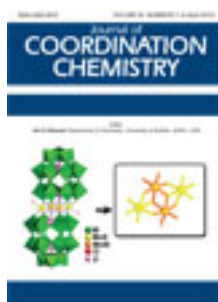


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Novel non-aggregated soluble metallophthalocyanines bearing carboxylic acid groups

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Synthesis and characterization of zinc and cobalt phthalocyanines substituted with biphenylmethylpropionic acids, methyl-*o*-tolylpropionic acids, and methyl-*p*-tolylpropionic acids are described in this study. The new compounds have been characterized by elemental analyses, FT-IR, UV-Vis, MALDI-TOF, and ¹H NMR spectroscopy. All new compounds are soluble in THF, DMF, DMSO, and dilute sodium hydroxide solution. The influence of the carboxylic acid and bulky biphenyl, ortho-methylbenzyl and para-methylbenzyl groups on the spectroscopic properties has been investigated. UV-Vis experiments suggest that the tendency of phthalocyanines to aggregate in polar solvents is significantly reduced owing to the carboxylic acid groups and bulky peripheral substituents.

Keywords: Phthalocyanine; Carboxylic acid; Hydrolysis; Absorption; Aggregation; Polar solvent

1. Introduction

Water solubility is a necessity in many fields, especially in biological and medical applications such as photodynamic therapy. Another application that is acquiring major interest is catalysis of reactions in aqueous media [1]. Water-soluble phthalocyanines (Pcs) are used widely as textile dyes and aggregation has significant effects on the light fastness and color quality of the dyestuff. Zinc phthalocyanines, and several other metallophthalocyanines, have been used as photosensitizing agents in photodynamic therapy at both cellular and animal levels [2–6]. Derivatization of the phthalocyanine ring with hydrophilic and bulky moieties enhances their use as photosensitizers in photodynamic cancer therapy. Water-soluble and non-aggregated phthalocyanines are therefore important and potentially useful materials, but the study of these compounds is still in its infancy [7].

The phthalocyanine macrocycle is a hydrophobic structure. Suitable hydrophilic groups in peripheral positions of the phthalocyanine structure can improve the solubility of phthalocyanines, especially in water [8]. The hydrophilic moieties which

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have been incorporated on the periphery of the phthalocyanine ring include sulfonates [9–15], carboxylates [16–18], phosphonates [19, 20], glucose [21, 22], polyoxyethylene [23–25], and quaternized amino groups [26–29]. Another type of water-soluble phthalocyanines contains hydrophilic groups as axial ligands coordinated to the central metal ion [30]. The water solubility of the Pcs strongly depends on its amphiphilicity and the pH of the aqueous medium [31].

The phthalocyanine ring system usually has a strong tendency to aggregate. In Pcs, the Q band arising from π - π^* transitions is dominant. In general, blue shift of the Q band indicates the presence of aggregated species. Several methods have been used to generate non-aggregated phthalocyanines, which include blocking the coplanar association of phthalocyanine rings with octahedral coordination of the complexed metal ion, and peripheral group substitution at the α - and β -positions on the phthalocyanine ring. These include steric crowding close to the point of attachment, flexible-chain substituents with long lengths, capping groups, and dendrimer substituents [32].

As part of our continuing interest in development of solubility and non-aggregation of phthalocyanines, we describe herein the preparation of six new metallophthalocyanines bearing carboxylic acid and biphenyl, ortho-methylbenzyl or para-methylbenzyl substituents. The sterically demanding phthalocyanines with hydrophilic moieties not only enhance the solubility of these macrocycles in polar media, but also prevent their aggregation.

2. Experimental

Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer and electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were performed on a Thermo Finnigan Flash EA 1112 instrument. ^1H NMR spectra were recorded on a Bruker 250 MHz using TMS as internal standard. Mass spectra were measured on a Bruker Daltonics MALDI-TOF mass spectrometer. All starting materials were purchased from major suppliers and used without purification. The homogeneity of the products was tested in each step by TLC. DMF was dried over 4 Å sieves and 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxymethyl)benzene (**2**) [33] was prepared from 1,2-dichloro-4,5-dicyanobenzene (**1**) [34] according to procedures described in the literature. Compounds **3a–c**, **4a–c**, and **5a–c** were obtained according to published procedures [35, 36].

2.1. General procedure for metallophthalocyanines (6a–c, 7a–c)

To a flask charged with anhydrous ethanol (10 mL) under nitrogen, sodium wire (46 equiv) was added under stirring. After the sodium was completely dissolved, **4a–c**, **5a–c** (0.100 g, 1 equiv) were added under N_2 . The reaction mixture was heated at reflux under N_2 for 24 h and then allowed to cool. The solvent was removed in *vacuum* and the residue was dissolved in water. Trace of undissolved particles were filtered off. When the water layer was acidified with 0.1 mol L⁻¹ aqueous HCl solution, a dark blue/green

product precipitated, was filtered, washed first water and then acetone, and dried in *vacuum*.

2.1.1. 2,9,16,23-tetra(carboxybiphenylmethyl)-3,10,17,24-tetrachloro-phthalocyaninato cobalt(II). (6a) 55 mg, 69%. IR, γ_{\max} (cm^{-1}): 2950–3400 (OH, acidic), 1710 (C=O, acid). MALDI-TOF-MS: 1606.82 $[\text{M}]^+$, 1563.35 $[\text{M}-\text{COOH}+2\text{H}]^+$. Calcd for $\text{C}_{92}\text{H}_{60}\text{Cl}_4\text{N}_8\text{O}_8\text{Co}$ (%): C, 68.79; H, 3.77; N, 6.98. Found (%): C, 68.84; H, 3.81; N, 6.91.

2.1.2. 2,9,16,23-tetra(carboxy-*o*-methylbenzyl)-3,10,17,24-tetrachloro-phthalocyaninato cobalt(II). (6b) 48 mg, 62%. IR, γ_{\max} (cm^{-1}): 2950–3400 (OH, acidic), 1709 (C=O, acid). MALDI-TOF-MS: 1358.22 $[\text{M}]^+$, 1312.73 $[\text{M}-\text{COOH}+\text{H}]^+$. Calcd for $\text{C}_{72}\text{H}_{52}\text{Cl}_4\text{N}_8\text{O}_8\text{Co}$ (%): C, 63.68; H, 3.86; N, 8.25. Found (%): C, 63.76; H, 3.73; N, 8.31.

2.1.3. 2,9,16,23-tetra(carboxy-*p*-methylbenzyl)-3,10,17,24-tetrachloro-phthalocyaninato cobalt(II). (6c) 0 mg, 65%. IR, γ_{\max} (cm^{-1}): 2950–3400 (OH, acidic), 1706 (C=O, acid). MALDI-TOF-MS: 1357.95 $[\text{M}]^+$, 1312.34 $[\text{M}-\text{COOH}+\text{H}]^+$. Calcd for $\text{C}_{72}\text{H}_{52}\text{Cl}_4\text{N}_8\text{O}_8\text{Co}$ (%): C, 63.68; H, 3.86; N, 8.25. Found (%): C, 63.76; H, 3.73; N, 8.31.

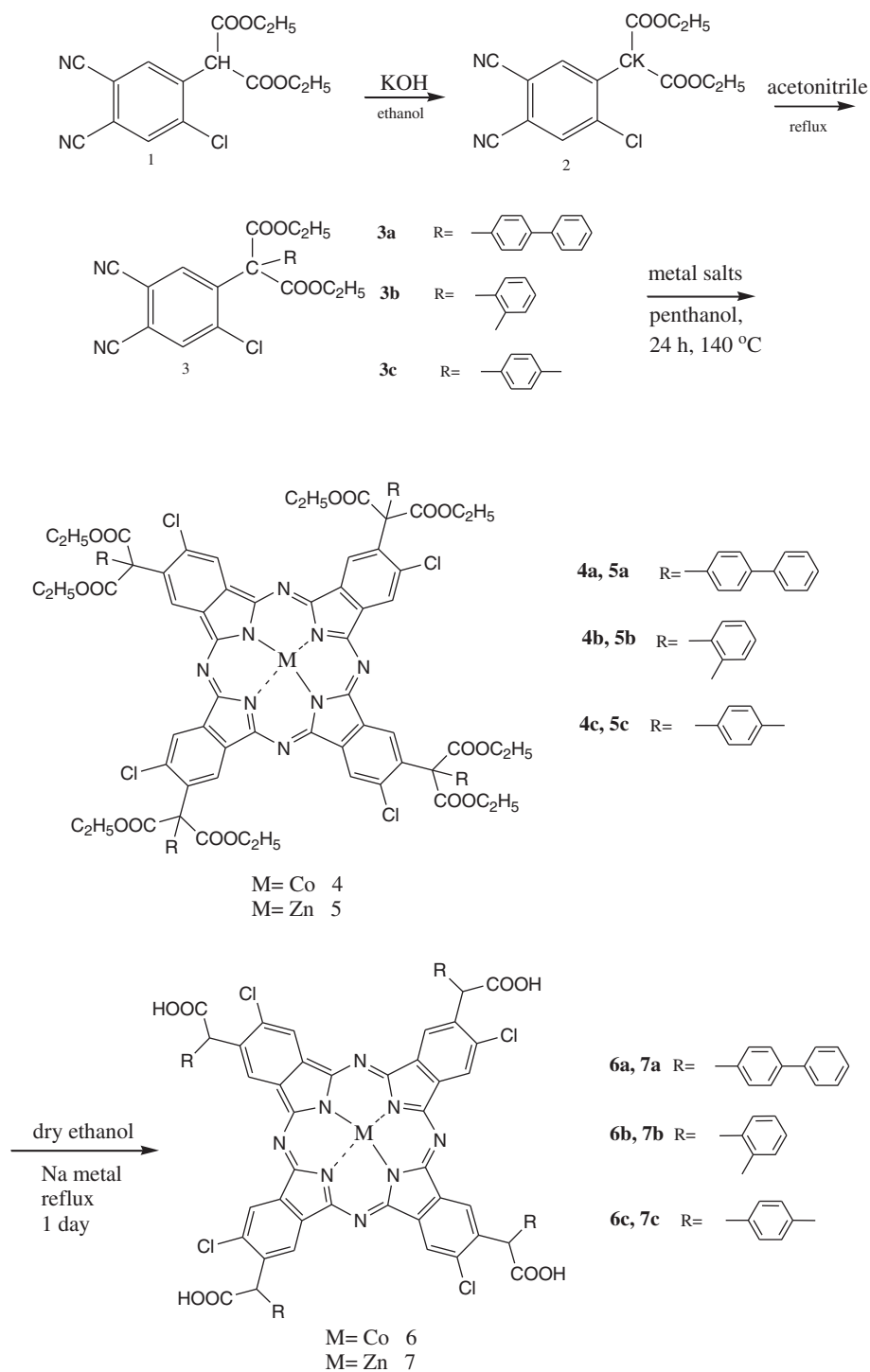
2.1.4. 2,9,16,23-tetra(carboxybiphenylmethyl)-3,10,17,24-tetrachloro-phthalocyaninato zinc(II). (7a) 151 mg, 64%. IR, γ_{\max} (cm^{-1}): 2950–3400 (OH, acidic), 1711 (C=O, acid). ^1H NMR (CDCl_3) δ : 10.26 (br, OH), 7.99–7.32 (m, 44 H, Ar-H), 4.72 (s, 4 H, CH), 3.29 (s, 8 H, CH_2). MALDI-TOF-MS: 1614.28 $[\text{M}+\text{H}]^+$. Calcd for $\text{C}_{92}\text{H}_{60}\text{Cl}_4\text{N}_8\text{O}_8\text{Zn}$ (%): C, 68.52; H, 3.75; N, 6.95. Found (%): C, 68.59; H, 3.82; N, 6.86.

2.1.5. 2,9,16,23-tetra(carboxy-*o*-methylbenzyl)-3,10,17,24-tetrachloro-phthalocyaninato zinc(II). (7b) 51 mg, 66%. IR, γ_{\max} (cm^{-1}): 2950–3400 (OH, acidic), 1708 (C=O, acid). ^1H NMR (CDCl_3) δ : 10.14 (br, OH), 7.98–7.01 (m, 24 H, Ar-H), 5.13–4.54 (br, 4H, CH), 3.95–3.63 (br, 8H, CH_2), 2.03–2.06 (br, 12H, CH_3). MALDI-TOF-MS: 1365.28 $[\text{M}]^+$. Calcd for $\text{C}_{72}\text{H}_{52}\text{Cl}_4\text{N}_8\text{O}_8\text{Zn}$ (%): C, 63.38; H, 3.84; N, 8.21. Found (%): C, 63.44; H, 3.76; N, 8.29.

2.1.6. 2,9,16,23-tetra(carboxy-*p*-methylbenzyl)-3,10,17,24-tetrachloro-phthalocyaninato zinc(II). (7c) 49 mg, 63%. IR, γ_{\max} (cm^{-1}): 2950–3400 (OH, acidic), 1711 (C=O, acid). ^1H NMR (CDCl_3) δ : 10.12 (br, OH), 9.51–7.01 (m, 24H, Ar-H), 5.07–4.40 (br, 4H, CH), 3.83–3.10 (br, 8H, CH_2), 2.30–2.21 (br, 12H, CH_3). MALDI-TOF-MS: 1365.01 $[\text{M}]^+$, 1320.91 $[\text{M}-\text{COOH}]^+$. Calcd for $\text{C}_{72}\text{H}_{52}\text{Cl}_4\text{N}_8\text{O}_8\text{Zn}$ (%): C, 63.38; H, 3.84; N, 8.21. Found (%): C, 63.45; H, 3.77; N, 8.27.

3. Results and discussion

In scheme 1, phthalocyanines (6a–c, 7a–c) were synthesized under the same conditions (reflux, anhydrous ethanol as solvent, sodium wire) and can reach higher yield and purity through a simple dissolving-precipitation method. During these conditions,

Scheme 1. Synthetic pathway to **6a-c** and **7a-c**.

a decarboxylation reaction also occurred [33, 37], thus the desired phthalocyanines were obtained with four carboxylic acid groups on the periphery.

The phthalocyanines (**6a–c**, **7a–c**) were analyzed by elemental analysis, IR, ^1H NMR, and mass spectrometry (MS). The analytical data for all compounds were in agreement with the proposed structures. In the ^1H NMR spectrum of **7a**, the carboxylic acid protons (COOH) appear as a broad peak at δ 10.26 ppm, the aromatic protons as a multiplet at δ 7.99–7.32 ppm, CH protons as a singlet at δ 4.72 ppm, and CH_2 protons as a singlet at δ 3.29 ppm. The ^1H NMR spectrum of **7b** showed the carboxylic acid protons (COOH) as a broad peak at δ 10.14 ppm, the aromatic protons as a multiplet at δ 7.98–7.01 ppm, CH protons as a broad peak at δ 5.13–4.54 ppm, CH_2 protons as a broad peak at δ 3.95–3.63 ppm, and the CH_3 protons as a broad peak at δ 2.03–2.06 ppm. The COOH protons for **7c** were observed as a broad peak at δ 10.12 ppm, the aromatic protons as a multiplet at δ 9.51–7.01 ppm, CH protons as a broad peak at δ 5.07–4.40 ppm, CH_2 protons as a broad peak at δ 3.83–3.10 ppm, and CH_3 protons as a broad peak at δ 2.30–2.21 ppm. The ^1H NMR spectra of the phthalocyanines are rather broad, owing probably to aggregation of the phthalocyanines which is frequently encountered at the concentrations used for NMR spectroscopy.

FT-IR spectra of **6a–c** and **7a–c** are provided in “Supplementary material.” Peaks around $1708\text{--}1711\text{ cm}^{-1}$ indicate the presence of $\text{C}=\text{O}$ groups, and the band at $2950\text{--}3400\text{ cm}^{-1}$ corresponds to OH of the COOH groups, respectively.

Elucidation of zinc phthalocyanines by proton spectra was possible as all signals of the various parts of the substituents, especially carboxylic acid protons around 10 ppm, appeared in specific regions. Structural clarification of zinc and cobalt phthalocyanines has also been realized using MS. MALDI-TOF-MS spectra gave clear evidence with the observed signals that could be explicitly ascribed to the ion mass peaks and fragment ions corresponding to the loss of carboxylic acid groups of phthalocyanines (**6a–c**, **7a–c**). Figure 1 shows that **6c** has the molecular ion peak $[\text{M}]^+$ at 1357.95 and fragment ion $[\text{M}-\text{COOH}+\text{H}]^+$ at 1312.34.

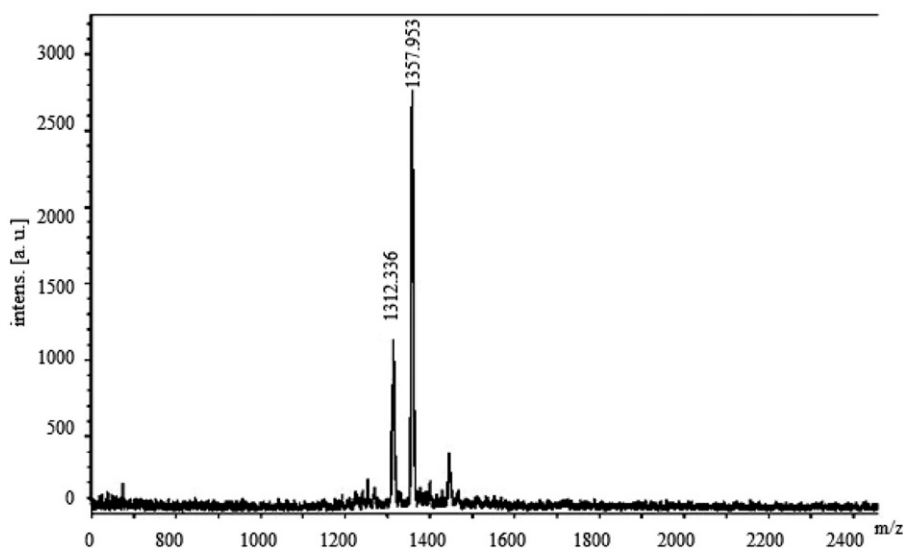


Figure 1. MALDI-TOF-MS spectrum of **6c**.

Cobalt and zinc phthalocyanines (**6a–c**, **7a–c**) were soluble only in THF, DMSO, and DMF. All products can also be dissolved in dilute sodium hydroxide solution because the dissociated carboxyl groups on the phthalocyanine rings increase the repulsion force and reduce the aggregation of phthalocyanine molecules, so improving the solubility of the complexes. As shown in figure 2, the absorption spectrum of **7c** showed the sharp Q band at 684 nm with a shoulder on the higher energy side at 636 nm. The intensities of the peaks at 684 nm and 636 nm increase with increasing concentration.

Products are soluble in THF, which is thought to be due to substitution of the functional groups (biphenyl, ortho-methylbenzyl, and para-methylbenzyl) on the phthalocyanine ring to enhance solubility.

The strongest absorption of M-Pcs in the visible region, the so-called Q band, can be attributed to the allowed highest occupied molecular orbital – lowest unoccupied molecular orbital ($\pi-\pi^*$) transition. Three cobalt and three zinc phthalocyanines were dissolved in THF and their electronic spectra evaluated (table 1). The Q band absorptions of zinc phthalocyanines move to longer wavelength by 6–10 nm in comparison with the cobalt phthalocyanines (table 1). The Q band shifts depend upon the change in electron distribution in the phthalocyanine ring caused by the substituents and their positions. Although the effect of the central metal on the energy of the Q band is usually small [38, 39], absorption maxima of **7a–c** are moved to longer wavelengths, and apparently increase with the ionic radius of the central metal.

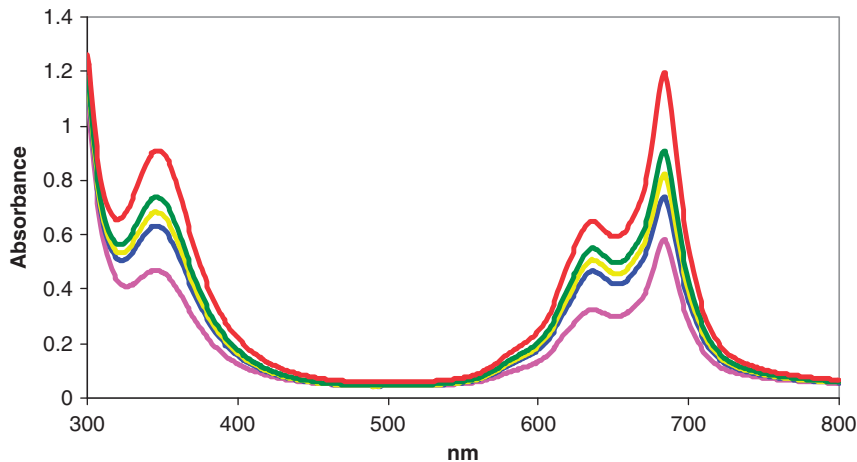


Figure 2. UV-Vis spectra of **7c** ($2.65 \times 10^{-5} \text{ mol dm}^{-3}$) (red line), ($2.39 \times 10^{-5} \text{ mol dm}^{-3}$) (green line), ($2.12 \times 10^{-5} \text{ mol dm}^{-3}$) (yellow line), ($1.86 \times 10^{-5} \text{ mol dm}^{-3}$) (blue line), ($1.32 \times 10^{-5} \text{ mol dm}^{-3}$) (pink line) in NaOH solution.

Table 1. B and Q band absorption data of **6a–c** and **7a–c** in THF.

λ_{max} (nm)	6a	7a	6b	7b	6c	7c
B-band	335	353	336	351	338	352
Q-band	667	677	670	676	669	676

The absorption spectra of **6a–c** and **7a–c** are typical of spectra due to monomeric phthalocyanines in DMF. The molar absorptivity of the Q-band around 670 nm for CoPcs and around 685 nm for ZnPcs remained essentially unchanged over a wide concentration range (2.0×10^{-6} – 1.0×10^{-5} mol dm⁻³), indicating that all phthalocyanines are relatively free from molecular aggregation under these conditions (figure 3a–c). The non-aggregated nature of metallophthalocyanines can be ascribed to the steric hindrance of the bulky biphenyl, ortho-methylbenzyl, and para-methylbenzyl moieties. This property is particularly important for photosensitizing applications.

The UV-Vis spectra of **6a–c** and **7a–c** in THF and DMF were typical for non-aggregated phthalocyanines. In the presence of NaOH, these compounds were also soluble in water giving similar spectral properties. As shown in figure 4, the absorption spectrum of **7c** shows the Q bands at 684 nm with high intensity and 636 nm with low intensity, indicating the presence of both monomeric and aggregated species, respectively. The intensities of the peaks at 684 nm and 636 nm decrease with lowering the pH of the solution. Under acidic conditions (pH = 2.4–3.7), the spectrum shows two broad maxima in the Q band range, indicating the presence of both monomeric and dimeric species. Phthalocyanines are usually highly aggregated in aqueous media due to the strong hydrophobic interactions. The low aggregated nature of **7c** (in the deprotonated form) can be ascribed to inherent repulsion of the negatively charged molecules and bulky substituents.

4. Conclusion

We have presented the syntheses of zinc and cobalt phthalocyanines (**6a–c** and **7a–c**) bearing carboxylic acid and bulky biphenylmethyl, *o*-methylbenzyl, *p*-methylbenzyl, and chlorides. Hydrolysis of the ester groups of phthalocyanine precursors (**4a–c** and **5a–c**) was accomplished in dry ethanol with sodium wire and under these conditions decarboxylation occurred, hence phthalocyanines having four carboxylic acid groups were obtained in good yields. All structures have been identified by elemental analysis, IR, ¹H NMR, and MS techniques. Owing to the presence of the carboxylic acid groups, all phthalocyanines are soluble in both common polar organic solvents and aqueous media. UV-Vis absorption spectra at concentrations ranging from 1.0×10^{-6} to 1.0×10^{-5} mol dm⁻³ in DMF indicated that steric isolation of the phthalocyanine macrocycles by bulky peripheral substituents is effective as shown by no Q band blue shift. Experiments conducted in aqueous medium show that steric isolation of the macrocycle by bulky peripheral substituents is relatively effective in polar protic solvents as shown by two Q-bands; the one on the lower energy side with significantly higher intensity corresponds to the monomer and the other blue shifted with lower intensity to the dimer. The reason for choosing this class of Pcs is that the bulky and ionic peripheral substituents on the Pcs core enhance solubility in organic and aqueous media and control the aggregation behavior. There are several water-soluble or non-aggregated phthalocyanines, but hydrophilic and non-aggregated phthalocyanines are extremely rare despite their great potential in photodynamic therapy and other photosensitizing applications.

In this study, carboxylic acid substituents enhance the solubility of phthalocyanines in polar media and bulky alkylbiphenyl and alkylbenzyl units prevent aggregation.

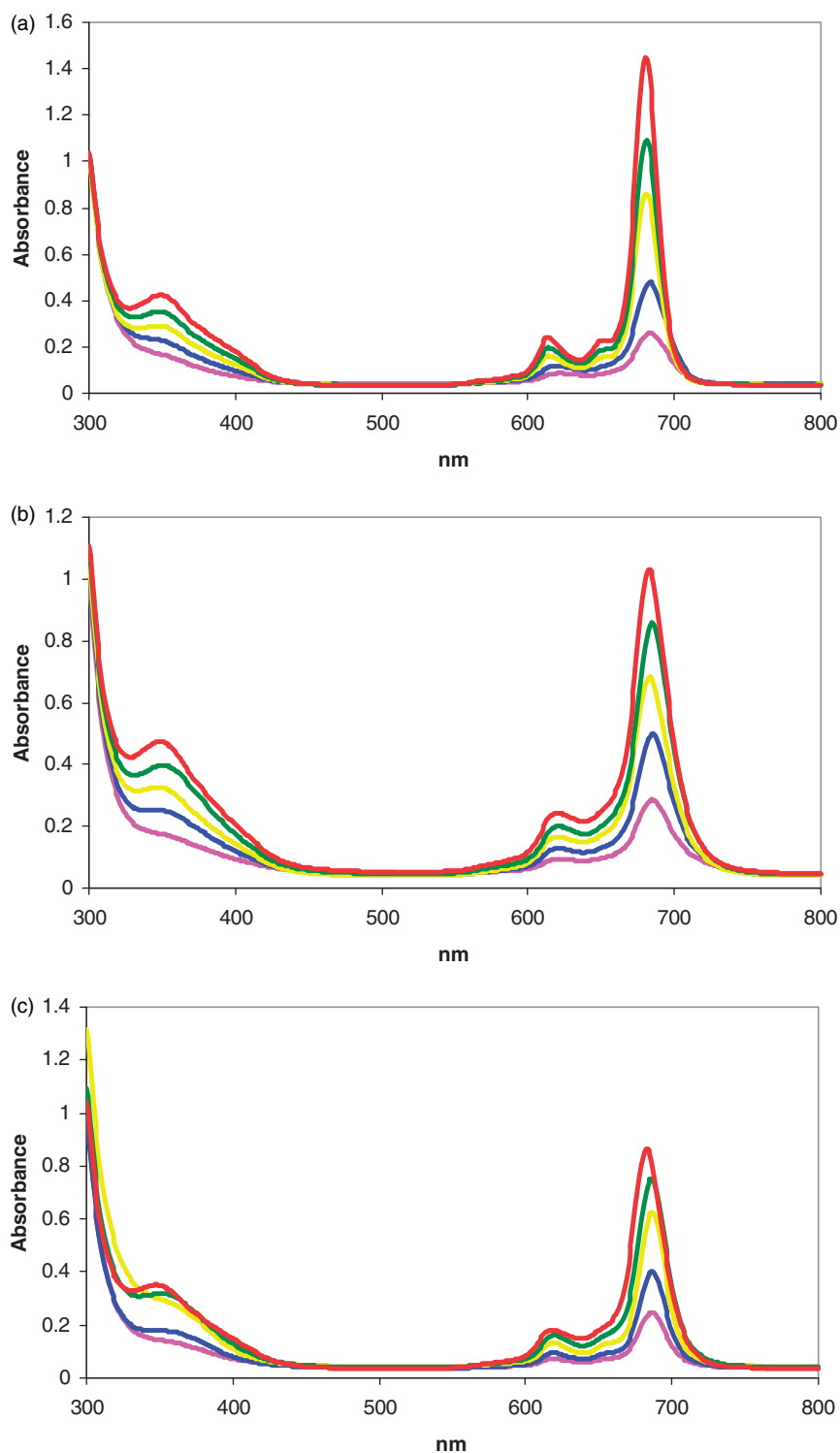


Figure 3. (a) UV-Vis spectra of **7a** (1×10^{-5} mol dm⁻³) (red line), (8×10^{-6} mol dm⁻³) (green line), (6×10^{-6} mol dm⁻³) (yellow line), (4×10^{-6} mol dm⁻³) (blue line), (2×10^{-6} mol dm⁻³) (pink line) in DMF. (b) UV-Vis spectra of **7b** (1×10^{-5} mol dm⁻³) (red line), (8×10^{-6} mol dm⁻³) (green line), (6×10^{-6} mol dm⁻³) (yellow line), (4×10^{-6} mol dm⁻³) (blue line), (2×10^{-6} mol dm⁻³) (pink line) in DMF. (c) UV-Vis spectra of **7c** (1×10^{-5} mol dm⁻³) (red line), (8×10^{-6} mol dm⁻³) (green line), (6×10^{-6} mol dm⁻³) (yellow line), (4×10^{-6} mol dm⁻³) (blue line), (2×10^{-6} mol dm⁻³) (pink line) in DMF.

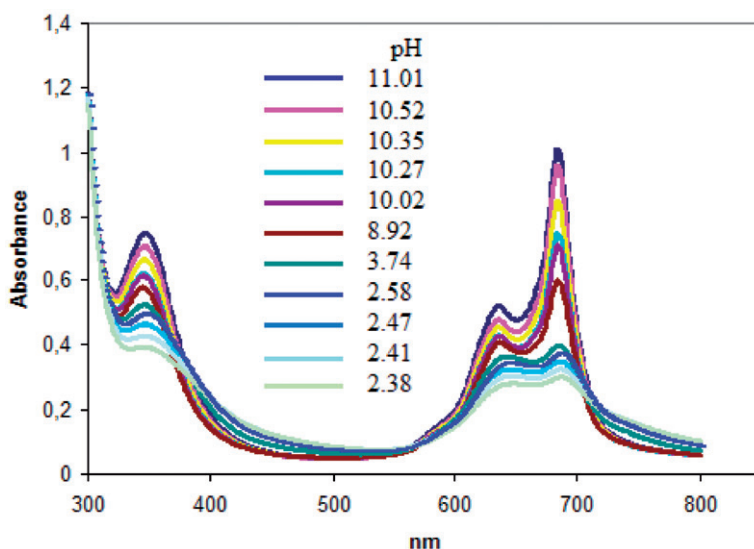


Figure 4. Changes in the UV-Vis spectra of **7c** in aqueous solution with respect to pH.

Thus we achieve soluble and non-aggregated phthalocyanine derivatives in polar media which is particularly important for photosensitizing applications. Preparation of asymmetric phthalocyanines carrying carboxylic acid function and bulky groups is currently underway.

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