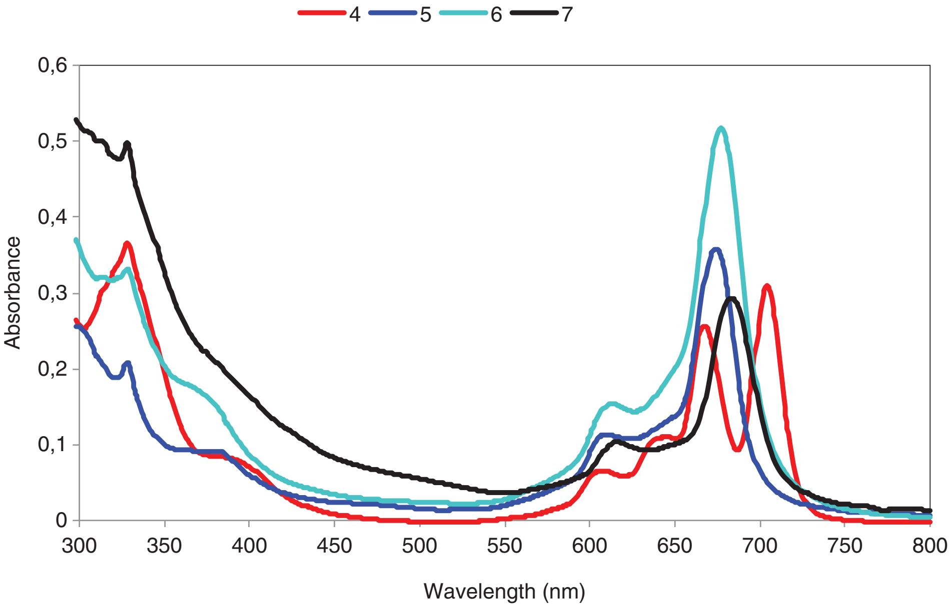


Figure 1. UV-Vis spectra of **4–7** in $CHCl_3$.

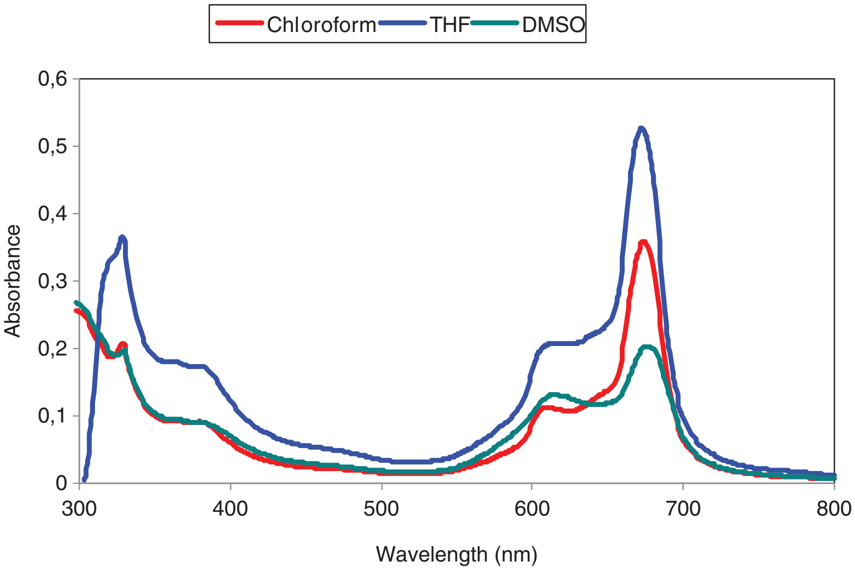


Figure 2. UV-Vis spectra of **5** in different solvents (concentration $= 10 \times 10^{-6}$ mol dm^{-3}).

but showed some in DMSO. Nickel(II) Pc **5** did not show any aggregation in chloroform but showed aggregation in THF and DMSO. Complex **6** did not show aggregation in chloroform but some in THF and DMSO. Copper(II) Pc **7** did not show any aggregation.

The aggregation behaviors of **4**–**6** were also investigated at different concentrations in chloroform. In chloroform, as the concentration was increased, intensity of absorbance of the Q band increased and there were no new bands (normally blue shifted) due to the aggregated species for any complex ("Supplementary material" section). The Beer–Lambert law was obeyed for all the compounds from 14×10^{-6} to $6 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}$.

4. Conclusion

This work has described the synthesis, characterization, and aggregation of tetra-(2-[2-(2-naphthyloxy)ethoxy]ethoxy) substituted metal-free and metallophthalocyanines. Solvent effect (chloroform, DMSO, and THF) on the aggregation of these tetra-substituted Pcs was determined. While **4** was monomeric in chloroform and THF, nickel(II) **5** and cobalt(II) **6** were only in chloroform. Complex **7** was monomeric in chloroform, DMSO, and THF. Complex **4** showed a little aggregation in DMSO, while **5** and **6** showed a little aggregation in THF and DMSO. We also studied aggregation behaviors of these new Pcs in different concentrations in chloroform. No aggregation was observed in chloroform for concentrations between 14×10^{-6} and $6 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}$. When we compared the results of this study with previous studies containing 4-(4-phenoxy-phenoxy) [47], (dihexylmalonate) [48], (phenyl, methyl, nitro, chloro-[1,3,4]) [49] groups in peripheral positions, long ethoxy groups extend the solubility of Pcs [50] compared to previous studies [51]. This tetra-substituted study has solubility advantages compared to other Pcs [52].

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