



Synthesis and photophysical properties of novel unsymmetrical metal-free and metallophthalocyanines



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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 phthalocyanine). 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 (^1H 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.

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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 centre of the ring [1,2,3]. Since their accidental discovery phthalocyanines have been used extensively as dyes and pigments in industry due to their blue-green colour [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) [6,7,8,9,10,11,12,13,14].

Despite the variety of synthetic routes developed to prepare symmetrically 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 diiminoisoindolines in 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 phthalocyanines 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 behaviour as well as photophysical (fluorescence

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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 ^1H 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 °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 °C. IR, (cm^{-1}): 3289 (N–H), 2955–2854 (Aliph.–H), 2206 ($\text{C}\equiv\text{C}$), 1260 (Ar–S–Aliph.), 741; ^1H NMR ($\text{CDCl}_3\text{-d}_6$), 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)): $\lambda_{\text{max}}/\text{nm}$ (log ϵ , L. $\text{mol}^{-1}\text{cm}^{-1}$): 282 (4.88), 327 (4.79), 700 (4.70), 723 (4.69); Anal. calc. for $\text{C}_{80}\text{H}_{94}\text{N}_8\text{S}_8$: 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 ($\text{Zn}(\text{CH}_3\text{COO})_2$) (0.038 g, 0.21 mmol) in dried DMF (2 mL) was heated at 145 °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 °C. IR, (cm^{-1}): 2953–2853 (Aliph.–H), 2206 ($\text{C}\equiv\text{C}$), 1259 (Ar–S–Aliph.), 740; ^1H NMR ($\text{CDCl}_3\text{-d}_6$), 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): $\lambda_{\text{max}}/\text{nm}$ (log ϵ , L. $\text{mol}^{-1}\text{cm}^{-1}$): 280 (4.79), 367 (4.90), 705 (5.31); Anal.

calc. for $\text{C}_{80}\text{H}_{92}\text{N}_8\text{S}_8\text{Zn}$, 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 °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 °C. IR, (cm^{-1}): 2954–2852 (Aliph.–H), 2207($\text{C}\equiv\text{C}$), 1261 (Ar–S–Aliph.), 741; UV–Vis (THF): $\lambda_{\text{max}}/\text{nm}$ (log ϵ , L. $\text{mol}^{-1}\text{cm}^{-1}$): 293 (5.24), 321 (5.14), 425 (4.90), 470 (4.87), 500 (4.81), 758 (5.13); Anal. calc. for $\text{C}_{80}\text{H}_{92}\text{ClMnN}_8\text{S}_8$: C, 63.53; H, 6.13; N, 7.41. Found: C, 63.57; H, 6.16; N, 7.45; MS: m/z 1532.85 [$\text{M} + \text{Na}$] $^+$, 1477.63 [$\text{M} - \text{Cl}$] $^+$

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 alkylthio 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 sulphur 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 °C under N_2 for 48 h.

The most usual method to prepare metal-free phthalocyanines is the cyclotramerisation 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 synthesizing 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

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