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A zincic phthalocyanine (Pc) derivative functionalized with four peripheral substituted tetrathiafulvalene (TTF) units has been synthesized. The intermediates and target compound have been characterized by  $^1\text{H}$ -nmr,  $^{13}\text{C}$ -nmr, ms, EA, uv-vis and mp. The molecular weight of  $\text{H}_2\text{Pc-TTF}_4$  can not be found in mass spectra.  $^1\text{H}$ -nmr spectra and mp determination show both  $\text{H}_2\text{Pc-TTF}_4$  and  $\text{ZnPc-TTF}_4$  are isomer-mixtures. Uv-vis spectra indicate that the aggregation of  $\text{H}_2\text{Pc-TTF}_4$  is solvent dependent and the introduction of Zn atom affects the solubility of the assembly.

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### Introduction.

Phthalocyanines (Pcs), both metallo and non-metallo derivatives as planar aromatic organic compounds, have been well known for *ca.* 70 years, not only as colorants with pretty colors but also an important class of organic functional materials due to their unique properties. They have the following fundamental characteristics: (1) being capable of diverse physical and chemical properties *via* changes in the identity of substituents attached to the ring system; (2) having intense color and thus efficient energy absorption; (3) being capable of adding or subtracting many electrons without changing molecular structure and stability; (4) permitting the facile design of special characteristics through symmetric and asymmetric substitution of the main phthalocyanine skeleton and through axial ligation to the central metal. These characteristics allow for applications in a wide range of fields [1]. Recently, they have been applied in such hi-tech applications as photosensitizer [2], electrophotographic photoconductor [3], photodynamic cancer therapy [4], solar energy conversion [5], gas sensors [6] *etc.*

Many compounds have been produced where identical substituents have been introduced to the benzenoid ring, giving tetra, octa substitution as well as higher orders of four. Thus, allowing for the modification of new molecules with a variety of properties.

Since the phthalocyanine core is an 18  $\pi$ -electron aromatic macrocycle, substituents such as tetrathiafulvalene (TTF) and its derivatives, the famous  $\pi$ -electron donors in the field of organic metals, have been introduced to its peripheral or non-peripheral places to form D- $\sigma$ -A assemblies as intramolecular charge transfer materials. For example, Cook and co-workers prepared a phthalocyanine system functionalized with one or two TTF units, which displayed liquid crystalline behavior [7]. Bryce and co-workers prepared Pc derivatives functionalized with four and eight peripheral substituted or un-substituted tetrathiafulvalene units. Their study on fluorescence spectroscopy indicated that rapid intramolecular electron transfer

occurred between the Pc core and a peripheral TTF [8,9].

It's noticeable that all the Pc-(TTF) $_x$  assemblies reported are nonmetallo. Our research towards metallo Pc-(TTF) $_x$  has been carried out and a zincic phthalocyanine derivative functionalized with four peripheral substituted tetrathiafulvalene units (see Figure 1) will be introduced in this paper. The mass spectra,  $^1\text{H}$ -nmr spectra and solution optical spectroscopy will also be discussed herein.

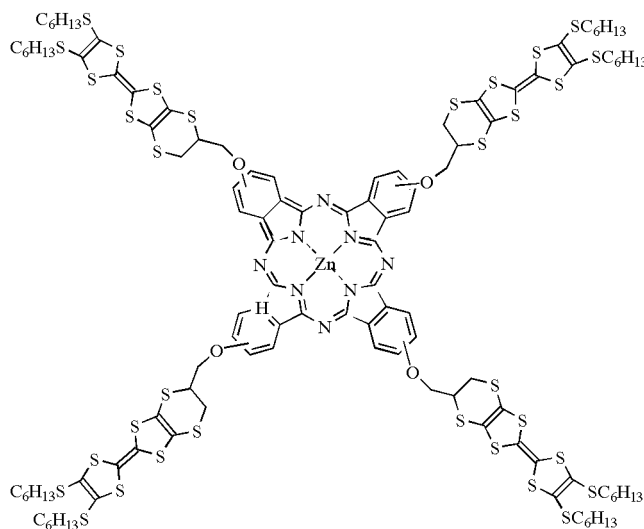


Figure. 1 The structure of target molecule **12**.

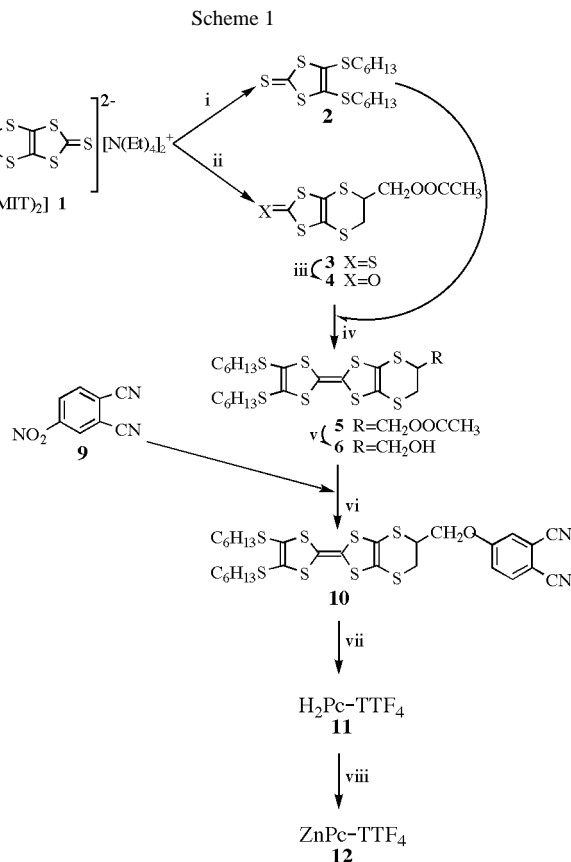
### Results and Discussion.

#### Syntheses.

The synthesis of the target molecule is shown in Scheme 1. Scherer [10] synthesized 4,5-bis(hexylthio)-1,3-dithiole-2-thione **2** *via* the reaction between 8 g of **1** and 9.46 g hexyl iodide in 600 mL acetone for 3 days at room temperature. The yield was *ca.* 90%. Nogami [11] pointed out that the yield would be poor without the dilution method. He used a large volume of acetone to set up a dilution system.

However, we find that the reaction can be completed within 4 hours, in even higher yield (96%) than those observed by Scherer, when the system is as concentrated as possible and is refluxed.

is mostly reported as 50 °C, and the molecular ratio of both precursors is 1:1. Young [12] used LiOH instead of K<sub>2</sub>CO<sub>3</sub>. However, in our work, we failed to obtain the product under those conditions. In addition, we found that an excess



Reagents and conditions: i, 1-bromohexane, acetone, reflux; ii, 2,3-dibromopropanyl acetate, acetone, reflux; iii, mercuric acetate, chloroform, acetic acid, room temperature; iv, triethyl phosphite, 120 °C; v, hydrazine monohydrate, chloroform, methanol, room temperature; vi, K<sub>2</sub>CO<sub>3</sub>, DMF, 90 °C; vii, sodium pentoxide, pentanol, 125 °C; viii, pentanol, zinc acetate, reflux.

One important intermediate for our target molecule is TTF derivative **6** which is the hydrolyzate of **5** obtained in 33.4% yield by the standard phosphite-induced cross-coupling of the 1,3-dithiole-2-one and 2-thione fragments **2** and **4**. The hydrolyzation can be realized by using either hydroxides (*e.g.* potassium, sodium hydroxide) or hydrazine monohydrate in methanol. The mixture obtained by hydrolyzation with sodium or potassium hydroxide was not stable during chromatography. Both the target compound and by-product turned into brown oils quickly. Though the yield was only 37.5%, we prefer choosing hydrazine monohydrate as alkali in this reaction.

To synthesize the key intermediate for phthalocyanine, base-catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile and TTF derivative **6** was carried out in dry DMF using K<sub>2</sub>CO<sub>3</sub>. The common reaction temperature

amount of 4-nitrophthalonitrile and higher temperature are necessary modifications to the reported approaches.

For the synthesis of **11** bearing four TTF units, we used sodium pentoxide/pentanol system and then treated the green residue with ethanol and acetic acid. The dark green air-stable solid **11** is soluble in a range of organic solvents, slightly soluble in DMF, but insoluble in alcohol. All the by-products are soluble in alcohol. Utilizing the solubility differences between product and byproducts, **11** was purified successfully by solvent (ethanol preferred) extraction for seven days.

Target compound **12** was prepared by refluxing **11** and zinc acetate in pentanol for 0.5 hour. Purification was then achieved by dissolving the mixture in acetate acid/ethanol solution and separating the green precipitate from the mixture after standing still for 24 hours. As a dark green solid,

**12** is appreciably soluble in DMF, however, it is insoluble in alcohol, chloroform and some other organic solvents. The change in the solubility of the assembly obviously results from the introduction of Zn.

Furthermore, **11** is a mixture of geometric isomers according to the observed melting point, which leads **12** to an isomer-mixture.

#### Mass Spectra.

The molecular weight of **11** was not found in mass spectra by EI, ESI or FAB, which is calculated as 2734.500. Only some fragments ions were observed during the measurement.

#### <sup>1</sup>H NMR Spectra.

<sup>1</sup>H NMR spectra of **11** show that the protons of phthalocyanine core, and those of substituted tetrathiafulvalene units near the core, are shielded by the four peripheral TTF units possessing long hexylthio substituents.

In addition, <sup>1</sup>H NMR spectra of **11** display broad peaks corresponding to the TTF substituents, resulting from 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. This agrees with the obtained melting point.

#### UV-VIS Spectra.

The UV-VIS spectra of compound **5**, **6**, **10**, **11** and **12** are listed in Table 1. Uv-visible spectra of **11** in chloroform show a typical split of Q-band at  $\lambda_{\text{max}}$  666.6, 702.6 nm, the weak absorption band at 639.4 is due to the dimer [13]. A shoulder beside the dimer band is a vibrational overtone of the Q-band. The bands between 300~500 nm show superimposed bands of the phthalocyanine and TTF species due to the existence of B-band (or Soret band) of Pc between 320~370 nm and typical absorption of TTF derivatives between 240~400nm in the ultra-violet region. When **11** is dissolved in DMF, no clear split peaks could be observed and the Q-band was bathochromically shifted to  $\lambda_{\text{max}}$  676.0 nm due to the slight solubility. The disappearance of Q-band at *ca.* 630 nm suggests that **11** is less aggregated in DMF than in chloroform.

The Q-band of **12**, a characteristic of non-aggregated metallo phthalocyanines, is observed at  $\lambda_{\text{max}}$  683.6 nm as a

strong absorption. The weak absorption band at  $\lambda_{\text{max}}$  614.6 nm is a vibrational overtone of the Q-band, which is stronger than for that of **11**.

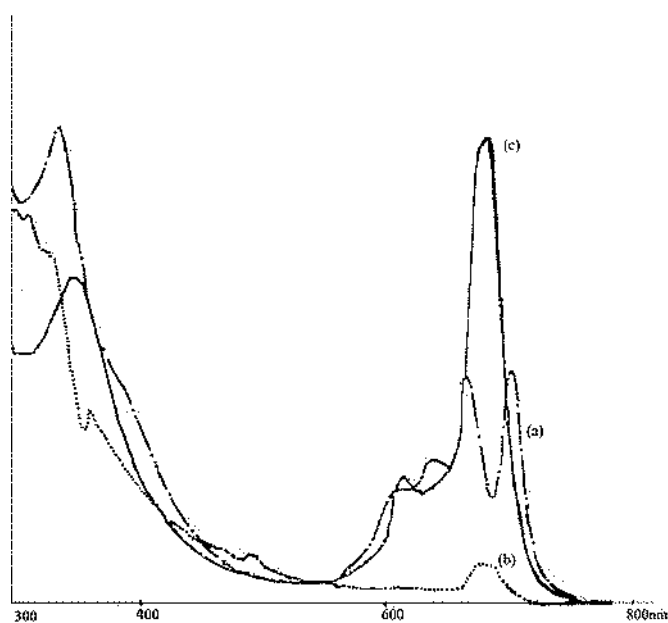


Figure. 2 The uv-visible absorption spectra of (a) H<sub>2</sub>Pc-TTF<sub>4</sub> in chloroform (b) H<sub>2</sub>Pc-TTF<sub>4</sub> in DMF (c) ZnPc-TTF<sub>4</sub> in DMF

## EXPERIMENTAL

### General.

All reagents and solvents were of commercial quality and distilled or dried when necessary using standard procedures. Light petroleum referred to the fraction with bp 60~90 °C. <sup>1</sup>H nmr and <sup>13</sup>C nmr spectra were obtained using a BRUCK AVANCE 500 spectrometer. Uv-vis spectra were recorded on a SHIMADZU UV365 spectrometer. Mass spectra were recorded on an HP-5989A spectrometer (EI) and MARINER ESI TOF-MS (ESI). Melting points were determined with X4 melting microscope (Pekin, China) and were not corrected. Element analytical data were obtained on an MOD1106 (Carol Ertra) instrument.

TEA<sub>2</sub>[Zn(DMIT)<sub>2</sub>] **1** and 2,3-dibromopropanyl acetate were prepared according to Zhao's methods[14].

### 4,5-Bis(hexylthio)-1,3-dithiole-2-thione (**2**).

A 100 mL acetone solution of 8 g (11.2 mol) TEA<sub>2</sub>[Zn(DMIT)<sub>2</sub>] **1** was heated to reflux in a 250 mL flask. A 50 mL acetone solution of 9.4 mL (60 mmol) 1-bromohexane was simultaneously dropped into the flask with vigorous stirring. The solution was then refluxed until **1** disappeared as shown by TLC. The mixture of the product was cooled to room temperature, and then filtered. The precipitate was separated from the mixture, and the acetone of the filtrate was evaporated. The residue was chromatographed on silica gel using chloroform: light petroleum=1:2 as an eluent. The second orange fraction contained **2**. Evaporating the eluent gave **2** as a red-orange oil, 7.8 g (96%), ms (EI): m/z 367 (14.119), 366 (27.196).

Table 1  
UV-VIS Spectra of Compound **5**, **6**, **10**, **11** and **12**

| Compound  | $\lambda_{\text{max}}$ (nm)  |
|-----------|--|
| <b>5</b>  | 265.4, 320, 345 (chloroform)   |
| <b>6</b>  | 265.2, 305.8, 335.8, 389.8 (chloroform)  |
| <b>10</b> | 246.2, 296.8, 328.4 (chloroform)   |
| <b>11</b> | 240.2, 287.6, 336.4, 639.4, 666.6, 702.6 (chloroform)<br>265.4, 310.8, 676.0 (DMF) |
| <b>12</b> | 352.4, 614.6, 683.6 (DMF)  |

Acetic Acid 2-Thioxotetrahydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-5-ylmethyl Ester (**3**).

Following the procedure described above, 7.2 g (10 mmol) TEA<sub>2</sub>[Zn(DMIT)<sub>2</sub>] **1** and 11.4 mL (80 mmol) 2,3-dibromopropyl acetate were used to synthesize compound **3**. The crude product was chromatographed on silica gel using ethyl acetate:light petroleum = 1:2 as an eluent. The fifth yellow fraction contained **3**. Evaporating the eluent gave compound **3** as a red-orange oil, 5.40 g (90%), ms (EI): *m/z* 296 (100.00).

Acetic Acid 2-Oxo-tetrahydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-5-ylmethyl Ester (**4**).

A mixture of 2.6 g (8.8 mmol) compound **3**, 20 mL chloroform, 20 mL acetic acid and 7.0 g (22 mmol) mercuric acetate was stirred at room temperature for 12 hours. The precipitate was filtered off and the filtrate was washed with water, and aqueous sodium carbonate. The organic layer was separated and dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuum and then gave a yellow oil, 2.4 g (98%), ms (EI): *m/z* 280 (100.00); <sup>1</sup>H nmr (CDCl<sub>3</sub>): δ<sub>H</sub> 4.35 (d, 2H), 3.4 (m, 3H), 2.1 (s, 3H).

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>S<sub>4</sub>: C, 34.29; H, 2.86. Found: C, 34.73; H, 3.24.

Acetic Acid 2-(4,5-Bis-hexylsulfanyl[1,3]dithiol-2-ylidene)-tetrahydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-5-yl Methyl Ester (**5**).

Compound **2** (0.36 g, 1 mmol) and 0.28 g (1 mmol) **4** were mixed with 5 mL triethyl phosphite and heated to 120 °C with stirring under argon for 5 hours. Removal of the solvent in vacuum gave a deep red oily residue which was then chromatographed on silica gel using light petroleum:ethyl acetate = 2:1 as an eluent to give **5** as a red-orange oil, 0.42 g (74%), ms (ESI): *m/z* 598.2 (5.45), 599.2 (1.55); <sup>1</sup>H nmr (CDCl<sub>3</sub>): δ<sub>H</sub> 0.89 (t, 6H), 1.25~1.44 (m, 12H), 1.57~1.64 (m, 4H), 2.10 (s, 3H), 2.79 (m, 4H), 3.13~3.25 (m, 2H), 3.80~3.95 (m, 1H), 4.25~4.37 (d, 2H); <sup>13</sup>C nmr (CDCl<sub>3</sub>): δ<sub>C</sub> 14.709, 21.431, 23.204, 28.854, 30.343, 30.950, 31.954, 32.744, 37.041, 42.535, 65.341, 77.447, 77.701, 77.955, 108.395, 114.358, 114.576, 115.926, 128.410, 171.074; uv-vis (chloroform): λ<sub>max</sub> 265.4, 320, 345nm.

*Anal.* Calcd. for C<sub>23</sub>H<sub>34</sub>O<sub>2</sub>S<sub>8</sub>: C, 46.11; H, 5.72. Found: C, 46.11; H, 5.73.

[2-(4,5-Bis-hexylsulfanyl[1,3]dithiol-2-ylidene)-tetrahydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-5-yl]-methanol (**6**).

A mixture of 2.7 g (4.5 mmol) **5**, 45 mL chloroform, 135 mL methanol and 3.4 mL (67 mmol) hydrazine monohydrate was stirred at room temperature until TLC showed that **5** disappeared. The solvents were evaporated and then the residue was extracted by chloroform (ca. 150 mL). The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuum and then chromatographed on a silica gel using light petroleum:chloroform:ethyl acetate = 10:1:4 as an eluent. The second orange fraction contained **6**. Evaporating the eluent afforded 0.94 g (37.5%) orange oil which was crystallized in a freezer. Recrystallization from light petroleum gave yellow crystals, mp 56~58 °C, ms (ESI): *m/z* 555.9 (6.97), 556.9 (1.96), 557.9 (2.91); <sup>1</sup>H nmr (CDCl<sub>3</sub>): δ<sub>H</sub> 0.88 (t, 6H), 1.25~1.36(m, 8H), 1.36~1.44 (m, 4H), 1.54~1.70 (m, 4H), 2.71~2.91 (m, 4H), 4.35(s, 1H); <sup>13</sup>C nmr (CDCl<sub>3</sub>): δ<sub>C</sub> 14.448, 22.957, 28.614, 30.116, 31.717, 36.797, 40.329, 77.183, 77.437, 77.691, 110.856, 113.691, 128.140, 131.627; uv-vis (chloroform): λ<sub>max</sub> 265.2, 305.8, 335.8, 389.8nm.

*Anal.* Calcd. for C<sub>21</sub>H<sub>32</sub>OS<sub>8</sub>: C, 45.28; H, 5.79. Found: C, 44.85; H, 5.64.

4-[2-(4,5-Bis-hexylsulfanyl-[1,3]dithiol-2-ylidene)-tetrahydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-5-ylmethoxy]-phthalonitrile (**10**).

A mixture of 0.3 g (0.5 mmol) **6**, 20 mL DMF (dried over MgSO<sub>4</sub>), 0.18 g (1 mmol) 4-nitrophthalonitrile **9** and 0.35 g (2.5 mmol) potassium carbonate (anhydride) was stirred at 90 °C until TLC showed **6** disappeared (ca. 30 days). The solvent was evaporated and then the residue was extracted by chloroform. The organic layer was separated, dried over MgSO<sub>4</sub>, concentrated in vacuum and then chromatographed on a silica gel using light petroleum:chloroform:ethyl acetate = 10:1:4 as an eluent. The second orange fraction contained **10**. Evaporating the eluent afforded 0.11 g (32.2%) dark red oil that crystallized in a freezer. Recrystallization from ethyl acetate gave red crystals, mp 87~88 °C; ms (EI): *m/z* 682 (100), 683 (58.86), 684 (42.48); <sup>1</sup>H nmr (CDCl<sub>3</sub>): δ<sub>H</sub> 0.85~0.93 (t, 6H), 1.25~1.35(m, 8H), 1.36~1.47 (m, 4H), 1.59~1.68 (m, 4H), 2.65~2.81 (m, 4H), 2.81~2.87 (m, 2H), 2.98~3.05 (d, 2H), 4.80~4.90 (t, 1H), 7.17~7.72 (m, Ar-3H); <sup>13</sup>C nmr (CDCl<sub>3</sub>): δ<sub>C</sub> 14.706, 23.206, 28.858, 30.359, 31.963, 36.559, 37.064, 77.446, 77.700, 77.954, 109.132, 109.680, 114.963, 115.558, 115.945, 118.606, 120.497, 121.399, 128.413, 131.023, 136.287, 159.867; uv-vis (chloroform): λ<sub>max</sub> 246.2, 296.8, 328.4nm.

*Anal.* Calcd. for C<sub>29</sub>H<sub>34</sub>OS<sub>8</sub>N<sub>2</sub>: C, 50.99; H, 5.02; N, 4.10. Found: C, 50.67; H, 5.03; N, 3.97.

Tetra-β-{2-[4,5-bis(hexylsulfanyl)-1,3-dithiol-2-ylidene]-tetrahydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-5-ylmethoxy}-phthalocyanine (**11**).

Compound **10** (580 mg) was added to the sodium pentoxide solution [prepared from sodium (2.34 g) and dry pentanol (30 mL)]. The mixture was heated to 130~135 °C and stirred under argon for 5 hours. 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 **11** was obtained as a dark green amorphous solid, 116 mg (20%), mp150~185 °C, ms (ESI): *m/z* 145 (41.68), 147(20.57), 220(24.43), 222(13.59), 258(13.52), 335(15.26), 342(12.42), 406(18.57), 426(100.00), 427(21.28), 428(64.48), 429(14.92), 430(11.32), 438(15.35), 440(10.07), 701(42.36), 702(19.19), 730(17.76); <sup>1</sup>H nmr (CDCl<sub>3</sub>): δ<sub>H</sub> 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); <sup>13</sup>C nmr (CDCl<sub>3</sub>): δ<sub>C</sub> 14.807, 23.387, 30.056, 30.396, 31.281, 38.118, 39.452, 125.732, 129.539, 131.569, 168.450; uv-vis (chloroform): λ<sub>max</sub> 240.2, 287.6, 336.4, 639.4, 666.6, 702.6nm; uv-vis (DMF): λ<sub>max</sub> 265.4, 310.8, 676.0nm.

*Anal.* Calcd. for C<sub>116</sub>H<sub>138</sub>O<sub>4</sub>S<sub>32</sub>N<sub>8</sub>: C, 50.95; H, 5.09; N, 4.10. Found: C, 51.31; H, 5.36; N, 3.97.

{{ Tetra-β-{2-[4,5-bis(hexylsulfanyl)-1,3-dithiol-2-ylidene]-tetrahydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-5-ylmethoxy}-phthalocyanine-nato} } zincic(II) (**12**).

A mixture of **11** (ca. 50 mg) and zinc acetate (ca. 50 mg) was refluxed in pentanol for 0.5 hour. A milky-greenish mixture was

then obtained, which was left overnight to form slightly green solution and green solid mixed with some white powder. The filter cake was dissolved in acetate acid/ethanol to form a transparent green solution. After standing for 24 hours, a green solid was separated by suction filtration, washed by ethanol and dried by vacuum at room temperature, *ca.* 40 mg (*ca.* 80%) **12** was obtained with satisfactory purity, uv-vis (DMF):  $\lambda_{\max}$  352.4, 614.6, 683.6 nm.

*Anal.* Calcd. for  $C_{116}H_{136}O_4S_{32}N_8Zn$ : C, 49.80; H, 4.90; N, 4.00. Found: C, 50.20; H, 5.22; N, 3.74.

#### Acknowledgements.

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