



## Original article

## Spectral and self-assembly properties of a series of asymmetrical pyrene derivatives



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## ABSTRACT

A series of pyrene derivatives with different asymmetrical substituents were successfully synthesized and characterized. The geometrical electronic structures of the asymmetrical pyrene derivatives were performed by density functional theory (DFT) calculations. The results of photophysical spectra and electrochemical analysis indicated that the optical or electric properties of the pyrene derivatives could be tuned by adjust the  $\pi$ -conjugation lengths of the substituents. Furthermore, through a phase exchange self-assembly method, the highly organized morphologies were observed by SEM.

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## 1. Introduction

In recent years, carbon-rich organic compounds with high  $\pi$  conjugation have received much attention because of their unique properties as ideal photoelectronic materials for applications such as organic light-emitting diodes [1], liquid crystal displays [2], thin film transistors [3], nonlinear optics [4], solar cells [5] and optical storage devices [6]. Among them, highly conjugated organic discoid molecules [7], for example, pyrene [8], perylene and triphenylene, have caused a great deal of excitement in the development of novel optoelectronic materials due to their low production cost and tunable electronic [9] and optical properties [10].

High charge-carrier mobility, which results from  $\pi$ - $\pi$  stacking in symmetric discoid molecules, also causes molecule aggregation, which in turn leads to fluorescence quenching [11]. In view of this, one of the great challenges for developing next generation highly efficient organic optoelectronic materials is to search for a trade-off between luminescence enhancement and charge carrier mobility tuning. The incorporation of dendrimers or asymmetrical groups around the fluorophore is an effective method to achieve this balance [12].

In this work, a series of novel asymmetrical pyrene derivatives were obtained by changing the carbonyl groups. The designed

groups were linked into pyrene, including one carbonyl group and three acetylene linkages. The photophysical and electrochemical properties of the compounds have been investigated and discussed. Furthermore, through a simple method for packing small organic molecules into nanostructures, the asymmetrical pyrene derivatives can form regular morphologies.

## 2. Experimental

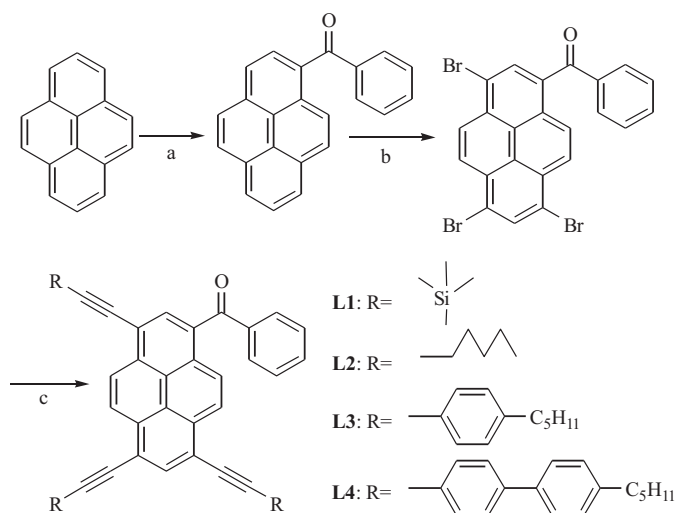
$^1\text{H}$  NMR spectra of the samples were recorded with a Varian 400 MHz instrument. MALDI-TOF-MS spectra were determined on a Shimadzu AXIMA-CFR mass spectrometer. FT-IR spectra were recorded on a Perkin Elmer LR-64912C spectrophotometer. All UV-vis spectra were recorded on a JASCO V-570 spectrophotometer, and all fluorescence spectra were recorded on a HITACHI F-4500 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) analyses were performed on a Perkin Elmer Pyris 6 instrument. The electrochemical behavior of the materials was investigated by cyclic voltammetry (CV) with a standard three electrode electrochemical cell in 0.1 mol/L tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) in  $\text{CH}_2\text{Cl}_2$  at room temperature under nitrogen with a scanning rate of 40 mV/s. It was calibrated using the ferrocene ( $\text{Fc}/\text{Fc}^+$ ) redox couple which has a formal potential of  $E_{1/2} = +0.18$  eV versus platinum wire.

## 2.1. Synthesis

The goal of these materials was to combine the high electronic density of ethynyl functional groups with the high hole-injection

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**Scheme 1.** Structures of **L1–L4** and the synthetic routes. (a) Benzoyl chloride,  $\text{AlCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ , 10 h; (b)  $\text{Br}_2$ , nitrobenzene,  $120^\circ\text{C}$ , 12 h; (c) Ethynyl,  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ ,  $\text{PPh}_3$ ,  $\text{CuI}$ ,  $\text{NEt}_3$ , THF,  $80^\circ\text{C}$ , 12 h.

ability of pyrene [10]. Meanwhile, through the introduction of single carbonyl groups, an asymmetrical structure will be achieved. We also expect that the long chain alkyl group will give better solubility, excellent thermal stability, and a low tendency to crystallize in devices.

The target molecules were synthesized in three steps, including the Friedel–Crafts acylation procedure [13] (a), the general bromination procedure (b) and the Hagihara–Sonogashira cross-coupling procedure [14] (c), as shown in Scheme 1. The final asymmetrical pyrene derivatives **L1–L4** were all characterized by  $^1\text{H}$  NMR, FT-IR and MS.

### 2.1.1. Synthesis of phenylpyren-1-yl-methanone (procedure a)

Pyrene (7.00 g, 34.8 mmol) and benzoyl chloride (5.40 g, 38.3 mmol) were dissolved in carbon disulfide (40 mL), the mixture was cooled to  $0^\circ\text{C}$ . After the gradual addition of  $\text{AlCl}_3$  (6.97 g, 52.2 mmol), the mixture was heated under reflux overnight, then poured into ice water. The resulting mixture was stirred until the color of the organic phase turned from red to yellow. The layers were then separated. The aqueous phase was extracted with dichloromethane. The combined organic phases were dried with  $\text{MgSO}_4$ , and the solvent was evaporated. The residue was purified by column chromatography to yield phenylpyren-1-yl-methanone (7.24 g, 68%).

### 2.1.2. Synthesis of phenyl-(3,6,8-tribromopyren-1-yl)-methanone (procedure b)

Phenylpyren-1-yl-methanone (6.12 g, 20.0 mmol, 1 equiv.) was dissolved in nitrobenzene. Under vigorous stirring, bromine (3.00 mL, 60.0 mmol, 3 equiv.) was added slowly. After complete addition, the temperature was increased to  $160^\circ\text{C}$  and maintained for 8 h. The cooled reaction suspension was poured into acetone, and the precipitate filtered off. Further drying of the precipitate in high vacuum gave the crude product phenyl-(3,6,8-tribromopyren-1-yl)-methanone (9.34 g, 86%), which was used without further purification. FT-IR (KBr,  $\text{cm}^{-1}$ ): 1658, 1595, 1466, 1328, 1246, 1120, 1007, 953, 814, 697.

### 2.1.3. Synthesis of the final compounds **L1–L4** (procedure c)

Phenyl-(3,6,8-tribromopyren-1-yl)methanone (0.500 mg, 0.921 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (18.9 mg, 0.0270 mmol),  $\text{CuI}$  (5.16 mg, 0.0270 mmol), and  $\text{PPh}_3$  (16.2 mg, 0.0600 mmol) were added to a degassed

solution of triethylamine (6.00 mL) and THF (10.0 mL) under argon. While stirring, the reaction mixture was heated to  $70^\circ\text{C}$ , and trimethylsiliconacetylene (0.300 g, 3.00 mmol) was injected. After 15 min of stirring at  $70^\circ\text{C}$ , the reaction was heated to  $80^\circ\text{C}$  and stirred overnight under argon atmosphere. The cooled reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$  and extracted with water. The organic phase was dried over  $\text{MgSO}_4$ , and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, petroleum ether) to afford **L1** (0.481 g, 88%), Hept-2-yne (0.270 g, 3.00 mmol), 1-ethynyl-4-pentylbenzene (0.510 mg, 3.00 mmol), or 1-ethynyl-4-dipentylbenzene (0.735 g, 3.00 mmol) was injected correspondingly and with the same procedure to afford **L2** (0.371 g, 85%), **L3** (0.616 mg, 82%), **L4** (0.826 mg, 86%), respectively.

**Phenyl(3,6,8-tris(trimethylsilyl ethynyl)pyren-1-yl)methanone (L1):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.37 (m, 27H,  $\text{CH}_3$ ), 7.50 (t, 2H, benzene), 7.64 (t, 1H, benzene), 7.88 (d, 2H,  $J = 7.2$  Hz, pyrene), 8.21 (s, 1H, pyrene), 8.28 (d, 1H,  $J = 9.2$  Hz, pyrene), 8.35 (1H, s, pyrene), 8.53 (d, 1H,  $J = 9.2$  Hz, pyrene), 8.71 (d, 2H,  $J = 7.2$  Hz, pyrene). FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2960, 2154, 1658, 1247, 854. MALDI-TOF-MS (dithranol) ( $m/z$ ): calcd. for  $\text{C}_{38}\text{H}_{38}\text{Si}_3\text{O}$ : 598.8, found: 599.1  $[\text{M}+1]^+$ .

**Phenyl(3,6,8-tris(butylethynyl)pyren-1-yl)methanone (L2):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.02 (m, 9H,  $\text{CH}_3$ ), 1.60 (m, 6H,  $\text{CH}_2$ ), 1.76 (m, 6H,  $\text{CH}_2$ ), 2.64 (m, 6H,  $\text{CH}_2$ ), 7.48 (t, 2H, benzene), 7.62 (t, 1H, benzene), 7.68 (d, 2H,  $J = 7.2$  Hz, benzene), 8.13 (s, 1H, pyrene), 8.19 (s, 1H, pyrene), 8.24 (d, 1H,  $J = 9.2$  Hz, pyrene), 8.49 (d, 1H,  $J = 9.2$  Hz, pyrene), 8.63 (d, 1H,  $J = 9.2$  Hz, pyrene), 8.62 (d, 1H,  $J = 9.2$  Hz, pyrene). FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2941, 2219, 1658, 1228, 835, 686. MALDI-TOF-MS (dithranol) ( $m/z$ ): calcd. for  $\text{C}_{41}\text{H}_{38}\text{O}$ : 550.6, found: 551.1  $[\text{M}+1]^+$ .

**Phenyl(3,6,8-tris(4-pentylphenyl)ethynyl)pyren-1-yl)methanone (L3):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.91 (m, 9H,  $\text{CH}_3$ ), 1.36 (m, 12H,  $\text{CH}_2$ ), 1.65 (6H, m,  $\text{CH}_2$ ), 2.65 (6H, m,  $\text{CH}_2$ ), 7.24 (m, 7H, benzene), 7.50 (t, 2H, benzene), 7.62 (m, 6H, benzene), 7.92 (d, 2H,  $J = 7.2$  Hz, benzene), 8.16 (s, 1H, pyrene), 8.18 (d, 1H,  $J = 8.0$  Hz, pyrene), 8.26 (s, 1H, pyrene), 8.32 (d, 1H,  $J = 9.2$  Hz, pyrene), 8.80 (d, 2H,  $J = 9.2$  Hz, pyrene). FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2931, 2192, 1658, 1519, 1247, 827. MALDI-TOF-MS (dithranol) ( $m/z$ ): calcd. for  $\text{C}_{62}\text{H}_{56}\text{O}$ : 822.8, found: 822.6  $[\text{M}+1]^+$ .

**Phenyl(3,6,1-tris(4'-pentylphenyl-4-yl)ethynyl)pyren-1-yl)methanone (L4):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.92 (m, 9H,  $\text{CH}_3$ ), 1.36 (m, 12H,  $\text{CH}_2$ ), 1.53 (m, 6H,  $\text{CH}_2$ ), 2.65 (m, 6H,  $\text{CH}_2$ ), 7.28 (m, 4H, benzene), 7.56 (m, 8H, benzene), 7.68 (m, 9H, benzene), 7.76 (m, 4H, benzene), 7.80 (d, 2H,  $J = 8.0$  Hz, benzene), 7.94 (d, 2H,  $J = 7.2$  Hz, benzene), 8.32 (s, 1H, pyrene), 8.37 (d, 1H,  $J = 8.0$  Hz, pyrene), 8.52 (s, 1H, pyrene), 8.73 (d, 1H,  $J = 7.2$  Hz, pyrene), 8.93 (m, 2H, pyrene). FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2916, 2189, 1667, 1598, 1504, 1248, 820. MALDI-TOF-MS (dithranol) ( $m/z$ ): calcd. for  $\text{C}_{80}\text{H}_{68}\text{O}$ : 1052.3, found: 1053.4  $[\text{M}+1]^+$ .

Compounds **L1–L4** have good solubility in all common organic solvents and relatively high melting points. For **L2–L4**, the melting point increased from  $83^\circ\text{C}$  to  $203^\circ\text{C}$  with increasing lengths of the rigid side chains.

## 2.2. Self-assembly

Molecules **L1–L4** with unbranched alkyl solubilizing groups were found to dissolve in solvents, such as tetrahydrofuran (THF), that have an affinity for alkyl and conjugated moieties and can also accept hydrogen bonds to compete with that molecule's self-assembly. Micro-ribbon self-assembly of **L4** molecules was achieved through the solvent-exchange method in the solution phase, which involves transferring the molecule from a good solvent (THF) into a poor solvent (ethanol, 25 mL). We drop cast  $10\ \mu\text{L}$  of the **L4** solution onto a clean glass

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