



# A novel pyromellitic diimide derivative: Synthesis, gelation and spontaneous colorimetric sensing of dihydroxybenzene isomers

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## ABSTRACT

We report on the synthesis and self-assembly of a new hydrazide derivative *N'*, *N'*-bis[4-octadecyloxybenzamidopyromellitic diimide (compound **1**) which formed gels in several apolar organic solvents such as benzene and 1, 2-dichloroethane. <sup>1</sup>H NMR, and FT-IR spectroscopy studies confirmed that the intermolecular hydrogen bonding and van der Waals interactions were major driving forces for the formation of self-assembling gels. The gelator can form noncovalent interactions with dihydroxybenzenes, exhibiting different colors when it complexes with different positional isomers, and thus can be used to sense the positional isomers of dihydroxybenzenes by the naked eyes. This sensing property was further investigated by UV/Vis, <sup>1</sup>H NMR, and <sup>1</sup>H NMR NOESY spectroscopy which revealed that the charge-transfer interaction between hydroxyl groups of the dihydroxybenzene isomers (donor) and compound **1** (acceptor) accounted for this property.

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## 1. Introduction

Low-molecular mass organogelators (LMOG) have attracted substantial attention [1–4] in supramolecular chemistry and materials science due to their unique characteristics and wide range of potential applications. For example, organogels could be used as templates for nanoscale inorganic materials [5,6], organic soft materials [7,8], optical sensors [9], slow drug-delivery systems [10] and so on. In an organogel the gelator molecules self-assemble into nanoscale superstructures, such as fibers, rods, and ribbons through noncovalent interactions (i.e., hydrogen bonding, π–π stacking, van der Waals, coordination, and charge-transfer interactions) [1,11]. Up to now, there have been reports on organogels that are responsive to pH changes [12], light [13], catalysis [14], and ion recognition [15]. Most of these sensors have been employed in solutions and based on spectroscopic instrumentation. This usually limits the practical applications of these sensors. For simplicity, convenience and low cost, the fabrication of small molecular sensors into colorimetric test kits is highly desirable [16–22].

Our interest in the development of 1D dianhydride diimide based on organogels is driven by the following motives: First, dianhydride diimide derivatives are versatile molecules with an extended π surface and have been applied in the design of conductive materials

[23–28] and artificial photosynthetic systems [29]. Second, the dianhydride diimide–alkoxybenzene system is an important supramolecular motif [30] that has been used in the design of a plethora of novel architectures. The selection of the type and relative length of the respective blocks can lead to a variety of well-defined supramolecular structures at nanometer-scale dimension [31].

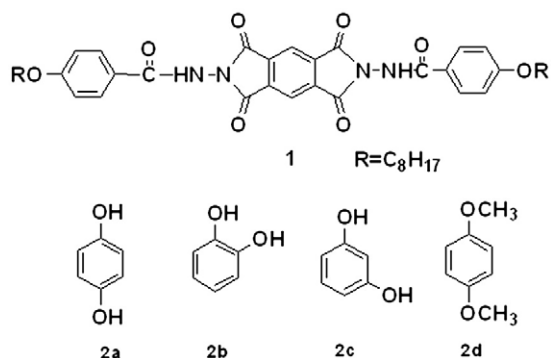
Herein, we report a compound (**1**, Scheme 1) that can form a 1D gel superstructure in several apolar organic solvents such as benzene and 1,2-dichloroethane. It is demonstrated that the driving forces for the gelation are intermolecular hydrogen bonding [32] and van der Waals interactions. Gelator **1** shows selective sensing of the polar, hydrophilic positional isomers of dihydroxybenzenes by virtue of its color changes.

Dihydroxybenzene isomers (**2a**, **2b**, **2c**) are known as environmental pollutants widely distributed in industrial effluents and pharmaceutical industries [33,34]. Because of their toxicity, their assay is generally required. So far various methods have been exploited for their detection, including electrochemistry [35,36], high-performance liquid chromatography (HPLC) [37], pH based-flow injection analysis [38], synchronous fluorescence [39], biosensor [40–42], etc. However, it is a challenge to distinguish these isomers because they present similar physiochemical property.

In the present work, we demonstrate that gelator **1** can be used to distinguish the positional isomers of the hydrophilic dihydroxybenzenes either in 1,2-dichloroethane or in the solid state by the naked eyes. To our best knowledge, there are only a few reports that gelators are utilized in colorimetric spontaneous sensing system [43], and the supramolecular chemistry sensing for the dihydroxybenzene isomers has not been reported yet.

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**Scheme 1.** The molecular structure of compound **1** and dihydroxybenzene isomers **2a**, **2b**, **2c** and **2d**.

## 2. Experiment

### 2.1. Characterization

$^1\text{H}$  NMR spectra were recorded with a Bruker Avance 300 MHz spectrometer, using deuterium dimethyl sulphoxide ( $d_6$ -DMSO) as solvent and tetramethylsilane (TMS) as an internal standard ( $\delta = 0.00$ ). FT-IR spectra were recorded with a Perkin-Elmer spectrophotometer (Spectrum One B). The samples were pressed tablet with KBr. SEM observations were taken with a JSM-6700F apparatus. X-ray diffraction (XRD) was carried out with a Bruker Avance D8 X-ray diffractometer. The UV/Vis spectrum was recorded on a Perkin-Elmer Lambda 900.

### 2.2. Synthesis experiment

All commercially available chemicals are of reagent grade and were used without further purification. Compound **1** was synthesized according to the route shown in **Scheme 2** in the atmospheric pressure conditions and purified by chromatography on silica gel using acetone/benzene (0.05/0.95) mixture as eluent and then vacuum-dried. The synthesis details are presented below.

#### 2.2.1. Diethyl 2,5-dicarboxyl terephthalate (**B**)

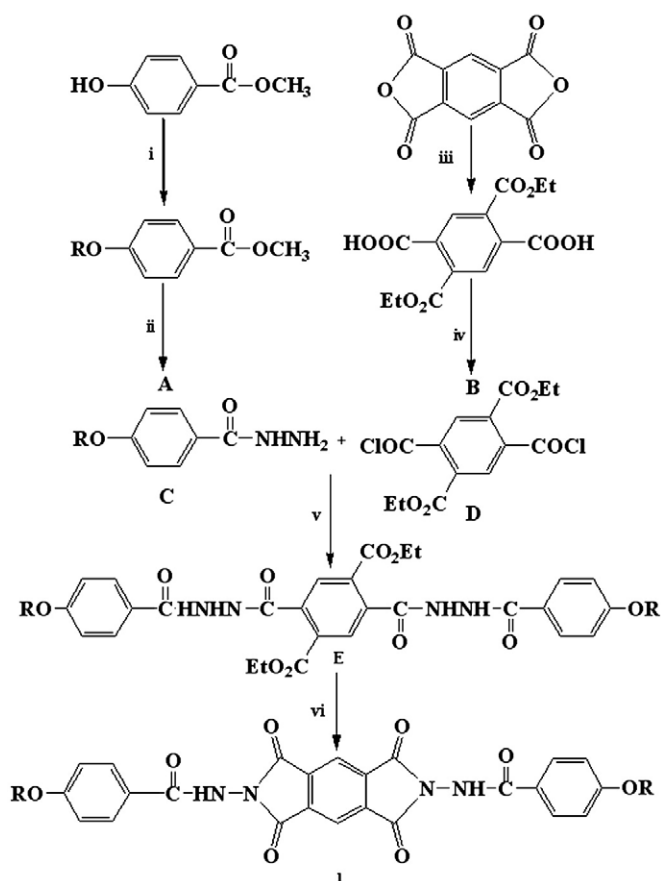
Phthalic anhydride (10.9 g, 0.05 mol) was dissolved in ethanol (120 mL), and the mixture was heated under reflux at  $80^\circ\text{C}$  for about 8 h. Then the reaction mixture was frozen for about 24 h and the crude product was precipitated by ethanol. The precipitate **B** was filtered, washed thoroughly with water, dried completely, and recrystallized from ether to give 4.65 g white crystal (yield 44.3%, mp  $235$ – $236.4^\circ\text{C}$ ).

$^1\text{H}$  NMR (deuterium dimethyl sulphoxide ( $d_6$ -DMSO) ppm from TMS, 300 MHz): 13.82 (s, 2H), 7.98 (s, 2H), 4.29–4.31 (q, 4H), 1.29 (t, 6H,  $J = 6.0$  Hz).

FT-IR (KBr disc  $\text{cm}^{-1}$ ): 2985, 2960, 2941, 2666, 2581, 1731, 1702, 1505, 1496, 1432, 1391, 1369, 1304, 1258, 1163, 1142, 1105, 1018, 918, 860, 794, 736, 654, and 574.

#### 2.2.2. 4-octaalkoxy-benzoyl dihydrazine (**C**)

Methyl 4-hydroxybenzoate (7.36 g, 0.04 mol), bromooctane (7.75 mL, 0.044 mol) and anhydrous  $\text{K}_2\text{CO}_3$  (15 g, 0.11 mol) were dissolved in anhydrous acetone (80 mL), and subsequently KI (1.0, 0.006 mol) were added. The reaction mixture was heated under reflux at  $56^\circ\text{C}$  for about 50 h. The hot reaction mixture was filtered and the residue was washed twice with acetone. The filtrates were collected and the solvent was removed with a rotary evaporator. The residual product (4-oxybenzoic acid methylester **A**) was collected. The obtained crude product and hydrazine monohydrate (20 mL) were then added into ethanol (40 mL), and the mixture was heated under reflux at  $80^\circ\text{C}$  for about 50 h. Upon cooling to  $-10^\circ\text{C}$  the product



**Scheme 2.** The synthesis procedure of compound **1**. (i) RBr ( $R = \text{C}_8\text{H}_{17}$ ), acetone,  $\text{K}_2\text{CO}_3$ , reflux 50 h; (ii) hydrazine monohydrate, ethanol, reflux, 50 h; (iii) ethanol, reflux 8 h; (iv)  $\text{SOCl}_2$ , RT, reflux 8 h; (v) THF, pyridine,  $0^\circ\text{C}$ –RT 10 h; (vi) pyridine/toluene (1/5, V/V), reflux 24 h.

precipitated from the reaction mixture. The crude product **C** was filtered and recrystallized from methanol to give 8.9 g white solid (yield 84%, mp  $108^\circ\text{C}$ ).

$^1\text{H}$  NMR ( $d_6$ -DMSO ppm from TMS, 300 MHz): 9.59 (s, 1H), 7.78 (d, 2H,  $J = 4.5$  Hz), 6.96 (d, 2H,  $J = 3.0$  Hz), 4.43 (s, 2H), 3.89 (t, 2H,  $J = 3.0$  Hz), 1.68 (t, 1H), 1.38–1.45 (m, 4H), 1.29–1.36 (m, 4H), 0.88 (t, 6H,  $J = 6.0$  Hz).

FT-IR (KBr disc  $\text{cm}^{-1}$ ): 3299, 3209, 2957, 2925, 2872, 2855, 1618, 1573, 1533, 1499, 1465, 1393, 1339, 1317, 1303, 1254, 1188, 1172, 1130, 1101, 1029, 1005, 968, 938, 843, 764, and 624.

#### 2.2.3. *N,N'*-bis[(4-octaalkoxyphenyl)-dihydrazide]-2,5-diethylphthalate (**E**)

**B** (3.01 g, 0.01 mol) was dissolved in thionyl chloride ( $\text{SOCl}_2$ ) (70 mL) and heated under reflux at  $79^\circ\text{C}$  for 15 h. Then  $\text{SOCl}_2$  was evaporated from the reaction mixture to give terephthaloyl chloride (**D**). Compound **D** was dissolved in tetrahydrofuran (THF) (70 mL), then **C** (5.28 g, 0.02 mol) and pyridine (6 mL) were added. The reaction mixture was cooled to  $0$ – $4^\circ\text{C}$  by using an ice bath and stirred for about 8 h. Then the crude product was frozen and precipitated from the reaction mixture and the product was collected through filtration and dried completely, yielding product **E**. **E** was recrystallized from methanol to give 6.1 g white powder (yield 67.5%, mp  $264^\circ\text{C}$ ).

$^1\text{H}$  NMR ( $d_6$ -DMSO ppm from TMS, 300 MHz) 10.61 (s, 2H), 10.49 (s, 2H), 8.02 (s, 2H), 7.92 (d, 4H,  $J = 6.0$  Hz), 7.13 (d, 4H,  $J = 4.5$  Hz), 4.32–4.34 (q, 4H), 3.94 (t, 4H,  $J = 3.0$  Hz), 1.48–1.75 (s, 2H), 1.29–1.45 (m, 22H), 0.90 (t, 12H,  $J = 9.0$  Hz).

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