

## Synthesis, thermo-responsive behavior of cyclodextrin modified Bi-perylene monoimide derivative

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### ARTICLE INFO

#### Keywords:

Perylene monoimide  
Thermo-responsive behavior  
Cyclodextrin  
Host-guest interaction  
Fluorescence

### ABSTRACT

Novel bi-perylene monoimide derivative with permethyl- $\beta$ -cyclodextrin grafts (**BPMI-CD**) was synthesized. **BPMI-CD** exhibited the maximum absorption and emission bands at 540 nm and 625 nm, showed a large Stokes shift of 81 nm with the fluorescence quantum of 30%, and possessed high water-soluble. More interestingly, **BPMI-CD** showed a thermo-responsive behavior because of self-inclusion effect. **BPMI-CD** exhibited the LCSTs from 32 °C to 48.2 °C under different concentrations, and showed host-guest controlled thermo-responsive behavior with water-soluble porphyrin and mono-6-O-(*p*-toluenesulfonyl)-permethyl- $\beta$ -cyclodextrin (**PMCD-Ts**) as a competitive host molecule.

### 1. Introduction

In recent years, thermo-responsive materials have been widely studied for their potential applications in disease treatments, drug delivery, cancer therapy, catalysis and tissue engineering [1–7]. Especially, thermo-responsive supramolecular materials have attracted more attentions because of their advantages on multiple dynamic interactions, reversible inclusion complexes and noncovalent interactions, and recyclability [8–10]. The poly(*N*-isopropylacrylamide) (PNIPAM) [11–17] and the oligoethylene glycol (OEG) [18–22] based thermo-responsive supramolecular materials have been extensively studied, and their mechanisms were revealed to alter the balance between hydrophilic and hydrophobic interactions [11–22]. However, a very few of example for the non-PNIPAM and the non-OEG based thermo-responsive materials has been reported [23].

Perylene bisimide derivatives are one of the most widely studied molecules due to their high molar absorptivity, prominent photochemical stability and excellent optical properties [24,25]. Various perylene bisimide derivatives have been extensively used in the field of biological materials, organic photovoltaic materials and light-harvesting materials [26–30]. However, thermo-responsive perylene bisimide derivatives were limited [31–34]. Würthner and coworkers

reported a series of hydrophobic perylene bisimide derivatives with hydrophilic OEG chains modification. The perylene bisimide derivative with ethylene diglycol monoethyl ether derivative modification showed a lower critical solution temperature (LCST) of 26 °C at the concentration of 50  $\mu$ M [35]. With changing the hydrophilic OEG units, the LCST temperature of tetraethylene glycol monomethyl ether derivative modified perylene bisimide derivative was raised to 69 °C at the concentration of 490  $\mu$ M [36]. Furthermore, an ethylene diglycol monomethyl ether derivative modified perylene bisimide derivative showed a LCST temperature of 51 °C. More interestingly, the LCST temperature could be turned between 26 °C and 51 °C by adjusting the molar fraction of the perylene bisimide derivatives with ethylene diglycol monomethyl ether derivative and ethylene diglycol monoethyl ether derivative [37]. Through the above works, we can know that thermo-responsive perylene bisimide derivatives were all PNIPAM and OEG based materials. Creation of non-PNIPAM and non-OEG based thermo-responsive materials possessing additional functions were an interesting issue.

In this paper, a novel bi-perylene monoimide derivative BPMI-CD (Fig. 1) with four permethyl- $\beta$ -cyclodextrin grafts was synthesized, in which the bi-perylene monoimide derivative served as the fluorescence group, the permethyl- $\beta$ -cyclodextrin acted for increasing water

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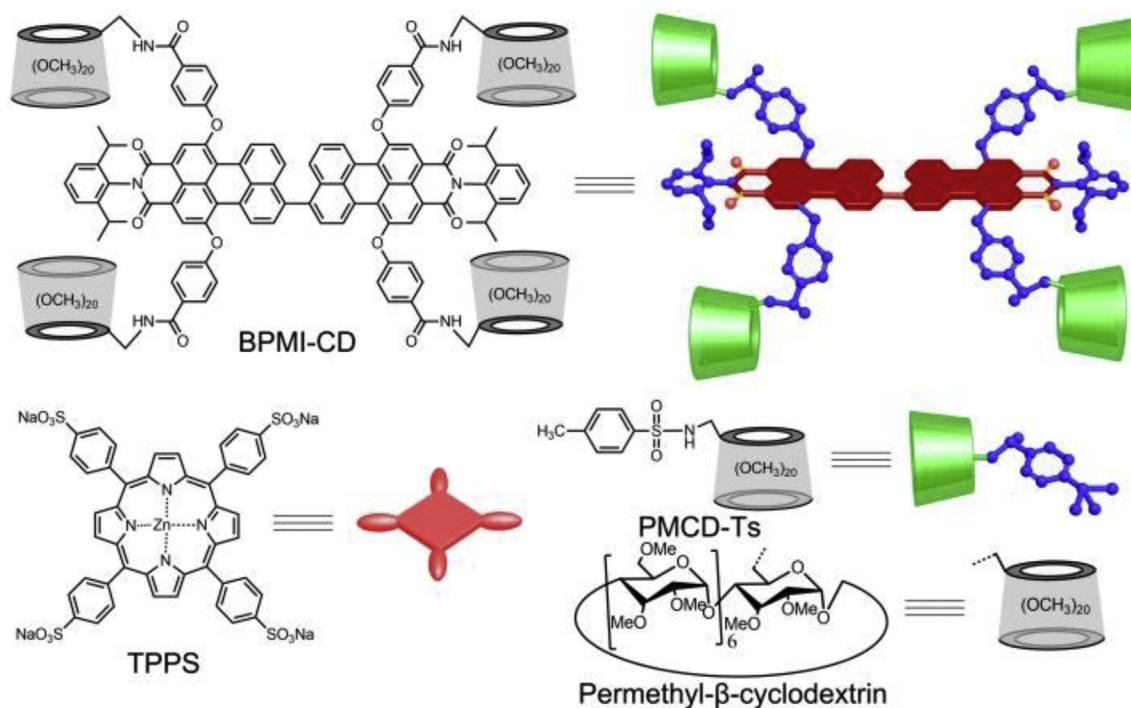


Fig. 1. The structural illustration of BPMI-CD, TPPS and PMCD-Ts.

solubility and for extending the further applications through altering the balance between hydrophilic and hydrophobic interactions by self-inclusion effect. Furthermore, its optical properties and reversible lower critical solution temperature (LCST) behaviors were investigated.

## 2. Experimental section

### 2.1. Materials

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker 600 spectrometer. HRMS analysis was performed on a FT-MALDI MS (Bruker Company). UV–Vis spectra were recorded in a quartz cell (light path 10 mm) on a Cary 5000 spectrophotometer equipped with a temperature controller. Fluorescence spectra were performed on F-7000 (Hitachi Instruments). The absolute fluorescence quantum yield was determined by an absolute method using an integrating sphere (Edinburgh Instruments FLS-980 fluorimeter) excited at 542 nm using a 150 W Xenon lamp. The fluorescence lifetimes were recorded on an Edinburgh Analytical Instruments FLS980 spectrometer, equipped with a supercontinuum ultrafast fiber lasers (Fianium), using the time correlated single-photon-counting (TCSPC) method. Typically, 10000 counts were collected at the peak channel, and the decay curves were fitted by least-squares deconvolution with original Edinburgh Instrument software; the quality of the parameters were judged by the reduced  $\chi^2$  values and the randomness of the weighted residuals.

### 2.2. Synthesis procedures and analytical data

#### 2.2.1. Synthesis of compound 1

3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) (1.00 g, 2.55 mmol), Zn (OAc)<sub>2</sub>·H<sub>2</sub>O (1.40 g, 7.65 mmol), H<sub>2</sub>O (3.0 mL), imidazole (10.20 g), and 2,6-diisopropylaniline (3.36 mL, 17.85 mmol) were heated under microwave irradiation at 170 °C and 80 W for 30 min. The reaction mixtures were dissolved by CH<sub>2</sub>Cl<sub>2</sub> (200 mL), and 200 mL of water was added. The solution was filtered, and separated. The organic solution was washed two times with 1 M HCl solution (300 mL), water (300 mL) and saturated NaCl solution. The residue was purified by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (v/

v = 2/1) as the eluent to give a red solid (785 mg, 64.1%). mp: 182.4–184.0 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  1.18 (d, 12H, *J* = 6.6 Hz, –CH<sub>3</sub>), 2.78 (m, 2H, –CH), 7.35 (d, 2H, *J* = 7.8 Hz, Ar–H), 7.48 (t, 1H, *J* = 7.8 Hz, Ar–H), 7.62 (t, 2H, *J* = 7.8 Hz, Ar–H), 7.89 (d, 2H, *J* = 7.8 Hz, Ar–H), 8.41 (m, 4H, Ar–H), 8.63 (d, 2H, *J* = 7.8 Hz, Ar–H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  23.00 (–CH<sub>3</sub>), 28.17 (–CH), 119.11, 119.99, 122.74, 122.98, 125.98, 126.92, 128.15, 128.40, 129.49, 129.87, 130.11, 130.90, 133.25, 136.42, 144.73, 162.96. HRMS: C<sub>34</sub>H<sub>28</sub>NO<sub>2</sub>, Calcd. for 482.2120, found 482.2112.

#### 2.2.2. Synthesis of compound 2

3.05 mL of Br<sub>2</sub> (59 mmol) was added dropwise to a reaction solution containing 500 mg of compound 1 (1.03 mmol) in CHCl<sub>3</sub> (50 mL), and the reaction mixture was heated at reflux for 3 h. The excess Br<sub>2</sub> was carefully washed by a saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (2 × 10 mL). The solvent was concentrated to dryness and the crude solid was purified by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub> and petroleum ether (4:1) as the eluent to give an orange solid of compound 2 (220 mg, 0.31 mmol, 30%). mp: > 250 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 1.11 (d, *J* = 6.6 Hz, 12H, –CH<sub>3</sub>), 2.63 (m, 2H, –CH), 7.28 (d, *J* = 7.8 Hz, 2H, Ar–H), 7.43 (t, *J* = 7.8 Hz, 1H, Ar–H), 7.70 (t, *J* = 7.8 Hz, 1H, Ar–H), 7.89 (d, *J* = 8.4 Hz, 1H, Ar–H), 8.35 (d, *J* = 7.8 Hz, 1H, Ar–H), 8.85 (d, *J* = 9.6 Hz, 2H, Ar–H), 9.01 (d, *J* = 8.4 Hz, 1H, Ar–H), 9.23 (d, *J* = 7.8 Hz, 1H, Ar–H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 24.02, 29.27, 119.03, 119.26, 120.87, 120.91, 124.18, 126.52, 126.76, 126.93, 127.52, 128.87, 129.59, 129.83, 130.26, 130.34, 130.68, 130.91, 131.61, 135.17, 135.39, 138.44, 145.62, 162.57. HRMS (MALDI-TOF): C<sub>34</sub>H<sub>25</sub>Br<sub>3</sub>NO<sub>2</sub>, Calcd. for 717.9415, found 717.9422.

#### 2.2.3. Synthesis of compound 3

In a 100-mL flask, 200 mg (0.28 mmol) of compound 2 were dissolved in 40 mL of *N*-methyl-2-pyrrolidone. Then, 1.0 g (7.24 mmol) of K<sub>2</sub>CO<sub>3</sub> and 108 g (0.56 mmol) of *tert*-Butyl 4-hydroxybenzoate were added, and the mixture was heated under N<sub>2</sub> atmosphere at 80 °C for 5 h. After the mixture was cooled to room temperature, 100 mL of 1 M HCl solution were added, and the resulting precipitate was filtered and washed with water until the filtrate became neutral. The solid obtained

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