The synthesis and photochemical characterization of *meso*-tetra-thienyl porphyrins

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Abstract

A series of *meso*-thienyl porphyrins were synthesized through Lindsey's procedure and characterized. Compared with H_2TPP (tetraphenyl-porphyrin), the absorption and fluorescence spectra of thienyl porphyrins have red shift obviously which show that thienyl substituents at *meso*-position change the electronic structure of tetrapyrrole ring. With protonation using CF_3COOH, the absorption bands of thienyl porphyrins are further red shifted. The absorption bands of *meso*-thienyl porphyrins change correspondingly with the variation of solvents' properties, however the maxima emission wavelengths corresponding to Q^* have little relation with solvents. And the fluorescence lifetime become so less even to 1.1 ns. The half-wave redox potential shows cathodic shift relative to H_2TPP. These changes above are all ascribed to the introduction of thienyl group at *meso*-position and the possibility of more planarity of *meso*-thienyl porphyrins for the small size of thienyl group which is helpful to the extending π-delocalization of thienyl groups to the tetrapyrrole ring.
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Keywords: Porphyrin; Thienyl; Absorption spectra; Fluorescence spectra; Solvent effect

1. Introduction

Porphyrins lie at the focal point of research because of their wide use in many fields, such as oxygen transfer [1], energy and electron transfer [2], light harvesting [3], molecular wires [4] and so on. Porphyrins can be synthesized flexibly by introducing different substituents at the *meso*- and β-position, and the photophysical and photochemical properties of porphyrins can be tuned for many applications [5]. The *meso*-substituted porphyrins are a subgroup of porphyrins with interesting properties [6,7]. *meso*-tetraarylporphyrins show attractive properties and have been used in a wide variety of model systems for their easy synthesis and functionalization. However, porphyrins with five-membered aromatic ring substituted at *meso*-position are seldom reported [8–10], although five-member ring substituted porphyrins

have potential application in material chemistry for their unusual electronic properties [10] and solid-state conductivity [8].

Takeo Shimidzu et al. synthesized porphyrins substituted by thiophene and oligo-thiophene at the *meso*-position and the *meso*-thienyl porphyrins had been found to have good film-forming properties and conductivity [10]. Effenberger et al. synthesized anthryloligothienylporphyrins containing anthryl as a donor, porphryin as acceptor and oligothiophene as bridge. This system offered efficient energy transfer from anthryl to porphyrin [11]. Li Zhongfang synthesized *meso*-thienyl porphyrins and characterized by ESR for their efficient photoelectron transfer [12]. The optical, redox, and axial ligation studies of *meso*-thienyl porphyrins were reported recently [13]. In the present work, we synthesized four porphyrins substituted at meso-position by thienyl group with different substituent through Lindsey's method [14] (see Scheme 1) and *meso*-tetra(5-methyl-thienyl) porphyrin (4) was unreported before. Then the absorption and fluorescent

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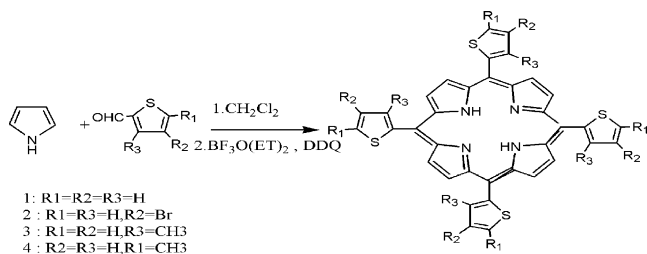
Scheme 1.

spectra of *meso*-thienyl porphyrins were discussed and expected some help for the future research work of thienyl porphyrins.

2. Experimental

^{1}H NMR spectra were recorded on DRX500 MHz using tetramethylsilane as internal standard and $CDCl_3$ as solvent. UV–vis spectra were measured on Varian Cary 500, and steady-state fluorescence spectra were obtained on Cary Eclipse Fluorescence Phosphospectrometer, respectively. Fluorescence lifetimes were obtained at EdinBurgh FL920. IR spectra were recorded as KBr discs on Nicolet Magna IR550 Spectrophotometer. EI–MS were obtained from Micromass GCT Spectrometer. Cyclic voltammograms were obtained from Shanghai Chenhua CHI 660B provided with three electrodes cell assembly.

meso-Thienyl porphyrin (**1**) was prepared by Lindsey's procedure from 2-thiophenealdehyde and pyrrole using $BF_3 \cdot O(ET)_2$ as catalyst at room temperature under the N_2 condition and the other three porphyrins were synthesized similarly.

2.1. The synthesis of meso-tetrathienyl porphyrin (1)

Fifty millilitres CH_2Cl_2 was added to a 100 ml three-neck round bottom flask equipped with magnetic stirring and fitted with a glass air bubbler with a rather porous tip, a gas outlet valve, and a rubber septum. Then the reaction flask was purged by N_2 for about 10 min, 345 μl pyrrole and 463 μl thiophenealdehyde were added through springe. After 5 min, 200 μl $BF_3 \cdot O(ET)_2$ solution (2.5 M stock solution in toluene) was added through springe and the color of the mixture became from colorless to yellow, red, and brown rapidly. The reaction was carried out at room temperature. Samples were taken via springe (30 μl) in the process of reaction and through absorption spectrum we can detect the formation of *meso*-thienyl porphyrin. At the end of 1 h, N_2 was removed and 0.6 g DDQ (dichlorodicyanobenzoquinone) was introduced. Stirring was continued for another hour, and the product concentration reached its top. Then triethylamine (TEA) was added to remove the excess acid. The porphyrin was introduced to the top of the column filled with silica gel (200–300 mesh). Using CH_2Cl_2 as eluent, the

band moving firstly was porphyrin and collected to dry. The porphyrin obtained used column to separate again and the pure porphyrin obtained as purple crystals (168 mg). Yields: 20.5%, mp > 300 °C; EI–MS: $C_{36}H_{22}N_4S_4$, calcd. av. mass, 638, obsd. m/z 638(M⁺); ^{1}H NMR ($CDCl_3$) δ: −2.76(s, 2H), 7.48–7.63(m, 4H), 8.20–8.56(m, 8H), 8.57–8.71(m, 8H); [12]

2.2. The synthesis of meso-tetra-(4-bromo-thienyl) porphyrin (2)

The synthesis of *meso*-tetra-(4-bromo-thienyl) porphyrin is similar to the up procedures, and the 2-thiophenealdehyde was replaced by 4-bromo-thiophenealdehyde (0.95 g). The product was purple crystals (226 mg). Yields: 18.5%, mp > 300 °C; EI–MS: $C_{36}H_{22}N_4S_4$, calcd. av. mass 954, obsd. m/z 954(M⁺); ^{1}H NMR ($CDCl_3$) δ: −2.76(s, 2H), 8.17(s,4H), 8.29(s, 4H), 8.67(s, 8H); [12].

2.3. The synthesis of meso-tetra-(3-methyl-thienyl) porphyrin (3)

The synthesis of *meso*-tetra-(5-methyl-thienyl) porphyrin is just like that of *meso*-tetra-thienylporphyrin, except that the 2-thiophenealdehyde was replaced by 3-methyl-thiophenealdehyde (0.63 g), porphyrin obtained as purple crystals (187 mg). Yields: 21%, mp > 300 °C; EI–MS: $C_{40}H_{30}N_4S_4$, calcd. av. Mass, 694, obsd. m/z 694(M⁺); ^{1}H NMR ($CDCl_3$) δ: −2.68(s, 2H), 2.08–2.20(m, 12H), 7.30–7.35(m, 4H), 7.70–7.76(m, 4H), 8.87–8.95(m, 8H); [12].

2.4. The synthesis of meso-tetra-(5-methyl-thienyl) porphyrin (4)

The synthesis of *meso*-tetra(5-methyl-thienyl) porphyrin is just like that of tetra-thienylporphyrin, except that the 2-thiophenealdehyde was replaced by 5-methyl-thiophenealdehyde (0.63 g). The *meso*-tetra(5-methyl-thienyl) porphyrin was obtained as purple crystals (200 mg). Yields: 22.7%, mp > 300 °C; EI–MS: $C_{40}H_{30}N_4S_4$, calcd. av. mass, 694, obsd. m/z 694(M⁺); ^{1}H NMR ($CDCl_3$) δ: −2.70(s, 2H), 2.78 (s, 12H), 7.15–7.17(d, 4H), 7.25–7.27 (m, 4H), 7.66–7.68(d, 8H); IR(KBr) ν: 3393, 2982, 1625, 1527, 1469, 960, 792 cm⁻¹.

3. Results and discussions

3.1. Steady-state absorption

The position of the absorption peak and molar extinction coefficients of *meso*-tetra-thienyl porphyrins and H_2TPP (tetraphenylporphyrin) are listed in Table 1. The absorption spectra and their dications' absorption spectra (inset) are shown in Fig. 1.

Table 1
Absorption data of tetra-thienyl porphyrins recorded in dichloromethane

Porphyrin	Soret band (nm) ($\varepsilon \times 10^{-5}$)	Q band (nm) ($\varepsilon \times 10^{-3}$)			
		Q_{y1}	Q_{y2}	Q_{x1}	Q_{x2}
H$_2$TPP	415 (2.749)	514 (19.5)	549 (8.1)	589 (5.6)	645 (4.4)
1	425 (2.579)	522 (13.6)	560 (6.7)	597 (4.8)	659 (3.9)
2	425 (2.574)	521 (15.3)	557 (6.4)	596 (5.0)	663 (6.3)
3	422 (2.885)	520 (24.5)	557 (8.1)	595 (8.3)	653 (2.1)
4	430 (2.341)	525 (11.7)	566 (8.3)	598 (5.0)	662 (4.1)

Compared to H$_2$TPP, the absorption bands of *meso*-tetra-thienyl porphyrins have red shift by 10–15 nm. Methyl substituted at different position of thiophene can show different influence on the position of absorption band. But the bromo atom has no obvious effect on absorption spectra. The thiophene ring is rich-electronic and can contribute electron to the π-system for the induction effect of S atom. According to the M. Gouterman's four orbital model, electron contributions of substituents at *meso*-position of porphyrin are known to effect energy of a_{2u} as the HOMO orbit [15]. Electron donating substituents cause an increase in a_{2u} orbit electron density and consequently cause a_{2u} HOMO to shift to higher energy, which induce a reduction band and absorption red shift [16]. The *meso*-tetra(3-methyl-thienyl) porphyrin has less red-shift spectrum because methyl at 3′-position of the thiophene ring close to tetrapyrrole ring and the extent of co-planarity and conjugation of system reduces and the Soret band locates at 422 nm. On the other hand, because of methyl group at 5′-position of thiophene ring, electron of thiophene ring in **4** is more rich and Soret band red shift to 430 nm. When the Br atom is introduced to thiophene ring, the position of absorption peak does not change obviously compared to **1**, which showing that Br atom has no distinct influence on the electron density of system. The dications generated
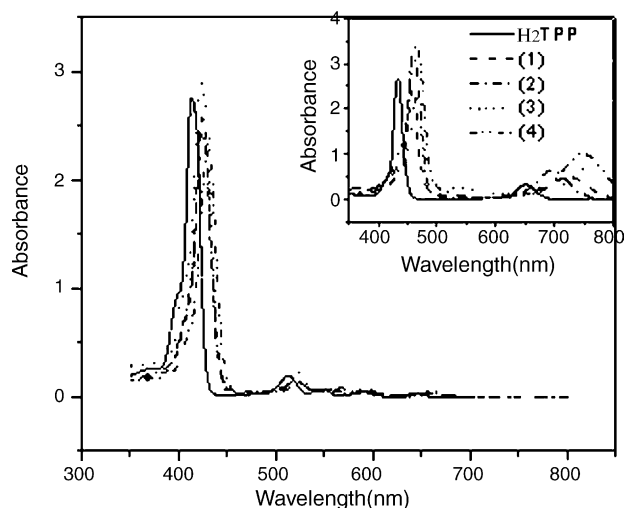
Table 2
Absorption data of dicationic porphyrins **1**–**4** and H$_2$TPP recorded in dichloromethane

Porphyrin	Soret band λ(nm) ($\varepsilon \times 10^{-5}$)	Q-band λ(nm) ($\varepsilon \times 10^{-5}$)
TPPH$_4^{2+}$	435 (2.95)	653 (0.52)
1 H$_4^{2+}$	458 (2.45)	724 (0.50)
2 H$_4^{2+}$	460 (3.18)	695 (0.65)
3 H$_4^{2+}$	466 (2.25)	765 (0.71)
4 H$_4^{2+}$	463 (3.36)	748 (1.01)

by addition of two drops of trifluoroacetic acid simplified the four Q-banded spectra to one Q-banded spectrum with one Soret band. The absorption bands of dications are further red shifted (Table 2, Fig. 1). It is shown that the red shift of Soret and Q-bands observed in the formation of dications is due to greater resonance interaction with thienyl groups with extension of conjugation in the dications [9]. Since the thienyl group is smaller than phenyl group, compared with H$_2$TPP the resonance interactions between tetrapyrrole ring and thienyl group are further increased, which reflected in the red shift of dications.

In dilute solution porphyrin molecules exist as single molecule and are surrounded by solvent molecules. But with the concentration increasing there are more and more porphyrin molecules aggregated. To determine the aggregation state of porphyrins, we measured the absorption of *meso*-thienyl porphyrin at different concentration in dichloromethane and the results were listed in Table 3. The porphyrin solution in dichloromethane was prepared before measurement without long term standing.

From Table 3 we can conclude that when concentration is less than 1×10^{-5} M, porphyrin molecules mostly exist as single molecule state in solution and the Soret band does not change obviously with the concentration. But with the concentration increasing Soret band even blue shift to 415.4 nm

Fig. 1. Comparison of absorption spectra of H$_2$TPP and tetra-thienyl porphyrins **1**, **2**, **3** and **4** recorded in dichloromethane. The inset shows the spectra of dications generated by addition of a drop of trifluoroacetic acid in dichloromethane.

Table 3
Soret band position of **1** at different concentration in dichloromethane

Concentration ($\times 10^{-5}$ M/L)	Soret band λ_{max} (nm)
0.1	425.6
0.5	425.6
1	425.4
2	422.0
4	419.4
6	415.4
8	416.0

Table 4
Absorption data of *meso*-tetrathienyl porphyrin **1** in different solvents

Solvents[a]	Absorption spectrum[b]				
	Soret band (nm)	Q_{y1} (nm)	Q_{y2} (nm)	Q_{x1} (nm)	Q_{x2} (nm)
n-Hexane	420.8	515.8	549.6	599.0	672.6
Dichloromethane	425.6	521.8	560.0	596.0	658.4
Tetrahydrofuran	462.2	–	–	–	659.6
Dimethylformamide	426.0	522.0	560.2	596.6	660.4
Ethanol	422.0	521.0	558.3	594.0	660.0
Ethanol (25% H_2O)[c]	422.4	522.1	–	594.3	665.1
Ethanol (50% H_2O)	431.1	527.1	–	598.8	667.7
Ethanol (75% H_2O)	424.8	525.8	–	598.6	668.0

[a] The polarity of the solvent increased in order.
[b] Spectral data in the table was measured at 25 °C, and concentration was 10^{-5} M.
[c] The concentration of ethanol solution including water was ratio of volume.

at 6×10^{-5} M. This maybe attribute to that aggregated porphyrins are mainly face to face and the excitation energy will rise [17,18], contrast to *J*-aggregates which have red shift absorption spectra in solution when porphyrin solution was kept for long time [18].

Porphyrins are low polar molecules and usually the maxima positions of their absorption spectra are not affected by solvents obviously [19,20]. But it is unexpected that *meso*-tetrathienyl porphyrins have obvious relation to the properties of the media. We selected different solvents for the porphyrins solution and measured their absorption spectra. The results were listed in Table 4 as above.

The data in Table 4 show that: (1) with the increasing of the solvent polarity, the Soret band and Q_y maxima position appear red shift, but Q_x shift to opposite direction. (2) In protic solvent the maxima of absorption differ from that of aprotic solvent. (3) In tetrahydrofuran there is a large red shift of Soret band unexpected. (4) When water molecule is added into the porphyrin solution in ethanol, the absorption spectra differ. Compared to H_2TPP, the characters of *meso*-tetrathienyl porphyrin absorption spectra have much relations to solvents although it should be a low-polar molecule estimated from the molecule structure. It maybe interpreted that the S_2 excited state of tetra-thienyl porphyrin can be stabilized efficiently for the existence of S atoms in molecule and the S_2 excited energy reduced accounting for the red shift of Soret band in polar solvents. According to Gouterman's interpretation [15], the polarity of solvents maybe have different effect on energy band between HOMO and two LUMO orbits which have symmetry e.g. accounting for Q_x and Q_y band shifting to opposite direction for the existence of S atom. In protic solvent there are maybe hydrogen bonds between solvents and the core of tetra-thienyl porphyrin, which disturb coplanarity, and the Soret band has just little red shift compared with the solvent with the similar polar medias [20]. Interestingly water molecules can affect tetra-thienyl porphyrin absorption obviously. With the concentration increasing of water the Soret band shifts to 430 nm from 422.4 nm although the polarity of solvent does not change evidently. It may be caused by the water molecules inserting into the core of the ring for its small size [19]. When the concentration of water

is up to 75%, the Soret band of porphyrins has blue shift to 424.8 nm. This may be due to the face-to-face aggregation of porphyrin formed at high concentration of water because of their poor solubility in water. The Soret band of porphyrins in tetrahydrofuran red shift to 462 nm shows that there are maybe porphyrin complexes formed in solution. The four Q bands of porphyrin become not clear without much alteration of absorption peak position unlike that of Soret band.

3.2. Fluorescence spectra

To specify the effect of substituents on their fluorescence spectra, H_2TPP and these four thienyl porphyrin's fluorescence spectra and fluorescence lifetimes were measured. The steady-state fluorescence spectra of *meso*-thienyl porphyrins are similar to that of H_2TPP's except the different maxima emission position. The maximum emission spectra corresponding to Q^* of *meso*-thienyl porphyrins are presented in the Fig. 2. And to show the relation of emission spectra and the solvents, we discussed their fluorescence spectra in different solvents. The maximum emission wavelengths in dif-
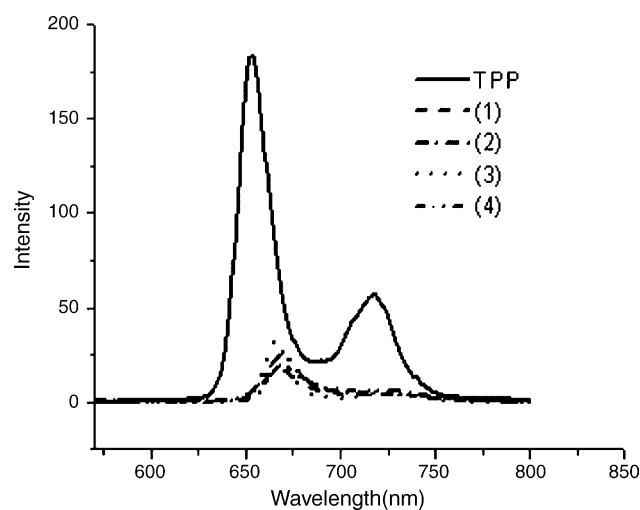

Fig. 2. Emission spectra of H_2TPP porphyrins **1**, **2**, **3** and **4** recorded in tetrahydrofuran at 1×10^{-5} M.

Table 5
Maximum emission wavelength of 1–4 in different solvents

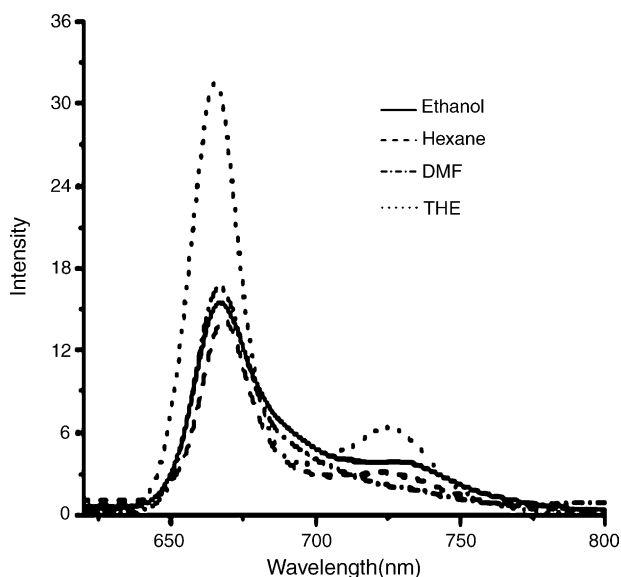| Solvents	Porphyrins			
	1 (nm)	2 (nm)	3 (nm)	4 (nm)
n-Hexane	664	667	666	666
Dichloromethane	667	668	662	668
Tetrahydrofuran	667	667	666	667
Dimethylformamide	668	667	667	672
Ethanol	663	666	665	665

Fig. 3. Emission spectra of meso-tetra-(3-methyl-thienyl) porphyrin 3 in ethanol, hexane, tetrahydrofuran and dimethylformamide.

ferent solvents are listed in Table 5. (The concentration of porphyrins solution here were about 1×10^{-5} M.) The typical emission spectra of tetra(5-methyl-thienyl) porphyrin in different solvents are shown in Fig. 3. The fluorescence decay signals is shown in Fig. 4. Excited state lifetimes of all porphyrins were obtained by an interactive non-linear deconvolution fitting procedure and all decay data were well
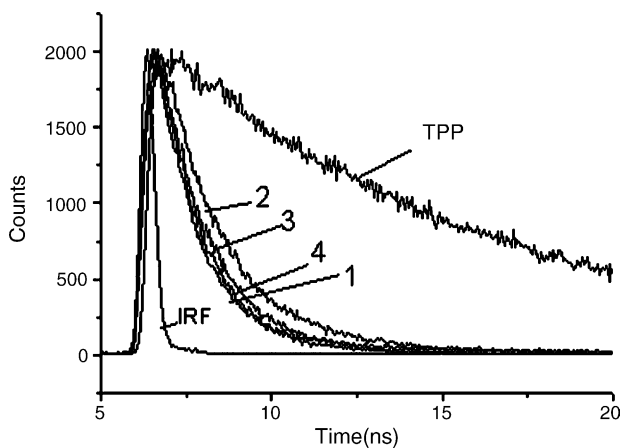

Fig. 4. Fluorescence decay signals of H_2TPP, 1, 2, 3 and 4. The detection wavelength is at 660 nm. IRF indicates instrumental response function.

Table 6
Photophysical properties of H_2TPP and thienyl porphyrin in toluene at ambient temperature

Compound	τ_f (ns)	Φ_f	k_f (1/ns)
H_2TPP	9.8	0.11[a]	0.102
1	1.11, 6.70[b]	0.01279	0.90
2	1.20, 2.53[b]	0.01729	0.83
3	1.47	0.01369	0.68
4	1.31	0.01425	0.76

[a] See Ref. [18].
[b] The minor component corresponding to 6.70 ns and 2.53 ns were assumed to be impurity.

fitted with single exponential except 2 and 3. The fluorescence quantum yields (Φ_f) and fitted fluorescence lifetime (τ_f) of all porphyrins are listed in Table 6.

From Fig. 2 and Fig. 3., we can find: (1) the maxima emission positions of $Q^*_{0–0}$ and $Q^*_{0–1}$ have little relation with the substituents and have red shift compared to H_2TPP, unlike that of meso-furyl porphyrins with one band in the emission spectra [9]. (2) The intensity of $Q^*_{0–1}$ have much relations to their structure. (3) In different solvents, there is no obvious change on the emission spectra unlike their absorption spectra. The emission spectra of thienyl porphyrins are similar to that of H_2TPP which have reverse mirror-image symmetry between absorption and fluorescence spectra [21]. When phenyl ring is replaced by thienyl ring, the extent of conjugation of this system become more efficient because of the induction of S atom and thiophene ring is smaller than phenyl ring resulting in the reduction of dihedral-angles between the porphyrin ring and thiophene ring which permits the greater π-conjugation in the S_1 excited state than in the ground state [21] and emission band shift to red. The induction of S atoms cause decrease of fluorescence lifetime and fluorescence quantum yields for their electron donation to the tetrapyrrole ring [13]. The intensity of $Q^*_{0–1}$ have much relations with substituents, which maybe be interpreted by the geometrical change such as dihedral angles between the thiophene ring and porphyrin ring. Solvents have no obvious effect on Q^* peak as shown in Table 5 and Fig. 3, although there are much relations between the solvents and absorption spectra. This maybe due to that the polarity of solvents can stabilize the excited state of porphyrin more than the ground state resulting in so little influence on position of emission band.

3.3. Redox potential

The electrochemical studies were performed on porphyrins to elucidate the effect of substituents on the porphyrin macrocycle. The redox data were listed in Table 7. All porphyrins showed 2 one-electron oxidation and 1 one-electron reduction potential. The observed values were similar to the literature values [13]. A representative cyclic voltammogram of 4 is shown in Fig. 5.

Notably thienylporphyrins show a cathodic shift in oxidation relative to H_2TPP. But there is no evident shift in

Table 7
Half-wave redox potentials (mV) of thienylporphyrins in CH_2Cl_2 using 0.1 M tetrabutylammonium perchlorate at 25 °C[a]

Porphyrin	Oxidation (mV)		Reduction (mV)
	I	II	I
H_2TPP[b]	1042	1335	−1155
1	918	1167	−1224
2	964	1229	−1133
3	876	1259	−1197
4	897	1214	−1225

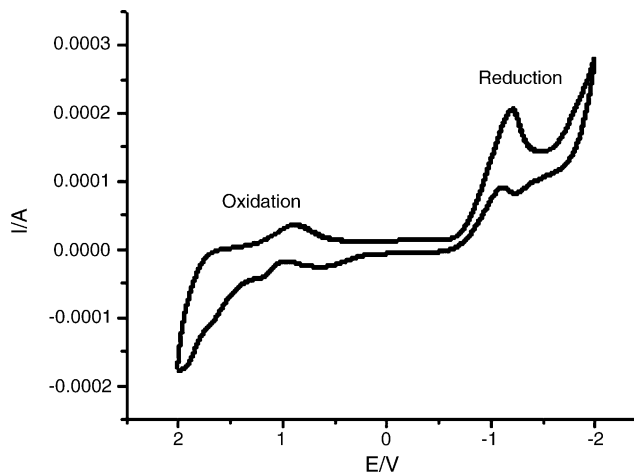[a] Versus calomel electrode.
[b] See Ref. [13].

Fig. 5. Cyclic voltammograms of **4** in CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte at 25 °C.

reduction potential. It can be seen that the thienylporphyrins are easy of oxidation relative to H_2TPP. The first oxidation of the porphyrins follow the trend: $H_2TPP > 2 > 1 > 4 > 3$. The cathodic shift in the first oxidation of thienylporphyrin can be ascribed to induction of S atoms in thienyl group. The substituents on thienyl group can affect the effective extent of induction of S atom and the co-planarity between thienyl group and porphyrin macrocycle. Corresponding with above the methyl group can contribute to the induction and Br atom can increase the deficiency of the porphyrin macrocycle accounting for the trend of first oxidation.

4. Conclusions

The *meso*-tetra-thienyl porphyrins were synthesized through Lindsey's procedure successfully. The existence of S atoms in the thiophene ring cause the absorption and emission shift to longer wavelength compared to H_2TPP. Their

dicationic compounds show large red shift too. Unlike other H_2TPP and its derivatives, the meso-tetrathienyl porphyrins' absorption spectra are affected by solvents obviously. When the concentration is more than 6×10^{-5} M, the porphyrin molecules exist mostly as face-to-face aggregation accounting for the blue shift of Soret band. Emission band of thienyl porphyrins have red shift to H_2TPP, and show similar spectra shape to the H_2TPP. The fluorescence lifetime become so less even to 1.1 ns. The half-wave redox potential shows cathodic shift relative to H_2TPP. These phenomenon are ascribed to the induction of S atoms and their geometrical structure alteration for the small volume of thienyl group.

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