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# Synthesis, crystal structure and photophysical properties of 5-mono- and 5,9-bis-(arylethynyl)-functionalized pyrenes



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## ABSTRACT

7-*tert*-Butyl-1,3-dimethylpyrene 5-carbaldehyde and 7-*tert*-butyl-1,3-dimethylpyrene 5,9-dicarbaldehyde were converted to the corresponding (4-methoxyphenylethynyl)pyrenes by the Wittig reaction with 4-methoxyphenyl methyl phosphonium ylide followed by bromination and dehydrobromination. Single-crystal X-ray analysis of 7-*tert*-butyl-5-(4-methoxyphenylethynyl)-1,3-dimethylpyrene revealed that there is a 1-D, slipped, face-to-face motif with off-set, head-to-tail stacked columns, which are clearly influenced by the single, bulky, *tert*-butyl group in the pyrene ring at the 7-position. Detailed studies on photophysical properties and electrochemical characteristics in solutions strongly indicate that they might be promising candidates for organic optoelectronic applications, such as organic light-emitting devices (OLEDs) or as models for investigating the fluorescent structure-property relationship of the alkyne-functionalized pyrene derivatives.

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## 1. Introduction

The fluorescence properties of pyrene molecule are well known that make it useful as a popular fluorescent probe. Pyrene and its derivatives have been widely used as fluorescent probes in many applications. For example, pyrene-labeled oligonucleotides have been used as probes to study DNA hybridization [1], and pyrene-labeled lipids have been used to study the depth-dependent quenching of fluorescence in lipid bilayers [2]. Recently, the synthesis of a pyrene-based fluorescent dendrimer has been reported wherein the core unit is a 1,3,6,8-tetrasubstituted pyrene and the peripheral units contain monosubstituted pyrene units [3–5]. In the applications of fluorescence techniques, it is desirable to design molecules that have emission in the visible region. The most common method to bathochromically shift the absorption and emission characteristics of a fluorophore to extend the  $\pi$ -conjugation is by introducing unsaturated functional groups to the core of the fluorophore.

One such group is the acetylenic group. In a recent paper the absorption and fluorescence emission properties of the dimer of 1-ethynylpyrene, namely 1,4-bis(1-pyrene)butadiyne, have been reported [6], and polymers of 1-ethynylpyrene and

1-trimethylsilylethynylpyrene have been also reported [7]. These polymers exhibit high thermal stability and absorb and emit in the visible region. In the present study, we have used acetylenic groups to extend the conjugation of the pyrene chromophore. Thus, there is substantial interest in investigating the synthesis of new alkyne-functionalized pyrenes, and several of its derivatives bearing both hydrophilic and hydrophobic substituents and studies on the electronic absorption and fluorescence emission properties of these molecules.

We previously reported the synthesis of 4,9- and 4,10-bis(arylethynyl)pyrenes by the Wittig reaction of 2,7-di-*tert*-butylpyrene-4,9-biscarbaldehyde and 4,10-biscarbaldehyde with aryl methyl phosphonium ylides followed by bromination and dehydrobromination [8]. On the other hand, we recently succeeded regioselective diacetylation arising from the twofold acetylation at the 5,9-positions to afford 5,9-diacetyl-7-*tert*-butyl-1,3-dimethylpyrene [9]. This result strongly suggests the *tert*-butyl group in the pyrene [10] ring protects the electrophilic attack at the 6,8-positions as well as the methyl groups at the 1,3-positions inhibiting the electrophilic attack at the 4,10-positions [11]. Accordingly, this results promote us to explore the synthesis of 5-mono- and 5,9-bis(arylethynyl)pyrenes and further to establish the structure-property relationships on electronic absorption and fluorescence emission in several arylethynylpyrenes functionalized at not only the active sites (*i.e.* 1-, 3-, 6-, and 8-positions) [5] but also the K-region (*i.e.* 4-, 5-, 9-, and 10-positions) [8]. We wish to report here the synthesis, crystal

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structure and photophysical properties of 7-*tert*-butyl-5-(4-methoxyphenylethynyl)-1,3-dimethylpyrene and 7-*tert*-butyl-5,9-bis(4-methoxyphenylethynyl)-1,3-dimethylpyrene.

## 2. Experimental

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at 300 MHz and 75 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with  $\text{Me}_4\text{Si}$  as an internal reference. The IR spectra were obtained as KBr pellets on a Nippon Denshi JIR-AQ20M spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed with a Yanaco MT-5 analyzer. UV–vis spectra were measured using a Shimadzu UV-3150 UV–vis–NIR spectrophotometer. Emission spectra were performed in a semimicro fluorescence cell (Hellma<sup>®</sup>, 104F-QS, 10 × 4 mm, 1400  $\mu\text{L}$ ) with a Varian Cary Eclipse spectrophotometer. Gas–liquid chromatograph (GLC) analyses were performed by Shimadzu gas chromatograph, GC-14A; silicone OV-1, 2 m; programmed temperature rise, 12  $^\circ\text{C min}^{-1}$ ; carrier gas nitrogen, 25 mL  $\text{min}^{-1}$ . Electrochemical properties of HOMO and LUMO energy levels were determined by Electrochemical Analyzer.

### 2.1. Synthesis

#### 2.1.1. Synthesis of 7-*tert*-butyl-1,3-dimethylpyrene 5-carbaldehyde (**2**)

To a stirred solution of **1** (106 mg, 0.37 mmol) and dichloromethyl methyl ether (74 mg, 0.64 mmol) in  $\text{CH}_2\text{Cl}_2$  (4 mL) was added a solution of titanium tetrachloride (0.1 mL, 0.91 mmol) in  $\text{CH}_2\text{Cl}_2$  (1 mL) at 0  $^\circ\text{C}$ . This mixture was stirred for 2 h at room temperature. The reaction mixture was poured into a large amount of ice-water and extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL × 2). The organic layer was washed with water (5 mL × 2), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The residue was recrystallized from hexane to afford the *title compound* **2** (98 mg, 85%) as pale yellow prisms, mp 268–269  $^\circ\text{C}$ ,  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$ : 3050, 2950, 1670 (C=O), 1570, 1470.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  ppm 1.62 (s, 9H, *t*Bu), 2.93 (s, 3H, *Me*), 2.95 (s, 3H, *Me*), 7.69 (s, 1H, Pyrene- $H_2$ ), 8.02 (d, 1H,  $J=9.2$  Hz, Pyrene- $H_9$ ), 8.12 (d, 1H,  $J=9.2$  Hz, Pyrene- $H_{10}$ ), 8.25 (d, 1H,  $J=2.0$  Hz, Pyrene- $H_8$ ), 8.61 (s, 1H, Pyrene- $H_4$ ), 9.73 (d, 1H,  $J=2.0$  Hz, Pyrene- $H_6$ ), 10.49 (s, 1H, CHO). FAB-MS ( $m/z$ ): 314 [ $\text{M}^+$ ]. Anal. calcd. (%) for  $\text{C}_{23}\text{H}_{22}\text{O}$  (314.41): C, 87.86; H, 7.05. Found: C, 87.85; H, 7.06.

#### 2.1.2. Synthesis of 7-*tert*-butyl-1,3-dimethylpyrene 5,9-dicarbaldehyde (**3**)

To a stirred mixture of **1** (286 mg, 1.0 mmol) and dichloromethyl methyl ether (463 mg, 4.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL), was added aluminum chloride (534 mg, 4.0 mmol) at 0  $^\circ\text{C}$ . After this addition, this mixture was stirred for 6 h at room temperature. The reaction mixture was poured into a large amount of ice-water and extracted with  $\text{CH}_2\text{Cl}_2$  (100 mL × 2). The organic layer was washed with water (50 mL × 3) and brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The residue was column chromatographed with hexane: chloroform (1:3) as eluent to give an orange solid. Recrystallization from hexane to afford the *title compound* **3** (325 mg, 95%) as orange-yellow prisms, mp 256–258  $^\circ\text{C}$ ,  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$ : 3050, 2950, 1670 (C=O), 1570, 1470.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  ppm 1.64 (s, 9H, *t*Bu), 3.05 (s, 6H, *Me*), 7.82 (s, 1H, Pyrene- $H_2$ ), 8.68 (2s, 2H, Pyrene- $H_{4,10}$ ), 9.84 (s, 2H, Pyrene- $H_{6,8}$ ), 10.56 (s, 2H, CHO). FAB-MS ( $m/z$ ): 342 [ $\text{M}^+$ ]. Anal. calcd. (%) for  $\text{C}_{24}\text{H}_{22}\text{O}_2$  (342.44): C, 84.18; H, 6.48. Found: C, 84.20; H, 6.45.

#### 2.1.3. Synthesis of 7-*tert*-butyl-5-[2-(4-methoxyphenyl)ethenyl]-1,3-dimethylpyrene (**E**-**5**)

The Wittig reagent was prepared from triphenylphosphine and 4-methoxybenzyl chloride in dry benzene. To a solution of this Wittig reagent (794 mg, 1.89 mmol) in dry THF (15 mL) was slowly added *n*-butyllithium in hexane (1.17 mL, 1.89 mmol) at 0  $^\circ\text{C}$  under argon. The mixture was stirring for 10 min and the solution of 7-*tert*-butyl-5-formyl-1,3-dimethylpyrene **2** (200 mg, 0.632 mmol) in dry THF (15 mL) was injected under same conditions. After this addition, the mixture was warmed to room temperature, stirred for 6 h under argon. The mixture was quenched by large amount of ice-water and extracted with ethyl acetate (100 mL × 2). The combined extracts were washed with water followed by drying with brine and  $\text{MgSO}_4$  and concentrated. The residue was adsorbed in silica gel and column chromatographed over silica gel (Wako C-300, 200 g) with hexane: dichloromethane (5:1) as eluent to give a mixture of (*E*)-**5** and (*Z*)-**5** in the ratio of 95:5 (NMR analysis) as light-yellow solids (240 mg, 90%). Recrystallization from hexane and dichloromethane afforded (*E*)-**5** (190 mg, 72%) as pale yellow prisms, mp 150–152  $^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  ppm 1.59 (s, 9H, *t*Bu), 2.94 (s, 3H, *Me*), 2.98 (s, 3H, *Me*), 3.88 (s, 3H, *OMe*), 7.00 (d, 2H,  $J=8.7$  Hz, Ar-*H*), 7.33 (d, 1H,  $J=15.9$  Hz, Pyrene- $\text{CH}=\text{CH}_b\text{-Ar}$ ), 7.65 (d, 2H,  $J=8.7$  Hz, Ar-*H*), 7.70 (s, 1H, Pyrene- $H_2$ ), 7.92 (d, 1H,  $J=15.9$  Hz, Pyrene- $\text{CH}_a=\text{CH-Ar}$ ), 8.02 (d, 1H,  $J=9.0$  Hz, Pyrene- $H_9$ ), 8.17 (d, 1H,  $J=9.0$  Hz, Pyrene- $H_{10}$ ), 8.21 (d, 1H,  $J=1.8$  Hz, Pyrene- $H_8$ ), 8.36 (s, 1H, Pyrene- $H_4$ ), 8.48 (d, 1H,  $J=1.8$  Hz, Pyrene- $H_6$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  ppm 19.73 (2Me), 31.98 (3Me), 35.34 (C), 55.38 (OMe), 114.22 (CH), 118.36 (CH), 121.08 (CH), 122.18 (CH), 123.48 (CH), 125.05 (CH), 126.53 (CH), 127.41 (CH), 127.48 (CH), 128.01 (CH), 129.97 (CH), 130.71 (CH), 131.15 (CH), 131.51 (CH), 131.79 (CH), 133.60 (CH), 148.45 (CH), 159.39 (CH). FAB-MS ( $m/z$ ): 418 [ $\text{M}^+$ ]. Anal. calcd. (%) for  $\text{C}_{31}\text{H}_{30}\text{O}$  (418.6): C, 88.95; H, 7.22. Found: C, 88.93; H, 7.24.

#### 2.1.4. Bromination of (*E*)-**5** with BTMA $\text{Br}_3$

To a solution of (*E*)-**5** (314 mg, 0.75 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL) was added BTMA  $\text{Br}_3$  (729 mg, 1.86 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 5 min, it was poured into a large amount of ice/water (100 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL × 2). The combined extracts were washed with water, dried with  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was recrystallized from hexane gave 560 mg (78%) of a mixture of two diastereomers **6** and **6'** in the ratio of 80:20 as colorless prisms, mp 200–202  $^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  ppm, **6**: 1.64 (s, 9H, *t*Bu), 2.92 (s, 3H, *Me*), 3.00 (s, 3H, *Me*), 3.86 (s, 3H, *OMe*), 6.00 (d, 1H,  $J=10.7$  Hz, Pyrene- $\text{CH}_b\text{Br-CH}_a\text{Br}$ ), 6.61 (d, 1H,  $J=11.4$  Hz, Pyrene- $\text{CH}_b\text{Br-CH}_a\text{Br}$ ), 6.98 (d, 2H,  $J=8.6$  Hz, Ar-*H*), 7.61 (d, 2H,  $J=8.61$  Hz, Ar-*H*), 7.88 (s, 1H, Pyrene- $H_2$ ), 8.03 (d, 1H,  $J=9.1$  Hz, Pyrene- $H_9$ ), 8.16 (d, 1H,  $J=9.1$  Hz, Pyrene- $H_{10}$ ), 8.22 (d, 1H,  $J=1.5$  Hz, Pyrene- $H_8$ ), 8.45 (s, 1H, Pyrene- $H_4$ ), 8.59 (d, 1H,  $J=1.5$  Hz, Pyrene- $H_6$ ); **6'**: 1.65 (s, 9H, *t*Bu), 2.92 (s, 3H, *Me*), 3.00 (s, 3H, *Me*), 3.86 (s, 3H, *OMe*), 6.13 (d, 1H,  $J=10.7$  Hz, Pyrene- $\text{CH}_b\text{Br-CH}_a\text{Br}$ ), 6.38 (d, 1H,  $J=11.4$  Hz, Pyrene- $\text{CH}_b\text{Br-CH}_a\text{Br}$ ), 7.02 (d, 2H,  $J=8.6$  Hz, Ar-*H*), 7.61 (d, 2H,  $J=8.6$  Hz, Ar-*H*), 7.88 (s, 1H, Pyrene- $H_2$ ), 8.03 (d, 1H,  $J=9.1$  Hz, Pyrene- $H_9$ ), 8.16 (d, 1H,  $J=9.1$  Hz, Pyrene- $H_{10}$ ), 8.23 (s, 1H, Pyrene- $H_4$ ), 8.33 (d, 1H,  $J=1.5$  Hz, Pyrene- $H_8$ ), 9.00 (d, 1H,  $J=1.5$  Hz, Pyrene- $H_6$ ). FAB-MS ( $m/z$ ): 576, 578, 580 [ $\text{M}^+$ ]. Anal. calcd. (%) for  $\text{C}_{31}\text{H}_{30}\text{Br}_2\text{O}$  (576.39): C, 64.38; H, 5.23. Found: C, 64.36; H, 5.24.

#### 2.1.5. Synthesis of 7-*tert*-butyl-5-(4-methoxyphenylethynyl)-1,3-dimethylpyrene (**7**)

To a solution of a mixture of **6** and **6'** (168 mg, 0.20 mmol) in *t*BuOH (24 mL) was added  $\text{KOtBu}$  (1.34 g, 10.5 mmol) at room

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