Synthesis and Photophysical Properties of Novel Unsymmetrical Metal-free and Metallophthalocyanines

İbrahim Özçeşmeci, Ayfer Kalkan Burat, Zehra Altuntaş Bayır

PII: S0022-328X(13)00801-2
DOI: 10.1016/j.jorganchem.2013.11.004
Reference: JOM 18348

To appear in: *Journal of Organometallic Chemistry*

Received Date: 25 July 2013
Revised Date: 4 October 2013
Accepted Date: 5 November 2013

Please cite this article as: İ. Özçeşmeci, A.K. Burat, Z.A. Bayır, Synthesis and Photophysical Properties of Novel Unsymmetrical Metal-free and Metallophthalocyanines, *Journal of Organometallic Chemistry* (2013), doi: 10.1016/j.jorganchem.2013.11.004.

Graphical abstract Synopsis

Synthesis and Photophysical Properties of a Novel Unsymmetrical, Metal-free and Metallophthalocyanines

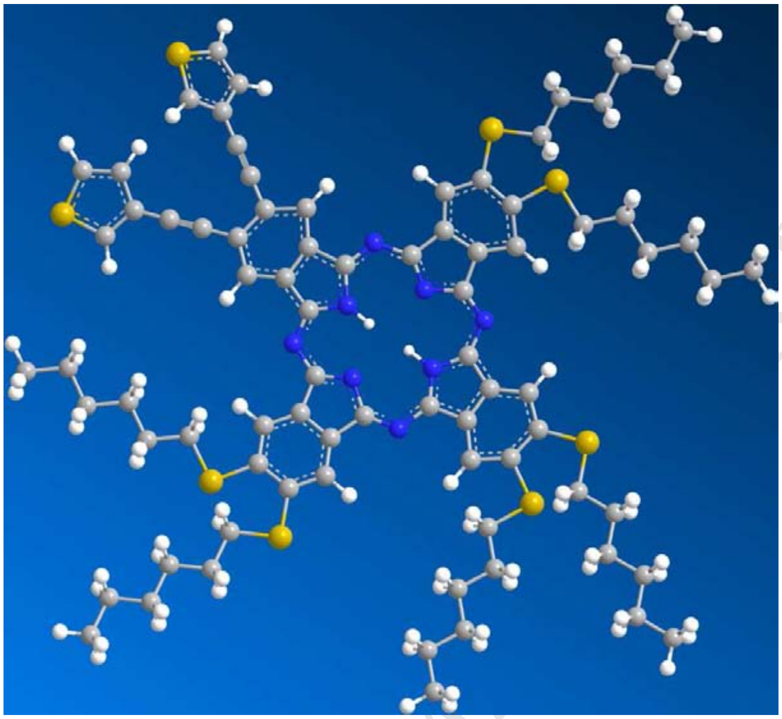
İbrahim Özçeşmeci, Ayfer Kalkan Burat and Zehra Altuntaş Bayır*

Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

Graphical Abstract

Novel, unsymmetrical, octasubstituted phthalocyanines bearing two ethynylthiophene moieties and six hexylthio substituents have been prepared and characterized. The aggregation properties of these compounds were investigated. General trends for fluorescence quantum yields and lifetimes of these phthalocyanines are also described. The fluorescence of these compounds is effectively quenched by 1,4-benzoquinone.

Graphical abstract



Synthesis and Photophysical Properties of Novel Unsymmetrical Metal-free and Metallophthalocyanines

İbrahim Özçeşmeci, Ayfer Kalkan Burat and Zehra Altuntaş Bayır*

**Istanbul Technical University, Faculty of Science and Letters, Department of Chemistry, 34469 Maslak, Istanbul, Turkey*

Abstract

The synthesis of novel, unsymmetrical, octasubstituted metal-free and metallo phthalocyanines (zinc, manganese) bearing two ethynylthiophene moieties and six hexylthio substituents was achieved by a statistical condensation reaction of 4,5-di(hexylthio) phthalonitrile with 4,5-bis(thiophen-3-ylethynyl)phthalonitrile in the presence of zinc and manganese salts (without metal salt for metal-free phthlocyanine). 4,5-Bis(thiophen-3-ylethynyl)phthalonitrile was obtained through Sonogashira coupling reaction. The new compounds have been characterized by using elemental analyses, mass, proton nuclear magnetic resonance (^{1}H-NMR), fourier transform infrared spectroscopy (FT-IR) and ultraviolet–visible spectroscopy (UV-vis) techniques. The aggregation properties of the compounds were investigated in different concentrations in tetrahydrofuran before and after addition of surfactant Triton X-100. General trends for fluorescence quantum yields and lifetimes of unsymmetrical phthalocyanines (metal-free and zinc) are also described in tetrahydrofuran (THF). The fluorescence of these compounds is effectively quenched by 1,4-benzoquinone (BQ) in THF.

Keywords: Ethynylthiophene, manganese, phthalocyanine, Sonogashira-coupling, unsymmetric, fluorescence.

---

*Corresponding author:Tel: +90 212 285 32 23; fax: +90 212 285 63 86.

*E-mail address:*bayir@ itu.edu.tr (Z. A. Bayır)

1. Introduction

Phthalocyanines (Pcs) are an important class of organic materials. They have a conjugated system of π-electrons and exhibit the ability to chelate metal ions at the center of the ring [1-3]. Since their accidental discovery phthalocyanines have been used extensively as dyes and pigments in indusrty due to their blue-green color [4, 5]. Phthalocyanines have found widespread industrial and medical applications, namely, chemical sensors, display devices, catalysts, data storage systems, and photosensitizers for photodynamic therapy (PDT) [6-14].

Despite the variety of synthetic routes developed to prepare symmetrcally substituted phthalocyanines, relatively few methods can be applied for preparing unsymmetrical phthalocyanines [15]. More recently, particular attention has been paid to the development of unsymmetrical phthalocyanines. This is because such phthalocyanines possess a number of unique physicochemical properties and improved organization capabilities, which render these compounds valuable applications in materials science, in particular in photodynamic therapy and non-linear optics for optical limiting applications [8, 16, 17].

The random condensation of two differently substituted phthalonitriles A and B is the most frequent method of the synthesis of unsymmetrical phthalocyanines. Although this method has been widely used for the synthesis of A_3B-type Pcs, it is often laborious, due to difficulty in separating similar chemical structures [18]. The second method is ring expansion of subphthalocyanines (SubPcs) developed by Kobayashi [19,20]. SubPcs are commonly used to form the unsymmetrically substituted phthalocyanines by ring expansion employing substituted phthalonitriles or diiminoisoindolines [21]. Good yields were obtained when the SubPc was treated with phthalonitriles or diiminoisoindolinesin the presence of a strong base, such as DBU, and a metal salt [22]. The last method is a polymer-support route in which one of the Pc precursors is covalently attached to a polymer support prior to the synthesis of phthalocyanine [23]. Following the synthesis of macrocycle, the polymer-bound Pc is obtained by filtration and the bond to the polymer is cleaved to yield pure 3:1 unsymmetrically substituted phthalocyanines. However, this method has not seen widespread application and only a few examples have been reported to date.

We have previously reported the synthesis of different unsymmetrical pthalocyanines bearing phenylethynyl [24], and morpholine groups [25] as peripheral substituents. In this regard, we report herein the synthesis of A_3B type unsymmetrically substituted metal-free (**3**) and metallophthalocyanines (**4**, **5**) carrying six hexylthio and two ethynylthiophene substituents on the periphery. We also report spectroscopic characterization, aggregation behavior as well as photophysical (fluorescence quantum yields and lifetimes) and quenching properties of novel unsymmetrical, octasubstituted phthalocyanines complexes.

2. Experimental

All chemicals and reagents were purchased from major suppliers and used without any further purification. All reported ^{1}H NMR spectra were recorded on an Agilent VNMRS 500 MHz spectrometer. Chemical shifts (δ, ppm) were determined with TMS as the internal reference. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer, electronic spectra were recorded on a Scinco LabProPlus UV/Vis spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer. Mass spectra were measured on a Bruker microflex LT MALDI-TOF MS spectrometer and Perkin Elmer Clarus 500 mass spectrometer. The isotopic patterns for all assigned signals are in agreement with the calculated natural abundance. Data have been given for the most abundant isotope only. Silica gel (Kieselgel 60, 200–400 mesh) was used in the separation and purification of compounds by column chromatography. The homogeneity of the products was tested in each step by TLC. 4,5-Di(hexylthio)phthalonitrile

(**1**) [26] and 4,5-bis(thiophen-3-ylethynyl)phthalonitrile (**2**) [27] were prepared according to the reported procedures.

*2.1 2,3,9,10,16,17-Hexakis(hexylthio)-23,24- bis(thiophen-3-ylethynyl)-29H, 31H-phthalocyanine (**3**)*

A mixture of dinitrile **1** (0.486 g, 1.45 mmol), dinitrile **2** (0.102 g, 0.30 mmol) and lithium metal (1.5 mg, 0.5 mmol) in n-pentanol (1.5 mL) was heated at 145 ^{o}C with stirring for 2 h under N_2. The resulting green suspension was cooled to ambient temperature. The reaction mass was then dissolved in dimethylformamide (DMF) (1 mL) and poured into 200 ml ice-water mixture with the addition of 4 mL conc. hydrochloric acid (HCl). In this mixture, the Li_2Pcs formed was converted into H_2Pcs. The precipitate was filtered off and washed with cold methanol and then dried in *vacuo*. The purification was carried out by column chromatography on silica gel using hexane/chloroform ($CHCl_3$) (1:6) as the eluent to afford **3** as a green solid. The yield was 10.53 % (0.045 g). M.p.>200 ^{o}C. IR, (cm^{-1}): 3289 (N-H), 2955-2854 (Aliph.-H), 2206 (C≡C), 1260 (Ar-S-Aliph.), 741; ^{1}H NMR ($CDCl_3$-d_6), δ, ppm: 8.38-7.18 (m, 14H, Ar-H), 3.47-3.01 (m, 12H, S-CH_2), 1.59-1.25 (m, 48H, -CH_2), 0.89 (b, 18H, -CH_3), -5.00 (b, 2H, -NH); UV-Vis (tetrahydrofuran (THF)) : λ_{max}/ nm (log ε, L. mol^{-1} cm^{-1}): 282 (4.88), 327 (4.79), 700 (4.70), 723 (4.69); Anal. calc. for $C_{80}H_{94}N_8S_8$: C, 67.47; H, 6.65; N, 7.87. Found: C, 67.56; H, 6.60; N, 7.82; MS: m/z 1423.15 [M]$^{+}$.

*2.2 2,3,9,10,16,17-Hexakis(hexylthio)-23,24-bis(thiophen-3-ylethynyl)-29H, 31H-phthalocyaninato zinc (II) (**4**)*

A mixture of phthalocyanine (**3**) (0.100 g, 0.07 mmol) and anhydrous zinc(II)acetate ($Zn(CH_3COO)_2$) (0.038 g, 0.21 mmol) in dried DMF (2 mL) was heated at 145 ^{o}C with stirring for 6 h under N_2. The resulting blue suspension was cooled to ambient temperature. The reaction mass was then poured into 100 mL ice-water mixture. The precipitate was filtered off and washed with cold water, ethanol and hexane. After dried in *vacuo*, the purification was carried out by column chromatography on silica gel using hexane/THF (1:4) as the eluent to afford **4** as a blue solid. The yield was 45.31 % (0.047 g). M.p.>200 ^{o}C. IR, (cm^{-1}): 2953-2853 (Aliph.-H), 2206 (C≡C), 1259 (Ar-S-Aliph.), 740; ^{1}H NMR (CDCl$_3$-d$_6$), δ, ppm: 8.35–7.19 (m, 14H, Ar-H), 3.13-2.78 (m, 12H, S-CH$_2$), 1.61-1.18 (m, 48H, -CH$_2$), 0.81 (b, 18H, -CH$_3$); UV-Vis (THF): λ_{max}/ nm (log ε, L. mol^{-1} cm^{-1}): 280 (4.79), 367 (4.90), 705 (5.31); Anal. calc. for $C_{80}H_{92}N_8S_8Zn$C, 64.59; H, 6.23; N, 7.53. Found: C, 64.56; H, 6.21; N, 7.55; MS: m/z 1485.57 [M]$^{+}$.

*2.3 2,3,9,10,16,17-Hexakis(hexylthio)-23,24- bis(thiophen-3-ylethynyl)-29H, 31H-phthalocyaninatomanganese-(III)chloride (**5**)*

A mixture of phthalocyanine (**3**) (0.100 g, 0.07 mmol) and manganese(II) chloride (MnCl$_2$) (0.026 g, 0.21 mmol) in dried DMF (2 mL) was heated at 145 ^{o}C with stirring for 6 h under N$_2$. The resulting brown suspension was cooled to ambient temperature. The reaction mass was then poured into 100 mL ice-water mixture. The precipitate was filtered off and washed with cold water, ethanol and hexane. After dried in *vacuo*, the purification was carried out by column chromatography on silica gel using hexane/THF (1:3) as the eluent to afford **5** as a brown solid. The yield was 38.02 % (0.040 g). M.p.>200 ^{o}C. IR, (cm-1): 2954-2852 (Aliph.-H), 2207(C≡C), 1261 (Ar-S-Aliph.), 741; UV-Vis (THF): λ_{max}/ nm (log ε, L. mol^{-1} cm^{-1}): 293 (5.24), 321 (5.14), 425 (4.90), 470 (4.87), 500 (4.81), 758 (5.13); Anal. calc. for $C_{80}H_{92}ClMnN_8S_8$: C, 63.53; H, 6.13; N, 7.41. Found: C, 63.57; H, 6.16; N, 7.45; MS: m/z 1532.85 [M+Na]$^{+}$, 1477.63 [M-Cl]$^{+}$

3. Results and Discussion

3.1 Synthesis and characterization

There are three approaches for preparing unsymmetrically substituted phthalocyanines: a statistical cyclization reaction of two different types of phthalonitriles [28], a solid-state reaction of two types of phthalonitriles on macromolecular carriers [29] and a ring-expansion treatment of subphthalocyanine with diiminoisoindoline [30,31]. In this work the statistical cyclization approach was used to synthesis of unsymmetrical Pcs. The rationale behind this choice is that both nitriles significantly differ in polarity.

4,5-Di(hexylthio)phthalonitrile (**1**) and 4,5-bis(thiophen-3-ylethynyl)phthalonitrile (**2**) were chosen as starting materials. It is well known that alkythio groups act as electron releasing, enhance the solubility of phthalocyanine in common organic solvents and reduce the aggregation of phthalocyanine. The insertion of alkylthio groups also facilitates the isolation of the desired A_3B product. The presence of ethynylthiophene moieties causes an extended π- conjugation on phthalocyanine complexes. The combination of the sulfur atoms and the alkynyl group influence the electronic spectra of Pcs and cause red shifting of the Q-band. Compound **1** was prepared from 4,5-dichlorophthalonitrile and hexanethiol in DMF at room temperature for 12 h. potassium carbonate (K_2CO_3) was used as the base for this nucleophilic aromatic displacement [26]. The synthesis of nitrile **2** was accomplished in 35% yield through Sonogashira cross-coupling reaction of 4,5-dichlorophthalonitrile with 3-ethynylthiophene in triethylamine using bis(triphenylphosphine)palladium(II)chloride and copper(I)iodide as catalysts [27]. The reaction was carried out 90 ^{o}C under N_2 for 48 h.

The most usual method to prepare metal-free phthalocyanines is the cyclotetramerisation of a phthalonitrile or diiminoisoindoline. A practical way of achieving this goal is the treatment of a phthalonitrile with lithium alkoxide, giving rise to the corresponding alkali metal phthalocyanines and it can be subsequently demetallated to the metal-free phthalocyanine with a mineral acid. In the present work, the latter was chosen for synthesising the A_3B type metal-free phthalocyanine (**3**). The mixed condensation of 4,5-di(hexylthio)phthalonitrile (**1**) with 4,5-bis(thiophen-3-ylethynyl)phthalonitrile (**2**) by using lithium in 1-pentanol, and then acidification with HCl resulted with the formation of **3** (Scheme 1). A 3:1 ratio of the two precursors was used to modify the relative amounts of the individual species, which are present within the reaction mixture [32,33]. The reaction of metal-free phthalocyanine (**3**) with metal salts ($Zn(CH_3COO)_2$, $MnCl_2$) in DMF at 145 °C under N_2 led to the formation of desired unsymmetrical metallophthalocyanines (**4** and **5**), respectively (Scheme 1). All of these new phthalocyanine compounds were purified by column chromatography. They were obtained in moderate yields (11% for **3**, 45.3 % for **4**, and 38% for **5**) and were characterized by elemental analysis and by their spectral data (^1H NMR, IR, mass and UV-Vis spectra). The data are consistent with the assigned structures.

In the IR spectrum of compound **1** (and **2**) the intense absorption band around 2233 cm^{-1} corresponding to C≡N vibrations, disappears after its conversion into the phthalocyanines. The IR spectra of the phthalocyanines **3**-**5** are very similar, except the metal-free (**3**), showing an NH stretching band peak at 3290 cm^{-1} in the inner core. The presence of alkylthio side chains was confirmed by the observation of an intense aliphatic C-H stretching around 2950-2850 cm^{-1} in the IR spectra of **3**-**5**. The C≡C vibration was observed around 2200 cm^{-1}.

The ^1H NMR spectra of compounds **3** and **4** are consistent with the proposed structure. In the ^1H NMR spectrum of metal-free phthalocanine (**3**) in $CDCl_3$ exhibited the aromatic protons at around 8.38-7.18 ppm as multiplet, the aliphatic SCH_2 and $SCCH_2$ protons of hexylthio group at 3.47 and 1.39 ppm as a triplet and a quintet, resectively, and the aliphatic CH_3 protons as a triplet at 0.89 ppm. The inner core protons of free-base phthalocyanine were monitored at around −5.00 ppm. For compound **4**, the aromatic protons of phthalocyanine core appeared at 8.35–7.19 ppm, the SCH_2 and $SCCH_2$ protons at 3.13and 1.61 ppm, respectively, and the CH_3 protons at 0.81 ppm.

The elemental analysis and the mass spectra confirmed our structural assignment. The peaks for the molecular ion were found at m/z= 1423.15 $[M]^+$ for the phthalocyanine **3**

(Figure 1), 1485.57 $[M]^+$ for **4**, m/z= 1532.85 $[M+Na]^+$ and m/z= 1477.63 $[M-Cl]^+$ for **5** (Figure 1), respectively.

3.2 Ground state electronic absorption spectra

In substituted metal-free and MPcs, strong absorption bands are detected in the visible region between the 600 and 700 nm, referred to as the Q band, and in the UV region between 300 and 350 nm, called the B (Soret) band [34-36]. The electronic absorption spectra of **4**, **5** recorded in THF exhibit intense Q bands at 705 (**4**), and 758 nm (**5**) and the B bands in the UV region, around 350 nm. The UV-Vis spectrum of manganese phthalocyanine **5** is clearly different from the spectrum of the zinc phtalocyanine (**4**). The oxidation state of Mn in the complex with Pc is +3, whereas the other metal Zn is in oxidation state +2. The Q band of MnPc (**5**) is shifted by 30-50 nm compared the Q band of the other phthalocyanines **3** and **4**. Furthermore, MnPc **5** shows absorption at 425 nm, 470 nm and 500 nm which was interpreted as a charge transfer absorption (phthalocyanine→metal, LMCT) [37-39]. For the metal-free phthalocyanine **3** in THF, a split Q band observed at 700 nm and 723 nm, while the B-band remained at 350 nm [40]. The UV-Vis spectra of compounds **3-5** in THF are shown in Figure 2. The presence of long hexylthio substituents in phthalocyanines **3**–**5** results in dramatic increase of solubility of these compounds in various common organic solvents compared with their symmetrical analogues which were synthesized in our recent work [27]. The Q bands of these new species are shifted to the blue compared with their symmetrical analogues which were synthesized in our recent work [27]. For the zinc (**4**) and mangenese (**5**) phthalocyanines, the Q-band positions are 705 and 758 nm, respectively. However the Q-band position of symmetrical analogues were observed around 722 nm for zinc and 775 nm for manganese phthalocyanine. Zn (II) (**4**) and Mn (III) (**5**) phthalocyanines have the same blue shifts (17 nm) compared with their symmetrical analogues [27].

When we compare the absorption bands of current phthalocyanines (**1-3**) with unsubstituted metal-free, Zn(II) and Mn(III) phthalocyanines [1], a significant red shift in Q band wavelengths were observed. The Q bands of **1-3** are shifted bathochromically because of the conjugation of the macrocyclic core and the ethynyl linkers [41]. The extension of the aromatic system was found to causes a shift of the Q-band maximum of about 70–80 nm [1, 27]. In our case, the bathochromic shifts of Q bands were observed around 60 nm for **1**, 40 nm for **2** and 50 nm compound **3**.

3.3 Aggregation Studies

Weaker absorptions of Pc’s compound on the lower wavelength side of Q bands indicate the presence of aggregated species which are generally observed together with the main Q bands essentially responsible for the intense absorption occurring due to the monomeric species [42]. When the electronic spectra of the metal-free phthalocyanine (**3**) and its metallo derivatives (**4, 5**) were examined, weak peaks were observed around 620-640 nm just on the higher energy side of the strong Q band. In order to see whether these bands are a consequence of aggregation or not has been investigated by measuring absorption spectra in a concentration range [43]. In the concentration ranges studied (10 – 01 x 10^{-6} M) for **4** (Figure 3a) and (20 - 1.25 x 10^{-6} M) for **5** (Figure 3b), no aggregation tendency has been discovered as the appearance of the Q-band absorption maxima remained unchanged as the concentration increases, as well as its apparent molar extinction coefficient remains almost constant indicating purely monomeric form which obeyed the Beer–Lambert Law in the outlined range of concentration (Figure 3c) [44]. In order to verify the presence of aggregation, Triton X, a surfactant, has been added to the Pc solutions as given in Figure 3d, but the results indicate no appreciable aggregation which can be decomposed by the addition of Triton X. By evaluating these observations, it can be clearly concluded that the phthalocyanine derivatives (**3-5**) did not show aggregation behaviour in THF at different concentrations [45].

3.4 Fluorescence Spectra

The fluorescence behavior of zinc phthalocyanine complexes (**3** and **4**) was studied in THF, upon excitation at the 670 nm Q-band vibration for **3** and excitation at the 635 nm Q-band vibration for **4**. Figure 4 shows the absorption, fluorescence emission and excitation spectra for complex **3** and **4** in THF. Fluorescence emission peaks were observed at 736 nm for **3** and 718 nm for **4** (Table 1). The observed Stokes shifts were within the region ~10-15 nm observed for phthalocyanine complexes and they were typical of phthalocyanine complexes [46]. Excition spectrum of **3** show two shoulder in the red spectral region and emission maxima of **3** appears at lower energy than those of the corresponding metallo derivative (**4**). It means that metal-free phthalocyanines shows red shift in emission maxima compared to metallophthalocyanines because of symmetry lowering [47]. The proximity of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for **4** suggest that the nuclear configurations of the ground and excited states are similar and are not affected by excitation in THF.

Fluorescence quantum yields (Φ_F) were determined by the comparative method (Eq. (1)) [48]: $\Phi_F = \Phi_F(_{Std})\ (F A_{Std} \eta^2 / F_{Std} A \eta^2_{Std})$ (1)

where F and F_{Std} are the areas under the fluorescence curves of phthalocyanines derivatives and the standard, respectively. A and A_{Std} are the respective absorbances of the sample and standard at the excitation and η and η_{Std} are the refractive indices of solvents used for the sample and standard, respectively. ZnPc was employed as a standard in DMF ($\Phi_F = 0.23$) [49]. Both the sample and the standard were excited at the same wavelength. Radiative or natural lifetimes (τ_o) were estimated using PhotochemCAD program which uses the Strickler-Berg equation [50]. Finally, the fluorescence lifetimes (τ_F) were calculated using the following equation (Eq. (2)):

$$\Phi_F = \tau_F / \tau_o \tag{2}$$

The fluorescence quantum yields (Φ_F) of **3** and **4** are given in Table 1. The measured fluorescence quantum yields for **3** and **4** were lower than those for ZnPc, for which, in DMF and unsubstituted ZnPc in THF [51], both quantum yield of 0.23 and 0.25 respectively at room temperature. This implies that the presence of peripheral ethynylthiophene and hexylthio substituents caused some fluorescence quenching of the parent **3** and **4**. The Φ_F values of the Zn (II) Pc compound (**4**) are higher than for the metal-free Pc compound (**3**) [52].

Fluorescence lifetime (τ_F) refers to the average time a fluorophore stays in its excited state before fluorescing, and its value is directly related to that of fluorescence quantum yield. Such factors include internal conversion and intersystem crossing shorten the fluorescence lifetime of a fluorophore indirectly decreases the value of Φ_F. As a result, the nature and the environment of a fluorophore determine its fluorescence lifetime. The τ_F values of the Pc complexes **3** and **4** (1.21 and 0.04 ns, respectively) are lower compared to unsubstituted ZnPc complexes in THF [53], suggesting more quenching by substitution. The natural radiative lifetime (τ_o) and the rate constants for fluorescence (k_F) values were also shown in Table 1. The k_F values of studied phthalocyanine complexes (**3** and **4**) are higher than unsubstituted ZnPc in THF.

3.5 Fluorescence quenching studies by 1,4-benzoquinone (BQ)

Fluorescence quenching experiments on phthalocyanine complexes (**3** and **4**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the complex, and the concentrations of BQ in the resulting mixtures were 0, 0.01, 0.02, 0.03, 0.04

and 0.05 M, respectively. The fluorescence spectra of compound **3-4** at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (SV) equation [54]:

$$\frac{I_0}{I} = 1 + K_{SV}[BQ] \tag{3}$$

where I_0 and I are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively. [BQ] is the concentration of the quencher and K_{SV} is the Sterne-Volmer constant which is the product of the bimolecular quenching constant (k_q) and the τ_F and is expressed in Eq. (4):

$$K_{SV} = k_q \times \tau_F \tag{4}$$

The ratios of I_0/I were calculated and plotted against [BQ] according to Eq. (4), and K_{SV} is determined from the slope.

The fluorescence quenching of studied phthalocyanine complexes (**3** and **4**) by benzoquinone (BQ) in THF was found to obey Stern-Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Figure 5 shows fluorescence emission spectral changes of **3** and Figure 6 shows fluorescence emission spectral changes of **4** on addition of different concentrations of BQ in THF. The Stern-Volmer plots for studied complexes (**3** and **4**) gave straight lines, depicting diffusion controlled quenching mechanisms (Figure 5-6). The slope of the plots shown at insert Figures 5 and 6 gave K_{SV} values, listed in Table 1. The bimolecular quenching constant (k_q) values for the BQ quenching of phthalocyanine complexes in THF are also listed in Table 1. The K_{SV} values of the phthalocyanine complexes **3** and **4** are lower than unsubstituted ZnPc in THF.

4. Conclusion

In this study, A_3B type metal-free and metallophtalocyanines (**3-5**) wee successfully prepared from 4,5-di(hexylthio)phthalonitrile (**1**) and 4,5-bis(thiophen-3-

ylethynyl)phthalonitrile (**2**). The statistical condensation reaction leads to a mixture of variously substituted phthalocyanine products. Thereby, it turned out that the choice of the phthalonitrile precursors having appropriate solubilizing groups plays a crucial role in the separation of the desired 3:1 type Pc from the mixture of different Pcs formed during the cyclotetramerization reaction. Desired A_3B type phthalocyanines (**3-5**) have been obtained in moderate yields after purifications. The synthesized, phthalocyanine complexes show very good solubility in a number of solvents such as THF, $CHCl_3$, dichloromethane. We show that the presence of sulfur atoms and ethynylthiophene groups at the peripheral positions of the phthalocyanine ring resulted in a shift of the Q-band to the near-IR region. The aggregation behavior, photophysical and photochemical properties of these novel A_3B type metal-free and metallophtalocyanines (**3-5**) have been also investigated. The phthalocyanines **3** and **4** show lower fluorescence quantum yields and shorter lifetimes when compared to unsubstituted zinc phthalocyanine in THF. The fluorescence of **3** and **4** are effectively quenched by 1,4-benzoquinone in THF.

Acknowledgements

This work was supported by the Research Fund of the Technical University of Istanbul.

References

[1] C.C. Leznoff, A.B.P. Lever, Phthalocyanines: Properties and Applications, vols. 1–4. New York: VCH; 1989–1996.

[2] M.P. Cormick, M. Rovera, E.N. Durantini, J. Photochem. Photobiol. A 194 (2008) 220-229.

[3] A. Diacon, L. Fara, C. Cincu, M.R. Mitroi, C. Zaharia, E. Rusen, C. Boscornea, C.Rosu, D. Comaneci, Opt. Mater. 32 (2010) 1583-1586.

[4] A.Braun, J. Tscherniac, Ber. Dtsch. Chem. Ges. 40 (1907) 2709-2714.

[5] P. Gregory, J. Porphyr. Phthalocyanines 4 (2000) 432-437.

[6] F.H. Moser, L.R. Thomas, Phthalocyanine Compounds, Reinhold, New York, 1963.

[7] G. Guillaud, J. Simon, J.P. Germain, Coord. Chem. Rev. 178 (1998) 1433-1484.

[8] G. De la Torre, P. Vazquez, F. Agullo-Lopez, T. Torres, Chem. Rev. 104 (2004) 3723-3750.

[9] S. Vagin, M. Barthel, D. Dini, M. Hanack, Inorg. Chem. 42 (2003) 2683-2694.

[10] M. Kimura, H. Ueki, K. Ohta, H. Shirai, N. Kobayashi, Langmuir 22 (2006) 5051-5056.

[11] J.W. Hoffman, F. Zeeland, S. Turker, H. Talsma, S.A. Lambrechts, D.V. Sakharov, W.E. Hennink, C.F. van Nostrum, J. Med. Chem. 50 (2007) 1485-1494.

[12] H. Kolarova, P. Nevrelova, R. Bajgar, D. Jirova, K. Kejlova, M. Strnad, Toxicology in Vitro 21 (2007) 249-253.

[13] S. Banfi, E. Carous, L. Buccafurni, R. Ravizza, M. Gariboldi, E. Monti, J. Organomet. Chem. 692 (2007) 1269-1276.

[14] E. Güzel, A. Atsay, S. Nalbantoglu, N. Saki, A.L. Dogan, A. Gül, M.B. Koçak, Dyes Pigm. 97 (2013) 238-243.

[15] G. de la Torre, C.G. Claessens, T. Torres, Eur. J. Org. Chem. (2000) 2821-2830.

[16] A. Yu Tolbin, L.G. Tomilova, N.S. Zefirov, Russ. Chem. Rev. 76 (2007) 681-692.

[17] A. Wang, L. Long, C.J. Zhang, Incl. Phenom. Macrocycl. Chem. 71 (2011) 1-24.

[18] H.Y.Y. Akkurt, A.İ. Okur, A. Gül, J. Porphyr. Phthalocyanines 16 (2012) 192-199.

[19] N. Kobayashi, R. Kondo, S. Nakajima, T. Osa, J. Am. Chem. Soc. 112 (1990) 9640-9641.

[20] S. Dabak, A. Gül, Ö. Bekaroğlu, Chem. Ber. 127 (1994) 2009-2012.

[21] N. Kobayashi, T. Ishizaki, K. Ishii, H. Konami, J. Am. Chem. Soc. 121 (1999) 9096-9110.

[22] S.V. Kudrevich, N. Brasseur, C. La Madeleine, S. Gilbert, J.E. van Lier, J. Med. Chem. 40 (1997) 3897- 3904.

[23] C.C. Leznoff, T.W. Hall, Tetrahedron Lett. 23 (1982) 3023-3026.

[24] A. Kalkan, A. Koca, Z.A. Bayır, Poyhedron 23 (2004) 3155-3162.

[25] A.K. Burat, A. Koca, J.P. Lewtak, D.T. Gryko, Synth. Met. 161 (2011) 1537-1545.

[26] A.G. Gürek, Ö. Bekaroğlu, J. Chem. Soc. Dalton Trans. (1994) 1419-1423.

[27] İ. Özçeşmeci, A.K. Burat, Y. İpek, A. Koca, Z.A. Bayır, Electrochim. Acta 89 (2013) 270-277.

[28] T. Kimura, N. Kanota, K. Matsui, I. Tanaka, T. Tsuboi, Y. Takaguchi, A. Yomogita, T. Wakahara, S. Kuwahara, F. Nagatsugi, T. Akasaka, Inorg. Chem. 47 (2008) 3577-3583.

[29] S.S. Erdem, I.V. Nesterova, S.A. Soper, R.P. Hammer, J. Org. Chem. 73 (2008) 5003-5007.

[30] N. Kobayashi, J Porphyr. Phthalocyanines 3 (1999) 453-467.

[31] N. Kobayashi, T. Nonomura, Tetrahedron Lett. 43 (2002) 4253-4255.

[32] M.J. Cook, J. Chem. Rec. 2 (2002) 225-236.

[33] G. De la Torre, T. Torres, J. Porphyr. Phthalocyanines 6 (2002) 274-284.

[34] M. Özçeşmeci, İ. Özçeşmeci, E. Hamuryudan, Polyhedron 29 (2010) 2710-2715.

[35] İ. Özçeşmeci, Synth. Met. 176 (2013) 128-133.

[36] A. Kalkan, Z.A. Bayır, Polyhedron 25 (2006) 39-42.

[37] J. Obirai, T. Nykong, Electrochim. Acta 50 (2005) 5427-5434.

[38] M.J. Stillman, T. Nykong, in: C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, VCH, New York, vol. 1, 1989.

[39] A.B.P. Lever, S.R. Pickens, P.C. Minor, S. Licoccia, B.S. Ramaswamy, K. Magnell, J. Am. Chem. Soc. 103 (1981) 6800-6806.

[40] M. Özçeşmeci, Ö.B. Ecevit, S. Sürgün, E. Hamuryudan, Dyes Pigm. 96 (2013) 52-58.

[41] E. Seikel, M. Grau, R. Käsmarker, B. Oelkers, J. Sundermeyer, Inorg. Chem. Acta 374 (2011) 119–126.

[42] İ. Özçeşmeci, S. Güner, A.İ. Okur, A. Gül, J. Porphyr. Phthalocyanines 11 **(**2007) 531-536.

[43] İ. Özçeşmeci, O. Güney, A.İ. Okur, A. Gül, J. Porphyr. Phthalocyanines 13 **(**2009) 753-759.

[44] E. Evren, A.K. Burat, İ. Özçeşmeci, B.Ş. Sesalan, Dyes Pigm. 96 (2013) 475-482.

[45] İ. Özçeşmeci, A. Gelir, A. Gül, Dyes Pigm. 92 (2012) 954-960.

[46] G. Gümrükçü, G.K. Karaoğlan, A. Erdoğmuş, A. Gül, U. Avcıata, Dyes Pigm. 95 (2012) 280-289.

[47] A. Ogunsipe, D. Maree, T. Nyokong, J. Mol. Struct. 650 (2003) 131-140.

[48] A. Ogunsipe, T. Nyokong, J. Photochem. Photobiol., A 173 (2005) 211-220.

[49] I. Scalise, E.N. Durantini, Bioorg. Med. Chem. 13 (2005) 3037-3045.

[50] H. Du, R.C.A. Fuh, J. Li, L.A. Corkan, J.S. Lindsey, Photochem. Photobiol. 68 (1998) 141-148.

[51] E.T. Saka, M. Durmuş H. Kantekin, J. Organomet. Chem. 696 (2011) 913-924.

[52] M. Çamur, M. Durmuş, M. Bulut, Polyhedron 30 (2011) 1935-1944.

[53] M. Durmuş, T. Nyokong, Spectrochim. Acta A 69 **(**2008) 1170-1177.

[54] J. Rose, Advanced Physico-chemical Experiments, 1st ed., Sir Isaac Pitman & Sons Ltd., London, 1964, pp. 257.

Table Captions

Table 1. Excitation spectra, emission spectra, photophysical and photochemical parameters along with fluorescence quenching data for **3** and **4** in THF.

Table(s)

Comp.	**Excitation λ Ex, (nm)**	**Emission λ Em, (nm)**	**Stokes shift (nm)**	**Φ_F**	**τ_F (ns)**	**τ_o (ns)**	**k_F (s^{-1})($x10^8$)[a]**	**K_{SV}**	**k_q/ ($x10^{11}$ s^{-1})**
3	719	736	13	0.13	1.21	8.99	1.11	17.34	0.14
4	706	718	12	0.22	0.04	0.16	55.00	43.12	10.78
ZnPc[b]	666[b]	673[b]	7[b]	0.25[b]	2.72[b]	10.9[b]	0.92[b]	48.48[b]	1.78[b]

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.

[b] Ref. [50].

Table 1.

Figure and Scheme Captions

Figure 1. Mass spectra of **3** and **5**.

Figure 2. Absorption spectra of **3-5** in THF(1.0 x 10^{-5} M).

Figure 3. Aggregation study of **3-5** in THF (**a-** Aggregation behavior of **4** in THF at different concentrations. **b-** Aggregation behavior of **5** in THF at different concentrations. **c-** Plot of the Log ε of **3-5** against concentration. **d-** Changes in the absorption spectra of **3** by the addition of Triton X-100 (1.0 x 10^{-5} M)).

Figure 4. Excitation and emission spectra for compound **3** and **4** in THF. Excitation wavelength = 670 nm for **3** and 635 nm for **4** in THF.

Figure 5. Fluorescence emission spectral changes of 3 (10^{-6} M) on addition of different concentrations of benzoquinone (BQ) in THF. [BQ] = 0, 0.01, 0.02, 0.03, 0.04, 0.05 M. (İnsert figure, Stern–Volmer plots for BQ quenching of **3**.)

Figure 6. Fluorescence emission spectral changes of **4** (10^{-6} M) on addition of different concentrations of benzoquinone (BQ) in THF. [BQ] = 0, 0.01, 0.02, 0.03, 0.04, 0.05 M. (İnsert figure, Stern–Volmer plots for BQ quenching of **4**.)

.**Scheme 1.** The synthesis of phthalocyanine complexes (**3-5)**. (**i)** Li, 1-pentanol, 140 ^{o}C, 2 h, HCl **ii)** $Zn(CH_3COO)_2$, DMF, 140 ^{o}C, 6h **iii)** $MnCl_2$, DMF, 140 ^{o}C, 6h.)

Figures

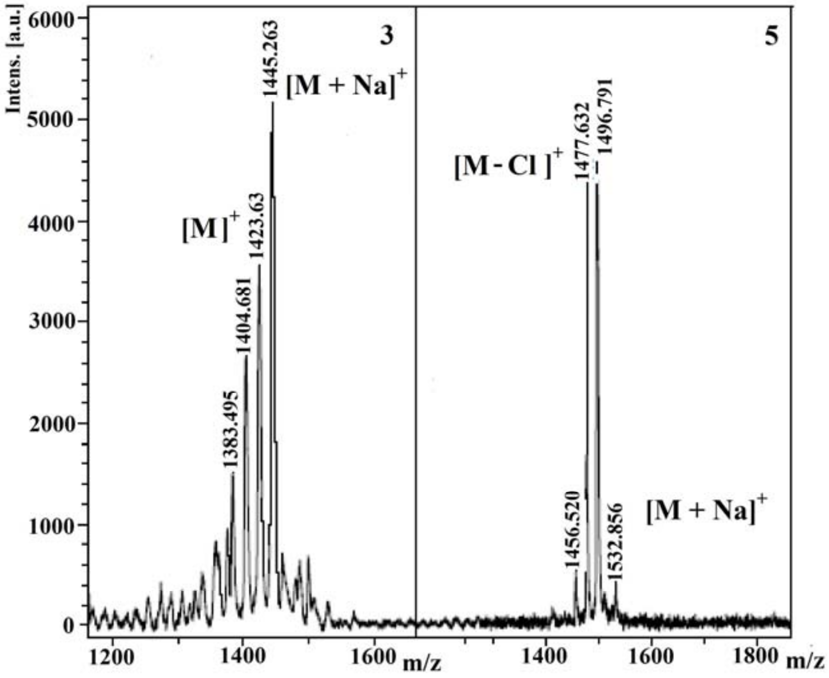


Figure 1.

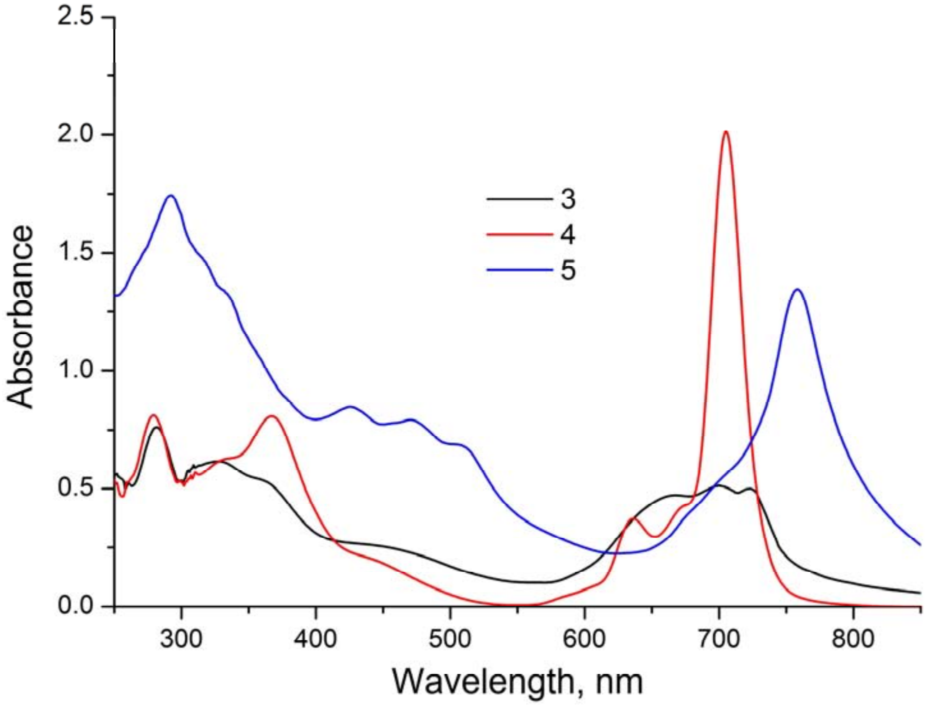


Figure 2.

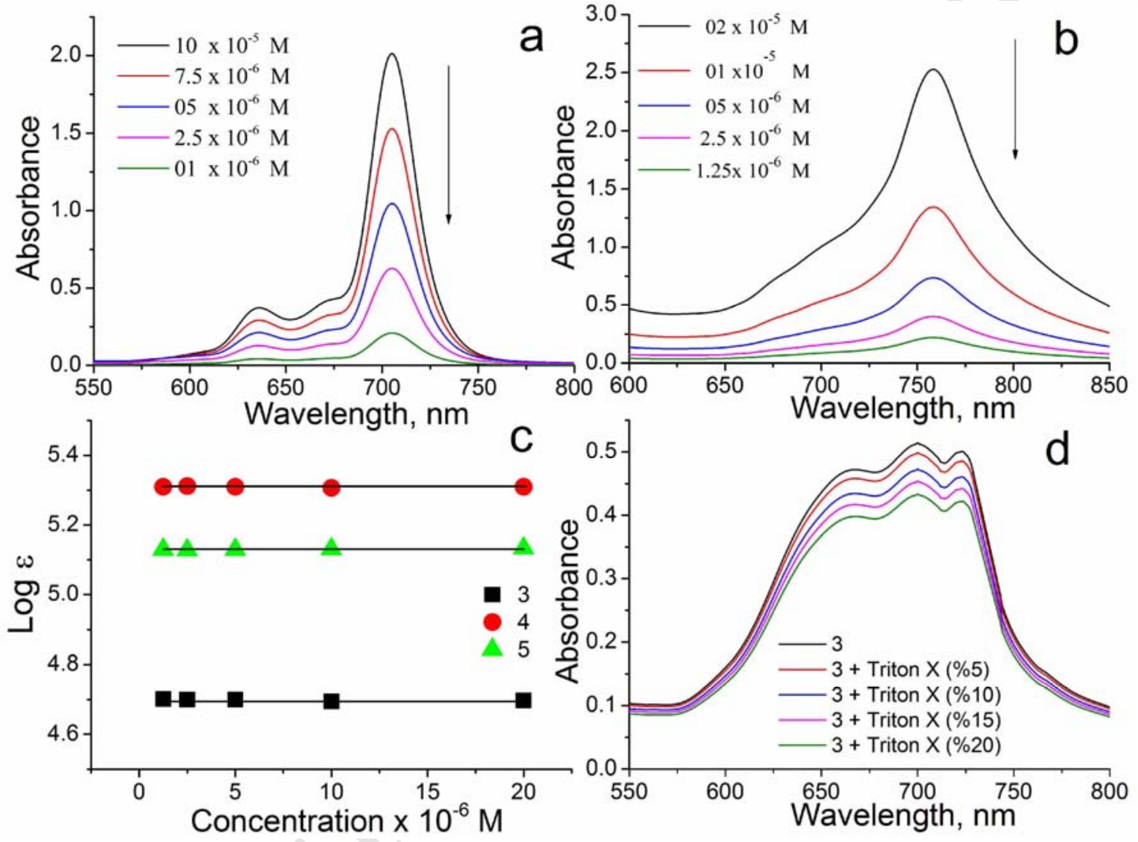


Figure 3.

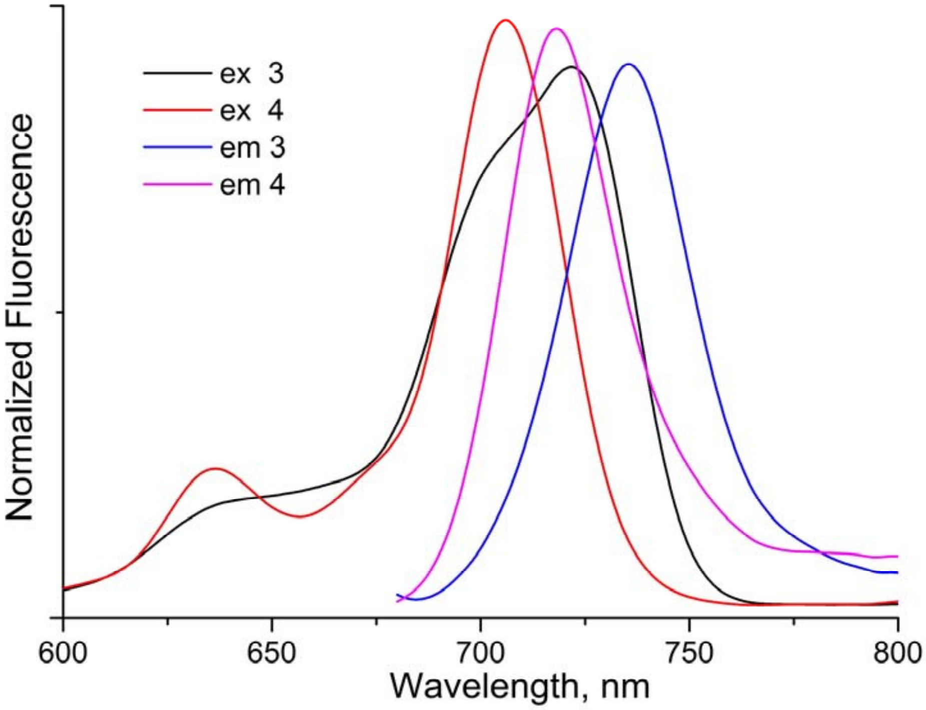

ex 3
ex 4
em 3
em 4
Normalized Fluorescence
600
650
700
750
800
Wavelength, nm

Figure 4.

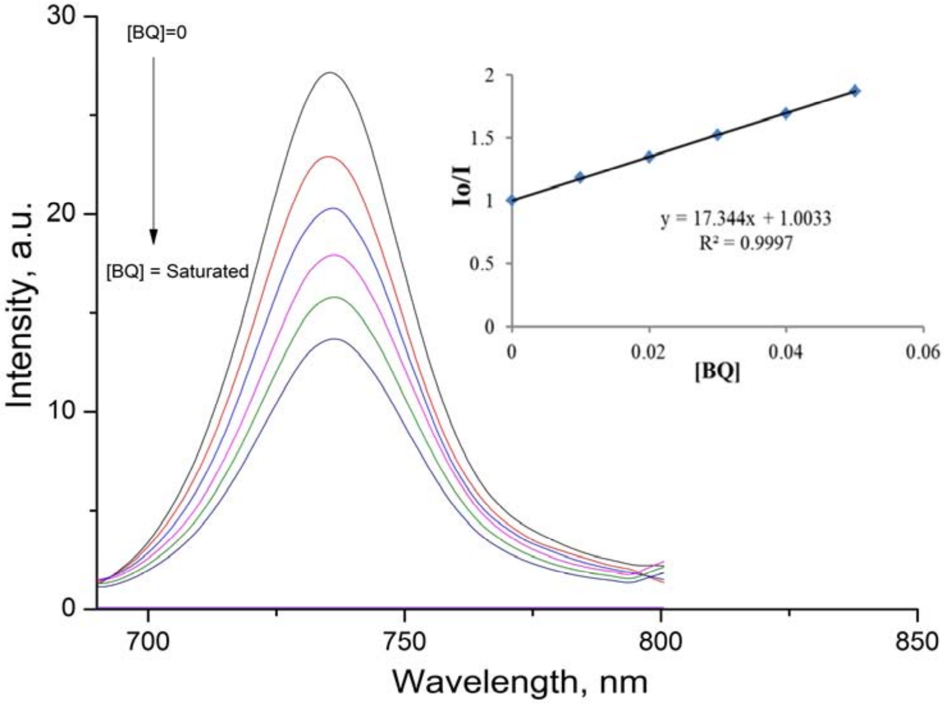

[BQ]=0
[BQ] = Saturated
Intensity, a.u.
0
10
20
30
700
750
800
850
Wavelength, nm
Io/I
[BQ]
y = 17.344x + 1.0033
R² = 0.9997
0
0.5
1
1.5
2
0
0.02
0.04
0.06

Figure 5.

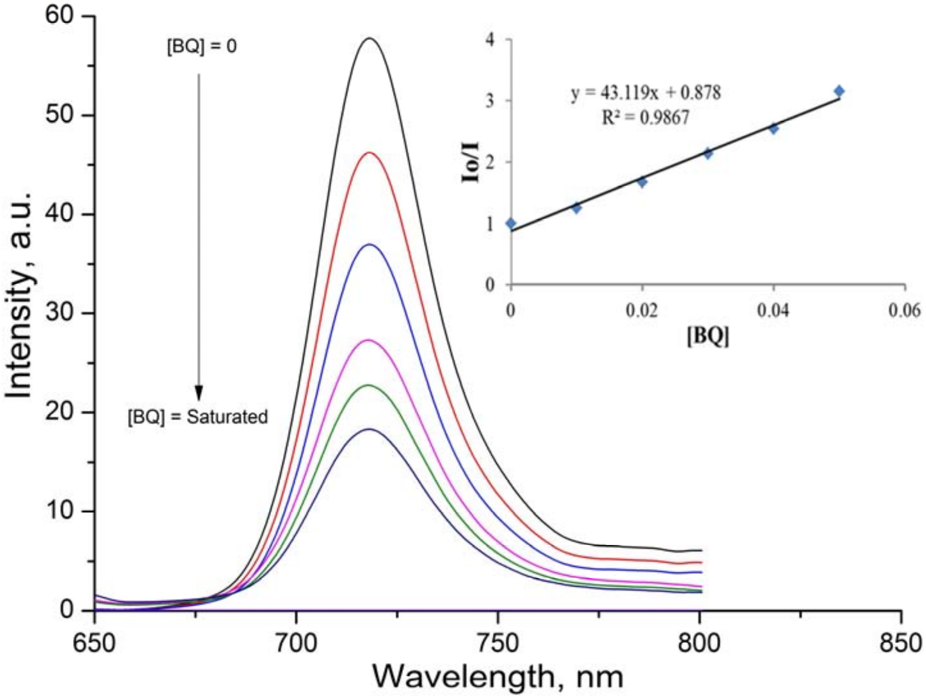
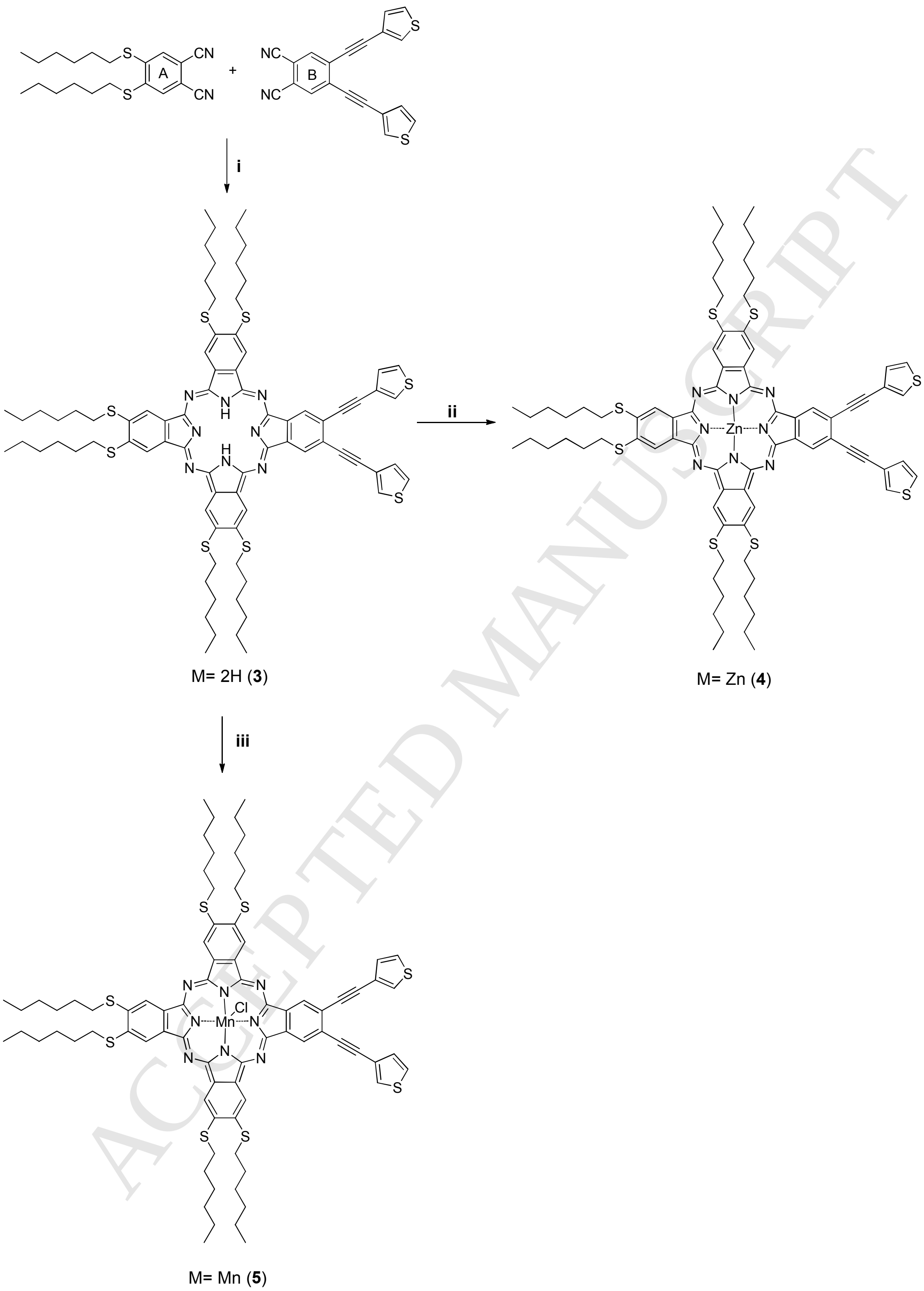


Figure 6.

Scheme



Scheme 1.

Research Highlights

- Unsymmetrical phthalocyanines bearing ethynylthiophene moieties were synthesized.
- These phthalocyanines show the enhanced solubility in organic solvents.
- Aggregation properties of these compounds were investigated.
- Photophysical properties of these phthalocyanines have been investigated.
- The fluorescence quenching behaviour of these phthalocyanines were also reported.