



Synthesis and Optical/Electrochemical Properties of *meso*-5,10,15,20-Tetrathienyl Substituted Porphyrins and Their Metal Complexes

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Two kinds of *meso*-5,10,15,20-tetrathienyl substituted porphyrin compounds, *meso*-5,10,15,20-tetra(2-thienyl)porphyrin (H_2TTP), *meso*-5,10,15,20-tetra(3-methyl-2-thienyl)porphyrin [$H_2T(3-M)TP$] and their metal complexes were synthesized and characterized by IR, 1H NMR. UV-visible absorption spectra, fluorescence spectra, photoluminescence spectra and the cyclic voltammograms of the synthesized porphyrins and metalloporphyrins. Optical properties reveal that zinc porphyrin possesses intensive fluorescence emission, whereas cobalt(II) and copper(II) porphyrins exhibit no fluorescence emission. When the complexation of H_2TTP and $H_2T(3-M)TP$ with metal ions occur, the electrochemical band-gaps (E_g) increase meanwhile the E_{LUMO} shows smaller change than that of the E_{HOMO} . The values of ionization potential, electronic affinity, HOMO energy level (E_{HOMO}) and LUMO energy level (E_{LUMO}) of the synthesized porphyrins and metalloporphyrins were also given in the paper.

Keywords: Porphyrin, Metalloporphyrin, Electrochemical properties, Optical properties, Zn(II), Co(II), Cu(II).

INTRODUCTION

In the past decades, great efforts have been made to the design and synthesis of new conjugated polymers due to their unique optoelectronic properties in organic devices^{1,2}. For polymer based solar cells, the power conversion efficiency needs to be further improved before commercialization, although conjugated polymers based devices have achieved over 9% recently³. One of the main efforts for this is to obtain new polymers with low band-gap (E_g) (as the donor materials), which is the key parameter to enhance the efficiency of photon absorption and improve the power conversion efficiency⁴. Porphyrins have attracted much attention due to their wide use in nature as one kind of tetrapyrrolic macrocycles with big π -orbital on the carbon-nitrogen framework, such as chlorophyll, haem and cytochrome, each consisted of tetrapyrrole compounds and Mg^{2+} , Fe^{3+} ions *etc*⁵. Because of the rigid flat structure and large conjugational effect of the tetrapyrrolic macrocycle, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital energy (LUMO) is relatively small, which leads to strongly absorption in the range of 400-700 nm with high molar absorbance coefficient and effective charge-transfer efficiency^{6,7}.

In recent years, metal porphyrins have been proved to be of great interest as photosynthetic model compounds in light-energy conversion applications^{8,9}; polythiophenes have been widely used in the polymer based solar cells (PSCs) as electron donors¹⁰. In this paper, we have synthesized a series of complexes of thiophene-porphyrins and their metal complexes in order to make better use of the advantages of porphyrins for preparing a low band-gap polythiophenes. The optical and electrochemical properties of the compounds are reported consequently.

EXPERIMENTAL

2-Thiophenecarboxaldehyde, 3-methylthiophene and pyrrole were purchased from Aladdin. Propanoic acid, DMF, $POCl_3$, nitrobenzene and all other solvents and chemicals used in this work were analytical grade and purchased from commercial sources without further purification before use. Column chromatography was carried out on silica gel (200-300 mesh). 1H NMR spectra and ^{13}C NMR were recorded on a Bruker AM-400 spectrometer using $CDCl_3$ as solvent in all cases. FT-IR analyses were performed on a Nicolet 380 spectrometer. UV-visible spectra and fluorescence spectra of the polymers were measured by HITACHI U-3310 spectrophotometer and HITACHI F-4500 fluorescence spectrophotometer, respec-

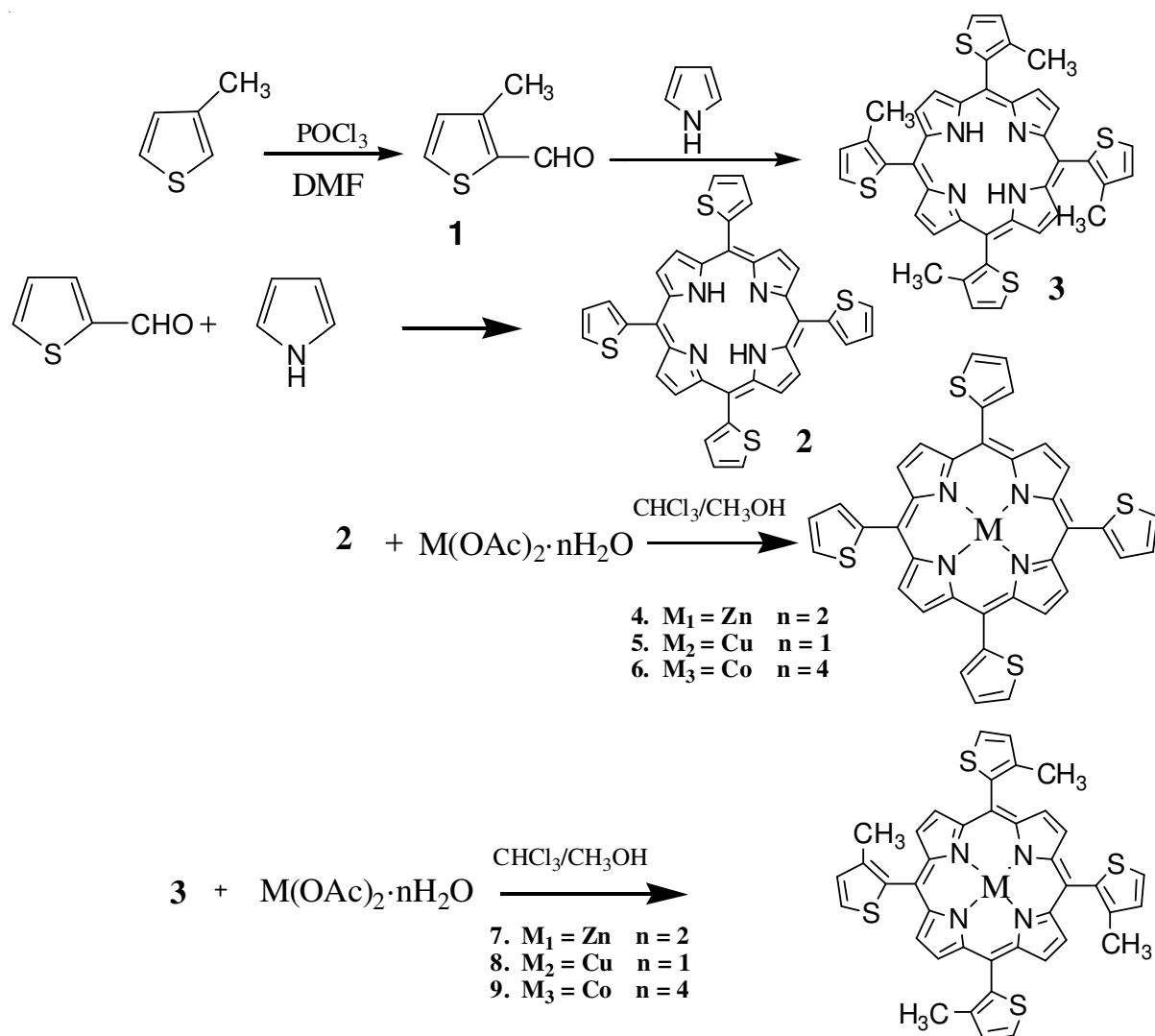
tively. Photoluminescence experiments were performed on a FL3-212-TCSPC fluorescence spectrophotometer. Cyclic voltammogram (CV) measurements were conducted on an electrochemistry workstation (LK-2005A, Tianjin) with the compound film on platinum (Pt) plate as the working electrode, Pt wire as counter electrode and Ag/AgCl electrode as a reference electrode with a scan rate of 50 mV/s. Tetrabutyl ammonium perchlorate (TBAP, 0.1 mol/L) and chloroform were used as supporting electrolyte and solvent, respectively. The measurements were calibrated using ferrocene as standard.

The synthetic routes of the *meso*-5,10,15,20-tetrathienyl substituted porphyrins and their metal complexes are shown in **Scheme-I**.

3-Methyl-2-thiophenecarboxaldehyde (compound 1): 9.62 mL (0.1 mol) 3-methylthiophene and 14 mL of anhydrous DMF were added into a 50 mL four-neck flask. The solution was cooled to 10 °C below by an ice-bath, 10.2 mL (0.11 mol) of POCl₃ was added slowly. After the addition, the cooling bath was removed and the reactant was stirred at ambient temperature for 1.5 h. The solution was refluxed until 3-methylthiophene was found disappeared by means of TLC. Then, the reaction mixture was poured into 25 mL of ice water, adjusted to pH 5-6 with 40 % sodium hydroxide solution and

extracted by diethyl ether 3 times. The organic layer was washed with saturated sodium carbonate solution and water and then dried with anhydrous MgSO₄. After the solvent was evaporated, dark red liquid as crude product was obtained. The crude product was distilled under vacuum to collect 7.7 g product (yield 61 %, 68-70 °C, 0.35 KPa, light yellow liquid). ¹H NMR (CDCl₃, 400 MHz): 10.042 (s, 1H), 7.633-7.645 (d, 1H), 6.971-6.983 (d, 1H), 2.586 (s, 3H).

***meso*-5,10,15,20-Tetra(2-thienyl)porphyrin (compound 2, H₂TTP):** 30 mL glacial acetic acid, 30 mL propionic acid and 15 mL of nitrobenzene were added into a 250 mL four-neck flask and the solution was heated under reflux at about 130 °C for 20 min. 2.8 mL (0.03 mol) 2-thiophenecarboxaldehyde in 30 mL propionic acid was added dropwise, meanwhile 2.07 mL (0.03 mol) of freshly distilled pyrrole in 30 mL acetic acid was added dropwise. After refluxing for 50-55 min, the reaction mixture was cooled to ambient temperature naturally. Then 25 mL of methanol was added, the solution was allowed to standing overnight. The precipitate was filtered and washed with hot water and ethanol for 3-4 times until the filtrate was nearly colorless. After drying for 24 h under vacuum, 2.1 g of purple powder was obtained as crude product. The crude product was purified by silica gel column chromatography



Scheme-I: Synthetic routes for the compounds of *meso*-5,10,15,20-tetrathienyl substituted porphyrins and their metal complexes

(chloroform/petroleum ether = 2:1), then 0.9 g desired blue-purple compound **2** was obtained (yield 18.8 %, mp. > 300 °C). IR (KBr, ν_{\max} , cm^{-1}): 3321, 3096, 2918, 2850, 1806, 1628, 1553, 1468, 1396, 1073, 1041, 967, 950, 794, 707, 632, 521. ^1H NMR (CDCl_3 , 400 MHz): 9.064 (s, 8H), 7.941-7.952 (d, 4H), 7.878-7.894 (d, 4H), 7.522-7.543 (m, 4H), -2.626 (s, 2H).

meso-5,10,15,20-Tetra(3-methyl-2-thienyl)porphyrin [compound 3, $\text{H}_2\text{T}(3\text{-M})\text{TP}$]: *meso*-5,10,15,20-Tetra(3-methyl-2-thienyl)porphyrin was synthesized in the similar way as H_2TTP with a yield of 16.5 %, m.p. > 300 °C. IR (KBr, ν_{\max} , cm^{-1}): 3321, 3095, 2920, 2851, 1647, 1545, 1460, 1334, 1056, 967, 795, 709, 617, 469. ^1H NMR (CDCl_3 , 400 MHz): 8.938 (s, 8H), 7.741-7.758 (d, 4H), 7.338-7.358 (d, 4H), 2.118-2.202 (m, 12H), -2.617 (s, 2H).

Zinc *meso*-5,10,15,20-tetra(2-thienyl)porphyrin (compound 4, ZnTTP): A mixture of compound **2** (0.14 g, 0.22 mmol) and $\text{Zn}(\text{OAc})_2$ (0.072 g, 0.33 mmol) in CHCl_3 (20 mL) and CH_3OH (6 mL) was refluxed for 2 h. After cooling to room temperature, the mixture was filtered and washed with water. After drying for 24 h under vacuum, the crude product was purified by the silica gel column chromatography (chloroform: petroleum ether = 1:1), then 0.126 g desired blue-purple compound **4** was obtained (yield 82 %, m.p. > 300 °C). IR (KBr, ν_{\max} , cm^{-1}): 3096, 2921, 2851, 1633, 1487, 1425, 1350, 1291, 1167, 1072, 972, 798, 702, 466. ^1H NMR (CDCl_3 , 400 MHz): 9.172 (s, 8H), 7.937-7.945 (d, 4H), 7.865-7.878 (d, 4H), 7.519-7.542 (m, 4H).

Copper(II) *meso*-5,10,15,20-tetra(2-thienyl)porphyrin (compound 5, CuTTP): Bright purple solid, yield 86 %, m.p. > 300 °C. IR (KBr, ν_{\max} , cm^{-1}): 3096, 2921, 2852, 1589, 1426, 1351, 1323, 1224, 1170, 1074, 973, 800, 701, 454.

Cobalt(II) *meso*-5,10,15,20-tetra(2-thienyl)porphyrin (compound 6, CoTTP): Bright purple solid, yield 80.5 %, m.p. > 300 °C. IR (KBr, ν_{\max} , cm^{-1}): 3096, 2921, 2852, 1649, 1461, 1328, 1224, 1169, 1071, 979, 815, 702, 463.

Zinc *meso*-5,10,15,20-tetra(3-methyl-2-thienyl)porphyrin [compound 7, $\text{ZnT}(3\text{-M})\text{TP}$]: A mixture of compound **3** (0.208 g, 0.3 mmol) and $\text{Zn}(\text{OAc})_2$ (0.1 g, 0.45 mmol) in CHCl_3 (20 mL) and CH_3OH (8 mL) was refluxed for 2 h. After cooling to room temperature, the mixture was filtered and washed with water. After drying for 24 h under vacuum, the crude product was purified by the silica gel column chromatography (petroleum ether: ethyl acetate = 5:1), then 0.19 g desired purple compound **7** was obtained (yield 83.7 %, m.p. > 300 °C). IR (KBr, ν_{\max} , cm^{-1}): 3095, 2920, 2852, 1653, 1515, 1458, 1378, 1329, 1063, 980, 818, 792, 702, 620, 464. ^1H NMR (CDCl_3 , 400 MHz): 9.031 (s, 8H), 7.732-7.745 (d, 4H), 7.347-7.357 (d, 4H), 2.131-2.224 (m, 12H).

Copper(II) *meso*-5,10,15,20-tetra(3-methyl-2-thienyl)porphyrin [compound 8, $\text{CuT}(3\text{-M})\text{TP}$]: Bright purple solid, yield 82.4 %, m.p. > 300 °C. IR (KBr, ν_{\max} , cm^{-1}): 3099, 2917, 2853, 1646, 1520, 1450, 1370, 1335, 1067, 984, 821, 794, 708, 618, 468.

Cobalt(II) *meso*-5,10,15,20-tetra(3-methyl-2-thienyl)porphyrin [compound 9, $\text{CoT}(3\text{-M})\text{TP}$]: Bright purple solid, yield 86.7 %, m.p. > 300 °C. IR (KBr, ν_{\max} , cm^{-1}): 3097, 2920, 2852, 1646, 1568, 1433, 1340, 1070, 991, 822, 794, 710, 618, 467.

RESULTS AND DISCUSSION

The IR spectra of $\text{H}_2\text{T}(3\text{-M})\text{TP}$ and H_2TTP show that the stretching vibrational absorption peak of N-H bond in pyrrole ring is at about 3321 cm^{-1} and the bending vibrational absorption peak of the N-H bond is at about 967 cm^{-1} . When the complexation of $\text{H}_2\text{T}(3\text{-M})\text{TP}$ and H_2TTP with metal ions occur, the two absorption peaks mentioned above disappear, which indicates that the bond between N-H in pyrrole ring is substituted by N-metal ions. This is the typical characteristic of the formation of metalloporphyrin complexes.

^1H NMR spectra of H_2TTP and $\text{H}_2\text{T}(3\text{-M})\text{TP}$ show that the chemical shift of the synthesized two kinds of porphyrin derivatives present negative position at -2.626 and -2.617, respectively, which can be attributed to the chemical shift of H in bond N-H. When the complexation of H_2TTP and $\text{H}_2\text{T}(3\text{-M})\text{TP}$ with metal ions occur, the corresponding peaks at negative position disappear, such as ^1H NMR of ZnTTP and $\text{ZnT}(3\text{-M})\text{TP}$. This indicates that the H in bond N-H is replaced by metal ions, meanwhile metal complexes of porphyrin formed. Owing to the paramagnetism, ^1H NMR of CuTTP , $\text{CuT}(3\text{-M})\text{TP}$, CoTTP and $\text{CoT}(3\text{-M})\text{TP}$ can not be measured in this work. In comparison with the ^1H NMR of H_2TTP , $\text{H}_2\text{T}(3\text{-M})\text{TP}$, ZnTTP and $\text{ZnT}(3\text{-M})\text{TP}$, we find that the chemical shift slightly decreases in compound $\text{H}_2\text{T}(3\text{-M})\text{TP}$, which is possibly due to the electronic effect of the methyl groups, while in the metal complexes, the chemical shift of corresponding H increases, which can be attributed to the electron-withdrawing metal ions.

The UV-visible absorption spectra of porphyrin derivatives in CHCl_3 solution are showed in Figs. 1 and 2. Owing to similar structures, conjugated macrocyclic system of porphyrin ring, porphyrin derivatives exhibit the strong absorption peaks located in the range of 400-440 and 500-600 nm which are attributed to $\pi \rightarrow \pi^*$ electron transition. Wherein, Soret-band is a single peak around 420 nm and weak Q-band includes four absorption peaks between 450 and 600 nm. The values of the absorption coefficient of Soret-band are about 10 to 20 times of Q-band. Q-band and Soret-band are attributed to the $a_{1u}(\text{p}) \rightarrow e_g(\text{p}^*)$ energy level transition and $a_{2u}(\text{p}) \rightarrow e_g(\text{p}^*)$ energy level transition of the porphyrin ring, respectively¹¹.

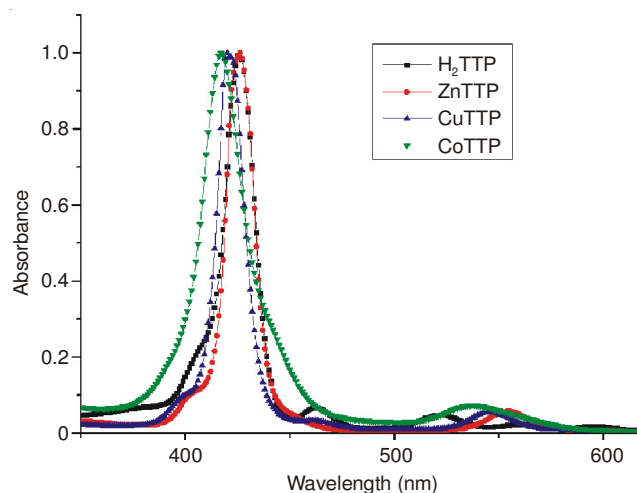


Fig. 1. UV-visible spectra of H_2TTP and its metal complexes

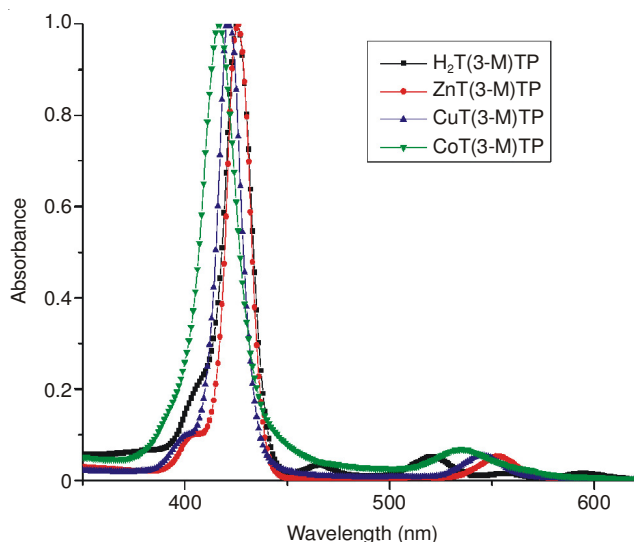


Fig. 2. UV-visible spectra of $H_2T(3-M)TP$ and its metal complexes

Fig. 1 shows the UV-visible spectra of H_2TTP and its metal complexes in $CHCl_3$ and Fig. 2 shows the UV-visible spectra of $H_2T(3-M)TP$ and its metal complexes in $CHCl_3$. In the visible region, both H_2TTP and $H_2T(3-M)TP$ exhibit the strong absorption peaks (Soret-band) and four weak absorption peaks (Q-band). When the metal complexes formed, the Q-band absorption peaks were reduced to one peak. The main reason is that compound H_2TTP and $H_2T(3-M)TP$ are D_{2h} point groups, which determine the Q-band is consist of four absorption peaks. When the metal ion was embedded into the porphyrin ring, the metal ion occupied the center of the porphyrin ring. Along with the four N atoms of porphyrin ring are coordinated with the metal ion, the symmetry of the metal complex and the degeneracy of molecular orbital increase, while the energy levels and the degree of the molecular orbital splitting decrease. The porphyrin metal complexes are D_{4h} point groups¹², which usually lead to the number and intensity of the Q-band absorption peaks decrease in UV-visible spectra. This is also the typical characteristic of the formation of metalloporphyrin complexes.

The UV-visible spectra absorption data of the synthesized porphyrin and metalloporphyrin complexes are shown in Table-1. It indicates that the metalloporphyrin complexes only have one Q-band absorption peak and the Soret-band absorption peaks of ZnTTP and ZnT(3-M) are red-shifted than H_2TTP and $H_2T(3-M)TP$. In contrast, compound CuTTP, CoTTP, CuT(3-M)TP and CoT(3-M)TP are blue-shifted. The Q-band absorption peaks of metalloporphyrin ZnTTP, ZnT(3-

TABLE-1
UV-VISIBLE SPECTRAL DATA OF
PORPHYRIN AND METALLOPORPHYRIN

| Compound | Soret band (nm) | Q band (nm) | | | |
|---------------|-----------------|-------------|-----|-----|-----|
| H_2TTP | 426 | 463 | 522 | 560 | 596 |
| ZnTTP | 427 | | | 554 | |
| CuTTP | 420 | | | 546 | |
| CoTTP | 417 | | | 538 | |
| $H_2T(3-M)TP$ | 426 | 466 | 521 | 557 | 595 |
| ZnT(3-M)TP | 427 | | | 553 | |
| CuT(3-M)TP | 421 | | | 545 | |
| CoT(3-M)TP | 416 | | | 535 | |

M), CuTTP, CuT(3-M)TP, CoTTP and CoT(3-M)TP are blue-shifted in contrast to the corresponding ligands in the order of $Zn < Cu < Co$, which indicates that the blue-shifted Q-band absorption peaks increase with the increase of metal atomic number.

The fluorescent studies are performed in $CHCl_3$ with scanning wavelength between 300 and 700 nm (Fig. 3) and the corresponding data are collected in Table-2. The Stokes shifts decrease when metal complexes are formed. Along with the complexation of H_2TTP and $H_2T(3-M)TP$ with Zn^{2+} , the fluorescence emission improves greatly, whereas the fluorescence quenching effect arises when the complexation of H_2TTP and $H_2T(3-M)TP$ with Cu^{2+} and Co^{2+} occur. This is possibly due to the electron-deficiency in 3d orbit of Cu^{2+} and Co^{2+} ¹³. Fig. 4 shows the photoluminescence spectra of H_2TTP , $H_2T(3-M)TP$, ZnTTP and ZnT(3-M)TP with excitation wavelength at 426 nm. It is shown that the maximum emission wavelength of H_2TTP , $H_2T(3-M)TP$, ZnTTP and ZnT(3-M)TP is at 724, 727, 666 and 654 nm, respectively. Similarly to the fluorescence, the photoluminescence of ZnTTP and ZnT(3-M)TP are blue-shifted in contrast to their ligands, while no photoluminescence occurs for compound CuTTP, CuT(3-M)TP, CoTTP and CoT(3-M)TP. The photoluminescence intensity of H_2TTP and $H_2T(3-M)TP$ are greater than that of ZnTTP and ZnT(3-M)TP, respectively.

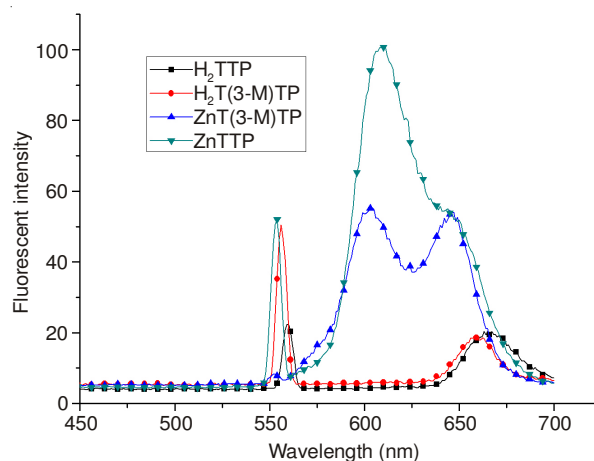


Fig. 3. Fluorescent spectra of H_2TTP , $H_2T(3-M)TP$, ZnTTP and ZnT(3-M)TP

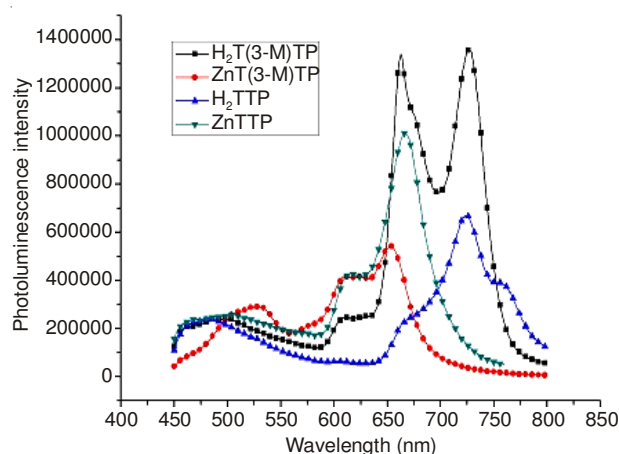


Fig. 4. Photoluminescence spectra of H_2TTP , $H_2T(3-M)TP$, ZnTTP and ZnT(3-M)TP

TABLE-2
FLUORESCENT SPECTRAL DATA OF
PORPHYRIN AND METALPORPHYRIN

| Compounds | E_x (nm) | E_m (nm) | Stokes shift (nm) |
|------------------------------|------------|------------|-------------------|
| H ₂ TTP | 560 | 667 | 107 |
| H ₂ T(3-M)TP M)TP | 557 | 659 | 102 |
| ZnTTP | 554 | 610 | 56 |
| ZnT(3-M)TP | 553 | 603, 645 | 50, 92 |

The electrochemical properties of all the synthesized compounds are obtained from cyclic voltammograms (Figs. 5 and 6). The onset of the oxidation and reduction are shown in Table-3. The ionization potential (I_p), electronic affinity (E_a), HOMO energy level (E_{HOMO}) and LUMO energy level (E_{LUMO}) are calculated using the equation¹⁴: $I_p = -E_{HOMO}$, $E_{HOMO} = -[E^{OX} + 4.4]$ eV, $E_a = E_{LUMO}$, $E_{LUMO} = -[E^{Red} + 4.4]$ eV, $E_g = E_{HOMO} - E_{LUMO}$. Table-3 shows that the E_{LUMO} change slightly than that of E_{HOMO} and meanwhile the electrochemical band-gaps (E_g) become larger when the complexation of H₂TTP and H₂T(3-M)TP with metal ions occur.

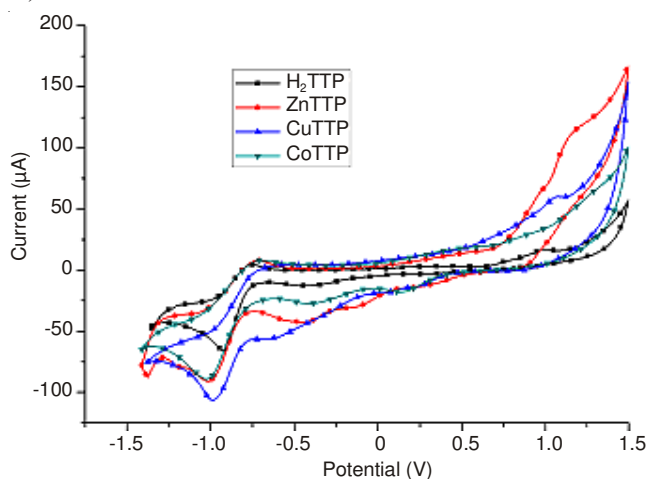


Fig. 5. Cyclic voltammograms of H₂TTP and its metal complexes

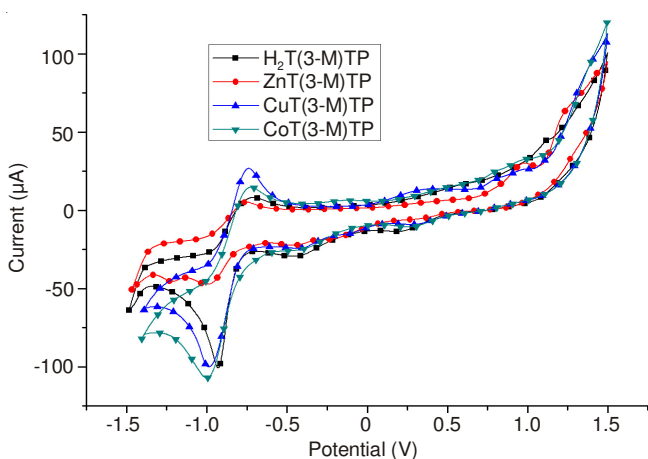


Fig. 6. Cyclic voltammograms of H₂T(3-M)TP and its metal complexes

Conclusion

Two kinds of *meso*-5,10,15,20-tetrathienyl substituted porphyrin compounds, *meso*-5,10,15,20-tetra(2-thienyl)-porphyrin (H₂TTP), *meso*-5,10,15,20-tetra(3-methyl-2-

TABLE-3
ELECTROCHEMICAL PROPERTIES OF H₂TTP,
H₂T(3-M)TP AND THEIR METAL COMPLEXES

| Compounds | E^{ox} (V) | I_p (eV) | E_{HOMO} (eV) | E^{red} (V) | E_a (eV) | E_{LUMO} (eV) | E_g (eV) |
|-------------------------|--------------|------------|-----------------|---------------|------------|-----------------|------------|
| H ₂ TTP | 0.66 | 5.06 | -5.06 | -1.25 | 3.15 | -3.15 | 1.91 |
| ZnTTP | 0.71 | 5.11 | -5.11 | -1.28 | 3.12 | -3.12 | 1.99 |
| CuTTP | 0.79 | 5.19 | -5.19 | -1.27 | 3.13 | -3.13 | 2.06 |
| CoTTP | 0.80 | 5.20 | -5.20 | -1.28 | 3.12 | -3.12 | 2.08 |
| H ₂ T(3-M)TP | 0.65 | 5.05 | -5.05 | -1.28 | 3.12 | -3.12 | 1.93 |
| ZnT(3-M)TP | 0.68 | 5.08 | -5.08 | -1.30 | 3.10 | -3.10 | 1.98 |
| CuT(3-M)TP | 0.74 | 5.14 | -5.14 | -1.26 | 3.14 | -3.14 | 2.00 |
| CoT(3-M)TP | 0.76 | 5.16 | -5.16 | -1.28 | 3.12 | -3.12 | 2.04 |

thienyl)porphyrin (H₂T(3-M)TP) and their cobalt, copper and zinc complexes were successfully synthesized. The optical properties, UV-visible absorption spectra, fluorescence spectra and photoluminescence spectra of them were investigated and their electrochemical properties such as band-gaps (E_g), ionization potential (I_p), electronic affinity (E_a), HOMO energy level (E_{HOMO}) and LUMO energy level (E_{LUMO}) were also recorded. The Soret-band absorption peak of the synthesized zinc porphyrin complex was red-shifted, in contrast, copper(II) and cobalt(II) porphyrin complexes were blue-shifted. With the increases of the metal atomic number, the Q-band absorption peak blue-shift increases in the order Zn < Cu < Co. When the synthesized two kinds of porphyrin compounds are coordinated with Zn²⁺, the fluorescence intensity enhances. The electrochemical properties indicate that E_{LUMO} has smaller change than E_{HOMO} , meanwhile the electrochemical band-gaps (E_g) became larger when metal complexes were formed.

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