



# Effect of central metals and peripheral substituents on the third-order nonlinear optical properties of tetra-benzimidazole and benzothiazole substituted phthalocyanines

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## ABSTRACT

A series of tetra substituted phthalocyanines bearing 2-mercaptobenzimidazole or 2-mercaptobenzothiazole units with different central metals (Zn and In) were synthesized. Their photophysical properties including the parameters of fluorescence and triplet state were studied. The benzothiazole substituted phthalocyanines exhibit stronger third-order nonlinear optical properties (NLO) absorption effects, higher triplet quantum yield ( $\Phi_T$ ) and faster intersystem crossing rate compared to the benzimidazole substituted phthalocyanines. With the same central metals, benzothiazole substituted phthalocyanine complexes have the lower fluorescence quantum yield ( $\Phi_F$ ), the higher triplet quantum yield ( $\Phi_T$ ) and the larger third-order NLO properties as a result of larger conjugated structure and spin-orbit coupling induced by sulphur atoms. The influences of the central metal atoms and the peripheral substituents on the third-order NLO properties are discussed using photophysical parameters.

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## 1. Introduction

The nonlinear optical (NLO) materials have been the research focus in many fields such as chemical sensors, storage, optical limiting and so on [1–3]. Phthalocyanine (Pc), an excellent NLO material has penetrated into the world of cutting-edge areas of science and technology at present because of its remarkable characteristics endowed by unique structure with aromatic macrocycles of an extensive delocalized 18- $\pi$  electron system. The presence of massive delocalized  $\pi$  electrons originated from highly conjugated system of Pc molecule, which confers on them dipole moments that response to the electric intensity, is the fundamental reason for the larger optical nonlinearities of Pcs [4,5]. It benefits from preferable NLO performance that Pcs are applied in many aspects including nonlinear optics, semiconductor devices, chemical sensors, optical storage devices and photosensitizers in photodynamic therapy (PDT) [6–10]. Research results show that phthalocyanine molecules

with the large conjugated systems, and the strong electron-withdrawing or electron-donating groups possess the larger optical nonlinearities [11,12]. Indium, a heavier metal atom, is diamagnetic and able to host axial ligands, which makes indium phthalocyanine derivatives as suitable candidates of photosensing devices and optical limiting materials reported in literatures [13,14].

Both benzimidazole and benzothiazole derivatives are very important species due to their pharmaceutical and biological activities [15–18]. The rigid plane structure and larger conjugated system make them possess preferable optical performance, such as photosensitizers, fluorescence probe and second-order nonlinear optical materials [19–21]. In this paper, the aim of the combination of phthalocyanine with benzimidazole or benzothiazole is designed to obtain larger  $\pi$ -conjugated system, improve the solubility for unsubstituted phthalocyanine in common organic solvents, and enhance the third-order NLO absorption effect. And the effect of pushing-drawing capacity of the peripheral substitutes and conjugation effect on the third-order NLO properties will be studied in this paper. Moreover, the photophysical properties, such as emission spectrum, and quantum yield, the triplet transient

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absorption coefficients and lifetimes, the triplet quantum yields, the rate constants of intersystem crossing have been obtained and used to discuss the mechanism of third-order NLO absorption effect for the phthalocyanines.

## 2. Experimental section

### 2.1. Materials

All initial raw materials such as 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, 4-nitrophthalonitrile, 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) were purchased from Sigma-Aldrich Co. LLC. Some reactive solvents, such as n-pentanol and DMF, were freshly distilled just before using.

### 2.2. Characterizations

The structures of the synthesized products were characterized by FT-IR, UV–vis,  $^1\text{H}$  NMR, MALDI-TOF and Elemental analysis. The Fourier transform infrared (FT-IR) spectra were obtained with a Perkin Elmer instruments Spectrum One FT-IR spectrometer (KBr disks). The UV–vis spectra were recorded by the Jena SPECORD S600 spectrophotometer in a 10 mm quartz cuvettes. The  $^1\text{H}$  NMR (400 MHz) spectra were recorded on a BRUKER AVANCE III 400 in  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$  solutions. The MALDI-TOF mass spectra were obtained by BRUKER Micro flex. Elemental analysis was taken on Elemental Vario MICRO.

### 2.3. Synthesis

The general synthetic routes of those four tetra-substituted metallophthalocyanine derivatives, namely Tetra[1*H*-Benzo(d)imidazol-2-yl]thiol phthalocyanine zinc (TBIT-ZnPc, **5**), Tetra[1*H*-Benzo(d)imidazol-2-yl]thiol phthalocyanine indium (TBIT-InClPc, **6**), Tetra[Benzo(d)thiazol-2-yl]thiol phthalocyanine zinc (TBIT-ZnPc, **7**) and Tetra[Benzo(d)thiazol-2-yl]thiol phthalocyanine indium (TBIT-InClPc, **8**) are given in Scheme 1. In summary, the preparation of targeted compounds was initially implemented by the popular method of cyclotramerization theoretically of 4-[[1*H*-Benzo(d)imidazol-2-yl]thiol]phthalonitrile (**3**) or 4-[[Benzo(d)thiazol-2-yl]thiol]phthalonitrile (**4**) in the presence of metal salts ( $\text{Zn}(\text{OAc})_2$  or  $\text{InCl}_3$ ) and the alkaline catalysts DBU in n-pentanol as the solvent at reflux temperature.

#### 2.3.14-[[1*H*-Benzo(d)imidazol-2-yl]thiol]phthalonitrile (3)

4-Nitrophthalonitrile (1.73 g, 0.01 mol) was dissolved in dry DMF (35 mL), 2-mercaptobenzimidazole (**1**) (1.50 g, 0.01 mol) was added into the above solution under nitrogen atmosphere, then the mixture solutions was stirred at 50 °C for 20 min. Anhydrous potassium carbonate ( $\text{K}_2\text{CO}_3$ ) (4.14 g, 0.03 mol) divided into eight sections were added into above mixture products within 2 h, and was stirred for 72 h at 50 °C. Three days later, the mixture was poured into ice-water, stirred for a moment, and was placed under the static condition at room temperature for 12 h. The gray solid was collected by filtration, washed with water until the filtrate was neutral, then washed with methanol for several times. Finally, the dried crude product was crystallized using methanol. Yield: 1.91 g (69%), m.p. = 157 °C. FT-IR ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 3382 (N-H), 3060, 3016 (Ar-CH), 2949, 2863 (C-H), 2236 ( $\text{C}\equiv\text{N}$ ), 1615, 1584 ( $\text{C}=\text{N}$ ), 1476, 1266 (C-S-C), 1116, 976, 866, 749 (Pc-Skeleton).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ) ( $\delta$ : ppm): 13.28 (s, 1H, -NH), 8.26 (d,  $J = 1.9$  Hz, 1H, Ar-H), 8.08 (d,  $J = 8.4$  Hz, 1H, Ar-H), 7.82 (dd,  $J = 8.3, 1.9$  Hz, 1H, Ar-H), 7.59 (m, 2H, Ar-H), 7.26 (m, 2H, Ar-H). MS (MALDI-TOF): Calculated: 276.32 [M]; Found: 277.27 [M+H] $^+$ . Anal. Calc. for  $\text{C}_{15}\text{H}_8\text{N}_4\text{S}$ : C, 65.20; H, 2.92; N, 20.28. Found: C, 64.92; H, 3.04; N, 20.15.

#### 2.3.2. 4-[[Benzo(d)thiazol-2-yl]thiol]phthalonitrile (4)

A mixture of 4-nitrophthalonitrile (1.73 g, 0.01 mol) and 2-mercaptobenzothiazole (**2**) (1.67 g, 0.01 mol) in dried DMF (35 mL) was stirred under nitrogen atmosphere at 50 °C for 20 min. Anhydrous potassium carbonate ( $\text{K}_2\text{CO}_3$ ) (4.14 g, 0.03 mol) was added in eight equal portions within 2 h and the mixture was allowed to stir at 50 °C for 72 h. Three days later, the mixture was instantly poured into ice-water and stirred for a moment, then remained stationary at room temperature for 12 h. The pale yellow solid was collected by filtration, washed with water until the filtrate was neutral, then washed with methanol for several times. Finally the dried crude product was crystallized using methanol. Yield: 1.96 g (67%), m.p. = 159 °C. FT-IR ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 3066, 3027 (Ar-CH), 2945 (C-H), 2230 ( $\text{C}\equiv\text{N}$ ), 1583 ( $\text{C}=\text{N}$ ), 1550, 1456, 1423, 1275 (C-S-C), 1074, 987, 865, 761, 683 (Pc-Skeleton).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ : ppm): 8.05–8.01 (m, 2H, Ar-H), 7.94 (dd,  $J = 8.3, 1.8$  Hz, 1H, Ar-H), 7.87 (d,  $J = 7.9$  Hz, 1H, Ar-H), 7.81 (d,  $J = 8.2$  Hz, 1H, Ar-H), 7.55 (t,  $J = 7.7$  Hz, 1H, Ar-H), 7.47 (t,  $J = 7.7$  Hz, 1H, Ar-H). MS (MALDI-TOF): Calculated: 293.37 [M]; Found: 292.02 [M] $^+$ . Anal. Calc. for  $\text{C}_{15}\text{H}_7\text{N}_3\text{S}_2$ : C, 61.41; H, 2.41; N, 14.32. Found: C, 61.12; H, 2.54; N, 14.15.

#### 2.3.3. The synthesis of metallophthalocyanines (5–6)

The compounds (**3**) (0.221 g, 0.8 mmol), anhydrous  $\text{Zn}(\text{OAc})_2$  (0.147 g, 0.8 mmol) or anhydrous  $\text{InCl}_3$  (0.177 g, 0.8 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.5 mL) were added into the dried n-pentanol (20 mL), stirred and refluxed for 24 h under nitrogen atmosphere. A day later, the dark green solution was cooled to room temperature and diluted with methanol until the solid was precipitated. The crude product was filtered and took turns to wash with n-hexane, hot ethanol and aether. Finally, the product was purified by column chromatography with silica gel. The related characterizations of the final products TBIT-ZnPc (**5**) and TBIT-InClPc (**6**) were given below.

##### 2.3.3.1 Tetra[1*H*-Benzo(d)imidazol-2-yl]thiol phthalocyanine (5)

Eluent for column chromatography: dichloromethane–methanol mixture (25:1). Yield: 71.2 mg (30.4%). FT-IR ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 3357 (N-H), 3049, 2929 (Ar-CH), 1643, 1600 ( $\text{C}=\text{N}$ ), 1485, 1380, 1266 (C-S-C), 1143, 1095, 908, 812, 744, 682 (Pc-Skeleton).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ) ( $\delta$ : ppm): 12.82 (s, 4H, Im-NH), 9.51–7.22 (m, 28H, Ar-H). MS (MALDI-TOF): Calculated: 1170.65 [M]; Found: 1169.41 [M] $^+$ . Anal. Calc. for  $\text{C}_{60}\text{H}_{32}\text{N}_{16}\text{S}_4\text{Zn}$ : C, 61.56; H, 2.76; N, 19.14. Found: C, 61.32; H, 2.92; N, 18.94.

##### 2.3.3.2 Tetra[1*H*-Benzo(d)imidazol-2-yl]thiol phthalocyanine (6)

Eluent for column chromatography: dichloromethane–methanol mixture (15:1). Yield: 63.5 mg (25.3%). FT-IR ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 3373 (N-H), 3051, 2952 (Ar-CH), 1643, 1599 ( $\text{C}=\text{N}$ ), 1479, 1389, 1267 (C-S-C), 1142, 1092, 909, 827, 740, 685 (Pc-Skeleton).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ) ( $\delta$ : ppm): 13.01 (s, 4H, Im-NH), 9.47–7.21 (m, 28H, Ar-H). MS (MALDI-TOF): Calculated: 1255.53 [M]; Found: 1254.46 [M] $^+$ . Anal. Calc. for  $\text{C}_{60}\text{H}_{32}\text{N}_{16}\text{S}_4\text{InCl}$ : C, 57.40; H, 2.57; N, 17.85. Found: C, 57.12; H, 2.65; N, 18.02.

#### 2.3.4. The synthesis of metallophthalocyanines (7–8)

The compounds (**4**) (0.235 g, 0.8 mmol), anhydrous  $\text{Zn}(\text{OAc})_2$  (0.147 g, 0.8 mmol) or anhydrous  $\text{InCl}_3$  (0.177 g, 0.8 mmol) and 20 mL dried n-pentanol were mixed and stirred, refluxed for 24 h under nitrogen atmosphere in the presence of 0.5 mL DBU as catalyst. After cooling down, the solution was diluted with methanol. The dark green solid was collected by filtration and washed with n-hexane, hot ethanol and aether, successively. The crude product was passed through a silica gel column using dichloromethane–methanol mixture as eluent. The related

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