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Synthesis and some optical results of long chain substituted phthalocyanines

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Abstract: Four metallo (zinc, copper, vanadyl, and indium) phthalocyanine derivatives bearing four aliphatic (hexylthio) groups were prepared from corresponding phthalonitrile compounds. The metallophthalocyanines were characterized with ultraviolet–visible spectroscopy (UV-Vis), proton nuclear magnetic resonance (¹H NMR), Fourier transform-infrared spectroscopy (FT-IR), and mass and elemental analyses techniques. Aggregation properties of metallophthalocyanines in solution were studied in varied concentration ranges. Thin films of metallophthalocyanines were obtained by spin coating technique. Optical measurements showed that transmittance values of metallophthalocyanine thin films obviously changed with respect to the metal ion in the phthalocyanines. Transmittance spectra of the phthalocyanines synthesized using different metal ions showed a variation of about 8% and 15% in transmittance spectra of the Q band region was obtained by mixing the two metal phthalocyanine (indium and zinc) solutions.

Key words: Phthalocyanine, aliphatic groups, aggregation, thin film, optical properties

1. Introduction

Phthalocyanines (Pcs) are an amazing class of compounds that have attracted remarkable interest due to their various applications in medicinal and materials chemistry. Pcs are especially noted for their high chemical, photochemical, and thermal inflexibility and have thus found a lot of uses in many fields.¹ Numerous adjustments can be made in the Pcs either by the insertions of different metal ions into the Pc's core or by the substitution of diverse aliphatic or aromatic groups at the Pc's ring. It is expected to increase the solubility in many solvents by introducing different substituents into the Pc ring and affects the electronic spectrum depending on the properties of substituted groups. Moreover, solvents may also change the photochemical and photophysical properties of Pcs.^{2,3}

Metallophthalocyanines (MPcs) are well-rounded conjugated macrocycles that have attracted a large amount of attention as effective components in organic/electronic materials. The charge transport behaviors, synthetic sophistication, and chemical and thermal stability of MPcs make them optimal candidate compounds for use in organic thin-film transistors.⁴ There are a lot of techniques that are used for obtaining MPc thin films: Langmuir–Blodgett film formation, self-assembled monolayer films, organic molecular beam epitaxy, vacuum deposition, and spin coating methods.⁵ Solution-process able MPcs are easily and practicably spin-coated onto the surface of the material.^{6–9}

In the present work we synthesized peripherally tetrahexylthio-substituted metallo (Zn, In, VO, Cu) phthalocyanine compounds. Similar alkyl unit-substituted Pcs were synthesized by the Matsuda group¹⁰ and

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different groups^{11–13} or hexylthio unit-containing Pcs were prepared by the Suda group.¹⁴ In this study, we used a relatively different synthesis method and a more detailed characterization study compared with those of the Suda group. In addition, we explored the effects of hexylthio units on the electronic absorption spectra and aggregation behaviors of MPcs (**2–5**) in tetrahydrofuran (THF) in different concentration ranges. We also obtained thin films of these MPcs with spin coating as the Suda group¹⁴ did and investigated their optical properties both separately and mixing a two Pc solution to see how the optical properties changed.

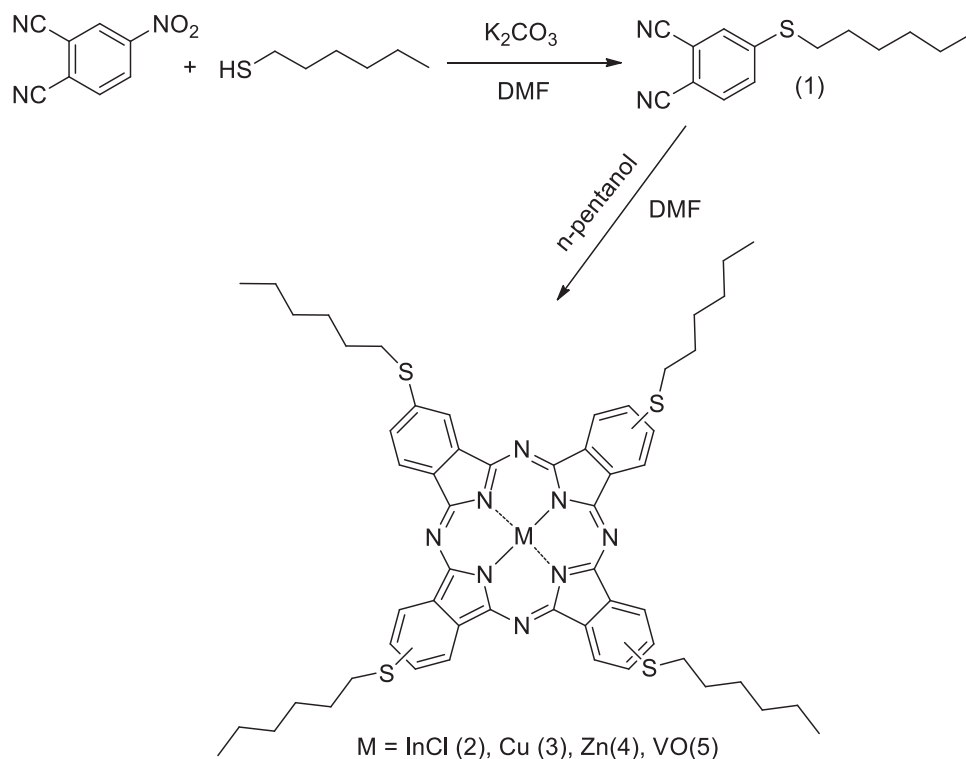
2. Results and discussion

2.1. Synthesis and characterization

A generally used synthetic path to soluble substituted MPcs requires aromatic nucleophilic substitution between nitrophthalonitrile and a suitable O- or S-nucleophile. This step was followed by cyclotetramerization of the resultant phthalonitrile derivatives.^{15,16} 4-(Hexylthio)phthalonitrile (**1**) was synthesized through base-catalyzed aromatic displacement of 4-nitrophthalonitrile with a hexylthiol group and purified according to reported methods.^{11,17,18} Tetrahexylthio-substituted metallophthalocyanine complexes (**2–5**) were prepared by cyclotetramerization of phthalonitrile derivatives (**1**) and anhydrous InCl_3 , CuCl_2 , $\text{Zn}(\text{CH}_3\text{COO})_2$, or $\text{VO}(\text{SO})_4$ in the presence of high boiling solvent (n-pentanol) with 2 drops of DBU under N_2 (Scheme).¹⁹ All of the MPcs (**2–5**) were purified by column chromatography. The MPcs (**2–5**) were obtained in satisfactory yields (between 40% and 50%) and were characterized by the spectral data (FT-IR, ^1H NMR, UV-Vis, and mass spectroscopies) together with elemental analysis. The characterization data of the MPcs (**2–5**) are consistent with the assigned formula. All MPcs (**2–5**) were extremely soluble in various organic solvents such as THF, chloroform, DMF, dichloromethane, and DMSO.

In the FT-IR spectrum of hexylthio-substituted MPcs (**2–5**), the typical $\text{C}\equiv\text{N}$ stretch at $\sim 2300\text{ cm}^{-1}$ of phthalonitriles (**1**) disappeared, indicative of MPc formation. MPcs (**2–5**) have characteristic vibration peaks due to aliphatic CH stretching at $2952\text{--}2855\text{ cm}^{-1}$. The ^1H NMR spectra of tetrahexylthio-substituted **4** are compatible with the proposed structure. The ^1H NMR spectrum of **4** in d-chloroform showed aliphatic protons between 3.43 and 0.96 ppm as a multiplet and the aromatic Pc protons appeared between around 8.88 and 7.88 ppm. The MPcs synthesized under these conditions are naturally a mixture of positional isomers. Therefore, the ^1H NMR spectrum of MPcs is expected to have chemical shifts that differ slightly from each other, causing the broadening of ^1H NMR peaks.²⁰ The elemental analysis results of **3–5** are consistent with the suggested structures. The mass spectra of **3–5** gave expected mass results as given in the experimental section. The molecular ion peaks of **3–5** were observed at $m/z = 1041.97$ $[\text{M} + 1]^+$ for **3**, $m/z = 1040.22$ $[\text{M}]^+$ for **4**, and $m/z = 1066.85$ $[\text{M} + \text{Na}]^+$ for **5**.

In substituted MPcs, strong absorption is observed in the visible region between 600 and 700 nm (Q band) and in the UV region between 300 and 350 nm (B (Soret) band). The Q and B bands both arise from $\pi\text{--}\pi^*$ transitions.²¹ The electronic absorption spectra of hexylthio-substituted MPcs (**2–5**) recorded in THF show intense Q bands at 689 nm (**3**), 687 nm (**4**), and 712 nm (**5**) (Figure 1). The B bands come out in the UV region around 345–362 nm. The Q band of VOPc (**5**) has been found to be more red shifted compared to other MPcs.²² The observation of a red shift for VOPc (**5**), containing V(IV) central metal, confirms that red shift in Q band absorption is favored for MPc complexes containing central metals in a high oxidation state. The red shift is a result of the lowering of the HOMO–LUMO gap, by either destabilizing the HOMO or stabilizing the LUMO by the central metal.²³



Scheme. Synthesis route of synthesized MPcs (2–5).

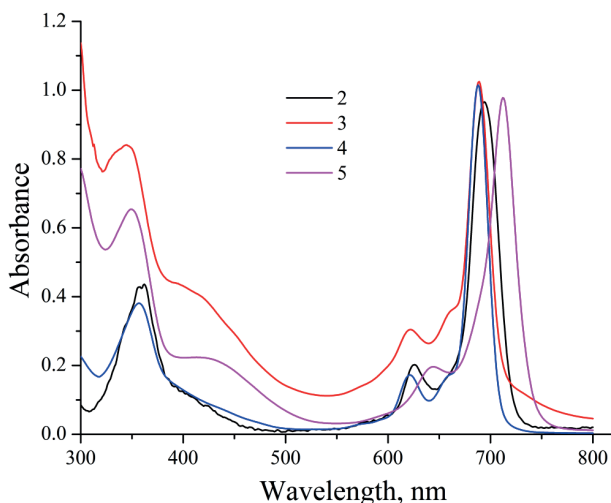


Figure 1. Absorption spectra of MPcs (2–5) in THF (5.0×10^{-6} M).

The aggregation behavior of Pcs can be followed effectively in solution by absorption studies and it is a good sign of the interactions between the aromatic macrocycles of the Pcs.^{24,25} In this study, the aggregation behaviors of the hexylthio-substituted MPcs (Figure 2A for **2**, Figure 2B for **3**, Figure 2C for **4**, and Figure 2D for **5**) were examined at diverse concentrations in THF (1.00×10^{-5} to 1.00×10^{-6} M) (Figure 2). As shown in Figures 2 and 3, the appearance of the Q-band absorption remains unaltered as the concentration changes (Figure 2) and its evident molar extinction coefficient stays almost constant (Figure 3), indicating the existence

of a purely monomeric form (i.e. no new blue-shifted band due to aggregation) for MPCs (**2–5**) that obeyed the Beer–Lambert law in the outlined range of concentration in THF.^{26,27}

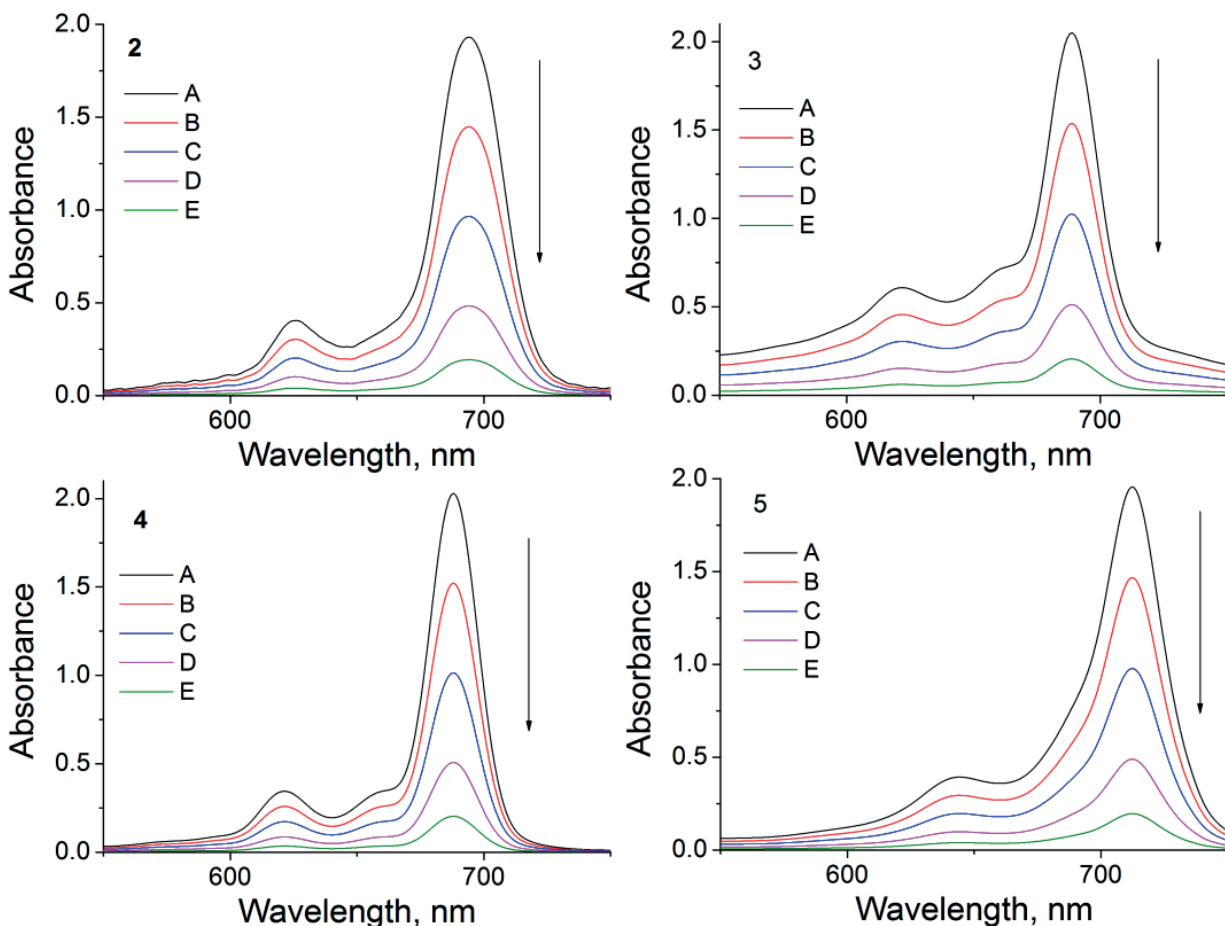


Figure 2. Changes in Q bands of **2–5** with different concentrations in THF (A - 1.0×10^{-5} M, B - 7.5×10^{-6} M, C - 5.0×10^{-6} M, D - 2.5×10^{-6} M, E - 1.0×10^{-6} M).

2.2. Optical properties

We prepared thin films of MPCs (**2–5**) by spin coating and investigated their optical properties. The spectral distribution of transmittance for deposited MPC thin films containing four different metal centers (InCl (**2**), Cu (**3**), Zn (**4**) and VO (**5**)) in the wavelength range of 200–1000 nm is shown in Figure 4. Transmittance values of the MPC films change with respect to the metal ions. Under these preparation conditions, from the transmittance measurements of **2** and **4**, it is seen that these films show more characteristic absorption peaks of MPCs. Transmittance of **3** and **5** shows that these films do not show the characteristic absorption peaks very well. The low solubility of **3** and **5** in THF compared to **2** and **4** may have led to the poor formation of these films. The transmittance values are about 87% and 85% around the wavelength of 550 nm for **2** and **4** films, respectively. However, transmittance measurement of these two films shows minima in the Q band absorption region and their transmittance values are 65% and 60% around 700 nm, respectively. While the absorption peak of **3** is around 82% in this region, this peak of **5** almost disappears.

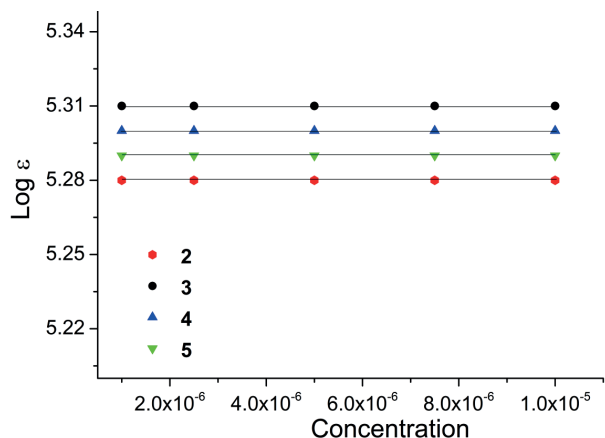


Figure 3. Plot of the $\text{Log } \epsilon$ of MPCs (2–5) against concentration.

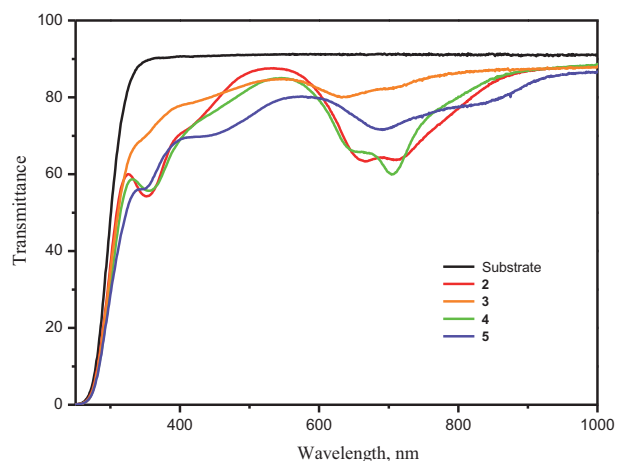


Figure 4. Transmittance spectra of MPCs (2–5) thin films.

The manipulation of the values of these absorption peaks is possible by varying the concentration of the solution of the film, which opens the way to the use of films as optical windows.³ In this work, we examined the solutions of **2** and **4** by mixing according to the $\text{InClPc}_{(x)} - \text{ZnPc}_{(1-x)}$ (which is indicated as $\mathbf{2}_{(x)}\mathbf{4}_{(1-x)}$ in Figures 5 and 6) formula, to see how the effect of mixing the two different solutions will change this manipulation. A graphical representation of the films obtained by mixing two different solutions is shown in Figure 5. Before mixing the **2** and **4** solutions, the transmittance values (65% and 60% for **2** and **4**, respectively) in the Q band absorption region of their films are reduced to 55% for $x = 0.50$ after mixing. In this region, after mixing two solutions, it means a relative difference of about 8% and 15% in transmittance. This is also evident from the absorption peaks in the Q band region of Figure 6.

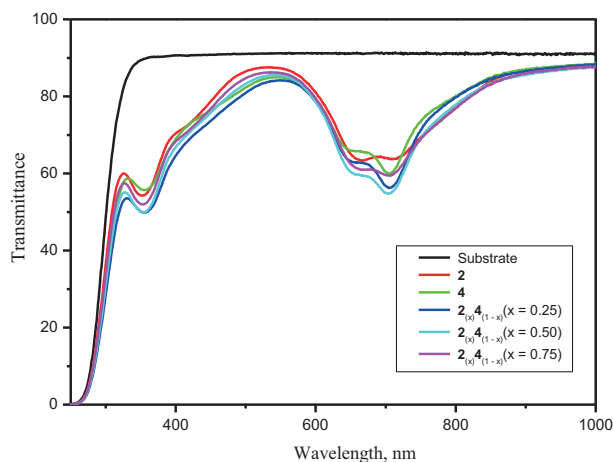


Figure 5. Transmittance spectra of $\text{InClPc}_{(x)} - \text{ZnPc}_{(1-x)}$ thin films.

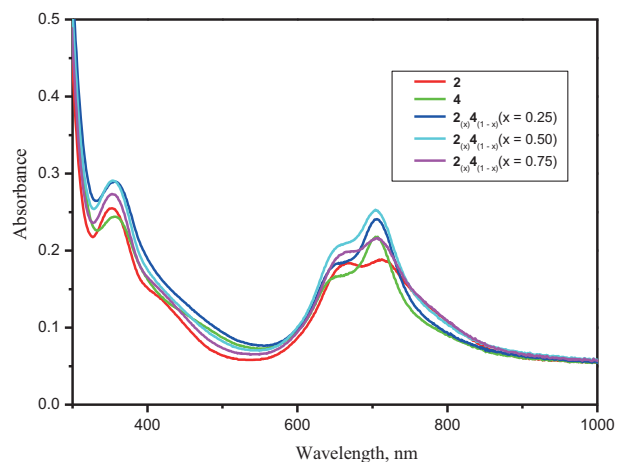


Figure 6. Absorption spectra of $\text{InClPc}_{(x)} - \text{ZnPc}_{(1-x)}$ thin films.

The optical energy band gap E_g is calculated according to the following relation [1]:

$$\alpha = A(h\nu - E_g)^m \quad (1)$$

where A is a constant independent of energy and m determines the type of transitions, equal to $1/2$ or 2 for

direct allowed and indirect allowed transitions, respectively. The graph of $(\alpha h\nu)^2$ vs. photon energy is plotted and shown in Figure 7. The band gap value is determined by extrapolating the straight line portion of $(\alpha h\nu)^2$ to the $h\nu$ axis. The optical energy band gap values range from 4.48 to 4.51 eV for Pc thin films of indium, zinc, and derived from their mixture. It is seen that the energy band gap values of the Pc thin films obtained by mixing the two solutions are slightly changed. The band gaps of the Pc thin films are also calculated (as shown in Figure 8) by employing the Tauc model for indirect band gap transition. The fundamental band gaps of the thin films, in this case, range from 3.70 to 3.78 eV and 1.63 to 1.88 eV for onset gaps.

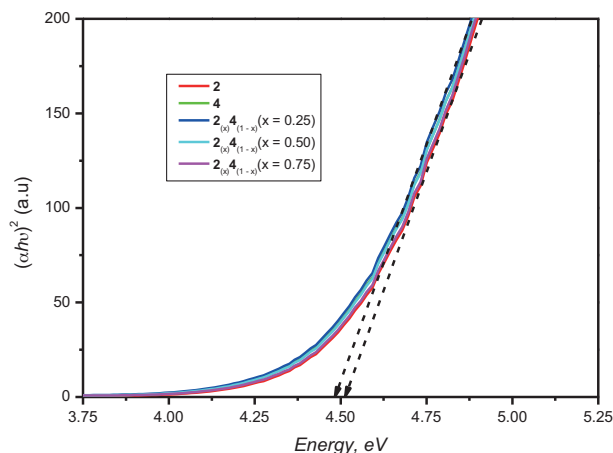


Figure 7. Relation between $(\alpha h\nu)^2$ vs. photon energy for $\text{InClPc}_{(x)}-\text{ZnPc}_{(1-x)}$ thin films.

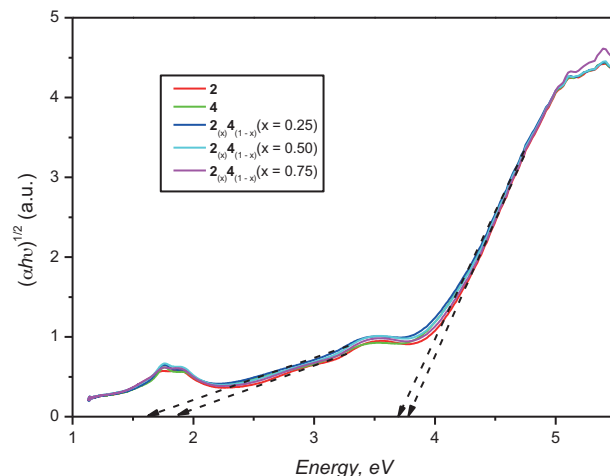


Figure 8. Relation between $(\alpha h\nu)^{1/2}$ vs. photon energy for $\text{InClPc}_{(x)}-\text{ZnPc}_{(1-x)}$ thin films.

In conclusion, we synthesized and characterized metallo (zinc, copper, vanadyl, and indium) phthalocyanine derivatives bearing four aliphatic (hexylthio) groups peripherally. Aggregation properties of the MPcs (**2-5**) in different concentrations of THF were reported. The MPcs (**2-5**) did not show aggregation behavior in the studied concentration range from 1.0×10^{-5} M to 1.0×10^{-6} M in THF. Thin films of MPcs were prepared by spin coating. Different transmittance spectra were obtained from the Pc synthesized using different metal ions. It was observed that the characteristic absorption peaks of **2** and **4** were more pronounced. The transmittance of the films obtained from two solutions mixed with each other in the Q band region varied between 8% and 15% with respect to the value before mixing. It was also observed that the results obtained by mixing **2** and **4** solutions with each other changed the energy band gap of the resulting films. Further manipulation of the transmittance and energy band gap in the Q and B band regions may be achieved by mixing two more concentrated solutions.

3. Experimental

3.1. Equipment and materials

FT-IR spectra were obtained on a PerkinElmer Spectrum One FT-IR spectrometer. Mass spectra were recorded on Ultima Fourier Transform and Varian 711 mass spectrometer. Elemental analyses were performed at the Instrumental Analysis Laboratory of the TÜBİTAK Marmara Research Centre. Electronic spectra were recorded on a Scinco SD 1000 single-beam ultraviolet-visible (UV-Vis) spectrophotometer at room temperature. ^1H NMR spectra were obtained on an Agilent VNMRS 500 MHz spectrometer using TMS as internal reference. All solvents and reagents were obtained from commercial suppliers. Furthermore, all solvents were purified and

dried as described previously.²⁸ The purity and homogeneity of the products were tested at each step by TLC (SiO₂). 4-Nitrophthalonitrile was synthesized according to a reported procedure.²⁹ 4-(Hexylthio)phthalonitrile (**1**) and tetrakis(hexylthio) indium(III)phthalocyaninechloride (**2**) were synthesized according to a procedure in the literature.^{11,30}

3.2. Synthesis procedures for metallophthalocyanines (3–5)

A mixture of starting compound (4-(hexylthio)phthalonitrile (**1**) (0.245 g, 1 mmol)) and 0.25 mmol of anhydrous metal salt [CuCl₂ (0.033 g), Zn(OAc)₂ (0.032 g), or VO(SO₄)₂ (0.065 g)] was reacted in a glass tube with 1–2 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in n-pentanol (2 mL). The solution was stirred and heated at 140 °C under N₂ overnight. The temperature of the resulting mixture was lowered to room temperature first and then the product was precipitated in ice-water. The green crude precipitate was filtered off and it was washed first with water and then with cold acetone, hexane, and cold ethanol consecutively and dried in vacuo. Purification of MPcs (**3–5**) was achieved by chromatography (on silica gel as solid phase) using a suitable eluent.

3.2.1. Tetrakis(hexylthio)copper(II)phthalocyanine (3)

Eluent: dichloromethane/ethanol (10:1). The yield was 105 mg (40.40%). Melting point > 200 °C. FT-IR, (cm⁻¹): 2952–2856 (alkyl-CH), 1258, 1072, 759; UV-Vis λ_{max} (nm) (log ϵ) in THF: 689 (5.31), 345 (5.22); MS: m/z 1041.97 [M + 1]⁺; Anal. calc. for C₅₆H₆₄CuN₈S₄: C, 64.61; H, 6.20; N, 10.76. Found: C, 64.56; H, 6.16; N, 10.72%.

3.2.2. Tetrakis(hexylthio)zinc(II)phthalocyanine (4)

Eluent: dichloromethane/ethanol (5:1). The yield was 131 mg (50.10%). Melting point > 200 °C. FT-IR, (cm⁻¹): 2950–2854 (alkyl-CH), 1256, 1036, 741; ¹H NMR (CDCl₃-d₆), δ : 8.88–7.88 (m, 12H, aromatic-H), 3.43 (t, 8H, alkyl-H), 2.06 (qnt, 8H, alkyl-H), 1.61–1.372 (m, 24H, alkyl-H), 0.96 (t, 12H, alkyl-H); UV-Vis λ_{max} (nm) (log ϵ) in THF: 688 (5.30), 356 (4.88); MS: m/z 1040.22 [M]⁺; Anal. calc. C₅₆H₆₄N₈S₄Zn: C, 64.50; H, 6.19; N, 10.75 Found: C, 64.54; H, 6.22; N, 10.77%

3.2.3. Tetrakis(hexylthio)vanadylphthalocyanine (5)

Eluent: dichloromethane/ethanol (20:1). The yield was 115 mg (44.06%). Melting point > 200 °C. FT-IR, (cm⁻¹): 2952–2855 (alkyl-CH), 1259, 1070, 740; UV-Vis λ_{max} (nm) (log ϵ) in THF: 712 (5.29), 349 (5.11); MS: m/z 1066.85 [M + Na]⁺; Anal. calc. C₅₆H₆₄N₈OS₄V: C, 64.40; H, 6.18; N, 10.73; Found: C, 64.35; H, 6.15; N, 10.70%.

3.3. Preparation of thin films

Each MPc solution was prepared by dissolving 10 mg of MPcs (**2–5**) in 1 ml of THF with stirring by a magnetic stirrer at room temperature for 5 min. Due to the high solubility of MPc in THF, a homogeneous solution is obtained. Thin films of MPcs (**2–5**) were obtained by spin coating at the rate of 2000 rpm for 15 s. All of the MPcs' (**2–5**) coatings were prepared on microscope glass substrates at room temperature (~25 °C). The transmittance of the MPc thin films was recorded in the 200–1000 nm wavelength range using a Thermo Scientific GENESYS10S UV-Vis spectrophotometer.

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