



# The synthesis, photophysical and electrochemical studies of symmetrical phthalocyanines linked thiophene substituents



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## ARTICLE INFO

### Article history:

Received 25 June 2014

Received in revised form 12 August 2014

Accepted 13 August 2014

Available online 21 August 2014

### Keywords:

Phthalocyanine

Thiophene

Phthalonitrile

## ABSTRACT

Tetrakis 4-(3-thienyl) and tetrakis 4-(5'-hexyl-2,2'-bithiophene) peripherally substituted zinc phthalocyanines were synthesized by using phthalonitrile derivatives. The phthalonitrile compounds were obtained through palladium catalyzed Suzuki–Miyaura cross-coupling reaction. The synthesized phthalocyanines were characterized by FT-IR, <sup>1</sup>H NMR and MALDI-TOF-MS methods. The absorption and emission properties were studied by using UV–Vis absorption and photoluminescence spectroscopies. The electrochemical behaviors of compounds were also investigated using cyclic voltammetry (CV) measurements. The 5'-hexyl-2,2'-bithiophene substituent shifted the absorption band to red region and decreased the HOMO–LUMO energy gap of phthalocyanines.

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## 1. Introduction

Phthalocyanines (Pc) and metallophthalocyanines (MPc) have received much attention as functional materials for various applications, including catalysis, photodynamic therapy, chemical sensors, and solar cells [1–4]. Such applications are based on unique optical, electrical, physical, chemical, and biological properties of the phthalocyanines [5,6]. Furthermore, the properties of Pcs can be altered by the introduction of appropriate substituents at the periphery of the phthalocyanine and by metal insertion. Many different substituents and over seventy metals used to modify the properties of phthalocyanine molecules and to enhance their potential application areas [7,8]. However, much less effort has been focused on the directly substitution of phthalocyanine at the  $\beta$  positions with thiophene derivatives [9,10]. Thiophenes have been widely investigated  $\pi$ -conjugated organic molecules due to their stability and the fact that their synthetic chemistry has been well-defined [11]. In addition, their structural planarity permits strong electronic conjugation within the structure. For these reasons, substitution of thienyl groups at the  $\beta$  positions of the Pc ring could result in the extension and refinement of the  $\pi$ -systems [10]. On the other hand, if the 2 or/and 5 position of the thiophene moiety is suitable, the phthalocyanine polymer films can be prepared by electrochemical method on electrodes for various application

areas. Özçeşmeci et al. reported the synthesis and electrochemical properties of phthalocyanines with ethynylthiophene substituent on periphery position and found that the metal center of the phthalocyanines affects the polymerization process [12]. Yavuz et al. synthesized the tetrakis 4-(2,5-di-2-thiophene-2-yl-pyrrol-1-yl) substituted nickel phthalocyanine (NiPc-SNS) and this molecule was polymerized by electrochemical method [13]. Muto et al. reported the synthesis of octabutoxyphthalocyanines having eight 2-thienyl and [2,2'-bithiophene]-5-yl groups at  $\beta$  positions and investigated their electrochemical and spectral features [10].

In this work, we have synthesized new symmetrical phthalocyanines linked 3-thienyl and 5'-hexyl-2,2'-bithiophene groups at peripheral positions. The electrochemical behavior, absorption and emission properties of the phthalocyanines were investigated by using CV, UV–Vis and PL measurements.

## 2. Experimental

### 2.1. Materials

4-Aminophthalonitrile, 3-thiopheneboronic acid, 5'-hexyl-2,2'-bithiophene boronic acid pinacol ester, CHCl<sub>3</sub>, THF, Hexane, Pd(PPh<sub>3</sub>)<sub>4</sub>, dimethoxy ethane (DME), 2-dimethylaminoethanol (DMAE), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU), zinc (II) acetate were purchased from Aldrich; Silica Gel 60 (0.04–0.063) was purchased from Merck.

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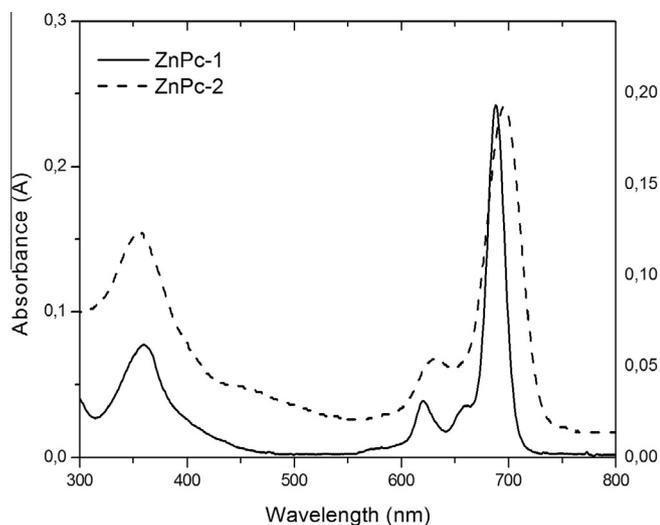


Fig. 1. Absorption spectra of ZnPc-1 and ZnPc-2 in THF.

FTIR spectra were measured between 400 and 4000  $\text{cm}^{-1}$  from KBr pellets on a Perkin Elmer Spectrum BX FTIR system (Beaconsfield, Buckinghamshire, HP91QA, England). The NMR (400 MHz) spectra were recorded using a Bruker Ultrashield Plus Biospin GmbH spectrometer in  $\text{CDCl}_3$ . The absorption spectra were recorded using Perkin Elmer Lambda 20 UV-Vis spectrometer. The fluorescence spectra were measured on Varian Cary Eclipse fluorescence spectrophotometer. Mass spectra were measured using Bruker Microflex LT MALDI-TOF mass spectrometer.

## 2.2. Synthesis of 4-iodophthalonitrile (1)

This compound was synthesized as described in literature [14]. Yield: 69%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) = 8.17 (d, 1H), 8.12 (dd, 1H,  $J = 8$  Hz), 7.52 (d, 1H,  $J = 6.8$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) = 142.48 (C-5), 142.07 (C-3), 134.01 (C-6), 117.04 (2C; CN), 114.94 (C-2), 113.85 (C-4), 99.69 (C-4). FTIR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3436, 3091, 3060, 3015, 2232 (–CN), 1946, 1811, 1680, 1572, 1543, 1468, 1372, 1277, 1265, 1205, 1178, 1101, 1071, 974, 907, 839, 581, 526, 475, 431, 410.

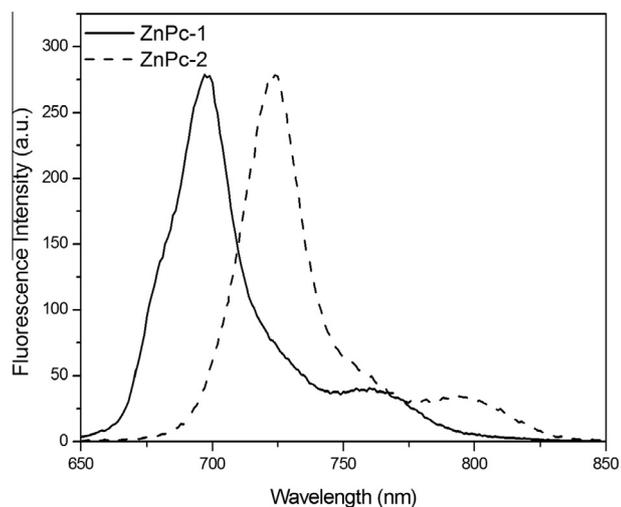


Fig. 2. Emission spectra of ZnPc-1 and ZnPc-2 in THF (Excitation: 600 nm).

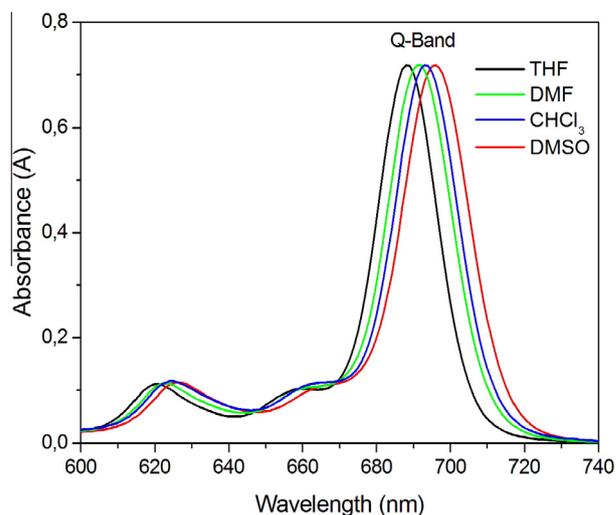


Fig. 3. Q-Band absorption of ZnPc-1 in different solvents.

Table 1

UV-Vis absorption and emission spectral data of ZnPc-1 in different solvents at 25 °C.

	$\lambda_{\text{max}}$ (nm) ( $\epsilon$ , $\text{M}^{-1} \text{cm}^{-1}$ )				$\lambda_{\text{max}}$ (nm)
	THF	DMF	$\text{CHCl}_3$	DMSO	
ZnPc-1	360 (4.65)	366 (4.87)	359 (4.53)	367 (4.74)	697
	621 (4.35)	623 (4.58)	625 (4.18)	626 (4.44)	
	688 (5.16)	691 (5.38)	693 (4.96)	696 (5.24)	
ZnPc-2	355 (5.02)	362 (5.01)	357 (4.70)	–	724
	634 (4.69)	632 (4.62)	638 (4.31)		
	696 (5.15)	697 (5.35)	700 (4.91)		

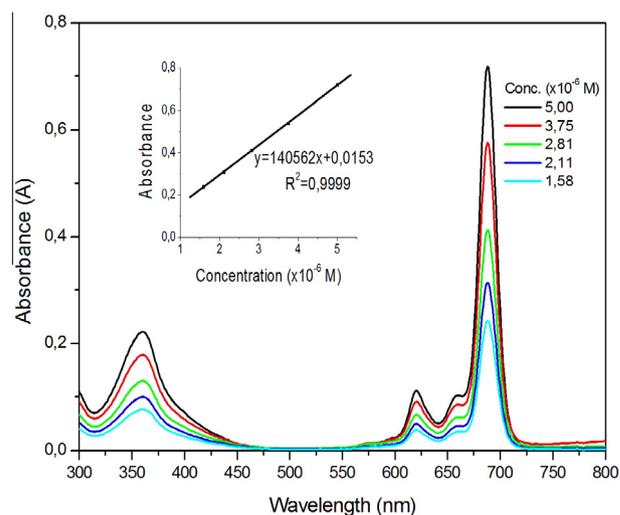


Fig. 4. Absorption spectra of ZnPc-1 in THF with different concentrations range from  $1.58 \times 10^{-6}$  to  $5.00 \times 10^{-6}$  M.

## 2.3. Synthesis of 4-(3-thienyl)phthalonitrile (2)

4-Iodophthalonitrile (127 mg, 0.5 mmol), 3-thienylboronic acid (70.05 mg, 0.55 mmol) and tetrakis (triphenylphosphine) palladium (0) (57.8 mg, 0.05 mmol) were dissolved in 20 ml of DME. To this aqueous solution of sodium carbonate (26.5 mg, 0.25 mmol)

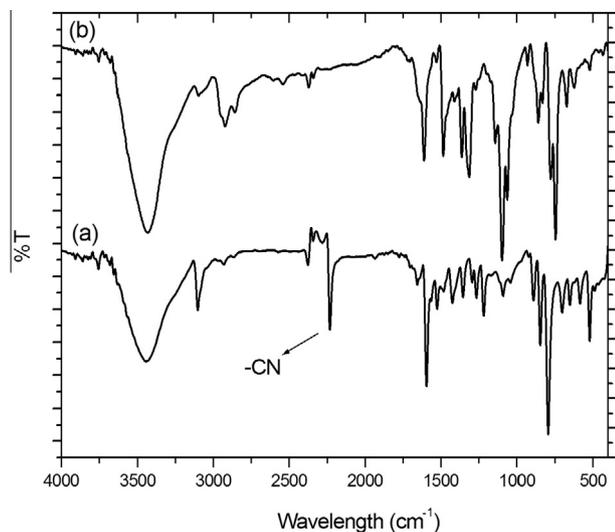


Fig. 5. FTIR spectra of 4-(3-thienyl)phthalonitrile (a) and ZnPc-1 (b).

was added. The resultant reaction mixture was heated at 80 °C under argon atmosphere for 16 h and then the reaction mixture is allowed to cool to room temperature. The reaction mixture was filtered and solvent was evaporated and the solid obtained was subjected to silica gel column chromatography and eluted with chloroform:hexane (3:1) mixture. Yield: 75%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) = 7.26 (m, 1H, Ar-H), 7.40 (m, 1H, Ar-H), 7.50 (m, 1H, Ar-H), 7.67 (m, 1H, Ar-H), 7.84 (m, 1H, Ar-H), 7.91–8.00 (m, 1H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) = 113.57, 115.39, 115.50, 116.66, 124.26, 125.52, 128.14, 130.36, 131.07, 134.08, 138.18, 140.78. FTIR (KBr)  $\nu$  (cm<sup>-1</sup>): 3102, 2230 (-CN), 1654, 1594, 1523, 1423, 1353, 1264, 1216, 1089, 891, 846, 794, 702, 651, 584, 521.

#### 2.4. Synthesis of 4-(5'-hexyl-2,2'-bithiophene)phthalonitrile (3)

4-Iodophthalonitrile (254 mg, 1 mmol), 5'-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester (414 mg, 1.1 mmol) and tetrakis(triphenylphosphine) palladium (0) (115.56 mg, 0.1 mmol) were dissolved in 20 ml of DME. To this aqueous solution of sodium carbonate (53 mg, 0.5 mmol) was added. The resultant reaction mixture was heated at 80 °C under argon atmosphere for 24 h and then the reaction mixture is allowed to cool to room temperature. The reaction mixture was filtered and solvent was evaporated and the solid obtained was subjected to silica gel column chromatography and eluted with chloroform:hexane (3:1) mixture. Yield: 58%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) = 0.94 (m, 3H, CH<sub>3</sub>), 1.36 (m, 2H, CH<sub>2</sub>), 1.42 (m, 2H, CH<sub>2</sub>), 1.72 (m, 2H, CH<sub>2</sub>), 2.84 (m, 2H, CH<sub>2</sub>), 6.76 (m, 1H, Ar-H), 7.11 (m, 1H, Ar-H), 7.29 (m, 1H, Ar-H), 7.79 (m, 1H, Ar-H), 7.80 (m, 1H, Ar-H), 7.86 (m, 1H, Ar-H), 7.97 (m, 1H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) = 14.07, 22.57, 28.74, 30.24, 31.54, 112.74, 115.24, 115.52, 116.73, 124.33, 124.76, 125.22, 127.38, 128.71, 129.48, 132.44, 134.04, 136.88, 139.29, 141.76, 147.38. FTIR (KBr)  $\nu$  (cm<sup>-1</sup>): 3106, 3067, 2954, 2920, 2841, 2229 (-CN), 1719, 1593, 1554, 1495, 1446, 1439, 1411, 1369, 1314, 1280, 1219, 1202, 1175, 1104, 1065, 905, 879, 837, 796, 777, 723, 521, 486, 430.

#### 2.5. Synthesis of meso-tetrakis(3-thienyl)phthalocyanine zinc(II) (ZnPc-1)

4-(3-Thienyl)phthalonitrile (105 mg, 0.5 mmol) and zinc (II) acetate (25 mg, 0.136 mmol) were dissolved in 10 ml of DMAE.

The mixture was added by three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and heated at 130 °C under argon atmosphere for 24 h. The reaction mixture was then allowed to cool to room temperature and the product was filtered and solvent was evaporated. The solid obtained was washed several times with MeOH:H<sub>2</sub>O (5:1) and the solid obtained was subjected to silica gel column chromatography and eluted with hexane:ethyl acetate (5:2) to give green product. Yield: 71%. FTIR (KBr)  $\nu$  (cm<sup>-1</sup>): 3432, 3097, 2921, 2857, 2541, 1609, 1482, 1361, 1313, 1140, 1095, 1062, 931, 859, 777, 746, 673, 624, 521. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) = 6.54–7.03 (12H, thienyl, Ar-H), 7.50–8.10 (12H, Ar-H). UV-Vis (THF):  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) = 360 (4.65), 621 (4.35) and 688 (5.16). MALDI TOF MS:  $m/z$ : calculated 906.43; found 905.96.

#### 2.6. Synthesis of meso-tetrakis(5'-hexyl-2,2'-bithiophene)phthalocyanine zinc(II) (ZnPc-2)

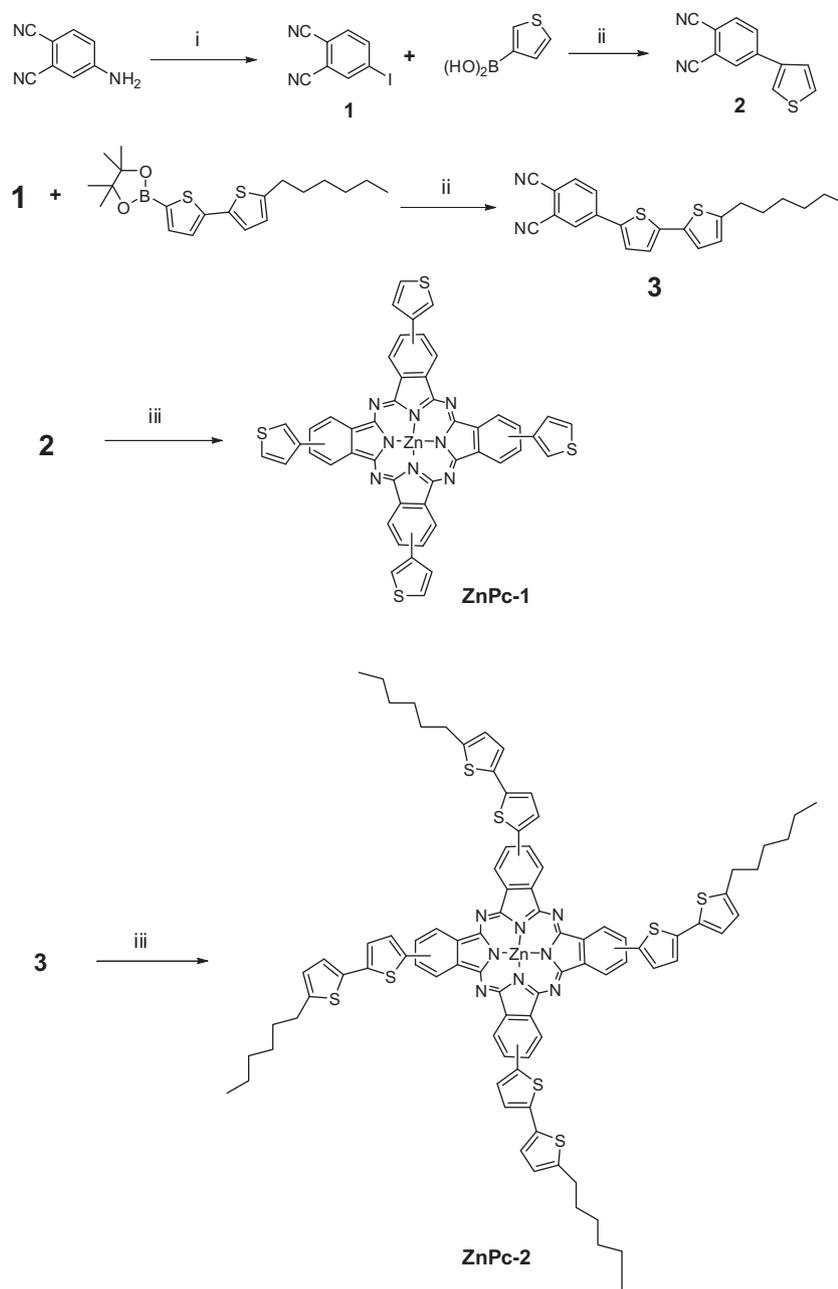
4-(5'-hexyl-2,2'-bithiophene)phthalonitrile (94.15 mg, 0.25 mmol) and zinc (II) acetate (12.61 mg, 0.069 mmol) were dissolved in 10 ml of DMAE. The mixture was added by three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and heated at 130 °C under argon atmosphere for 24 h. The reaction mixture was then allowed to cool to room temperature and the product was filtered and solvent was evaporated. The solid obtained was washed several times with MeOH:H<sub>2</sub>O (5:1) and the solid obtained was subjected to silica gel column chromatography and eluted with hexane:THF (5:1) to give green product. Yield: 62%. FTIR (KBr)  $\nu$  (cm<sup>-1</sup>): 3634, 3435, 3059, 2918, 2855, 1724, 1613, 1481, 1443, 1391, 1325, 1132, 1094, 1055, 883, 785, 748, 733, 465. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) = 0.91–2.84 (several m, 52H, alkyl), 6.54–7.33 (28H, Ar-H). UV-Vis (THF):  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) = 355 (5.02), 634 (4.69) ve 696 (5.15). MALDI TOF MS:  $m/z$ : calculated 1571.56; found 1572.10.

### 3. Results and discussion

The synthesis of symmetrical zinc phthalocyanines was illustrated in the Schema 1. The phthalonitrile compounds **2** and **3** were obtained through Suzuki–Miyaura cross-coupling reaction of 4-iodophthalonitrile with 3-thienylboronic acid and 5'-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester, respectively. ZnPc-1 and ZnPc-2 were prepared through **2** and **3**, in DMAE solution in the presence of DBU and zinc salt. Usually, the tetra-substituted Pcs which are prepared from 4-substituted phthalonitriles give a mixture of four positional isomers with D<sub>2h</sub>, D<sub>4h</sub>, C<sub>2v</sub> and C<sub>s</sub> symmetries [15]. Separation of these four isomers is extremely difficult with common column chromatography or recrystallization. Therefore, both ZnPc-1 and ZnPc-2 were obtained as a mixture of isomers.

#### 3.1. Absorption and emission results

The absorption spectra of phthalocyanines are shown in Fig. 1. The strong absorption of phthalocyanines in the visible region are assigned as the Q-band, which are attributed to the  $\pi$ - $\pi^*$  transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring [16]. ZnPc-1 and ZnPc-2 exhibited a strong absorption peak at 688 and 696 nm, respectively. In addition, both phthalocyanines exhibited absorption band around 360 nm known as Soret band. ZnPc-2, additionally present a weak absorption around 400 nm, which is assigned to the  $\pi$ -conjugated bithiophene substituent [17].



**Scheme 1.** Synthesis of phthalonitrile derivatives and phthalocyanines. (i)  $\text{H}_2\text{SO}_4$ ,  $\text{NaNO}_2$ ,  $\text{KI}$ . (ii)  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{DME}$ ,  $80\text{ }^\circ\text{C}$ ,  $24\text{ h}$ . (iii)  $\text{Zn}(\text{OAc})_2$ ,  $\text{DMAE}$ ,  $\text{DBU}$   $130\text{ }^\circ\text{C}$ ,  $24\text{ h}$ .

Fluorescence spectra of ZnPc-1 and ZnPc-2 are shown in Fig. 2. The excitation wavelength is 600 nm. ZnPc-1 exhibited a maximum emission peak at 697 nm, while ZnPc-2 exhibited red shifted emission peak at 724 nm. Conjugated bithiophene moiety shifted the emission maxima to red region by 31 nm in ZnPc-2.

The compounds ZnPc-1 and ZnPc-2 show an extended  $\pi$ -conjugation system, which produces a redshift in the absorption and emission maximum, in comparison with the unsubstituted zinc phthalocyanine (ZnPc). ZnPc shows a Q-band absorption at 668 nm in THF [18], whereas ZnPc-1 and ZnPc-2 dyes show a maximum absorbance at 688 and 696 nm, respectively. The use of conjugated 3-thienyl and 5'-hexyl-2,2'-bithiophene substituents enhanced the conjugation length of the phthalocyanine macrocycle.

Fig. 3 depicts the Q-band absorption of ZnPc-1 in different solvents. Q-bands were red-shifted by about 3 nm, 5 nm and 8 nm by replacing THF with DMF,  $\text{CHCl}_3$  and DMSO, respectively. Table 1

summarizes the UV-visible absorption spectral data of the compounds at different solvents and emission data in THF.

The aggregation behaviors of the Pcs were investigated in THF. Fig. 4 shows the absorption spectra of ZnPc-1 at different concentrations. As shown in the figure, the intensity of absorption bands increases with increasing concentration and no new bands were observed signifying no aggregation behavior at these concentrations. This is probably due to the bulky nature of the ring substituents. The same behaviors were also observed for ZnPc-2. Lambert-Beer's law was observed for two complexes at the concentrations less than  $5 \times 10^{-6}\text{ M}$  [19].

### 3.2. FTIR studies

Fig. 5 shows the FT-IR spectra of 4-(3-thienyl)phthalonitrile and ZnPc-1. The characteristic CN stretching of phthalonitrile were observed at  $2230\text{ cm}^{-1}$ . The disappearance of the characteristic

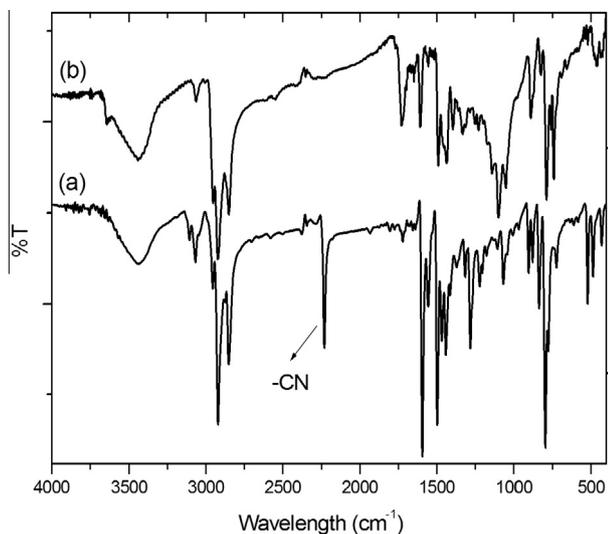


Fig. 6. FTIR spectra of 4-(5'-hexyl-2,2'-bithiophene)phthalonitrile (a) and ZnPc-2 (b).

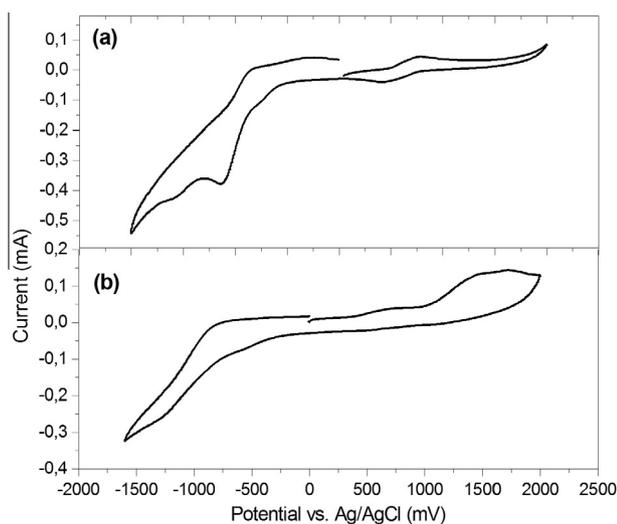


Fig. 7. Cyclic voltammograms of ZnPc-1 (a) and ZnPc-2 (b) in 0.1 M TBAPF6 + DMF:DCM (1:1) on ITO working electrode. Scan rate: 25 mV/s.

Table 2  
Electrochemical and optical properties of ZnPc-1 and ZnPc-2.

	$E_{ox}^{on}$ (V) <sup>a</sup>		$E_{red}^{on}$ (V) <sup>b</sup>	HOMO (eV)	LUMO (eV)	$E_g^{elec}$ (eV)
ZnPc-1	0.55	1.40	-0.92	-4.78	-3.31	1.47
ZnPc-2	0.42	1.03	-0.93	-4.65	-3.30	1.35

<sup>a</sup> Oxidation onset potential.

<sup>b</sup> Reduction onset potential vs. Ag/AgCl reference electrode.

CN band confirms the formation of phthalocyanine [20]. The bands at around 3100 and 3097  $\text{cm}^{-1}$  are assigned to the aromatic C–H vibrations. While phthalonitrile shows aromatic C=C stretching at 1594  $\text{cm}^{-1}$ , phthalocyanine shows the same stretching peak at 1609  $\text{cm}^{-1}$ . Fig. 6 shows the FT-IR spectra of 4-(5'-hexyl-2,2'-bithiophene)phthalonitrile and ZnPc-2. The characteristic CN stretching of phthalonitrile were observed at 2229  $\text{cm}^{-1}$ . FT-IR spectrum of phthalonitrile shows aromatic C–H stretching peak at 3106 and

3067  $\text{cm}^{-1}$  and aliphatic C–H symmetric stretching at 2954, 2920 and 2851  $\text{cm}^{-1}$  which indicates the hexyl group. The aliphatic C–H stretching in ZnPc-2 was observed at 2952, 2918 and 2855  $\text{cm}^{-1}$ . The C=C stretching of phthalonitrile and ZnPc-2 was observed at 1593 and 1613  $\text{cm}^{-1}$ , respectively. The band at 1440  $\text{cm}^{-1}$  is assigned to the C=C stretching of bithiophene in the both structure [21].

### 3.3. Electrochemical studies

The electrochemical behavior of the compounds was investigated using cyclic voltammetry (CV). Fig. 7 shows the cyclic voltammograms (CVs) of ZnPc-1 and ZnPc-2 in DMF solution containing 0.1 M TBAPF6 as an electrolyte. ZnPc-1 shows a reversible oxidation wave at 0.6 V ( $E_{1/2}$ ) which assigned to the phthalocyanine ring. The onset oxidation and onset reduction potentials are given in Table 2. The HOMO–LUMO level energy gap also known as electrochemical band gap is estimated from the difference between the first oxidation and the first reduction potential from cyclic voltammograms [10]. The HOMO energy level, LUMO energy level, and electrochemical band gap ( $E_g^{elec}$ ) were calculated as follows:

$$\text{HOMO} = -[E_{ox}^{on} - E_{1/2}(\text{ferrocene}) + 4.8]\text{eV},$$

$$\text{LUMO} = -[E_{red}^{on} - E_{1/2}(\text{ferrocene}) + 4.8]\text{eV},$$

$$E_g^{elec} = (\text{LUMO} - \text{HOMO})\text{eV},$$

where  $E_{1/2}(\text{ferrocene})$  is the ferrocene half-wave potential (0.57 mV),  $E_{ox}^{on}$  is the oxidation onset potential,  $E_{red}^{on}$  is the material reduction onset potential, and 4.8 eV is the energy level of ferrocene below the vacuum level. The HOMO–LUMO gaps obtained from the onset oxidation–reduction potentials were calculated at 1.47 eV for ZnPc-1 and 1.35 eV for ZnPc-2, respectively. In addition, both of the Pcs showed oxidation over 1.2 V. The HOMO–LUMO gap of ZnPc-1 and ZnPc-2 decreased upon increasing the conjugation length [22], in comparison with the unsubstituted ZnPc [23]. Muto et al. reported the similar observation for 2-thienyl and [2-2'-bithiophene]-5-yl substituted 1,4,8,11,15,18,22,25-octa-butoxyphthalocyanines ((OBu)<sub>8</sub>Pcs) [10]. The calculated HOMO and LUMO energy levels of ZnPcs are summarized in Table 2.

## 4. Conclusions

In summary, the syntheses of two peripherally tetra-substituted zinc phthalocyanines were presented. Spectral and electrochemical characterizations were carried out. The 5'-hexyl-2,2'-bithiophene substituent shifted the absorption band to red region and decreased the HOMO–LUMO energy gap of phthalocyanine. It was also found that the phthalocyanines have no aggregation in low concentrations.

## Acknowledgements

This work was supported financially by the grant of Suleyman Demirel University, Scientific Research Projects (2950-D-11).

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