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### 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 tradeoff 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

<sup>1</sup>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 (Bu<sub>4</sub>NPF<sub>6</sub>) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature under nitrogen with a scanning rate of 40 mV/s. It was calibrated using the ferrocene (Fc/Fc<sup>+</sup>) redox couple which has a formal potential of  $E_{1/2} = +0.18$  eV versus platinum wire.

#### 2.1. Synthesis

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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, AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 10 h; (b) Br<sub>2</sub>, nitrobenzene, 120 °C, 12 h; (c) Ethynyl, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, PPh<sub>3</sub>, Cul, NEt<sub>3</sub>, THF, 80 °C, 12 h.

ability of pyrene [10]. Meanwhile, through the introduction of single carbonyl groups, an asymmtrical 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 crosscoupling procedure [14] (c), as shown in Scheme 1. The final asymmetrical pyrene derivatives **L1–L4** were all characterized by <sup>1</sup>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 °C. After the gradual addition of AlCl<sub>3</sub> (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 MgSO<sub>4</sub>, and the solvent was evaporated. The residue was purified by column chromatography to yield phenyl-pyren-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 °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-tribromo-pyren-1-yl)-methanone (9.34 g, 86%), which was used without further purification. FT-IR (KBr, cm<sup>-1</sup>): 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), Pd(PPh\_3)\_2Cl\_2 (18.9 mg, 0.0270 mmol), Cul (5.16 mg, 0.0270 mmol), and 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 °C, and trimethylsiliconeacetylene (0.300 g, 3.00 mmol) was injected. After 15 min of stirring at 70 °C, the reaction was heated to 80 °C and stirred overnight under argon atmosphere. The cooled reaction mixture was diluted with  $CH_2Cl_2$  and extracted with water. The organic phase was dried over MgSO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, petroleummether) 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*(*trimethylsilylethynyl*)*pyren*-1-*yl*)*methanone* (**L1**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.37 (m, 27H, CH<sub>3</sub>), 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, cm<sup>-1</sup>):  $\nu$  2960, 2154, 1658, 1247, 854. MALDI-TOF-MS (dithranol) (*m*/*z*): calcd. for C<sub>38</sub>H<sub>38</sub>Si<sub>3</sub>O: 598.8, found: 599.1 [M+1]<sup>+</sup>.

*Phenyl*(3,6,8-*tris*(*butylethynyl*)*pyren*-1-*yl*)*methanone* (L2): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.02 (m, 9H, CH<sub>3</sub>), 1.60 (m, 6H, CH<sub>2</sub>), 1.76 (m, 6H, CH<sub>2</sub>), 2.64 (m, 6H, CH<sub>2</sub>), 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, cm<sup>-1</sup>): ν 2941, 2219, 1658, 1228, 835, 686. MALDI-TOF-MS (dithranol) (*m*/*z*): calcd. for C<sub>41</sub>H<sub>38</sub>O: 550.6, found: 551.1 [M+1]<sup>+</sup>.

*Phenyl*(3,6,8-*tris*((4-*pentylphenyl*)-*ethynyl*)*pyren*-1-*yl*)*methanone* (**L3**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.91 (m, 9H, CH<sub>3</sub>), 1.36 (m, 12H, CH<sub>2</sub>), 1.65 (6H, m, CH<sub>2</sub>), 2.65 (6H, m, CH<sub>2</sub>), 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, cm<sup>-1</sup>):  $\nu$  2931, 2192, 1658, 1519, 1247, 827. MALDI-TOF-MS (dithranol) (*m*/*z*): calcd. for C<sub>62</sub>H<sub>56</sub>O: 822.8, found: 822.6 [M+1]<sup>+</sup>.

Phenyl (3,6,1-tris((4'-pentyldiphenyl-4-yl)ethynyl)pyren-1-yl) methanone (**L4**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.92 (m, 9H, CH<sub>3</sub>) 1.36 (m, 12H, CH<sub>2</sub>), 1.53 (m, 6H, CH<sub>2</sub>), 2.65 (m, 6H, CH<sub>2</sub>), 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, benzen), 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, cm<sup>-1</sup>):  $\nu$  2916, 2189, 1667, 1598, 1504, 1248, 820. MALDI-TOF-MS (dithranol) (*m*/*z*): calcd. for C<sub>80</sub>H<sub>68</sub>O: 1052.3, found: 1053.4 [M+1]<sup>+</sup>.

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 °C to 203 °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 µL of the **L4** solution onto a clean glass substrate. The drop remained stationary at the location of drop casting and was allowed to dry in a covered Petri dish. The resulting dried film was sputter coated with 10 nm of carbon and imaged by SEM.

#### 3. Results and discussion

#### 3.1. Photophysical properties

The photophysical properties of compounds **L1–L4** were examined by UV–vis spectra and fluorescence spectra in dilute CH<sub>2</sub>Cl<sub>2</sub> solution, as shown in Fig. 1. All the data were summarized in Table 1, including the compounds' melting points ( $T_m$ ), absorption maxima ( $\lambda_{abs}$ ), PL emission maxima ( $\lambda_{em}$ ) and Stokes shifts.

The normalized UV/vis absorption spectra shown in Fig. 1(a) are complex with multiple overlapping broad bands, and all the absorption spectra have three well-resolved, sharp absorption bands. All four compounds exhibit broad absorption in the region (200–500 nm). In general, the spectra display absorptions resulting from the combination of pyrene, benzene and alkynyl chromophores. The spectra also show a slight bathochromic shift from **L1** to **L4**, concomitant with increasing conjugation length.

For the same reason, the emission characteristics of pyrene derivatives **L1–L4** in Fig. 1(b) have been bathochromatically tuned in the visible region from 467 nm to 517 nm. The colors of the lights emitted from the samples visibly changed from bright blue to green.

On the whole asymmetrical pyrene derivatives **L1–L4** exhibited similar absorption and emission spectra to ymmetric pyrene derivatives with acetylene linkages [15], and this means that the introduction of the carbonyl group onto these asymmetrical pyrene derivatives did not significantly affect the spectral characteristics.

#### 3.2. Fluorescence quantum yield

Fluorescence quantum yield  $(\phi_f)$  is a basic and important parameter which can describe the capability of a material to convert absorbed light energy into fluorescence. The fluorescence quantum yield is the ratio of photons absorbed to photons emitted through fluorescence and gives the probability of the excited state being deactivated by fluorescence. Absolute values are calculated using the standard samples, which have a fixed and known fluorescence quantum yield value, according to the following

#### Table 1

Physical properties of materials L1-L4.

Compd.	$T_m^{\mathbf{a}}$ (°C)	$\lambda_{abs} (nm)$	λ <sub>em</sub> (nm)	Stokes shift (cm <sup>-1</sup> )	$\phi_{\!f}^{\mathrm{b}}$
L1	260	232, 306, 426b	467	1061	0.32
L2	83	252, 306, 416b	479	3161	0.41
L3	113	245, 331, 457b	511	2360	0.43
L4	203	232, 348, 466b	517	2117	0.51

<sup>a</sup> Melting point  $T_m$  was obtained from DSC measurements in nitrogen atmosphere at a heating rate of 5 °C/min.

 $^{\rm b}$  Measured in  $\rm CH_2Cl_2$  solution using quinine sulphate as a standard at room temperature.

equation:

$$\phi_f = \phi_L \times \frac{n_f^2}{n_L^2} \times \left(\frac{\text{GRAD}_f}{\text{GRAD}_L}\right) \tag{1}$$

where the subscripts *L* and *f* denote standard and test samples, respectively,  $\phi$  is the fluorescence quantum yield, Grad is the gradient from the plot of integrated fluorescence intensity versus absorbance, and n is the refractive index of the solvent. Quinine sulphate was used as the standard sample because it fluoresces at the excitation wavelength of choice for these samples.

Current fluorescence emission research on 1,3,6,8-tetraethynylpyrene derivatives showed that the fluorescence quantum yield of 1,3,6,8-tetrakis(phenylethynyl)pyrene is only 0.18 [15]; but in this research the values of  $\phi_f$  obtained in this way were from 0.32 to 0.51. This revealed that the pyrene derivatives possessed excellent luminescence properties, because the incorporation of asymmetrical groups around the fluorophore well reduced the tendency for molecules to aggregate and cause fluorescence quenching. These new derivatives have potential to be a new type of organic photoelectric materials.

#### 3.3. Electrochemical properties

The HOMO (highest occupied molecular orbital) and LUMO (lowest occupied molecular orbital) energy levels of the materials are very crucial parameters for organic optoelectronic devices configuration. The electrochemical properties of **L1–L4** were studied by cyclic voltammogram (CV) as showed in Fig. 2. A reversible oxidation potential and two reduction potentials were observed in CH<sub>2</sub>Cl<sub>2</sub> for **L1**, **L3** and **L4**, and two reversible oxidation potentials for **L1–L4** were located at 0.29, 0.28, 0.27, and 0.20 eV, and the onset



Fig. 1. UV-vis absorption spectra (a) and fluorescence emission spectra (b) of L1-L4 in CH<sub>2</sub>Cl<sub>2</sub>.



Fig. 2. Cyclic voltammograms of L1-L4 in dichloromethane/Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of 40 (mV/s).

reduction potentials were located at -1.13, -1.18, -1.27 and -1.19 eV respectively.

The HOMO and LUMO energy levels were estimated according to the equation  $HOMO = -([E_{onset}]_{ox} + 4.8) eV$  and  $LUMO = -([E_{onset}]_{re} + 4.8) eV$  [16]. Subsequently, the HOMO and LUMO energy levels were estimated respectively (shown in Fig. 3). Subsequently, the band gaps were estimated by combining the HOMO energy levels together with the LOMO energy levels.

The corresponding HOMO energy levels were thus estimated to be 5.09, 5.08, 5.07, 5.00 (eV) for **L1–L4** respectively. The slight increasing of HOMO from **L1** to **L4** corresponded with the increasing  $\pi$ -conjugation length of the side chains [17].

To gain insight into the geometrical and electronic structures of the new pyrene derivatives, we performed density functional theory (DFT) calculations on the compound **L4** by using the Gaussian03 program package [18]. The orbital spatial distributions of HOMO and LUMO for **L4** were shown in Fig. 4. It is obvious that the HOMO and LUMO of **L4** both localize at the



Fig. 3. The HOMO and LUMO energy levels for L1-L4.

central pyrene ring. The asymmetrical chains show different distributions of their electron clouds which leads to different energy levels. The theoretical estimation of the HOMO–LUMO gaps for L4 (2.53 eV) is in good agreement with the measured band gaps (Fig. 3).

#### 3.4. Self-assembly

Most high performance organic optoelectronic devices are based on highly ordered molecular packing with strong  $\pi$ – $\pi$ 



**Fig. 4.** Molecular orbital distributions for **L4**, energy levels estimated by density functional theory (DFT) calculations.



Fig. 5. SEM micrographs of bundled fibers formed from a 5 (wt%) L4 solution on glass.

interactions and thus, show high crystallinities when they are assembled in the solid state [19]. Molecular packing frustration as a result of the  $\pi$ - $\pi$ \* conjugation was expected to play a significant role during drying in the self-assembly of this molecule under kinetic versus thermodynamic control. A simple solvent-exchanging method was used to form the self-assembly structure in the solution phase (for details, see the experimental section).

For L1, the regular morphology cannot be observed because of its highly steric trimethylsilylethynyls in the molecule structure. Correspondingly, the other three materials easy self-assemble into fibrous. As an example, the micrograph of L4 is shown in Fig. 5. The observed structures can be tens of micrometers long and range in diameter from hundreds to thousands of nanometers with the long axis of the bundles parallel to the substrate. The molecular length with nanometer-scale of L4 was estimated by molecular modeling to be about 4.7 (nm) in its extended conformation. The molecular length is significantly smaller than the observed diameters in the SEM, indicating the occurrence of a high extent of bundling. We expect that L2-L4 does not adhere to the substrate because of the glass's low surface energy. It is implies that the fibrous assembly of molecules occurs in solution, precipitates, and then grows as the solution dried. Because the flexible chains on the benzene rings are steric, the onedimensional linear stacking was formed by assembly of molecules driven by the  $\pi$ - $\pi$  interaction between the pyrene rings. These fibrous structures are common for self-assembling molecules similar to **L2–L4** [20], and we assume that the  $\pi$ – $\pi$  stacking direction is parallel to the long axis of the bundled fibers. This onedimensional linear structure of the materials can expand the application prospects in the field of organic optoelectronics, such as photodiodes, sensors and OLED [21].

#### 4. Conclusion

In order to reduce the  $\pi$ - $\pi$  stacking quenching effect, a series of pyrene derivatives with asymmetrical groups was synthesized in excellent yield by using a three-step reaction. The photophysical properties of compounds **L1–L4** were examined by UV–vis spectra and fluorescence spectra in dilute CH<sub>2</sub>Cl<sub>2</sub> solution. It was found that the spectra both show a slight bathochromic shift from **L1** to **L4**, concomitant with increasing the conjugation length. The emission characteristics of pyrene derivatives **L1–L4** have been bathochromatically tuned in the visible region from 467 nm to 517 nm, and the fluorescence quantum yields increased from 0.32

to 0.51 with the extending  $\pi$ -conjugation. The colors of the lights emitted from the samples changing from bright blue to green can been seen. The fibrous structure was carried out through a phase exchange method for packing small organic molecules of **L4** into nanostructures. Results in this work have made great contribution to the further application of asymmetrical discoid molecules as organic optoelectronic devices.

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