2,6-Bis(phenylethynyl)biphenyls and Their Cyclization to Pyrenes

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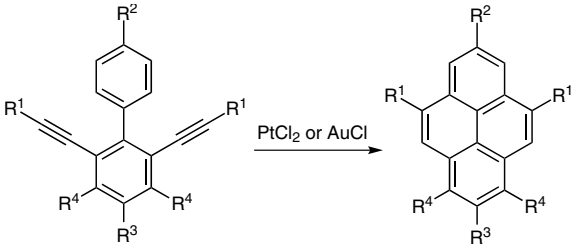
Abstract: We present a new protocol for pyrene synthesis via transition-metal cross-couplings. The initially prepared 2,6-bis(phenylethynyl)biphenyls were transformed to pyrenes with uncommon 4,10-disubstitution through an electrophilic cyclization. The precursors were synthesized by Suzuki–Miyaura cross-coupling, which provides 2,6-dibromobiphenyls; these were subsequently coupled with phenylethynyl derivatives via Kumada cross-coupling.

Key words: alkynes, biaryls, pyrenes, cyclizations, transition metals

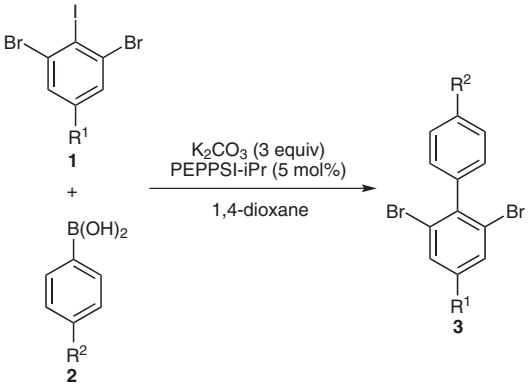
Pyrenes are associated with attractive electronic and optoelectronic properties for use as building blocks for organic electronics, and they are already in use in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaic devices (OPVs).[1–4] A special property of pyrenes is their blue emission fluorescence when substituents are placed so that undesirable face-to-face π–π stacking interactions are avoided.[2] Traditional synthetic pathways to substituted pyrenes typically involve electrophilic halogenation of the parent pyrene and its derivatives leading to substitution in the 1-, 1,3-, 1,6-, 1,8-, 2,7-, 1,3,6,8- and 4,5,9,10-positions, but mostly not with different substituents.[4,5] Alternatively, 2,6-diethynylbiphenyls and analogous phenanthrene derivatives have been proposed as precursors for electrophilic cyclizations to form pyrenes with diverse and complementary substitution patterns (Scheme 1). Davis' approach[3] and our approach[6] utilizing electrophile-induced ring closures[6–8] enables the introduction of substituents in positions 4 and 10 without substitution in positions 5 and 9. Furthermore, the use of electrophilic cyclizations is a viable path to achieve uncommonly functionalized pyrene derivatives without employing toxic preformed pyrene.

Here, we present an extension of this strategy to prepare functionalized pyrenes from 2,6-bis(phenylethynyl)biphenyls, anticipating that the latter can also be conveniently employed for cyclization reactions.[8,9] We found that various cyclization attempts utilizing the established procedures of Fürstner and Mamane were to no avail.[7] We also tackled the question of what factors prevent such systems from giving pyrenes. In order to elucidate this unexpected behavior, we compared our systems with those of the pioneering work of Larock and co-workers (see Figure 2) and employed density functional theory (DFT) computations to gain insight into the geometric constraints of the cyclization precursors.



Scheme 1 Davis' pyrene synthesis: R^1 = I, H; R^2–R^4 = various substituents (OBu, NBoc, OMe, etc.), generally leading to a uniform substitution pattern

In addition to the use of our ethynyl precurors for pyrene cyclizations, these materials are also valuable building blocks for a unique family of compounds for various applications, such as liquid crystal engineering and drug design.[10] The 4′-substituted 2,6-dibromobiphenyls **3** are known compounds but have not yet been fully characterized in the literature.[11] 2,6-Dibromobiphenyls **3a**–**e** were synthesized in moderate to good yields (Scheme 2) by Suzuki–Miyaura cross-coupling, starting from the appropriate 2,6-dibromoiodobenzene **1** and boronic acid **2**, utilizing Organ's PEPPSI-iPr catalyst.[12]



Scheme 2 R group definitions: **1a** R^1 = H, **1b** R^1 = F; **2a** R^2 = H, **2b** R^2 = F, **2c** R^2 = OMe, **2d** R^2 = CF_3; **3a** R^1 = R^2 = H, 62%; **3b** R^1 = H, R^2 = F, 45%; **3c** R^1 = H, R^2 = OMe, 49%; **3d** R^1 = H, R^2 = CF_3, 18%; **3e** R^1 = F, R^2 = H, 58%.

Purification by flash chromatography (**3a**–**c** and **3e**) gave colorless crystals. Compound **3d** was purified by prepara-

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tive GC and was also obtained as colorless crystals. All the biphenyls were characterized spectroscopically and by X-ray crystal structure analyses. Structure **3a** is shown in Figure 1 with its elementary cell; the X-ray crystal structures of compounds **3c** and **3e** were measured (see Supporting Information). These structures were also used for structural validation of the optimized computed geometries at the M06-2X/6-31G(d,p)[13] level of theory, for which we found that the experimental bond lengths and angles were well reproduced.

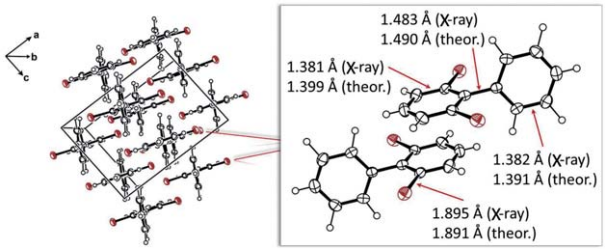
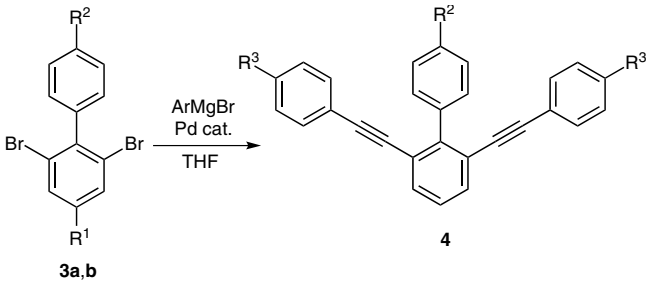


Figure 1 X-ray structure of 2,6-dibromobiphenyl (**3a**) with selected bond lengths compared with the computed M06-2X/6-31G(d,p) values

Coupling of 2,6-dibromobiphenyls **3** with phenylacetylenes via Sonogashira–Hagihara cross-coupling[14] gave, if at all, the twofold coupling product in low yields; often, the singly phenylethynylated biphenyl was formed instead. However, Kumada coupling of the 2,6-dibromobiphenyls with phenylethynylmagnesium bromides in tetrahydrofuran readily gave the 2,6-bis(phenylethynyl)biphenyls **4a**–**d** (Scheme 3). The catalyst $(Ph_3P)_2PdCl_2$ was used for compounds **4a**, **4b** and **4d**; for **4c**, $Pd_2(dba)_3$ proved to be more suitable. Flash chromatography was mostly adequate for purification; compound **4a** required purification by preparative HPLC.



Scheme 3 ArMgBr prepared from phenylacetylene (**6a**) or 4-fluorophenylacetylene (**6b**) via H–MgBr exchange with EtMgBr; catalyst = $(Ph_3P)_2PdCl_2$ or $Pd_2(dba)_3$; **3a** $R^1 = R^2 = H$, **3b** $R^1 = H$, $R^2 = F$; **4a** $R^2 = R^3 = H$, 53%; **4b** $R^2 = R^3 = F$; **4c** $R^2 = H$, $R^3 = F$, 15%; **4d** $R^2 = F$, $R^3 = H$, 40%.

DFT computations at the M06-2X/6-31G(d,p) level indicate that **4a** is twisted, with the phenyl substituent in the 1-position being almost exactly perpendicular (89°) to the plane of the other aryl moieties. The twisted structure lies 14.7 kcal·mol^{-1} below a hypothetical planar arrangement, which is not a stationary point on the potential energy hypersurface. In contrast, the corresponding energy difference of the rotational profile of Larock's 2-phenylethynylbiphenyl system is only about 7.2 kcal·mol^{-1}.[15] Between the carbon atoms in **4a** that eventually form the new carbon–carbon bond we observed a distance of 3.85 Å, while an angle of 79° was determined between these two carbon atoms and the ethynyl-substituted carbon atom of the biphenyl; Larock's precursor has a critical angle of 73° and a distance of 3.40 Å (Figure 2). Hence, the steric arrangement of structure **4a** is rather unfavorable for the desired 1,6-cyclization.

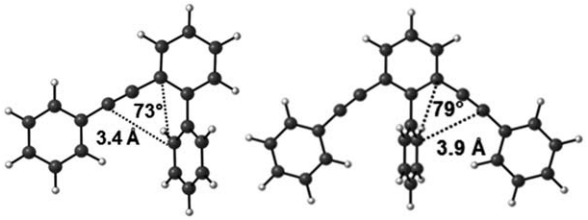
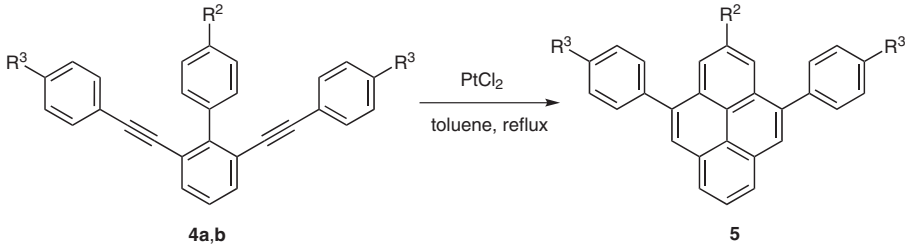


Figure 2 Optimized geometries of Larock's structure (left) vs **4a**: different spatial adjustment of the unsubstituted phenyl ring in the biphenyl [M06-2X/6-31G(d,p) level]

Owing to the larger distances and angles between the crucial C atoms, we expected our system to require higher reaction temperatures; however, the cyclization of **4a** and **4b** in refluxing toluene with platinum(II) chloride resulted in the expected pyrenes **5a** and **5b** (Scheme 4).[16] After purification by preparative HPLC and subsequent high-vacuum sublimation, **5a** was characterized by ^1H and ^{13}C NMR spectroscopy with the aid of HSQC and DEPT-135 experiments.

The optimized geometry of pyrene **5a** also shows twisted (almost perpendicular) phenyl substituents, which is supported by the spectroscopic finding that **5a** displays pronounced blue fluorescence and does not therefore display undesirable π–π stacking.

The main quality for the potentional use of these pyrene derivatives in optical devices is their strong fluorescence.



Scheme 4 1,6-Cyclization towards functionalized pyrenes **5a** ($R^2 = R^3 = H$) and **5b** ($R^2 = R^3 = F$)

We recorded a blue shift (–20 nm) of the absorption bands compared to the parent pyrene (338 nm).[17] The emission spectrum of **5a** (as an example) shows a maximum at about 380 nm and nicely mirrors the UV–vis absorptions (Figure 3). The Stokes shift was determined to be around 50 nm. We identified the long-wavelength absorption at 310 nm of pyrene **5a** as a $\pi \rightarrow \pi^*$ transition, which mainly involves the HOMO–LUMO transition (B → A) of the S_0 ground state to the open-shell singlet state S_1.

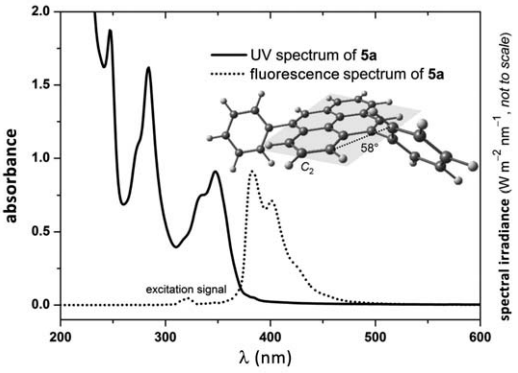


Figure 3 UV–vis absorption (left) and emission (right) spectra of **5a** (λ_{exc} = 310 nm) in CH_2Cl_2, and optimized geometry [M06-2X/6-31G(d,p) level]

In conclusion, we have synthesized the 2,6-dibromobiphenyls **3a–e** from their respective boronic acid precursors **2a–d** using Suzuki–Miyaura cross-couplings as the decisive step. The 2,6-dibromobiphenyls can be readily coupled with alkynyl derivatives. The resulting 2,6-bis(phenylethynyl)biphenyls were electrophilically cyclized to pyrene derivatives with a substitution pattern that is not readily available utilizing common approaches to pyrenes.

^{1}H NMR spectra were recorded at 400 MHz or 600 MHz, and ^{13}C NMR spectra at 100 MHz or 151 MHz, on a Bruker AV 400 or AV 600 spectrometer, respectively. Chemical shifts are reported in ppm (δ scale) using TMS as internal standard or the solvent signal as secondary standard. Structural assignments were made using 2D NMR spectra (HSQC) and DEPT-135 NMR spectra. UV–vis spectra were measured with a HP 8423 spectrometer (mercury lamp). Emission spectra were measured with an Ocean Optics SD 200 spectrometer (lamp: Beckmann Xe 1045, monochromatic illuminator: Beckmann GM 1139). Preparative GC was carried out using an OV-17 column and a temperature program 100 °C to 250 °C, with 4 °C/min ramping. Preparative HPLC was carried out using a Knauer HPLC Pump 64 system (RP-18 column). Melting points are not corrected and were measured with a Büchi Dr. Tottoli Typ S apparatus or with a Krüss KSP I N melting point meter. HRMS were recorded using a Finnigan MAT 95 instrument under electron impact (EI) conditions. Solvents were dried according to literature procedures. Compounds **1a**, **1b**, **2a–d** and **6b** were prepared according to literature procedures.[18]

2,6-Dibromobiphenyl (3a)
A 100-mL nitrogen flask was charged with 2,6-dibromoiodobenzene (**1a**; 1.8 g, 5 mmol), PEPPSI-IPr (0.2 g, 0.25 mmol, 5 mol%), K_2CO_3 (2.48 g, 18 mmol) and dioxane (25 mL) under argon and anhydrous conditions. The mixture was stirred at r.t. for 1 h, then phenylboronic acid (**2a**; 0.6 g, 5 mmol) was added and the solution was refluxed for 36 h. Sat. aq $NaHCO_3$ (80 mL) was added and the crude product was extracted with CH_2Cl_2 (100 mL). The extract was dried over $MgSO_4$ and purified by column chromatography [R_f = 0.32 (pentane–CH_2Cl_2, 99:1)]. Evaporation of the eluent provided colorless crystals; yield: 0.97 g (3.1 mmol, 62%); mp 71 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (t, *J* = 8.0 Hz, 1 H), 7.20 (d, *J* = 7.2 Hz, 2 H), 7.4–7.5 (m, 3 H), 7.62 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.54 (2 *C*Br), 128.06 (Ar*C*H), 128.19 (2 Ar*C*H), 129.14 (2 Ar*C*H), 129.81 (2 Ar*C*H), 131.78 (Ar*C*H), 141.14 (ArC_q), 143.02 (ArC_q).

HRMS: *m*/*z* calcd for $C_{12}H_8Br_2$: 309.899; found: 309.897.

2,6-Dibromo-4′-fluorobiphenyl (3b)
Into a 100-mL nitrogen flask were placed 2,6-dibromoiodobenzene (**1a**; 1.8 g, 5 mmol), PEPPSI-IPr (0.2 g, 0.25 mmol, 5 mol%), K_2CO_3 (2.48 g, 18 mmol) and dioxane (25 mL) under argon and anhydrous conditions. The mixture was stirred at r.t. for 1 h, then 4-fluorophenylboronic acid (**2b**; 0.7 g, 5 mmol) was added and the solution was refluxed for 36 h. Sat. aq $NaHCO_3$ (80 mL) was added and the crude product was extracted with CH_2Cl_2 (100 mL). The extract was dried over $MgSO_4$ and purified by column chromatography [R_f = 0.26 (pentane–CH_2Cl_2, 99:1)]. This afforded colorless crystals; yield: 0.74 g (2.24 mmol, 45%); mp 56 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04–7.18 (m, 5 H), 7.61 (d, *J* = 8.9 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.3 (d, $^2J_{C\text{-}F}$ = 22 Hz, 2 Ar*C*H), 124.7 (2 *C*Br), 130.04 (2 Ar*C*H), 131.04 (d, $^3J_{C\text{-}F}$ = 8.2 Hz, 2 Ar*C*H), 131.87 (Ar*C*H), 137.01 (ArC_q), 142.02 (ArC_q), 162.77 (d, $^1J_{C\text{-}F}$ = 243 Hz, Ar*C*F).

HRMS: *m*/*z* calcd for $C_{12}H_7Br_2F$: 327.889; found: 327.890.

2,6-Dibromo-4′-methoxybiphenyl (3c)
A 100-mL nitrogen flask was charged with 2,6-dibromoiodobenzene (**1a**; 1.8 g, 5 mmol), PEPPSI-IPr (0.17 g, 0.25 mmol, 5 mol%), K_2CO_3 (2.48 g, 18 mmol) and dioxane (25 mL) under argon and anhydrous conditions. The mixture was stirred at r.t. for 1 h, then 4-methoxyphenylboronic acid (**2c**; 0.76 g, 5 mmol) was added and the solution was refluxed for 36 h. Sat. aq $NaHCO_3$ (80 mL) was added and the crude product was extracted with CH_2Cl_2 (100 mL). The extract was dried over $MgSO_4$ and purified by column chromatography [R_f = 0.1 (hexane–CH_2Cl_2, 95:5)]. This afforded colorless crystals; yield: 0.83 g (2.43 mmol, 49%); mp 60 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 6.97 (d, *J* = 8.7 Hz, 2 H), 7.03 (t, *J* = 8.05 Hz, 1 H), 7.13 (d, *J* = 8.4 Hz, 2 H), 7.60 (d, *J* = 7.9 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.2 (O*C*H$_3$), 113.5 (2 Ar*C*H), 125.2 (2 *C*Br), 129.7 (ArC_q), 130.4 (2 Ar*C*H), 131.8 (2 Ar*C*H), 133.7 (Ar*C*H), 142.7 (ArC_q), 159.2 (*C*O).

HRMS: *m*/*z* calcd for $C_{13}H_{10}Br_2O$: 339.909; found: 339.911.

2,6-Dibromo-4′-(trifluoromethyl)biphenyl (3d)
Into a 100-mL nitrogen flask were placed 2,6-dibromoiodobenzene (**1a**; 0.362 g, 1 mmol), PEPPSI-IPr (0.1 g, 0.15 mmol, 15 mol%), K_2CO_3 (0.42 g, 3 mmol) and dioxane (10 mL) under argon and anhydrous conditions. The mixture was stirred at r.t. for 1 h, then 4-(trifluoromethyl)phenylboronic acid (**2d**; 0.19 g, 1 mmol) was added and the solution was refluxed for 36 h. Sat. aq $NaHCO_3$ (20 mL) was added and the crude product was extracted with CH_2Cl_2 (60 mL). The extract was dried over $MgSO_4$ and subsequently purified by preparative GC. This afforded colorless crystals; yield: 0.07 g (0.18 mmol, 18%); mp 46 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (t, *J* = 8.1 Hz, 1 H), 7.33 (d, *J* = 8 Hz, 2 H), 7.63 (d, *J* = 8.1 Hz, 2 H), 7.71 (d, *J* = 8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.75 ($^1J_{C\text{-}F}$ = 273 Hz, *C*F$_3$), 124.0 (2 *C*Br), 125.3 ($^3J_{C\text{-}F}$ = 4 Hz, 2 Ar*C*H), 129.8 (2 Ar*C*H), 130.1

($^2J_{C-F}$ = 32 Hz, ArC_q), 131.1 (2 Ar*C*H), 132.9 (Ar*C*H), 141.7 (ArC_q), 144.5 (ArC_q).

HRMS: *m*/*z* calcd for $C_{13}H_7Br_2F_3$: 377.886; found: 377.885.

2,6-Dibromo-4-fluorobiphenyl (3e)

Into a 100-mL nitrogen flask were placed 2,6-dibromo-4-fluoroiodobenzene (**1b**; 1.9 g, 5 mmol), PEPPSI-IPr (0.17 g, 0.25 mmol, 5 mol%), K_2CO_3 (2.1 g, 15 mmol) and dioxane (25 mL) under argon and anhydrous conditions. The mixture was stirred at r.t. for 1 h, then phenylboronic acid (**2a**; 0.6 g, 5 mmol) was added and the solution was refluxed for 36 h. Sat. aq $NaHCO_3$ (80 mL) was added and the crude product was extracted with CH_2Cl_2 (100 mL). The extract was dried over $MgSO_4$ and purified by column chromatography [R_f = 0.35 (hexane–CH_2Cl_2, 9:1)]. This afforded colorless crystals; yield: 0.96 g (2.9 mmol, 58%); mp 110 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 7.3 Hz, 2 H), 7.4–7.5 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.4 ($^2J_{C-F}$ = 23 Hz, 2 Ar*C*H), 124.4 (2 *C*Br), 128.3 (3 Ar*C*H), 129.4 (2 Ar*C*H), 139.4 ($^4J_{C-F}$ = 4 Hz, ArC_q), 140.3 (ArC_q), 161.1 ($^1J_{C-F}$ = 254 Hz, Ar*C*F).

HRMS: *m*/*z* calcd for $C_{12}H_7Br_2F$: 327.889; found: 327.890.

2,6-Bis(phenylethynyl)biphenyl (4a)

To a stirred mixture of **3a** (0.312 g, 1 mmol) and $(Ph_3P)_2PdCl_2$ (0.105 g, 0.15 mmol) in THF (15 mL) under argon atmosphere and anhydrous conditions was added phenylethynylmagnesium bromide [prepared beforehand from ethynylmagnesium bromide (1 equiv) and phenylacetylene (**6a**, 6 mmol) by transmetalation at –40 °C]. The solution was refluxed for 48 h. Then, NH_4Cl (50 mL) was added to the dark brown solution and the mixture was extracted with CH_2Cl_2 (150 mL). The crude product was purified by preparative HPLC (MeCN–H_2O, 80:20; 3 mL/min; 220 nm). This afforded a pale yellow, viscous oil; yield: 0.19 g (0.53 mmol, 53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.1–7.2 (m, 10 H), 7.24 (t, *J* = 8 Hz, 1 H), 7.34–7.43 (m, 3 H), 7.52–7.55 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 88.9 (2 CCAr), 92.9 (2 CCAr), 123.2 (2 ArC_q), 123.3 (2 ArC_q), 127.1 (Ar*C*H), 127.4 (Ar*C*H), 127.7 (2 Ar*C*H), 128.2 (6 Ar*C*H), 130.4 (2 Ar*C*H), 131.4 (4 Ar*C*H), 132.1 (2 Ar*C*H), 139.1 (ArC_q), 146.4 (ArC_q).

HRMS: *m*/*z* calcd for $C_{28}H_{18}$: 354.140; found: 354.139.

4′-Fluoro-2,6-bis(4-fluorophenylethynyl)biphenyl (4b)

To a stirred mixture of **3b** (0.330 g, 1 mmol) and $(Ph_3P)_2PdCl_2$ (0.105 g, 0.15 mmol) in THF (15 mL) under argon atmosphere and anhydrous conditions was added 4-fluorophenylethynylmagnesium bromide [prepared beforehand from ethynylmagnesium bromide (1 equiv) and 4-fluorophenylacetylene (**6b**, 6 mmol) by transmetalation at –40 °C]. The solution was refluxed for 48 h. Then, NH_4Cl (50 mL) was added to the dark brown solution and the mixture was extracted with CH_2Cl_2 (150 mL). The crude product was purified by flash column chromatography with silica gel [R_f = 0.18 (hexane–CH_2Cl_2, 95:5)] to provide a pale yellow solid; conversion almost complete (probable spectroscopically invisible impurity); mp 82 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.96 (t, *J* = 8.6 Hz, 4 H), 7.1–7.2 (m, 6 H), 7.34 (t, *J* = 7.5 Hz, 1 H), 7.5 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 88.2 (2 CCAr), 92.1 (2 CCAr), 114.3 ($^2J_{C-F}$ = 21 Hz, 2 Ar*C*H), 115.6 ($^2J_{C-F}$ = 22 Hz, 4 Ar*C*H), 119.05 ($^4J_{C-F}$ = 3 Hz, 2 Ar*C*H], 123.3 (2 ArC_q), 127.4 (Ar*C*H), 131.3 (ArC_q), 132.1 (2 Ar*C*H), 133.2 ($^3J_{C-F}$ = 8 Hz, 2 Ar*C*H), 135.0 (2 Ar*C*H), 145.0 (ArC_q), 161.3 ($^1J_{C-F}$ = 245 Hz, 2 Ar*C*F), 163.8 ($^1J_{C-F}$ = 248 Hz, Ar*C*F).

HRMS: *m*/*z* calcd for $C_{28}H_{15}F_3$: 408.113; found: 408.112.

2,6-Bis(4-fluorophenylethynyl)biphenyl (4c)

To a stirred mixture of **3a** (0.312 g, 1 mmol) and $Pd_2(dba)_3$ (0.137 g, 0.15 mmol) in THF (10 mL) under argon atmosphere and anhydrous conditions was added 4-fluorophenylethynylmagnesium bromide [prepared beforehand from ethynylmagnesium bromide (1 equiv) and 4-fluorophenylacetylene (**6b**, 6 mmol) by transmetalation at –40 °C]. The solution was refluxed for 48 h. Then, NH_4Cl (50 mL) was added to the dark brown solution and the mixture was extracted with CH_2Cl_2 (150 mL). The crude product was purified by flash column chromatography with silica gel [R_f = 0.36 (cyclohexane–CH_2Cl_2, 95:5)] to provide a pale yellow, viscous oil; yield: 0.057 g (0.15 mmol, 15%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.93 (t, *J* = 8.8 Hz, 4 H), 7.12–7.16 (m, 4 H), 7.30 (t, *J* = 8.8 Hz, 1 H), 7.4–7.5 (m, 3 H), 7.56–7.58 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 88.5 (2 *C*CAr), 91.9 (2 C*C*Ar), 115.5 ($^2J_{C-F}$ = 21 Hz, 4 Ar*C*H), 119.2 ($^4J_{C-F}$ = 4 Hz, 2 ArC_q), 123.1 (2 ArC_q), 127.1 (Ar*C*H), 127.4 (Ar*C*H), 127.7 (2 Ar*C*H), 130.3 (2 Ar*C*H), 132.0 (2 Ar*C*H), 133.3 ($^3J_{C-F}$ = 8.5 Hz, 4 Ar*C*H), 139.1 (ArC_q), 146.4 (ArC_q), 163.7 ($^1J_{C-F}$ = 250 Hz, 2 Ar*C*F).

HRMS: *m*/*z* calcd for $C_{28}H_{16}F_2$: 390.122; found: 390.121.

4′-Fluoro-2,6-bis(phenylethynyl)biphenyl (4d)

To a stirred mixture of **3b** (0.330 g, 1 mmol) and $(Ph_3P)_2PdCl_2$ (0.105 g, 0.15 mmol) in THF (10 mL) under argon atmosphere and anhydrous conditions was added phenylethynylmagnesium bromide [prepared beforehand from ethynylmagnesium bromide (1 equiv) and phenylacetylene (**6a**, 6 mmol) by transmetalation at –40 °C]. The solution was refluxed for 48 h. Then, NH_4Cl (50 mL) was added to the dark brown solution and the mixture was extracted with CH_2Cl_2 (150 mL). The crude product was purified by flash chromatography [R_f = 0.17 (hexane–CH_2Cl_2, 95:5)] to provide a pale yellow, viscous oil; yield: 0.148 g (0.40 mmol, 40%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.1–7.3 (m, 5 H, ArH), 7.5–7.6 (m, 12 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 88.6 (2 CCAr), 93.1 (2 CCAr), 114.5 ($^2J_{C-F}$ = 21 Hz, 2 Ar*C*H), 123.0 (2 ArC_q), 123.4 (2 ArC_q), 127.2 (2 Ar*C*H), 128.3 ($^3J_{C-F}$ = 6 Hz, 3 Ar*C*H), 129.4 (4 Ar*C*H), 131.4 (4 Ar*C*H), 132.1 (2 Ar*C*H), 135.0 (ArC_q), 145.1 (ArC_q), 163.7 ($^1J_{C-F}$ = 243 Hz, Ar*C*F).

HRMS: *m*/*z* calcd for $C_{28}H_{17}F$: 372.131; found: 372.130.

4,10-Diphenylpyrene (5a)

Biphenyl **4a** (118 mg, 0.6 mmol) and $PtCl_2$ (40 mg, 0.6 mmol) were placed in a nitrogen flask, and degassed and purged with argon. Anhyd toluene (3 mL) was added and the mixture was heated at reflux for 20 h. The reaction mixture was filtered through Celite® and the dark brown solid was purified by preparative HPLC (MeCN–H_2O, 80:20; 3 mL/min; 220 nm) and sublimation [UHV (10^{-6} mbar), heating with a heat gun]. This afforded a pale yellow solid; yield: 28 mg (0.08 mmol, 13%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.47–7.58 (m, 8 H, 8 ArH), 7.65–7.7 (m, 4 H, 4 pyrene-H), 8.03–8.05 (m, 2 H, 2 pyrene-CH), 8.18–8.24 (m, 4 H, 2 pyrene-H, 2 ArH).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 124.1 (Ar*C*H), 125.0 (Ar*C*H), 127.5 (Ar*C*H), 128.7 (Ar*C*H), 130.1 (Ar*C*H), 130.6 (C_q), 131.8 (C_q), 139.7 (C_q), 140.9 (C_q).

HRMS: *m*/*z* calcd for $C_{28}H_{18}$: 354.141; found: 354.142.

2-Fluoro-4,10-bis(4-fluorophenyl)pyrene (5b)

Fluorinated biphenyl **4b** (122 mg, 0.3 mmol) and $PtCl_2$ (8 mg, 0.03 mmol) were placed in a nitrogen flask, and degassed and purged with argon. Anhyd toluene (1.5 mL) was added and the mixture was heated at reflux for 20 h. The reaction mixture was filtered through Celite® and the dark brown solid was purified by preparative HPLC (MeCN–H_2O, 80:20; 3 mL/min; 220 nm) and then sublimation

[UHV (10^{-6} mbar) heating with a heat gun]. The NMR spectra were not analyzed because of unidentified side products.

HRMS: *m*/*z* calcd for $C_{28}H_{15}F_3$: 408.112; found: 408.112 (the fragmentation pattern of the mass spectrum unambiguously supports the assignment of **5b**).

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