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Synthesis, optical spectroscopy and electrochemistry of TTF-derived metallophthalocyanine complexes

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Abstract

Two tetrathiafulvalene (TTF)-derived metallophthalocyanine complexes were synthesized. The structures of the target compounds and their intermediates have been characterized by NMR, MS, EA, UV–VIS and mp. The results of cyclic voltammetry indicated that the presence of zinc or magnesium phthalocyanine slightly affected the first oxidation of 4,5-ethylenedithiotetrathiafulvalene (EDT-TTF) unit. The EDT-TTF unit on the peripheral sites of the zinc phthalocyanine core could be more easily oxidized than the one on the same sites of the magnesium phthalocyanine core.

Keywords: Zinc phthalocyanine; Magnesium phthalocyanine; 4,5-Ethylenedithiotetrathiafulvalene; Ultraviolet–visible spectra; Cyclic voltammetry

1. Introduction

Both phthalocyanine (H_2Pc) and metallophthalocyanines (MPcs) are well known colorants. Besides their intense color and efficient energy absorption, more remarkable properties have been discovered due to their 18 (or 16)-π-electron conjugated system. This has attracted the attention of scientists to design different structures through symmetric and asymmetric substitution of the phthalocyanine core and through altering the central metals. Such modified phthalocyanines have been applied in a wide range of hi-tech fields such as photosensitizer [1], electrophotographic photoconductor [2], photodynamic cancer therapy [3], solar energy conversion [4], gas sensors [5] etc.

As a path to obtain functional phthalocyanines, redox active substituents such as tetrathiafulvalene (TTF) can be introduced to the peripheral or non-peripheral sites. For example, Michael J. Cook and co-workers prepared a phthalocyanine system functionalized with one or two TTF units that presented liquid crystalline behaviour [6]. Martin R. Bryce and co-workers prepared phthalocyanine derivatives containing four or eight peripheral substituted or unsubstituted tetrathiafulvalene units [7,8]. Some flexible and saturated spacers, such as alkoxyl, were inserted between the donor and acceptor groups to form D–σ–A assemblies possessing intramolecular charge transfer (ICT) property. Alternatively, different central metal ions of the Pc core have effect on the properties of Pc [9–12].

In our recent paper, a zinc phthalocyanine derivative with four peripheral TTF units has been reported, which is the first metallophthalocyanine bearing tetrathiafulvalene units [13]. Unfortunately, its electrochemistry was not possibly studied due to its unsatisfactory solubility.

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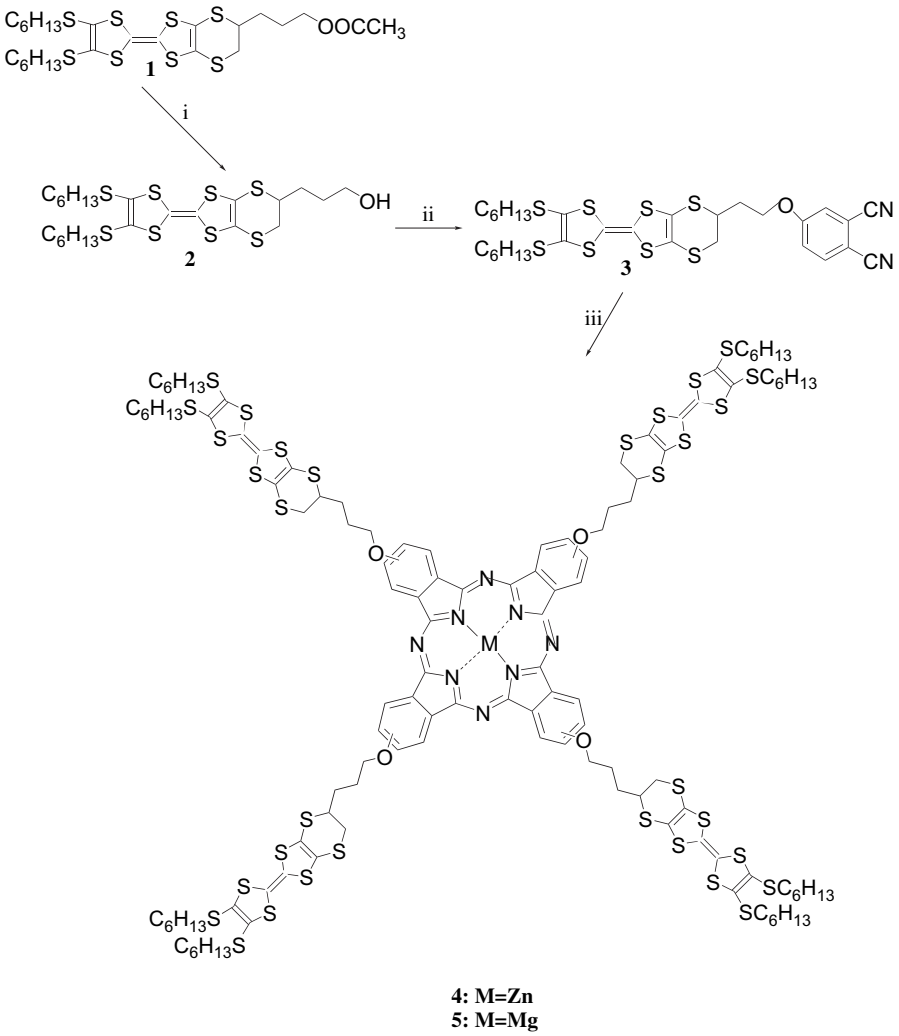

Scheme 1. Reagents and conditions: i, chloroform, methanol, potassium hydroxide, r.t.; ii, 4-nitrophthalonitrile, K_2CO_3, DMSO, 50 °C; iii, zinc acetate or magnesium acetate, *n*-pentanol, reflux.

To obtain more information about such metallophthalocyanines derived by substituted tetrathiafulvalenes, it is necessary to lengthen the spacers or modify the synthetic method of cyclotetramerisation, so that the solubility of products can be improved.

As an extension of our research, we now report the synthesis, optical spectroscopy and electrochemistry of zinc and magnesium phthalocyanines bearing four EDT-TTF (4,5-ethylenedithiotetrathiafulvalene) units on peripheral sites, which are soluble in many organic solvents, such as chloroform, dichloromethane. Hence, the ultraviolet–visible spectra and cyclic voltammetry of our target compounds are reported.

2. Results and discussion

2.1. Synthesis

The synthetic route to our target molecules is presented in Scheme 1.

The method of synthesizing [2-(4,5-Bis-hexylsulfanyl [1,3]dithiol-2-ylidene)-tetrahydro-[1,3]dithiolo[4,5-*b*][1,4] dithiin-5-yl]-methanol, a homologous compound of compound 2, has recently been introduced [4]. Hydrazine monohydrate was utilized as base. However, there was insignificant reaction between compound 2 and hydrazine monohydrate even after 8 days, with a yield of only 28.9% at most. We found that the hydrolysis of compound 2 could be realized by using potassium hydroxide in the place of hydrazine monohydrate. Due to the good solubility of potassium hydroxide in methanol, the solution could be added to compound 2 dissolved in chloroform dropwise under room temperature. A yield of 53.4% was obtained. An alternative path using potassium carbonate as catalyst instead of potassium hydroxide, gave a yield of 43.0%. When a mixture containing compound 2 and potassium hydroxide or potassium carbonate was refluxed, the yield decreased to 27%, indicating that EDT-TTF cannot tolerate the presence of strong base under high temperature.

To synthesize the key intermediate of our target compounds, 4-nitrophthalonitrile and compound 2 underwent potassium carbonate-catalyzed nucleophilic aromatic nitro displacement in neat DMSO at 50 °C. The reaction was accelerated by the rapid addition of potassium carbonate in one portion compared with the more popular addition in small portions over a long period.

Target compound 4 or 5 was prepared directly by refluxing compound 3 with zinc or magnesium acetate in *n*-pentanol, respectively. We previously synthesized a zinc phthalocyanine derived from tetrathiafulvalene on peripheral sites via the two-step procedure including cyclotetramerisation and introduction of zinc atom to the center. The purification of zinc phthalocyanine produced a bulky aggregate that reduced the solubility significantly. The one-step procedure reported here solved the problem and provided target compounds with good solubility. The crude compounds were simply washed with acetone; in this way, pure products were achieved, which could be dissolved in chloroform, dichloromethane very well. Due to good solubility, optical and electrochemical properties can be studied further. No molecular ion peak could be detected. Instead, the peak of a fragment, quarter of the whole molecular weight, was noticed at 711.0.

2.2. UV–VIS spectra

The UV–VIS spectra of compounds 4 and 5 are depicted in Fig. 1. The values of λ_{max} are listed in Table 1.

In the ultraviolet region of compounds 4 and 5, B-band (or Soret band) of metallophthalocyanine between 320 and 370 nm and typical absorption of EDT-TTF derivatives between 240 and 400 nm lead to the superimposed bands.

Compound 4 possesses Q-band of typical metallophthalocyanine at λ_{max} 685.0 nm. The Q-band of compound 5 indicates a bathochromic shift to λ_{max} 695.0 nm whose peak is broadened due to the cofacial aggregation in chloroform. The bathochromic shift compared with unsubstituted zinc phthalocyanine core (λ_{max} 674 nm) [14] and magnesium phthalocyanine core (λ_{max} 668 nm) [15] depends on the change of electron distribution in the phthalocyanine macrocycle arising from the D–σ–A system derived by four EDT-TTF substituents on their peripheral positions. No Q-band of dimers was observed in the visible region.

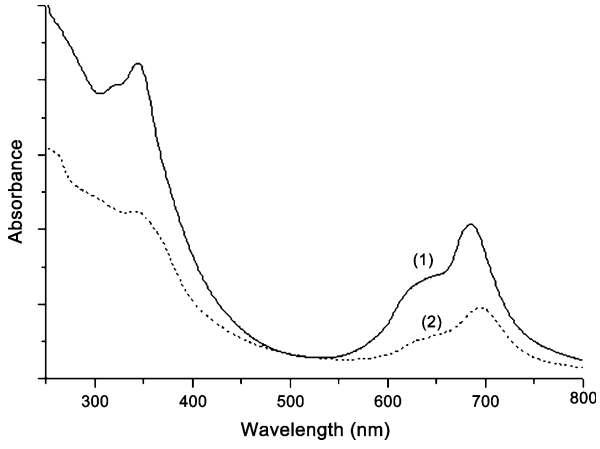

Fig. 1. UV–VIS spectra of (1) compound 4 and (2) compound 5.

Table 1
Values of λ_{max}

Compound	λ_{max} (Chloroform, nm)
4	322.0, 344.0, 685.0
5	342.0, 695.0

2.3. Cyclic voltammetry

Cyclic voltammetric (CV) studies on compounds 4 and 5 were performed in dichloromethane. Fig. 2 depicts their cyclic voltammogram. Their values of redox potential together with their parent material 3 are listed in Table 2.

Compounds 4 and 5 exhibit two TTF redox waves at $E_{1/2}{}^1 = 0.612$ V and 0.620 V, $E_{1/2}{}^2 = 0.884$ V and 0.903 V in dichloromethane, respectively. The scan rate of these two compounds were very low (12.5 mV/s), otherwise, no redox peaks could be observed, possibly due to the aggregation and instability of the one- and two-electron oxidation of EDT-TTF unit. Compared with compound 3, their value of $E_{1/2}{}^1$ is not significantly changed, which means the formation of

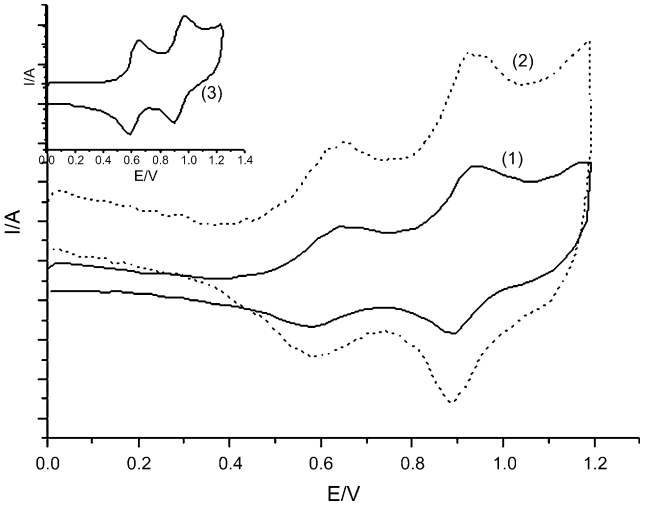

Fig. 2. Cyclic voltammogram of (1) compound 4: scan rate 12.5 mV/s, $E_{1/2}{}^1 = 0.612$ V, $E_{1/2}{}^2 = 0.884$ V; (2) compound 5: scan rate 12.5 mV/s, $E_{1/2}{}^1 = 0.620$ V, $E_{1/2}{}^2 = 0.903$ V; (3) compound 3: scan rate 100 mV/s, $E_{1/2}{}^1 = 0.612$ V, $E_{1/2}{}^2 = 0.935$ V.

Table 2
Redox potential values of compounds 3–5

Compound	$E_{1/2}^1$ (V)	$E_{1/2}^2$ (V)	Scan rate (mV/s)
3	0.612	0.935	100
4	0.612	0.884	12.5
5	0.620	0.903	12.5

Electrodes – working: Pt; counter: Pt; reference: SCE. Supporting electrolyte: ca. 0.1 M $Et_4N^+BF_4^-$. Medium: dichloromethane.

macro-π-conjugated system and introduction of zinc and magnesium atoms only affect the first oxidation of EDT-TTF slightly. The cathodal shift of 51 mV and 32 mV in their value of $E_{1/2}^2$ compared with compound 3 indicates that the second oxidation of EDT-TTF unit in zinc phthalocyanine can be more easily achieved.

3. Experimental

3.1. General

All reagents and solvents were of commercial quality. DMSO was dried over $MgSO_4$ before use. Light petroleum is of the fraction with b.p. 60–90 °C. ^{1}H NMR spectra were obtained on a Bruker ADVANCE 500 spectrometer operating at 500.13 MHz: chemical shifts were quoted downfield of TMS. *J* values were in Hz. ^{13}C NMR spectra were obtained on a Bruker ADVANCE 500 spectrometer operating at 125.76 MHz. UV/VIS spectra were recorded on a SHIMADZU UV365 spectrophotometer. EI spectra were recorded using an HP-5989A spectrometer. Melting points were obtained on an X4 melting microscope apparatus (Shanghai, China) and were uncorrected. Element analytical data were obtained on a Vario El III (Elementar) instrument. Cyclic voltammetry was carried out on an EG&G PARC Model 283 Potentiostat/Galvanostat. The counter, working and reference electrodes were Pt wire, Pt disc and saturated calomel electrode (SCE), respectively. The supporting electrolyte was tetraethylammonium tetrafluoroborate (ca. 0.1 M) and dichloromethane was utilized as the medium. Concentration of compounds 4 and 5 for the determination of optical spectra and cyclic voltammetry was 0.04 mg/mL (ca. 0.014 mmol/L).

Acetic acid 2-(4,5-Bis-hexylsulfanyl[1,3]dithiol-2-ylidene)-tetrahydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-5-yl propyl ester, compound 1, was prepared according to the method introduced [13].

3.2. Synthesis

3.2.1. [2-(4,5-Bis-hexylsulfanyl[1,3]dithiol-2-ylidene)-tetrahydro[1,3]dithiolo[4,5-b][1,4]dithiin-5-yl]-propanol (2)

A total of 0.91 g (16.2 mmol) potassium hydroxide dissolved in 65 mL methanol was added dropwise to the mixture of 2.61 g (4.2 mmol) (1) and 22 mL chloroform with stirring. When TLC showed that compound 1 disappeared (ca. 24 h), the mixture was concentrated in vacuum and then extracted with chloroform. The organic layer was separated, dried over Na_2SO_4, concentrated in vacuum followed by chromatography on silica gel using light petroleum:ethyl acetate = 1:3 as an eluent. The second orange fraction contained compound 2. Evaporating the eluent afforded compound 2 as orange oil (1.20 g, 53.4%), mp < 30 °C (from light petroleum), *m*/*z* (%) 584.1(100.00), 585.1(M^+, 20.42), 586.1(26.42). Found: C, 47.34; H, 6.27. Calc. for $C_{23}H_{36}OS_8$: C, 47.22; H, 6.20%. δ_H (500 MHz; $CDCl_3$; TMS) 0.80–0.95(t, 6H, 13.78), 1.22–1.35(m, 8H, 37.45), 1.35–1.44(m, 4H, 29.42), 1.56–1.65(m, 4H, 29.75), 1.65–1.90(m, 4H, 115.89), 2.70–2.87(t, 4H, 14.71), 3.02–3.33(m, 2H, 128.47), 3.51–3.60(m, 1H, 24.20), 3.63–3.72(t, 2H, 12.39). δ_C (125.76 MHz; $CDCl_3$): 14.643, 23.130, 28.785, 30.281, 30.331, 31.889, 36.214, 36.961, 44.743, 62.659, 113.612, 114.533, 114.664, 128.318. UV/VIS (chloroform): λ_{max} 242.4, 316.4, 343.0 nm.

3.2.2. 4-[2-(4,5-Bis-hexylsulfanyl[1,3]dithiol-2-ylidene)-tetrahydro[1,3]dithiolo[4,5-b][1,4]dithiin-5-ylpropoxy phthalonitrile (3)

A mixture of 1.2 g (2.1 mmol) compound 2 and 15 mL neat DMSO was heated to 50 °C with stirring followed by the addition of 1.3 g (9.3 mmol) potassium carbonate and 0.4 g (2.1 mmol) 4-nitrophthalonitrile. Another portion of 0.6 g (4.3 mmol) potassium carbonate and 0.18 g (1.05 mmol) 4-nitrophthalonitrile was added after 24 h. The system was stirred. When TLC showed that compound 2 disappeared, the mixture was poured into water followed by extraction with chloroform. The organic layer was separated, dried over Na_2SO_4, concentrated in vacuum and then purified by chromatography on silica gel using light petroleum: chloroform:ethyl acetate = 10:1:4 as an eluent. The second red fraction contained compound 3. Evaporating the eluent afforded compound 3 as dark red oil (0.94 g, 63.2%), mp 72–74 °C (from ethyl acetate), *m*/*z* (%) 710.1(M^+, 0.55), 366.1(100.00), 127.0(12.35). Found: C, 52.26; H, 5.31; N, 4.04. Calc. for $C_{31}H_{38}OS_8N_2$: C, 52.35; H, 5.39; N, 3.94%. δ_H (500 MHz; $CDCl_3$; TMS) 0.85–0.93(t, 6H, 13.78), 1.25–1.32(m, 8H, 34.18), 1.37–1.42(m, 4H, 31.23), 1.59–1.68(*tert*, 4H, 22.55), 1.90–2.15(m, 4H, 79.36), 2.77–2.83(t, 4H, 14.72), 3.07–3.13(*tert*, 1H, 19.75), 3.28–3.41(*tert*, 1H, 16.11), 3.55–3.62(m, 1H, 22.92), 4.03–4.13(*tert*, 2H, 14.84), 7.16–7.19(t, Ar–H, 11.27), 7.24–7.26(d, Ar–H, 2.51), 7.71–7.72(d, Ar–H, 8.12). δ_C (125.76 MHz, $CDCl_3$): 13.051, 21.545, 28.716, 29.344, 30.310, 30.918, 34.674, 35.388, 42.694, 67.512, 106.351, 106.961, 113.326, 114.266, 114.692, 118.622, 124.500, 126.798, 127.834,

129.933, 134.267, 160.828. UV/VIS (chloroform): λ_{max} 259.0, 306.4, 341.0 nm.

3.2.3. {Tetra-β-{2-[4,5-bis(hexylsulfanyl)-1,3-dithiol-2-ylidene]-tetrahydro[1,3]dithiolo[4,5-b][1,4]dithiin-5-ylpropoxy}phthalocyaninato} zinc(II) (4)

A mixture of 186 mg (0.26 mmol) compound 3, 14 mg (0.0654 mmol) zinc acetate and 10 mL *n*-pentanol was refluxed and stirred for 12 h. The dark green solution was cooled to room temperature followed by the addition of 20 mL methanol. The green solid was collected by suction, and then washed with acetone until the filtrate was colorless. An intense green solution was obtained by dissolving this solid in chloroform. It was then filtered and evaporated in vacuum, giving compound 4 as green amorphous solid (169 mg, 89.0%). Found: C, 49.91; H, 5.03; N, 4.56. Calc. for $C_{124}H_{152}N_8O_4S_{32}Zn$: C, 51.18; H, 5.26; N, 4.65%. UV/VIS (chloroform): λ_{max} 322.0, 344.0, 685.0 nm.

3.2.4. {Tetra-β-{2-[4,5-bis(hexylsulfanyl)-1,3-dithiol-2-ylidene]-tetrahydro[1,3]dithiolo[4,5-b][1,4]dithiin-5-ylpropoxy} phthalocyaninato} magnesium (II) (5)

A mixture of 720 mg (1.01 mmol) compound 3, 54 mg (0.253 mmol) magnesium acetate and 15 mL *n*-pentanol was refluxed with stirring for 12 h. The dark green solution was cooled to room temperature followed by the addition of 25 mL methanol. Black solid was separated out by suction, which was washed with acetone until the filtrate was colorless. An intense green solution was obtained by dissolving this solid in chloroform. It was then filtered and evaporated in vacuum, giving compound 5 as green amorphous solid (107 mg, 15.7%). Found: C, 51.75; H, 5.05; N, 4.17. Calc. for $C_{124}H_{152}MgN_8O_4S_{32}$: C, 51.91; H, 5.34; N, 3.92%. UV/VIS (chloroform): λ_{max} 342.0, 695.0 nm.

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