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Synthesis, Spectroscopy, and Electrochemistry of Metallophthalocyanines Substituted by Propylenedithiotetrathiafulvalene Derivatives

Yingyu Hu[1], **Guoqiao Lai**[2], **Yongjia Shen**[1,*], and **Yongfang Li**[3]

[1] Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, P.R. China
[2] Institute of New Materials, Hangzhou Normal College, Zhejiang 310036, P.R. China
[3] Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, P.R. China

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Summary. Zinc(II) and magnesium(II) phthalocyanines bearing four substituted propylenedithio-tetrathiafulvalene (*PDT-TTF*) units were synthesized and characterized by NMR, MS, EA, and UV/VIS spectra. The absorption peaks of two target molecules were hypsochromically shifted compared with the phthalocyanine parent compound. Studies using cyclic voltammetry indicated that introduction of Zn and Mg as central metals enhanced the electronwithdrawing between the phthalocyanine core and the *PDT-TTF* unit, thus losing one electron to form (*PDT-TTF*)$^+$ becomes more difficult.

Keywords. Propylenedithiotetrathiafulvalene; Metallophthalocyanine; Optical spectroscopy; Cyclic voltammetry.

Introduction

Tetrathiafulvalene (*TTF*) and its derivatives are nonaromatic planar molecules that are easily oxidized to form reversibly the radical cation and dication species [1]. In the field of organic metals, *TTF* and its derivatives have been intensively studied during the past three decades on account of their unique π-electron donor properties. Progress in synthetic *TTF* chemistry paves the way for the application of *TTF* and its derivatives as donor moieties in the intramolecular charge transfer (*ICT*) system, which can be linked to electron acceptors such as phthalocyanine.

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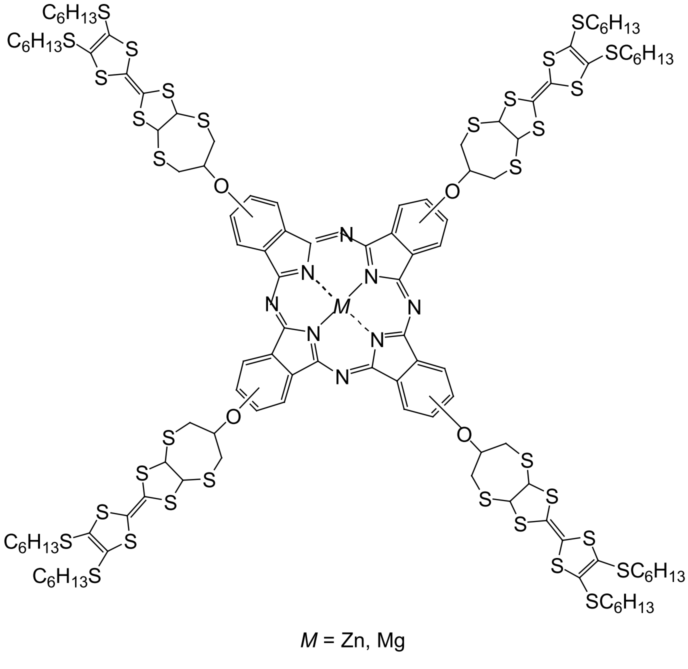
* Corresponding author. E-mail: yjshen@ecust.edu.cn

The phthalocyanines or metallophthalocyanines have been used as pigments since they were first produced. Recently, due to their 18-(or 16)-π-electron conjugated system, modified phthalocyanines with remarkable properties have been applied in several 'high-tech' fields [2] by varying central metal ions and peripheral substituents.

Some D-σ-A systems (the assemblies of electron donor and electron acceptor linked by spacers, such as saturated alkoxy groups) formed by association of the phthalocyanine core with *TTF* units have been described previously. *Cook et al.* synthesized a phthalocyanine system functionalized with one or two *TTF* units that showed the behaviour of liquid crystals [3]. *Bryce et al.* prepared phthalocyanine derivatives substituted by four or eight peripheral substituted or unsubstituted tetrathiafulvalene units [4, 5].

Tetrathiafulvalenylmetallophthalocyanine attracted our attention. We once introduced a zinc(II) phthalocyanine derivative functionalized with four peripheral tetrathiafulvalene units as the first assembly of metallophthalocyanine bearing tetrathiafulvalene units [6]. Unfortunately, its electrochemical properties could not be measured due to its unsatisfactory solubility. We recently reported a magnesium(II) phthalocyanine bearing four *EDT-TTF*s (4,5-ethylenedithiotetrathiafulvalenes) on its non-peripheral sites, which was soluble in both chloroform and dichloromethane [7].

As an extension of our previous research we report the synthesis, optical spectroscopy, and electrochemistry of zinc(II) and magnesium(II) phthalocyanines bearing four propylenedithiotetrathiafulvalenes (*PDT-TTF*) on the peripheral sites, which can be well dissolved in both chloroform and dichloromethane. The structures of the target compounds are shown in Fig. 1.



M = Zn, Mg

Fig. 1. Target compounds

Results and Discussion

Mass Spectra

The molecular weight of each target compound could not be observed directly by mass spectrometry. Instead only some data of fragments were collected during the measurements.

^{1}H NMR Spectra

^{1}H NMR spectra of the two target molecules show that the protons of the phthalocyanine core are shielded by the four peripheral *PDT-TTF* units possessing long hexylthio substituents. In addition, their ^{1}H NMR spectra display the broadening peak of *TTF* substituents, corresponding to the eight different environments that these groups may experience in the four isomers possible for a tetra-substituted phthalocyanine containing one substituent on each benzene ring.

UV/VIS Spectra

Figure 2 depicts the UV/VIS spectra of compound **3** and **4**. The optical spectra of **2** is displayed in Fig. 3.

In the ultraviolet region of **2**, **3**, and **4**, *B*-band (or *Soret* band) of phthalocyanine between 320–370 nm and typical absorption of *PDT-TTF* derivatives between 240–400 nm lead to the superimposed bands.

Compared with the *Q*-band of **2**, typical split of nonmetallophthalocyanine derivatives at $\lambda_{max} = 666.6$, 702.6 nm (see Fig. 3), **4** possesses a *Q*-band of a typical metallophthalocyanine at $\lambda_{max} = 693.0$ nm. The *Q*-band of **3** is hypsochromically shifted to $\lambda_{max} = 686.0$ nm, which is broadened due to the cofacial aggregation in chloroform. The hypsochromic shift compared with the nonmetallophthalocyanine core depends on the change of the electron distribution in the phthalocyanine

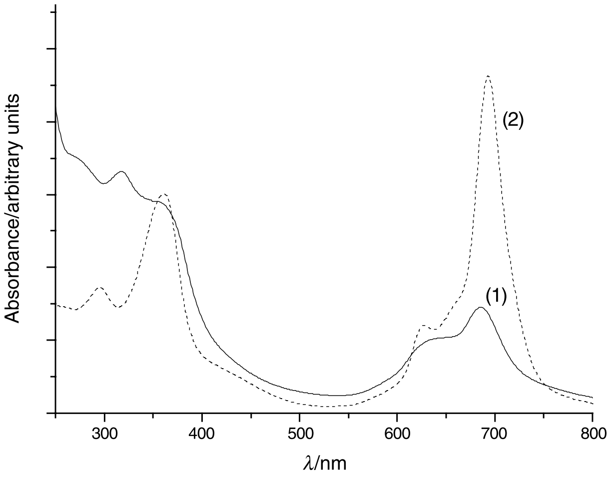


Fig. 2. UV/VIS spectra of (1) compound **3**, (2) compound **4**

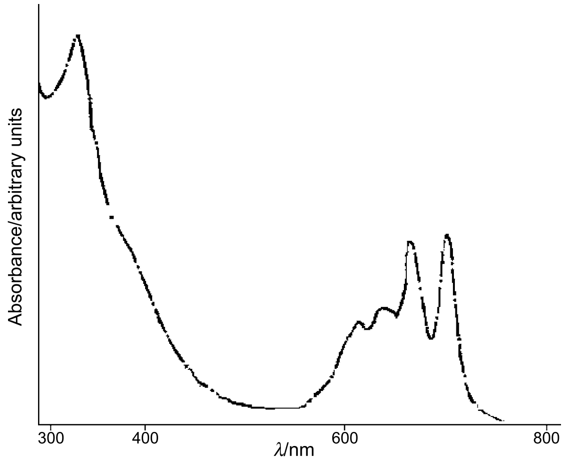


Fig. 3. UV/VIS spectra of compound **2**

macrocycle. In addition, the Q-band of dimers at $\lambda_{\max} = 627.0$ nm was observed in the visible region of **4**.

Cyclic Voltammetry

Cyclic voltammetric (CV) studies on **3** and **4** were performed in dichloromethane. Figure 4 depicts their cyclic voltammogram together with that of **2**.

The compounds **2**, **3**, and **4** undergo the classical two-step-oxidation of *TTF* derivatives. An anodic shift of the first oxidation peak can be detected between the phthalocyanine parent compound (**2**, $E^1{}_{1/2} = 0.646$ V) and the metallophthalocyanine derivatives (**3**, $E^1{}_{1/2} = 0.655$ V; **4**, $E^1{}_{1/2} = 0.660$ V). The introduction of Zn

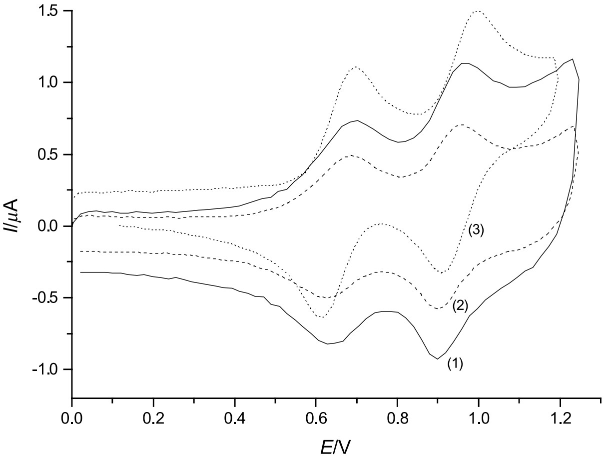


Fig. 4. Cyclic voltammogram of (1) compound **2**: scan rate 50 mv/s, $E^1{}_{1/2} = 0.646$ V, $E^2{}_{1/2} = 0.929$ V; (2) compound **3**: scan rate 25 mv/s, $E^1{}_{1/2} = 0.655$ V, $E^2{}_{1/2} = 0.928$ V; (3) compound **4**: scan rate 5 mv/s, $E^1{}_{1/2} = 0.660$ V, $E^2{}_{1/2} = 0.948$ V

and Mg as central metals changes the density of the electron cloud in the macro-π-conjugated system, therefore the electronwithdrawing between the phthalocyanine core and the *PDT-TTF* unit is enhanced. Thus losing one electron to form (*PDT-TTF*)$^+$ becomes more difficult. In addition, the magnesium atom has more influence on the second oxidation peak of the *PDT-TTF* unit than the zinc atom.

Experimental

All reagents and solvents were of commercial quality and were distilled or dried when necessary using standard procedures. ^{1}H NMR spectra were obtained on a *Bruker* AVANCE *500* spectrometer operating at 500.13 MHz. ^{13}C NMR spectra were obtained on a *Bruker* AVANCE *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. Elemental analyses were carried out with a Vario El III (Elementar) instrument; their results agreed with calculated values.

The synthesis of the precursor of our target compounds, [2-(4,5-bishexylsulfanyl[1,3]dithiol-2-ylidene)hexahydro[1,3]dithiolo[4,5-b][1,4]dithiin-5-yloxy]phthalonitrile (**1**), has been reported [8].

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 the solvent was dichloromethane.

Tetra-β-{2-[4,5-bis(hexylsulfanyl)[1,3]dithiol-2-ylidene]hexahydro[1,3]dithiolo[4,5-b][1,4]dithiin-5-yloxy}phthalocyanine (**2**)

Compound **1** (580 mg) was added to the sodium pentanolate solution (prepared from sodium (2.34 g) and dry pentanol (30 cm^3)). The mixture was heated to 130–135°C and stirred under argon for 5 h. The solvent was removed in vacuum. Ethanol was added to the green residue, followed by the addition of acetic acid. The mixture was left overnight. A dark green solid was obtained by decantation and suction filtration. The solid was extracted with boiling ethanol until the solvent was colorless. Then the residue was dissolved in chloroform to obtain an intense green solution. This solution was filtered through celite, and then evaporated in vacuum. Compound **2** was obtained as a dark green amorphous solid. Yield, 116 mg (20%); MS (EI): $m/z = 145$, 147, 220, 222, 258, 335, 342, 406, 426, 427, 428, 429, 430, 438, 440, 701, 702, 730; ^{1}H NMR (CDCl$_3$): $\delta = 0.75$–1.08 (t, 6H), 1.13–1.50 (m, 12H), 1.50–1.75 (m, 4H), 2.65–3.00 (m, 4H), 3.13–3.20 (t, 1H) ppm; ^{13}C NMR (CDCl$_3$): $\delta = 14.807$, 23.387, 28.678, 30.056, 31.281, 36.628, 37.241, 68.868, 129.539, 131.569, 168.450 ppm; UV/VIS (chloroform): $\lambda_{\max} = 287.6$, 336.4, 639.4, 666.6, 702.6 nm.

{Tetra-β-{2-[4,5-bis(hexylsulfanyl)[1,3]dithiol-2-ylidene]hexahydro[1,3]dithiolo[4,5-b][1,4]dithiin-5-yloxy}phthalocyaninato} zinc(II) (**3**)

A mixture of 420 mg (0.62 mmol) of **1**, 55 mg (0.154 mmol) of zinc acetate, and 25 cm^3 of *n*-pentanol was stirred and refluxed for 12 h. The dark green solution was cooled to room temperature followed by an addition of 50 cm^3 of methanol. A dark brown solid was precipitated and then separated by suction filtration. The precipitate was washed with acetone until the filtrate was colorless. An intense green solution was obtained by dissolving this solid in chloroform, which was filtered and then evaporated in vacuum, giving 219 mg (51%) of **3** as green amorphous solid. MS (EI): $m/z = 145$, 147, 220, 222, 258, 335, 342, 406, 426, 427, 428, 429, 430, 438, 440, 701, 702, 730; ^{1}H NMR (CDCl$_3$): $\delta = 0.75$–1.08 (t, 6H), 1.13–1.50 (m, 12H), 1.50–1.75 (m, 4H), 2.65–3.00 (m, 4H), 3.13–3.20 (t, 1H) ppm; ^{13}C NMR (CDCl$_3$): $\delta = 14.807$, 23.387, 28.678, 30.056, 31.281, 36.628, 37.241, 68.868, 129.539, 131.569, 168.450 ppm; UV/VIS (chloroform): $\lambda_{\max} = 317.0$, 686.0 nm.

{Tetra-β-{2-[4,5-bis(hexylsulfanyl)[1,3]dithiol-2-ylidene]hexahydro[1,3]dithiolo[4,5-b][1,4]dithiin-5-yloxy}phthalocyaninato} magnesium(II) (**4**)

A mixture of 560 mg (0.82 mmol) of **1**, 44 mg (0.205 mmol) of magnesium acetate, and 25 cm^3 of *n*-pentanol was stirred and refluxed for 12 h. The dark green solution was cooled to room temperature followed by the addition of 70 cm^3 of methanol. A dark brown solid was precipitated and separated by suction filtration. The precipitate was washed with ethanol until the filtrate was colorless. An intense green solution was obtained by dissolving this solid in chloroform, which was filtered and then evaporated in vacuum, giving 69 mg (12%) of **4** as green amorphous solid. MS (EI): $m/z = 145$, 147, 220, 222, 258, 335, 342, 406, 426, 427, 428, 429, 430, 438, 440, 701, 702, 730; ^{1}H NMR ($CDCl_3$): $\delta = 0.75$–1.08 (t, 6H), 1.13–1.50 (m, 12H), 1.50–1.75 (m, 4H), 2.65–3.00 (m, 4H), 3.13–3.20 (t, 1H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.807$, 23.387, 28.678, 30.056, 31.281, 36.628, 37.241, 68.868, 129.539, 131.569, 168.450 ppm; UV/VIS (chloroform): $\lambda_{max} = 295.0$, 361.0, 627.0, 693.0 nm.

Acknowledgements

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