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Ir-Catalyzed Direct Borylation at the 4-Position of Pyrene

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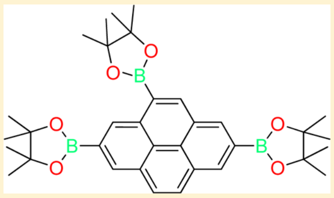
Supporting Information

ABSTRACT: The first direct borylation of a C−H bond at the 4-position of pyrene was achieved using $[Ir(COD)Cl]_2$/dtbpy as the catalyst precursor and B_2pin_2 as the boron source. The position-related photophysical properties of pyrene derivatives are reported.



Boron plays an important role in modern organic chemistry, both for synthetic methodology[1] and for functional materials.[2−4] In particular, aryl boronates (boronic acids, boronate esters, and trifluoroborate salts) are widely used as key intermediates for a variety of cross-coupling reactions.[5−7] Boronates can be prepared either from halo-substituted arenes via reactive lithium or Grignard reagents or via transition metal catalyzed borylation.[1] Recently, the direct borylation of C−H bonds has attracted great attention.[8] Thus, Ishiyama, Miyaura and Hartwig,[9,10] Smith[11] and Marder[12] and their co-workers showed that an Ir-complex can be used for borylation of aromatic C−H bonds under mild conditions. Ground breaking experimental and theoretical studies have been carried out to examine the mechanism[13,14] and extend the use of this borylation reaction from aryl and heteroaryl systems to fused polycyclic aromatics and even polymers.[15−21] The Ir-catalyst, normally prepared in situ via the reaction of $[Ir(COD)Cl]_2$ or $[Ir(COD)OMe]_2$ with 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy), borylates arenes with unusual sterically driven regioselectively, typically avoiding positions ortho to either substituents or to ring junctions.[8] This selectivity is due to the crowded nature of the five-coordinate trisboryl species $[Ir(dtbpy)(Bpin)_3]$, which is believed to be the key intermediate in the catalytic cycle responsible for the C−H activation.[13]

Pyrene-based materials for organic electronics have been the subject of tremendous investigation.[22] From a synthetic viewpoint, the chemistry of pyrene is strongly position-dependent. The 1-, 3-, 6-, and 8-positions of pyrene are the active sites for electrophilic aromatic substitution (S_EAr) reactions, and most pyrene derivatives are prepared via such processes.[22] Thus, monobromination is known to occur preferentially at the C1 position of pyrene.[23] For substitution at the unfavorable 2,7 and 4,5,9,10 positions, an indirect multistep route normally has to be employed. For example, Pd/C catalyzed reduction of pyrene with H_2 to give 4,5,9,10-tetrahydropyrene, which followed by substitution and subsequent rearomatization, gives 2,7-substituted pyrenes,[24] while the ruthenium-catalyzed oxidation at the K-region of pyrene[25,26] or Lewis acid catalyzed bromination of 2,7-di-*tert*-butyl pyrene can extend pyrene at the 4,5,9,10 positions.[27] Itami and co-workers have very recently reported the palladium-catalyzed oxidative direct arylation of pyrene at the 4-position.[28] However, there are no reports of direct borylation of pyrene at the 4-position due to the steric-selectivity of the Ir-catalyst mentioned above.

Thus, Marder et al. reported a one-step Ir-catalyzed direct borylation of pyrene at the 2- or 2,7-positions with high selectivity,[19] which provided a rapid and efficient route to functionalized pyrenes,[29−31] and even rich crystallographic behaviors.[19c] Furthermore, the authors also noted that trace amounts of a triborylated pyrene were observed by EI/MS after extended reaction times of 3−4 days, when 2.2 mol equiv of B_2pin_2 were used, although they had not separated and characterized it at that time.[19a]

Herein, we examine the regio-selectivity of the Ir-catalyzed borylation of pyrene, which has previously been substituted at the 2,7 positions by bulkyl groups such as *tert*-butyl and/or Bpin, and demonstrate the position-related photophysical properties of pyrene derivatives (Scheme 1).

First, pyrene was selectively mono- or di-*tert*-butylated using *tert*-butyl chloride and aluminum chloride to afford mono- or di-*tert*-butyl-pyrene depending on the number of equivalents of *tert*-butyl chloride.[32] The orientation of the substituents has been shown by crystal structure analysis,[33] and it is unique, because of the extreme bulk of the *tert*-butyl groups, that electrophilic substitution takes place at the 2,7-positions. In a typical borylation reaction, equimolar quantities of substrate and B_2pin_2 (normally 10 mmol) and a catalytic amount of $[Ir(COD)Cl]_2$ (1 mol % Ir) and dtbpy (1 mol %) were reacted

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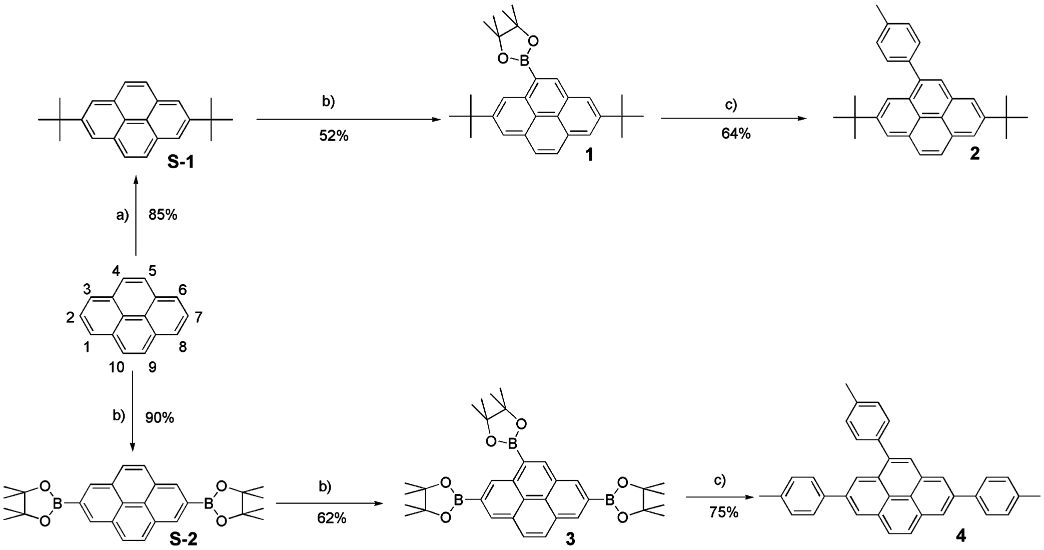
Scheme 1. Borylation of Pyrene Derivatives[a]



[a](a) t-BuCl, $AlCl_3$, DCM, rt, 16 h; (b) B_2pin_2, $[Ir(COD)Cl]_2$, dtbpy, hexane, 80 °C, 48 h; (c) 4-bromo-toluene, $Pd(PPh_3)_4$, Na_2CO_3, toluene/H_2O, 80 °C, 16 h.

in hexane (15 mL) under N_2 at 80 °C for 48 h. When 2-*tert*-butyl-pyrene was used, the Ir-catalyzed monoborylation clearly took place at the 7-position in nearly 100% yield, confirmed by NMR spectroscopy and crystal structure analysis.[19b] The borylation of di-*tert*-butylpyrene was also quite clean, affording **1** in 52% yield after workup. Although the yield is moderate, the product is very easily purified, and most of the unreacted di-*tert*-butylpyrene can be recovered and recycled. Further efforts to increase the yield by using larger amounts of B_2pin_2 or extending the reaction time always increased the quantity of byproduct (i.e., a mixture of diborylated pyrenes).

The product of the borylation of di-*tert*-butylpyrene was fully characterized by NMR, MS, and elemental analysis, and its structure was confirmed by single-crystal X-ray diffraction, demonstrating that this borylation occurred exclusively at the 4-position as expected. Its ^1H NMR spectral pattern is quite similar with that reported for 4-bromo-2,7-di-*tert*-butylpyrene.[34] In the single crystal structure (Figure S4, Supporting Information) of **1**, two types of disorder involving methyl and Bpin groups precluded our obtaining highly accurate structural parameters, but the data confirmed that boron is connected to the 4-position of pyrene. Interestingly, the space group of the crystals of **1** is C_C, such that all molecules of **1** pack along one polar axis.

Encouraged by this result, the borylation of 2,7-di-Bpin-pyrene (**S-2**) under the same conditions was examined, and 2,4,7-tri-Bpin-pyrene (**3**) was successfully isolated in 62% yield. The positions of borylation in compound **3** were also confirmed by single-crystal X-ray diffraction (Figure S4, Supporting Information). Compound **3** crystallizes in the noncentrosymmetric spacegroup $P2_1$; however, it is partly disordered. The disorder was refined employing a suitable split-atom model. The three borolane rings are nearly coplanar with the pyrene skeleton as indicated by the small angles of 5.3(9)° to 19.3(7)° between the mean plane of the pyrene skeleton and the respective O—B—O planes. The bond lengths of the three B—C bonds are in a narrow range around 1.57 Å. Thus, Ir-catalyzed borylation can also occur at a C—H bond ortho to a ring junction when more sterically favored positions are occupied. A related finding in the borylation of phenacenes was recently reported.[35]

Considering that previous reports indicated relatively sluggish reactivity of 2,7-di-Bpin-pyrene in Suzuki—Miyaura cross-coupling reactions,[19b,36] compared with -$B(OH)_2$ or -BF_3K analogues,[19b] the reactivity of the 4-Bpin-substituted pyrenes was also examined. First, 4-bromo-toluene and **1** were used as coupling partners, employing the $Pd(PPh_3)_4$-Na_2CO_3-toluene system for Suzuki—Miyaura coupling. This reaction worked well and gave the 4-arylated product **2** in high yield, indicating good reactivity of the 4-Bpin group. To our surprise, compound **3** also coupled readily with 4-bromotoluene under the same conditions. Interestingly, all three Bpin groups reacted giving 2,4,7-tri-4-tolylpyrene **4** in 75% yield. Compared with **S-2**, it appears that the lower symmetry of the 4-substituted derivatives may activate the Bpin groups at the 2,7-postions. In contrast with the reported 2,7-Ph_2-pyrene,[36b] in the solid state, the tolyl moieties at the 2,7-positions in **4** are nearly coplanar with the pyrene skeleton, with angles between the respective mean planes of 16.67(7) and 3.98(9)°. However, maybe because of steric hindrance, the tolyl groups at the 4-position are twisted, with angles between the respective mean planes of 64.8(1)° in **2** and 54.58(6)° in **4** (Figure S5, Supporting Information). Note that **2** forms a 1:1 π-stacked cocrystal with C_6F_6 (see Figure S6, Supporting Information, ref 19c and references therein).

Pyrene is a prototypical and widely used fluorophore.[22] The photophysical properties of pyrene derivatives can be tuned not only by the substituent but also by its position. In our recent paper,[30] we demonstrated and discussed the differences between 1- and 2-substituted pyrene derivatives. Although several 4-subsititutted pyrenes have been reported,[25−28,37] few studies of the relationship between substitution position and basic photophysical properties have appeared.[37] We therefore recorded absorption and emission spectra, fluorescence quantum yields and lifetimes of compounds **1**−**4**, and for comparison, 2,7-$^tBu_2$-pyrene (**S-1**), 2-^{t}Bu-7-Bpin-pyrene (**5**)[19b] and 2-^{t}Bu-6-Bpin-pyrene (**6**)[38] (Figure 1 and Table 1).

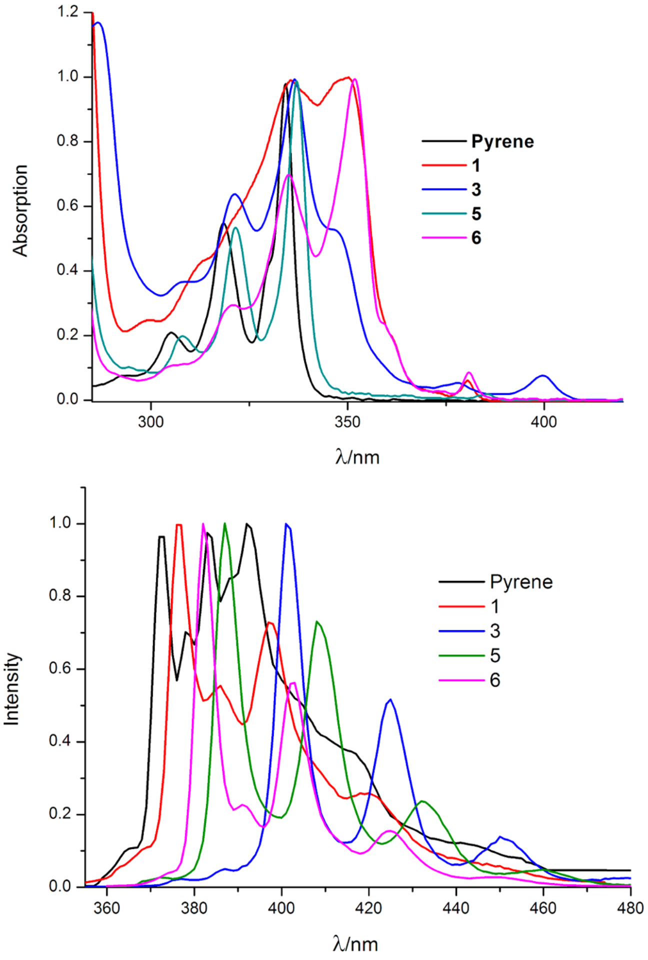


Figure 1. Normalized absorption (top) and emission (bottom) spectra of pyrene and 1-, 2-, and 4-borylated pyrenes.

Table 1. Spectroscopic Data for Pyrene Derivatives in Degassed Hexane

	R	λ_{abs}/ nm	ε/mol^{-1} cm^{-1} L	λ_{em}/ nm	Φ	τ/ ns
S-1	R_2 = *t*-butyl	376	800	378	0.42	78
	R_7 = *t*-butyl	337	67000	388		
	R_4 = H	322	45000	398		
1	R_2 = *t*-butyl	380	2600	381	0.66	45
	R_7 = *t*-butyl	350	34000	391		
	R_4 = Bpin	336	37000	402		
2	R_2 = *t*-butyl	342	60000	381	0.55	60
	R_7 = *t*-butyl	328	48000	391		
	R_4 = *p*-tolyl			400		
3	R_2 = Bpin	399	5000	402	0.62	42
	R_7 = Bpin	347	29000	425		
	R_4 = Bpin	337	55000	450		
4	R_2 = *p*-tolyl	345	50000	420	0.44	52
	R_7 = *p*-tolyl	336	64000			
	R_4 = *p*-tolyl	320	62000			
5	R_2 = *t*-butyl	385	1200	386	0.49	74
	R_7 = Bpin	337	74000	408		
	R_4 = H	322	45000	432		
6	R_2 = *t*-butyl	381	7300	382	0.83	40
	R_6 = Bpin	352	69000	391		
	R_7 = R_4 = H	335	51000	402		

As shown in Figure 1, the absorption spectrum of 2-Bpin-7-*t*-butyl-pyrene (**5**) is quite similar to that of unsubstituted pyrene with only a 3 nm red-shift.[30] However, borylation at the "1-position" (2-*t*-butyl-6-Bpin-pyrene, **6**) causes a red-shift of 17 nm and a 6 fold increase in ε for the lowest energy transtion. These are in accordance with the observation that substitution at the 2,7-positions has little influence on the $S_2 \leftarrow S_0$ absorption but a large influence on the $S_1 \leftarrow S_0$ absorption, whereas 1-substitution influences both $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ absorptions.[30] However, the absorption maximum of the 4-Bpin substituted compound **1** is fairly similar to that of **6**, including the $S_1 \leftarrow S_0$ absorption at 380 nm, but its pattern is quite different. The main $S_2 \leftarrow S_0$ absorption band (i.e., 330–360 nm for **1**) has become a broad band comprising two weak peaks with much lower extinction coefficients. The absorption of tri-Bpin substituted **3** shows a significant red-shift vs the other Bpin derivatives, and again, evidence that symmetry breaking makes the $S_1 \leftarrow S_0$ transition more allowed.

For the emission spectra of the substituted compounds, some of the fine structure observed for pyrene is lost, and the main emission peaks are significantly red-shifted. The spectral profile for compound **1** is nearly the same as that of **6**. Compound **3** fluoresces at longer wavelength than the others but shows a similar pattern to that of **5**. In addition, the fluorescence lifetimes of 4-substituted **1** and **3** are also similar to that of **6**, but only half of that of **5**. For the tolyl substituted compounds **2** and **4**, the typical $S_2 \leftarrow S_0$ absorption observed in pyrene around 334 nm appears as broad bands with unresolved vibrational structures, and the weak $S_1 \leftarrow S_0$ pyrene absorption at 372 nm was not observed.

In summary, we have shown that an Ir catalyst will borylate pyrene at the 4-position, which is ortho to ring junctions, if the 2- and 7-positions are occupied. Moreover, the 4-Bpin compounds show good reactivity for Suzuki–Miyaura coupling, and the asymmetry induced seems to activate Bpin groups at 2,7-positions as well. The absorption and emission properties of 4-substituted compounds also show much similarity to those of 1-substituted pyrenes, i.e., spectral patterns and peak positions. We expect this borylation process to be of use in extending the chemistry of pyrene.

■ EXPERIMENTAL SECTION

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. NMR spectra were obtained in $CDCl_3$ using 400 MHz spectrometers. Chemical shifts are reported relative to tetramethylsilane and are referenced to residual proton or carbon resonances in $CDCl_3$. High-Res MS (HRMS) were record in MALDI (DHB matrix, FTMS) or ESI (Q-TOF positive ion) modes. The melting points were measured on a DSC at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere. UV–vis absorption spectra and fluorescence emission spectra were recorded with $C = 1.0 \times 10^{-5}$ mol·L^{-1} in hexane. For luminescence quantum yield and lifetime measurements, dilute solutions (C = 2.0–5.0 × 10^{-6}) of the compounds were carefully degassed via three freeze–pump–thaw cycles to remove any dissolved oxygen.

4-Bpin-2,7-di-*tert*-butylpyrene (1). In a dry nitrogen-filled glovebox, the precatalyst $[Ir(COD)Cl]_2$ (33.5 mg, 0.1 mmol Ir), ligand dtbpy (27 mg, 0.1 mmol) and a small amount of B_2pin_2 (ca. 50 mg) were mixed in 2 mL of hexane in a Schlenk tube and stirred vigorously until the solution turned brown. Then di-*tert*-butylpyrene (**S-1**, 3.14 g, 10.0 mmol) and B_2pin_2 (2.54 g, 10.0 mmol) and 20 mL of hexane were add into this tube under N_2, the tube was sealed with Teflon cap, and the mixture was stirred at 80 °C for 48 h to give a dark red solution. The mixture was filtered through a short silica pad to remove the Ir-containing catalyst and then concentrated. Removal of the volatiles and subsequent column chromatography on silica gel, eluting with hexane: $CHCl_3$ = 1:1, resulted in two colorless compounds, **1** and **S-1** in 52 and 45% yields, respectively. The product was recrystallized from hexane to give colorless prismatic crystals: mp 173−174 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ = 9.18 (d, *J* = 2 Hz, 1 H), 8.66 (s, 1 H), 8.23 (d, *J* = 2 Hz, 1 H), 8.19 (d, *J* = 2 Hz, 1 H), 8.16 (d, *J* = 2 Hz, 1 H), 8.00 (AB quartet), 1.59 (s, 9H), 1.56 (s, 9H), 1.51 (12 H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz), δ = 148.5, 148.4, 138.5, 133.1, 130.8, 130.7, 130.0, 127.9, 126.7, 124.0, 123.5, 122.9, 122.81, 122.75, 121.9, 83.8, 35.4, 35.2, 31.97, 31.95, 25.1. Anal. Calcd: for $C_{30}H_{37}BO_2$; C 81.81, H 8.47; found C, 81.68; H, 8.43. HRMS (MALDI/DHB) Calcd for $C_{30}H_{37}{}^{10}BO_2$ 440.2881; found 440.2887. HRMS (ESI) Calcd for $C_{30}H_{38}{}^{10}BO_2$ 441.2965; found 441.2975.

4-Tolyl-2,7-di-*tert*-butylpyrene (2). Compound **1** (0.40 g, 1.0 mmol) and 4-bromo-toluene (0.34 g, 2.0 mmol) were placed in a 100 mL Schlenk tube, which was evacuated and purged with nitrogen gas three times. $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), toluene (∼10 mL) and a saturated aqueous solution of Na_2CO_3 (∼0.5 mL) were added under nitrogen. The tube was sealed with a Teflon cap and stirred at 80 °C for 16 h before it was quenched. The mixture was extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated in vacuo. Purification by column chromatography (silica gel using chloroform-petroleum ether (1: 6)) gave a colorless oil in 64% yield. The product was recrystallized from hexane with addition of hexafluorobenzene to give colorless needle-like crystals: mp 121−123 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ = 8.29 (d, *J* = 2 Hz, 1 H), 8.20 (d, *J* = 1 Hz, 1H), 8.18 (s, 2 H), 8.05 (d, *J* = 2 Hz, 2 H), 7.974 (s, 1 H), 7.60 (d, *J* = 8 Hz, 2 H), 7.38 (d, *J* = 8 Hz, 2 H), 2.52 (s, 3 H), 1.58 (s, 9 H), 1.48 (s, 9 H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz), δ = 148.8, 148.3, 139.5, 138.2, 137.0, 131.0, 130.8, 130.6, 130.1, 129.9, 129.1, 128.4, 127.9, 127.7, 127.2, 123.2, 122.4, 122.1, 121.8, 121.2, 35.3, 35.2, 32.0, 31.9, 21.3. Anal. Calcd: for $C_{31}H_{32}$: C 92.03, H 7.97; found C 91.97; H, 8.01. HRMS (MALDI/DHB) Calcd for $C_{31}H_{32}$ 404.2499; found 404.2496. HRMS (ESI) Calcd for $C_{31}H_{33}$ 405.2582; found 405.2547.

2,4,7-Tri-Bpin-pyrene (3). In a dry, nitrogen-filled Schlenk tube, in a glovebox, the precatalyst $[Ir(COD)Cl]_2$ (33.5 mg, 0.1 mmol Ir), ligand dtbpy (27 mg, 0.1 mmol) and a small amount of B_2pin_2 (ca. 50 mg) were mixed in 2 mL of hexane and stirred vigorously until the solution turned brown. Then 2,7-di-Bpin-pyrene (**S-2**) (2.27 g, 5 mmol), B_2pin_2 (2.54 g, 10 mmol) and 20 mL of hexane were added under N_2 into this tube, and the system was sealed with a Teflon cap and stirred at 80 °C for 48 h to give a dark red solution. The mixture was filtered through a short silica pad to remove the Ir-containing catalyst and then concentrated. Removal of the volatiles and subsequent column chromatography on silica gel, eluting with hexane:$CHCl_3$ = 1:1, resulted in two colorless compounds, **3** and **S-2** in 62 and 30% yields, respectively. The product was recrystallized from hexane to give colorless prismatic crystals: mp 260−262 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ = 9.43 (s, 1 H), 8.69 (s, 1 H), 8.66 (s, 1 H), 8.62 (s, 1 H), 8.58 (s, 1 H), 8.05 (AB quartet, 2 H), 1.51 (s, 12 H), 1.45 (s, 12 H), 1.44 (12 H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz), δ = 138.3, 133.2, 132.5, 132.1, 132.0, 131.03, 130.96, 130.8, 130.0, 128.1, 127.4, 127.0, 126.3, 84.1, 84.0, 25.11, 25.08, 25.05. Anal. Calcd: for $C_{34}H_{43}B_3O_6$; C 70.39, H 7.47; found C, 70.42; H, 7.45. HRMS (ESI) Calcd for $C_{34}H_{44}B_3O_6$ 581.3417; found 581.3414.

2,4,7-Tri-4-tolyl-pyrene (4). Compound **3** (0.58 g, 1.0 mmol) and 4-bromo-toluene (1.00 g, 6.0 mmol) were placed in a 100 mL Schlenk tube, which was evacuated and purged with nitrogen gas three times. $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), toluene (∼10 mL) and a saturated aqueous solution of Na_2CO_3 (∼0.5 mL) were added under nitrogen. The tube was sealed with a Teflon cap and stirred at 80 °C for 16 h before it was quenched. This mixture was extracted with dichloromethane, dried over $MgSO_4$, and concentrated in vacuo. Purification by column chromatography (silica gel using chloroform/petroleum ether (1:6)) gave a colorless oil in 75% yield. The product was recrystallized from toluene to give colorless single crystals: mp 202−204 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ = 8.43 (d, *J* = 1 Hz, 1 H), 8.39 (d, *J* = 1 Hz, 1H), 8.38 (s, 2 H), 8.15 (s, 2 H), 8.06 (d, 1 H), 7.80 (d, *J* = 8 Hz, 2 H), 7.66 (d, *J* = 8 Hz, 2 H), 7.62 (d, *J* = 8 Hz, 2 H), 7.38 (m, 4 H), 7.31 (d, *J* = 8 Hz, 2 H), 2.51 (s, 3 H), 2.47 (s, 3 H), 2.43 (s, 3 H); ^{13}C {H} NMR ($CDCl_3$, 100 MHz), δ =140.1, 139.0, 138.9, 138.7, 137.9, 137.28, 137.25, 137.14, 131.7, 131.5, 131.3, 130.9, 130.0, 129.8, 129.7, 129.3, 128.3, 128.1, 127.93, 127.85, 127.75, 124.1, 123.9, 123.74, 123.69, 123.5, 123.2, 122.8, 21.4, 21.2, 21.2. Anal. Calcd: for $C_{37}H_{28}$: C 94.03, H 5.97; found C 94.07; H, 5.93. HRMS (MALDI/DHB) Calcd for $C_{37}H_{28}$ 472.2182; found 472.2185. HRMS (ESI) Calcd for $C_{37}H_{29}$ 473.2269; found 473.2261.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of NMR, HRMS, and crystallographic data in CIF format for **1**−**4**, absorption and excitation spectra of **1**, **3**, **5**, **6**, and absorption and emission spectra of **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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