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Synthesis of 2- and 2,7-Functionalized Pyrene Derivatives: An Application of Selective C–H Borylation

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Abstract: An efficient synthetic route to 2- and 2,7-substituted pyrenes is described. The regiospecific direct C–H borylation of pyrene with an iridium-based catalyst, prepared in situ by the reaction of [{Ir(μ-OMe)cod}$_2$] (cod = 1,5-cyclooctadiene) with 4,4′-di-*tert*-butyl-2,2′-bipyridine, gives 2,7-bis(Bpin)pyrene (**1**) and 2-(Bpin)pyrene (**2**, pin = $OCMe_2CMe_2O$). From **1**, by simple derivatization strategies, we synthesized 2,7-bis(R)-pyrenes with R = BF_3K (**3**), Br (**4**), OH (**5**), $B(OH)_2$ (**6**), and OTf (**7**). Using these nominally nucleophilic and electrophilic derivatives as coupling partners in Suzuki–Miyaura, Sonogashira, and Buchwald–Hartwig cross-coupling reactions, we obtained 2,7-bis(R)-pyrenes with R = (4-$CO_2C_8H_{17}$)C_6H_4 (**8**), Ph (**9**), C≡CPh (**10**), C≡C[{4-B(Mes)$_2$}C_6H_4] (**11**), C≡CTMS (**12**), C≡C[(4-NMe_2)C_6H_4] (**14**), C≡CH (**15**), N(Ph)[(4-OMe)C_6H_4] (**16**), and R = OTf, R′ = C≡CTMS (**13**). Lithiation of **4**, followed by reaction with CO_2, yielded pyrene-2,7-dicarboxylic acid (**17**), whilst borylation of 2-*t*Bu-pyrene gave 2-*t*Bu-7-Bpin-pyrene (**18**) selectively. By similar routes (including Negishi cross-coupling reactions), monosubstituted 2-R-pyrenes with R = BF_3K (**19**), Br (**20**), OH (**21**), $B(OH)_2$ (**22**), [4-B(Mes)$_2$]C_6H_4 (**23**), B(Mes)$_2$ (**24**), OTf (**25**), C≡CPh (**26**), C≡CTMS (**27**), (4-CO_2Me)C_6H_4 (**28**), C≡CH (**29**), $C_3H_6CO_2Me$ (**30**), $OC_3H_6CO_2Me$ (**31**), $C_3H_6CO_2H$ (**32**), $OC_3H_6CO_2H$ (**33**), and $O(CH_2)_{12}Br$ (**34**) were obtained from **2**. These derivatives are of synthetic and photophysical interest because they contain donor, acceptor, and conjugated substituents. The crystal structures of compounds **4**, **5**, **7**, **12**, **18**, **19**, **21**, **23**, **26**, and **28–31** have also been obtained from single-crystal X-ray diffraction data, revealing a diversity of packing modes, which are described in the Supporting Information. A detailed discussion of the structures of **1** and **2**, their polymorphs, solvates, and co-crystals is reported separately.

Keywords: C–H activation · cross-coupling · fluorescence · polycyclic aromatic · sensors

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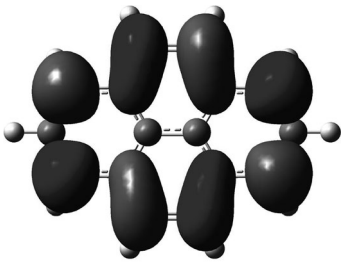
Introduction

Pyrene is a fundamental polycyclic aromatic system that can undergo stacking by π–π interactions, both in solution and in the solid state, and also an important chromophore.[1] The π–π interactions between pyrene and carbon nanotubes have allowed its derivatives to be used to solubilize and disentangle nanotubes,[2a–c] as well as to attach external substrates, such as molecular magnets, quantum dots, porphyrins, and enzymes.[2d–h] Discotic liquid crystals make use of the stacking ability of pyrene derivatives.[3] Polypyrene dendrimers with interesting photophysical properties also benefit from the rigid structure of the pyrene units, leading to a strongly twisted 3D structure because of the steric hindrance upon coupling two pyrene units at the 1-position.[4] Pyrene also displays a long fluorescence lifetime of τ = 354 ns (in toluene) and its emission is very sensitive to changes in the local environment. The π–π interactions between molecules of pyrene can lead to the formation of excimers, which display different luminescence behavior to the monomer, an important property, e.g., for the detection of

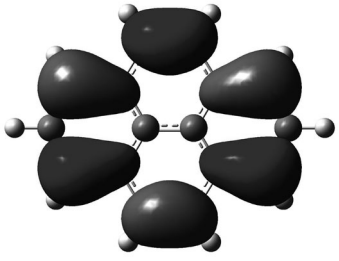
toxic metals.[5] Pyrene-based chromophores have also been widely used as fluorescent labels for nucleic acids.[6]

Pyrene derivatives that are substituted at the 2- and 7-positions are of particular interest because the few examples known exhibit useful properties. The long axis of 2,7-pyrene derivatives makes them attractive for the synthesis of metal–organic frameworks (MOFs) and covalent organic frameworks (COFs), which require rigid, linear linkers.[7] An MOF consisting of zinc ions linked by 2,7-bis(carboxylato)-pyrenes (compare compound **17**) was found to adsorb molecular hydrogen with high uptake.[7b] The optoelectronic properties of several COFs, synthesized from pyrene-2,7-bis(boronic acid) (**6**), have been studied.[7c,d] Pyrene with two ethynyl triptycyl groups attached at the 2,7-positions has been examined as a molecular rotor, the molecule undergoing frictional rotation at temperatures as low as 25 K.[8] Symmetrical star-shaped molecules, designed to investigate energy transfer and storage in chromophore aggregates, have also been synthesized from 2,7-substituted pyrenes.[9]

However, owing to the fact that nodal planes pass through the 2,7-positions in both the HOMO and the LUMO of pyrene (Figure 1), substituents at these positions should exert less perturbation on the electronic properties of the pyrene moiety than substituents at the 1-, 3-, 6-, and 8-positions. For example, calculations and photophysical studies on a 2-substituted pyrene-modified deoxyuridine nucleoside showed that it retained the optical properties of pyrene, with weak electronic coupling to the nucleoside, in contrast to the strong electronic interaction shown by its 1-pyrenyl analogue.[10] Thus, the investigation of electron transfer in DNA benefits from the absence of spectral signals owing to π-orbital overlap of the pyrenyl group with the uracil moiety in the 2-substituted system. Therefore, the assignment of the electron-transfer dynamics in the spectra is much more straightforward. Intriguingly, a DNA duplex containing a 2-pyrenyl-modified deoxyuridine nucleoside, which was located adjacent to a deoxyadenosine nucleoside in the counter strand, showed a significantly blue-shifted long-wavelength absorption maximum and substantially increased fluorescence intensity relative to duplexes in which it was aligned with the other three DNA bases. This result was attributed to base-pairing of the (pyren-2-yl)deoxyuridine with deoxyadenosine, leading to a relocation of the pyrene chromophore out of the DNA helix. Notably, this phenomenon was not observed in analogous duplexes with (pyren-1-yl)deoxyuridine.[10] 2-Phenylethynylpyrenes have also been used as fluorescence labels for DNA and were compared with their 1- and 4-phenylethynyl-substituted counterparts.[11]



LUMO



HOMO

Figure 1. HOMO (bottom) and LUMO (top) of pyrene.

An electrochemical study of oligomers, consisting of two (Pyr_2) and three (Pyr_3) pyrene moieties connected at the 2,7-positions,[12] showed that the first reduction potentials are independent of the number of pyrene units (Pyr_2: $E_1 = -2.24$ eV, Pyr_3: $E_1 = -2.27$ eV). Furthermore, the Coulomb repulsions upon dianion ($E_1 - E_2 = 0.16$ eV) and trianion ($E_2 - E_3 = 0.07$ eV) formation were small. The dianion was found to exist as a diradical with the zero-field splitting almost equal to that in $[Pyr_3]^{2-}$, suggesting that two adjacent pyrene units are charged instead of the two terminal ones. In both of these studies, the electronic interaction between pyrene units connected at the 2- and 7-positions was shown to be very weak.

Despite the increasing interest in and demand for 2,7-substituted pyrenes, relatively few examples have been described in the literature. The difficulty in synthesizing the desired pyrene derivatives results from the presence of nodal planes in both the HOMO and the LUMO (Figure 1), which lie perpendicular to the molecule and pass through the 2- and 7-positions. Maximum contributions of the HOMO can be found at the 1-, 3-, 6-, and 8-carbon atoms; therefore, pyrene derivatives, synthesized by electrophilic aromatic substitution, are substituted at these positions. Reactions at the 2- and 7-positions are only known to take place using $AlCl_3$ and *t*BuCl, as a result of unfavorable steric interactions precluding reactions at the normal 1-, 3-, 6-, and 8-positions.[13]

Alternative synthetic strategies must be employed to obtain other 2- and 2,7-subsituted derivatives. For example, the preparation of 2,7-dimethylpyrene through catalytic oxidation of 5,13-dimethyl[2.2]metacyclophane has been achieved by using Pd/C at 290–310 °C,[14] and several 2-substituted pyrenes have been formed in excellent yields from 5-substituted 8-methoxy[2.2]metaparacyclophane-1,9-dienes by using $TiCl_4$ as a catalyst.[15] However, since these routes involve the laborious preparation of cyclophanes, 2- and 2,7-substituted pyrenes are usually prepared from electrophilic aromatic substitution of the hydrogenated pyrene derivative

4,5,9,10-tetrahydropyrene (THP), followed by subsequent dehydrogenation.[16] Although THP has been prepared through photochemical ring closure of 2,2′-divinylbiphenyl,[12,17] the most common routes involve the hydrogenation of pyrene, either with hydrogen gas and catalytic Pd/C or with lithium in ammonia (Birch reduction). The Pd-catalyzed preparation of THP can now be achieved in good yields,[11b,16g] but it requires prior purification of the commercial pyrene by column chromatography or stirring over Raney nickel, the use of elevated pressures and extended reaction times (64–72 h), and the separation of the product from side products by column chromatography. In contrast, the alternative route involves an initial Birch reduction of pyrene to 1,9-dihydropyrene, followed by an acid-mediated isomerization to form 4,5-dihydropyrene, and then another Birch reduction, the reaction time of which has to be carefully monitored to prevent over-reduction.[16e] Both pyrene and 4,5-dihydropyrene must be purified by column chromatography prior to the reduction to give satisfactory conversions, and the THP product also needs to be separated from unreacted starting materials by charge-transfer chromatography. Notably, a report exists of the small-scale photochemical reduction of pyrene to THP in reasonable yield using an excess of triethylamine and triphenyltin hydride without generation of any other hydrogenated side products.[18] We note that THP is commercially available, but that current prices make it a rather unattractive starting material.

More recently, as part of our work on the metal-catalyzed borylation of aromatic C–H and C–X bonds,[19] we reported the direct Ir-catalyzed borylation of the C–H bonds at the 2- and 7-positions of pyrene, giving 2,7-bis(Bpin)pyrene (**1**) and 2-(Bpin)pyrene (**2**, pin = $OCMe_2CMe_2O$).[20] The catalyst,[21] prepared in situ by the reaction of [{Ir(μ-OMe)cod}$_2$] with 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy), is known to borylate arenes selectively at unhindered positions, that is, not *ortho* to a substituent or ring junction.[19g] The sterically driven selectivity is attributed to the crowded nature of the five-coordinate trisboryl species [Ir(dtbpy)(Bpin)$_3$], which is the key intermediate in the catalytic cycle responsible for the C–H activation step.[19g]

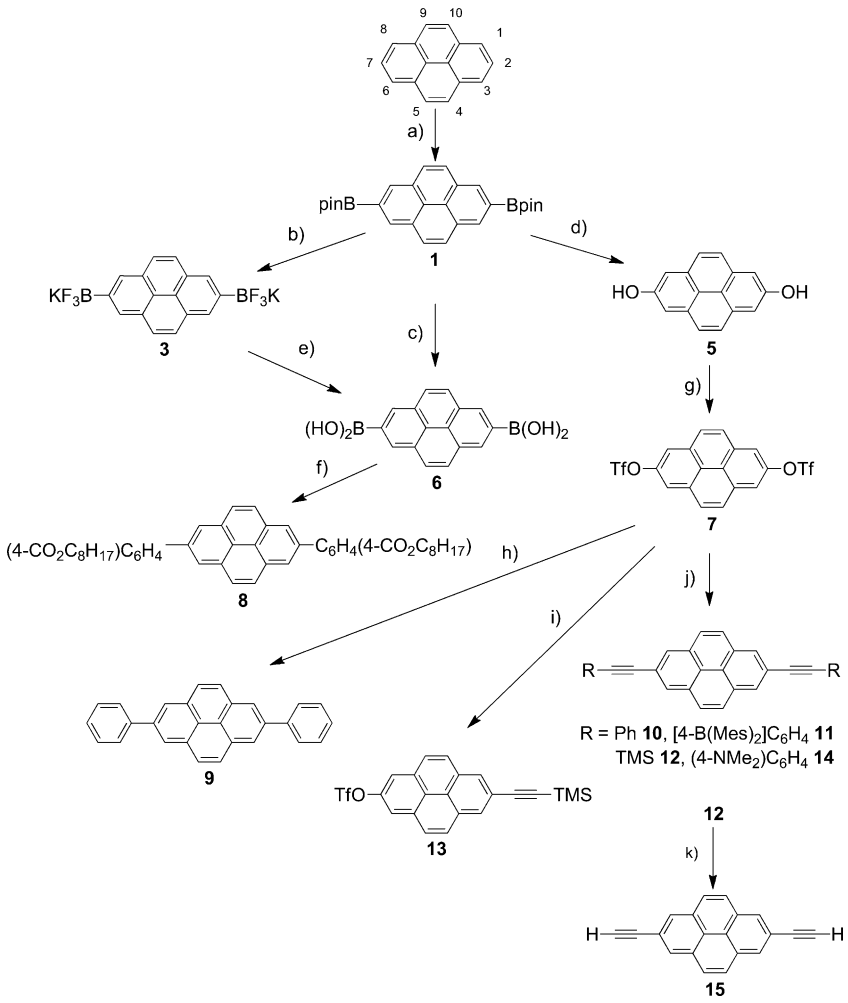
Our one-step, high-yielding synthesis of **1** and **2** directly from pyrene provides a straightforward entry point for the preparation of 2- and 2,7-substituted pyrene derivatives. Indeed, while our work was in progress, several groups employed **1** or **2** directly in Suzuki–Miyaura coupling reactions, although yields were typically low and conditions rather harsh.[22] In addition, both compounds have been used in the preparation of mono- and digold(I) complexes.[23] Herein, we report the synthesis and characterization of a library of 2-mono- and 2,7-bisfunctionalized pyrenes by efficient conversion of the boronic esters **1** and **2** to derivatives that can serve as nucleophilic or electrophilic partners in cross-coupling reactions. We demonstrate the utility of this approach through Suzuki–Miyaura, Sonogashira, Buchwald–Hartwig and Negishi cross-coupling reactions, leading to synthetically and photophysically interesting systems. In a separate paper,[24] we presented, in detail, the photophysical properties of the pyrene derivatives obtained by our methodology and provided a discussion of theoretical approaches to understand the nature of the electronic transitions in these systems.

Results and Discussion

Synthesis and Characterization: The regiocontrolled C–H borylation of pyrene to give **1** and **2** can be carried out on multigram scales and with much lower catalyst loadings (1 mol% [{Ir(μ-OMe)cod}$_2$]) than we initially reported.[20a] The reaction of pyrene with 2.2 equivalents of B_2pin_2 in THF at 80°C for 16 h gave **1** in 94% isolated yield (Scheme 1 a), which is only marginally lower than that obtained previously with a 5 mol% catalyst loading (97%).[20a] In the case of **2**, competing disubstitution to give **1** lowers the yield of the monosubstituted product. However, the reaction of pyrene with 1.1 equivalents of B_2pin_2 in the less polar solvent hexane at 80°C for 16 h improves selectivity, leading to a higher isolated yield (65%) of **2** after column chromatography (Scheme 3 b), again only slightly lower than when a 5 mol% catalyst loading was used (68%). Borylation of 2-*tert*-butylpyrene[13] in hexane gave 2-*t*Bu-7-Bpinpyrene (**18**) in 85% isolated yield (Scheme 3 a).

Although aryl boronate esters have been used extensively in Suzuki–Miyaura cross-coupling reactions,[25] we found **1** and **2** to exhibit unusually low reactivity. While our work was in progress, **2** was successfully coupled to 5-iodo-2′-deoxyuridine using large amounts of a [$PdCl_2$(dppf)] as catalyst (>10 mol%).[10] Very recently, **1** has been coupled to various aryl bromides in low to moderate yields using 3–10 mol% [$Pd(PPh_3)_4$] in toluene at 90–110°C in the presence of phase-transfer reagents.[22] Our approaches to prepare pyrene derivatives from **1** and **2** are summarized in Schemes 1–4. All reactions were monitored by GC-MS and ^{1}H NMR spectroscopy, and the isolated compounds were fully characterized. Whilst several of these compounds are known, previously reported characterization data for them are sparse. The crystal structures of compounds **4**, **5**, **7**, **12**, **18**, **19**, **21**, **23**, **26**, and **28**–**31** have also been obtained from single-crystal X-ray diffraction data, revealing a diversity of packing modes, which are described in the Supporting Information. A detailed discussion of the structures of **1** and **2**, their polymorphs, solvates, and co-crystals will be reported separately.[26]

We converted the boronate esters **1** and **2** to their corresponding boronic acids **6**[7c] and **22**[27] in 78 and 80% yields, respectively, using $NaIO_4$ in THF/H_2O (Schemes 1 c and 3 e).[28] We found the boronic acids to be more reactive than the Bpin esters towards Suzuki–Miyaura cross-coupling reactions. Compound **6** was coupled to 2 equivalents of *n*-octyl 4-bromobenzoate in DMF at 80°C by using 7 mol% [$PdCl_2$(dppf)] and anhydrous K_3PO_4 as a base to give pyrenyl-2,7-bis[4-(benzoic acid *n*-octyl ester)] (**8**, 75% yield, Scheme 1 f). Analogously, **22** was coupled to methyl 4-iodobenzoate under similar conditions, but with only 2 mol%



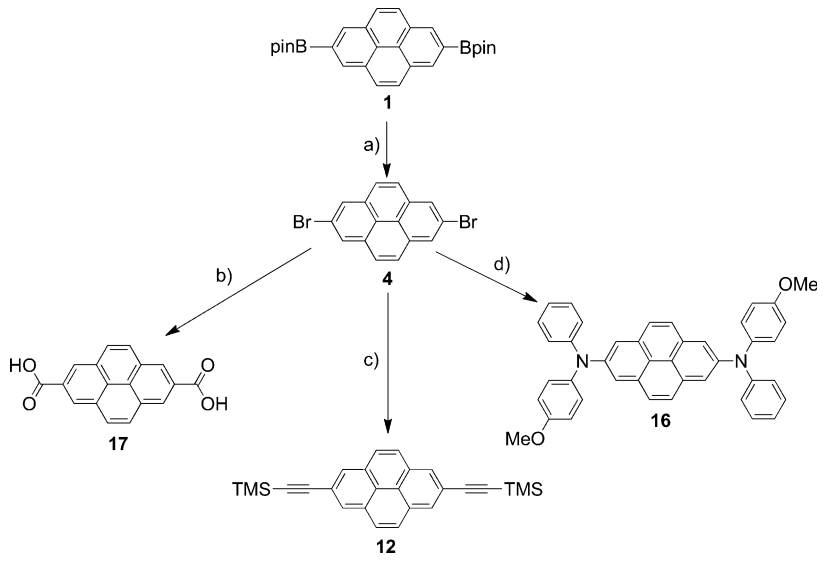
Scheme 1. a) B_2pin_2 (2.2 equiv), [{Ir(μ-OMe)cod}$_2$] (1 mol%), dtbpy (2 mol%), THF, 80°C, 16 h, 94%; b) KHF_2 (12 equiv), THF/H_2O (3:1), RT, 16 h, 79%; c) $NaIO_4$ (8 equiv), THF/H_2O (4:1), RT, 48 h, 78%; d) H_2O_2 (6 equiv), NaOH (6 equiv), THF/H_2O, RT, 4 h, 89%; e) LiOH·H_2O (18 equiv), THF/H_2O (5:1), RT, 16 h, 89%; f) 1-Br-(4-$CO_2C_8H_{17}$)C_6H_4 (2 equiv), [$PdCl_2$(dppf)] (7 mol%), K_3PO_4 (5 equiv), DMF, 80°C, 72 h, 75%; g) Tf_2O (6 equiv), pyridine/hexane (3:1), −10°C to RT, 16 h, 60%; h) $PhB(OH)_2$ (2 equiv), [$PdCl_2$(dppf)] (3 mol%), K_3PO_4 (3 equiv), DMF/H_2O (19:1), 80°C, 16 h, 79%; i) TMSA (2 equiv), [$PdCl_2(PPh_3)_2$] (3 mol%), CuI (2 mol%), DMF/Et_3N (2:1), 80°C, 16 h, 22%; j) HC≡CR [R = Ph, [4-B(Mes)$_2$]C_6H_4, TMS, (4-NMe_2)C_6H_4] (2 equiv), [$PdCl_2(PPh_3)_2$] (3 mol%), CuI (2–3 mol%), DMF/Et_3N (2:1), 80°C, 16 h, 50, 31, 51, and 40%; k) Na_2CO_3 (7.5 equiv), MeOH/H_2O (10:1), RT, 16 h, 86%.

[$PdCl_2$(dppf)], to afford 4-(pyren-2-yl)benzoic acid methyl ester (**28**) in 60% yield (Scheme 3 k). The addition of H_2O to increase the solubility of the K_3PO_4 in the synthesis of **8** reduced the yield to 12%.

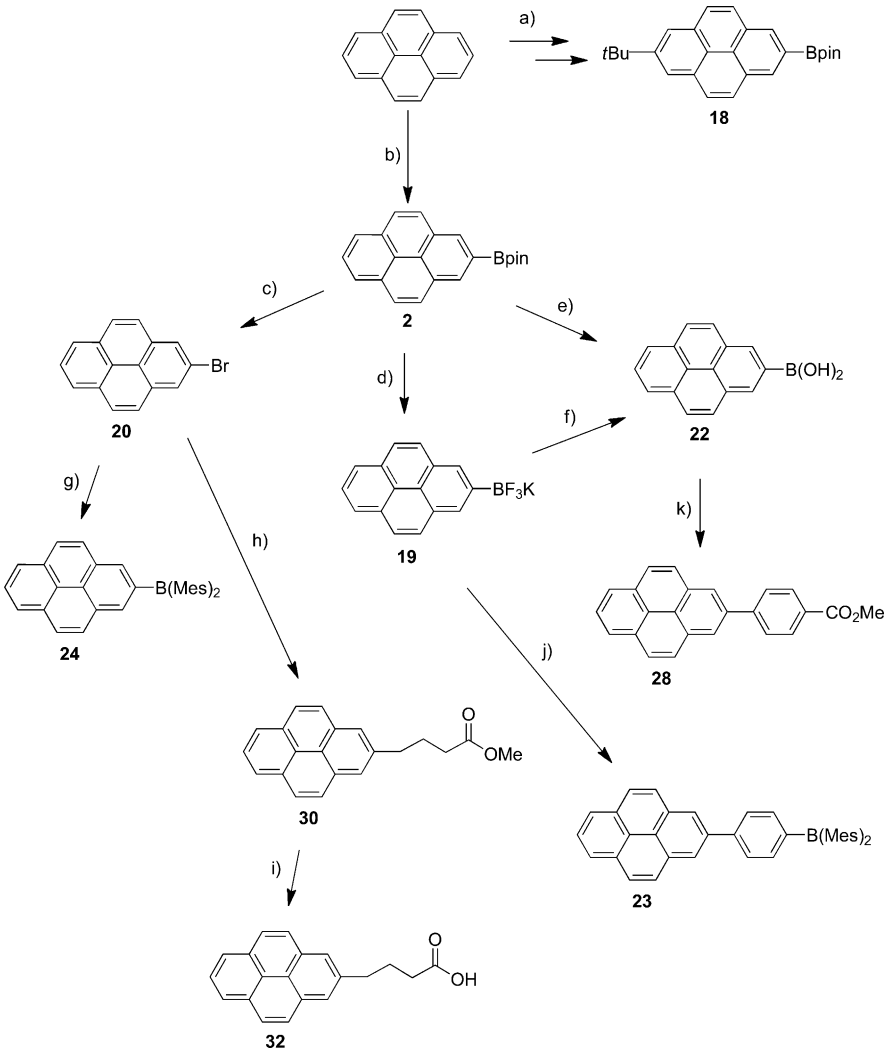
The boronic acids **6** and **22** show evidence (MALDI-TOF MS) of condensation to form oligomers,[7c,d] as is usual for arylboronic acids. Therefore, we also prepared their respective potassium trifluoroborates because such compounds have been shown to be efficient reagents in Suzuki–Miyaura cross-couplings.[29] The reaction of **1** with KHF_2 in THF/H_2O at room temperature[30] gave poorly soluble K_2-[2,7-(BF_3)$_2$pyrene] (**3**)[31] with complete conversion, as shown by in situ NMR spectroscopy (Scheme 1 b). The addition of 6 equivalents of [18]crown-6 to the reaction mixture resulted in the isolation of soluble **3**·1.5([18]crown-6) (**3b**) in 70% yield. The reaction of **2** with 4 equivalents of KHF_2 in refluxing MeOH/H_2O (2:1) for 1 h gave K[2-(BF_3)-pyrene] (**19**) in an excellent yield of 94% after recrystallization from EtOH (Scheme 3 d). The reaction of **3** and **19** at room temperature with 18 and 2 equivalents, respectively, of LiOH·H_2O in THF/H_2O (4:1), followed by acidification, provided an alternative route[30] to the boronic acids **6** and **22** in slightly higher yields (89 and 85%, respectively, Schemes 1 e and 3 f) and with easier purification relative to their preparation by the oxidation of **1** and **2**.

π-Conjugated organic compounds, containing three-coordinate boron centers, have had a significant impact in the area of materials chemistry[32] because these functional molecular and polymeric materials display useful linear, nonlinear, and electro-optical properties. Thus, they have potential applications in organic light-emitting diodes (OLEDs), sensors, solar cells, and other optical materials. For these reasons, our group has been examining the linear and nonlinear optical properties,[32d,e,33] including two-photon absorption,[34] of species containing dimesitylboron moieties, which serve as efficient π-acceptors.[32,33a–g] With this in mind, we reacted **19** with 1-iodo-4-(dimesitylboryl)benzene at 80°C for 16 h in EtOH by using 1 mol% [$PdCl_2$(dppf)] as catalyst and K_2CO_3 as base to give 2-[4-(dimesitylboryl)phenyl]pyrene (**23**) in a 65% yield after recrystallization, demonstrating the efficient Suzuki–Miyaura cross-coupling of **19** (Scheme 3 j).

All of the above cross-coupling reactions have employed the pyrenyl boron reagent as a masked carbon nucleophile. A complementary approach to employ 2,7-substituted pyrene systems in cross-coupling reactions would be to convert the pyrene compound into an electrophile. Common electrophilic reagents for cross-couplings are aryl halides, and the conversion of aryl boronate esters to the corresponding bromides using $CuBr_2$ has been reported.[35] The reaction of compound **1** with 6 equivalents of $CuBr_2$ at 90°C for 16 h in MeOH/H_2O/THF (3:3:1) gave 2,7-dibromopyrene (**4**, Scheme 2 a), and the analogous reaction of **2** with 3



Scheme 2. a) $CuBr_2$ (6 equiv), MeOH/H_2O/THF (3:3:1), 90 °C, 16 h, 70 %; b) *n*BuLi (8 equiv), CO_2 (excess), Et_2O, −78 °C to RT, H^+, 96 %; c) TMSA (2 equiv), $[PdCl_2(dppf)]$ (4 mol %), CuI (4 mol %), Et_3N/THF (5:2), 80 °C, 16 h, 44 %; d) Ph-N(H)-(4-OMe)C_6H_4 (2.2 equiv), $[Pd_2(dba)_3]$ (6 mol %), P*t*Bu_3 (11 mol %), NaO*t*Bu (6.7 equiv), toluene, 110 °C, 4 h, 92 %.

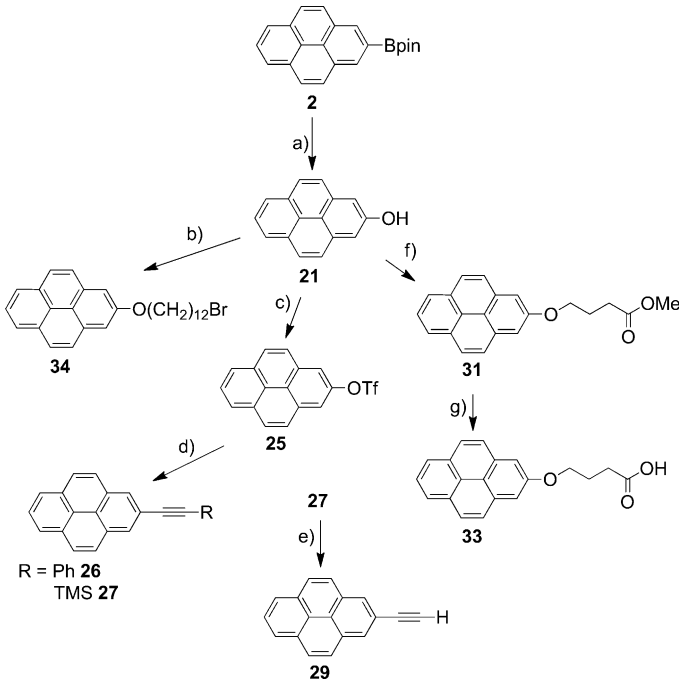


Scheme 3. a) *t*BuCl, $AlCl_3$, CH_2Cl_2, 80 °C, 16 h; then B_2pin_2 (1.3 equiv), [{Ir(μ-OMe)cod}$_2$] (1 mol %), dtbpy (2 mol %), hexane, 80 °C, 16 h, 85 %; b) B_2pin_2 (1.1 equiv), [{Ir(μ-OMe)cod}$_2$] (1 mol %), dtbpy (2 mol %), hexane, 80 °C, 16 h, 65 %; c) $CuBr_2$ (3 equiv), MeOH/H_2O (1:1), 90 °C, 16 h, 83 %; d) KHF_2 (4 equiv), MeOH/H_2O (2:1), 80 °C, 1 h, 94 %; e) $NaIO_4$ (3 equiv), THF/H_2O (4:1), RT, 48 h, 80 %; f) LiOH·H_2O (2 equiv), THF/H_2O (4:1), RT, 20 h, 85 %; g) *n*BuLi (1.3 equiv), Et_2O, −78 °C to RT, 1 h; then $FB(Mes)_2$ (1 equiv), Et_2O, −78 °C to RT, 16 h, 31 %; h) $BrZnC_3H_6CO_2Me$ (1.2 equiv), $[PdCl_2(PPh_3)_2]$ (2 mol %), DMF, RT, 16 h, 74 %; i) LiOH·H_2O (2.5 equiv), THF/H_2O (4:1), RT, 16 h, 80 %; j) 1-I-[4-$B(Mes)_2$]C_6H_4 (1 equiv), $[PdCl_2(dppf)]$ (1 mol %), K_2CO_3 (2 equiv), EtOH, 80 °C, 16 h, 65 %; k) 1-I-(4-CO_2CH_3)C_6H_4 (1 equiv), $[PdCl_2(dppf)]$ (2 mol %), K_3PO_4 (3 equiv), DMF, 80 °C, 16 h, 60 %.

equivalents of $CuBr_2$ in MeOH/H_2O (1:1) gave 2-bromopyrene (**20**, Scheme 3 c). Aryl bromides **4** and **20** were isolated in 70 and 83 % yields, respectively, since they precipitated from the reaction mixture as colorless solids, which were easily purified by filtration and washing with water and hexane. The synthesis of **4** by dehydrogenation of 2,7-dibromo-4,5,9,10-tetrahydropyrene,[16b] as well as the synthesis of **20** from a $TiCl_4$-catalyzed reaction of a [2.2]metaparacyclophane,[15] the dehydrogenation of 2-bromo-4,5,9,10-tetrahydropyrene with *o*-chloranil,[16c] and the reaction of diazotized 2-aminopyrene with hydrobromic acid[36] have been previously reported. However, our method allows the target compounds to be obtained in high yields and in only two simple steps from pyrene, avoiding high-pressure hydrogenation and several additional steps. Very recently, the syntheses of **4** and **20** have been reported by using the same method, although experimental details were not provided.[1] Furthermore, we have carried out the C−H borylation/bromination

sequence as a "one-pot" process,[35] isolating **4** in 70% yield from pyrene. In the analogous one-pot synthesis of **20**, a mixture of unreacted pyrene and **20** was recovered, which proved difficult to separate. However, this mixture could be used for further reactions, such as cross-couplings, where the separation of the unreacted pyrene from the final products could be easier. The lithiation of 2,7-dibromopyrene **4**, followed by reaction with CO_2, is known to yield pyrene-2,7-dicarboxylic acid (**17**, Scheme 2 b).[7a,b,37] Again, using our route to synthesize **4** reduces the number of reaction steps and gives straightforward access in high yields to a compound that was previously laborious to synthesize. Lithiation of **20** with 1.3 equivalents of *n*BuLi and subsequent addition of 1 equivalent of dimesitylboron fluoride in Et_2O gave 2-(dimesitylboryl)pyrene (**24**) in a moderate yield of 31% (Scheme 3 g). The photophysical properties of **24** were compared with those of 1-(dimesitylboryl)pyrene[38] in our previous paper.[24]

Aryl triflates have also been used as electrophiles in many coupling reactions, and the conversion of boronate esters to alcohols and then triflates is known.[39] The oxidation of **1** at room temperature with H_2O_2/NaOH for 4 h in THF/H_2O gave 2,7-dihydroxypyrene (**5**)[40] in 89% yield (Scheme 1 d); analogously, **2** was converted to 2-hydroxypyrene (**21**) in 84% yield (Scheme 4 a). Compound **21** has been previously prepared in moderate yield from **20** by the formation of its Grignard reagent and subsequent reaction with diborane



Scheme 4. a) H_2O_2 (3 equiv), NaOH (3 equiv), THF/H_2O, RT, 4 h, 84%; b) $Br(CH_2)_{12}Br$ (5 equiv), NaO*t*Bu (1 equiv), DMF, 80°C, 16 h, 72%; c) Tf_2O (3 equiv), pyridine, 0°C to RT, 16 h, 69%; d) HC≡CR [R = Ph, TMS] (1.5, 3.3 equiv), [$PdCl_2(PPh_3)_2$] (3 mol%), CuI (3 mol%), DMF/Et_3N (5:2), 80–90°C, 16 h, 78%, 75%; e) Na_2CO_3 (3.5 equiv), MeOH/H_2O (10:1), RT, 16 h, 81%; f) $BrC_3H_6CO_2Me$ (4.3 equiv), NaO*t*Bu (1.1 equiv), DMF, 80°C, 16 h, 75%; g) LiOH·H_2O (2.5 equiv), THF/H_2O (4:1), RT, 16 h, 66%.

and alkaline H_2O_2.[16c] The π-stacking properties of **5** have been investigated recently after conversion to its more soluble dibenzyl ether, which allowed its complexation with macrocyclic systems.[41] The reaction of **5** and **21** with triflic anhydride in dry pyridine gave 2,7-bis(trifluoromethanesulfonyl)pyrene (**7**) and 2-(trifluoromethanesulfonyl)pyrene (**25**) in 60 and 69% yields, respectively (Schemes 1 g and 4 c).

The synthetic routes demonstrated above not only provided pyrenes substituted with weak π-donors (Br, OH, OTf) or strong π-acceptors (CO_2H, $BMes_2$) at the 2- and 2,7-positions, but also allowed us to expand our library of pyrene compounds and, in particular, to increase the conjugation length of the system by cross-coupling reactions utilizing compounds **7** and **25**. Thus, the Suzuki–Miyaura cross-coupling of **7** with 2 equivalents of phenylboronic acid in DMF/H_2O (19:1) at 80°C for 16 h by using 3 mol% [$PdCl_2$(dppf)] and 3 equivalents of K_3PO_4 afforded 2,7-diphenylpyrene (**9**) in 79% yield (Scheme 1 h). Recently, compound **9** has been synthesized from **1** by a Suzuki–Miyaura cross-coupling reaction,[22b] but the reaction took 36 h and the yield was only 39%.

The Sonogashira cross-coupling reactions of **7** with 2 equivalents of phenylacetylene, 1-ethynyl-4-(dimesitylboryl)-benzene, trimethylsilylacetylene (TMSA), and 4-ethynyl-*N*,*N*-dimethylaniline in a DMF/Et_3N (2:1) mixture for 16 h at 80°C by using 3 mol% [$PdCl_2(PPh_3)_2$] and 2–3 mol% CuI gave the corresponding products 2,7-bis(phenylethynyl)pyrene (**10**), 2,7-bis[4-(dimesitylboryl)phenylethynyl]pyrene (**11**), 2,7-bis(trimethylsilylethynyl)pyrene (**12**), and 2,7-bis[4-(*N*,*N*-dimethylamino)phenylethynyl]pyrene (**14**) in yields of 50, 31, 51, and 40%, respectively (Scheme 1 j). During the work up of compound **12**, we also isolated 2-(trifluoromethanesulfonyl)-7-(trimethylsilylethynyl)pyrene (**13**), as a mono-coupled byproduct, in 22% yield (Scheme 1 i). Further derivatization should be possible through the triflate moiety in **13**, leading to interesting unsymmetrically disubstituted pyrenes. Under similar conditions, the couplings of **25** with 1.5 equivalents of phenylacetylene and 3.3 equivalents TMSA gave 2-(phenylethynyl)pyrene (**26**) and 2-(trimethylsilylethynyl)pyrene (**27**) in 78 and 75% yields, respectively (Scheme 4 d). The synthesis of **27** from **20** has been reported previously, but only MS data were published.[16f] To demonstrate the synthetic value of 2,7-dibromopyrene (**4**) in cross-coupling reactions, it was coupled with 2.1 equivalents of TMSA as an alternative route to **12**. Initially, [$PdCl_2(PPh_3)_2$] was used as the catalyst, but, after overnight heating, incomplete conversion was observed by GC-MS. However, using 4 mol% [$PdCl_2$(dppf)] in Et_3N/THF led to complete conversion after 16 h at 80°C, giving **12** in 44% isolated yield after column chromatography (Scheme 2 c). Hydrodesilylation of **12** and **27** with Na_2CO_3 in MeOH/H_2O gave the terminal alkynes 2,7-diethynylpyrene (**15**) and 2-ethynylpyrene (**29**) in 86 and 81% yields, respectively (Schemes 1 k and 4 e). Compounds **15** and **29** have been synthesized previously from their 2-hydroxyisopropyl-protected analogues through base-induced retro-Favorskii reactions.[42] In addi-

tion, **29** has also been prepared by hydro-desilylation of **27**[16f] and from 2-acetylpyrene by either Vilsmeier–Haack–Arnold transformation and Bodendorf fragmentation[11b] or by dichloro-deoxygenation with PCl_5 and subsequent base-induced HCl elimination.[43]

N,*N*,*N*',*N*'-Tetraaryl-1,1'-biphenyl-4,4'-diamines (TPDs) are an important class of hole transporters for OLEDs.[44] To demonstrate the utility of the Buchwald–Hartwig amination methodology for the synthesis of analogous 2,7-bis(diarylamino)pyrenes, **4** was reacted with 2.2 equivalents of *N*-(4-methoxyphenyl)-*N*-phenylamine in toluene by using 6 mol% [$Pd_2(dba)_3$], 11 mol% P*t*Bu_3, and NaO*t*Bu to give 2,7-bis[*N*-(4-methoxyphenyl)-*N*-phenylamino]pyrene (**16**)[45] in 92% yield (Scheme 2 d). In contrast to the recent report[46] of the synthesis of the 1,6-isomer of **16** from 1,6-dibromopyrene, which employed only [$Pd_2(dba)_3$] without any phosphine ligand as the catalyst, the synthesis of **16** from **4** required a more active catalyst system. Similar to the Sonogashira couplings of **4** (see above), this again demonstrates the lower reactivity of 2,7-dibromopyrene in cross-coupling reactions compared to that of pyrenes substituted at the 1-, 3-, 6-, and 8-positions. Presumably, this results from the fact that neither the HOMO nor the LUMO of pyrene have a contribution at C2 or C7, owing to the presence of nodal planes passing through these carbon atoms.

Commercially available 4-(pyren-1-yl)butyric acid is used to determine oxygen concentrations in biological systems[47] and to investigate intracellular delivery of bioactive molecules.[48] For comparison of their photophysical properties with those of 4-(pyren-1-yl)butyric acid, we synthesized 4-(pyren-2-yl)butyric acid (**32**) and 4-(pyren-2-yloxy)butyric acid (**33**). The 2-pyrenyl derivative **32** has a high fluorescence quantum yield and a longer fluorescence lifetime than the 1-pyrenyl isomer[24] and should thus be even more effective in cellular oxygen sensing. To demonstrate the application of a Negishi coupling reaction, the alkylation of pyrene at the 2-position was performed. Zinc powder and a catalytic amount of iodine were used to form the zinc reagent[49] from 4-bromobutyric acid methyl ester, which was then cross-coupled with **20** at room temperature in DMF by using 2 mol% [$PdCl_2(PPh_3)_2$] to give 4-(pyren-2-yl)butyric acid methyl ester (**30**) in a 74% yield (Scheme 3 h). Deprotonation of **21** with 1.1 equivalents of NaO*t*Bu, followed by the addition of 4-bromobutyric acid methyl ester, gave 4-(pyren-2-yloxy)butyric acid methyl ester (**31**) in 75% yield (Scheme 4 f). Hydrolysis of compounds **30** and **31** in THF/H_2O gave acids **32** and **33** in 80 and 66% yields, respectively (Schemes 3 i and 4 g). Compound **32** has been synthesized previously from (pyren-2-yl)acetaldehyde by a multistep route.[50] Similar to the synthesis of **31**, the reaction of 5 equivalents of 1,12-dibromo-*n*-dodecane with **21** in the presence of NaO*t*Bu gave 2-(12-bromo-*n*-dodecyloxy)pyrene (**34**) in 72% isolated yield (Scheme 4 b). Compound **34** has the potential for further derivatization at the bromo end of the carbon chain to facilitate, for example, the introduction of polar moieties, thus allowing it to be used as a fluorescence probe in biological systems.

Conclusion

Substitution chemistry of pyrenes is typically limited to reactions at the 1-, 3-, 6-, and 8-positions. The reactions at the 2- and 2,7-positions along the main twofold axis of the molecule are normally precluded because both the HOMO and the LUMO have a nodal plane coincident with this axis. However, iridium-catalyzed borylation of pyrene, which is sterically rather than electronically controlled, provides direct access to the useful 2,7-bis(Bpin)pyrene (**1**) and 2-(Bpin)pyrene (**2**) derivatives. These were readily converted in high yields into nominally electrophilic (e.g., Br, OTf) and nucleophilic (e.g., $B(OH)_2$, BF_3K) pyrene derivatives, which were further utilized in Suzuki–Miyaura, Sonogashira, Buchwald–Hartwig, and Negishi cross-coupling reactions. Using this methodology, we prepared a library of 2- and 2,7-substituted pyrenes bearing donor and acceptor groups, including aryl, ethynyl, arylethynyl, alkyl, hydroxy, alkoxy, diarylamino, carboxylic acid, and diarylboryl derivatives.

Our high-yielding methodology provides rapid access to derivatives that maintain the long twofold rotational axis of pyrene and, as such, are expected to be particularly useful in the synthesis of conjugated rigid-rod systems, molecular rotors, and organic and metal–organic frameworks. In addition, the unusually long fluorescence lifetimes of the 2- and 2,7-substituted pyrenes, as discussed in detail in our companion paper,[24] make these compounds well suited for use as fluorescence probes in biological and other systems.

Experimental Section

General methods: Reagents purchased from commercial suppliers were tested for purity before use. Pyrene (Aldrich, 98%) was purified before use by passage through a 5 cm silica plug (eluent: hexane). Dimesitylboron fluoride was obtained by the reaction of mesitylmagnesium bromide with $BF_3{\cdot}OEt_2$[51] and was used to synthesize 1-iodo-4-(dimesitylboryl)-benzene,[33f] which in turn was used to synthesize 1-ethynyl-4-(dimesitylboryl)benzene[52] and 1-Bpin-4-(dimesitylboryl)benzene. The starting materials 2-*tert*-butylpyrene,[13b] *N*-(4-methoxyphenyl)-*N*-phenylamine,[53] 4-ethynyl-*N*,*N*-dimethylaniline,[54] and 4-bromobutyric acid methyl ester[55] were synthesized as previously reported. The reactions were monitored by GC-MS, TLC, or by ^{1}H NMR spectroscopy to assure consumption of starting materials prior to work up. GC-MS analyses were performed on an Agilent Technologies 6890 N gas chromatograph equipped with a 5973 inert mass selective detector and a 10 m fused silica capillary column (5% cross-linked phenylmethylsilicone) by using the following operating conditions: injector temperature 250 °C, detector temperature 300 °C, the oven temperature was ramped from 50 to 300 °C at 20 °C min^{-1}. UHP helium was used as the carrier gas. NMR spectra were recorded on Bruker Avance-400, Varian Mercury-400, Varian Inova-500, and Varian VNMRS-600 and 700 spectrometers at the following frequencies: ^{1}H: 400, 500, and 700 MHz; ^{13}C{^{1}H}: 100, 125, 151, and 176 MHz; ^{19}F{^{1}H}: 376 MHz; ^{11}B{^{1}H}: 128 and 225 MHz. The spectra were obtained at room temperature, unless otherwise stated. It was observed that the chemical shifts of the signals in the ^{1}H NMR spectra often differed by several hundredths of a ppm depending on sample concentration, which is presumably attributable to aggregation effects in solution. Mass spectra were obtained by using a Waters Xevo QTOF equipped with an Atmospheric Solids Analysis Probe (ASAP), a Thermo-Finnigan LTQ FT mass spectrometer for high-resolution ESI spectra, and an Applied Biosystems Voyager-DE STR spectrometer for MALDI-TOF analyses. High-resolu-

tion EI mass spectra were recorded by the EPSRC National Mass Spectrometry Service at Swansea (UK) by using a Finnigan MAT 95 XP spectrometer. Elemental analyses were performed by using an Exeter Analytical E440 machine. Melting points were measured on a Sanyo Gallenkamp apparatus and are uncorrected.

Pyrene-2,7-bis(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane) [2,7-bis(Bpin)pyrene)] (1):[20] In a nitrogen-filled glove box, [{Ir(μ-OMe)cod}$_2$] (0.060 g, 0.09 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy, 0.048 g, 0.18 mmol), and B_2pin_2 (0.10 g, 0.39 mmol) were dissolved in THF (5 mL). The mixture was added to a Young's tube containing pyrene (1.80 g, 8.90 mmol) and B_2pin_2 (4.86 g, 19.1 mmol). After addition of THF (10 mL), the tube was sealed and the reaction mixture was stirred at 80 °C for 16 h. Then, the reaction mixture was passed through a 5 cm silica plug (eluent: CH_2Cl_2) and the solvent was removed under reduced pressure. The pale-yellow residue was purified by sublimation (150 °C at 6×10^{-4} Torr) and then washed with refluxing hexane (100 mL) to afford **1** (3.80 g, 94 %) as a white solid. M.p. 331–333 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.63$ (s, 4H), 8.09 (s, 4H), 1.46 ppm (s, 24H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta=131.3$, 131.0, 127.8, 126.5, 84.4, 25.1 ppm (*C*–B not observed); ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): $\delta=32.1$ ppm; MS (EI): *m/z*: 454 $[M]^+$, 354 $[M-C_6H_{12}O]^+$, 254 $[M-(C_6H_{12}O)_2]^+$, 228 $[M-C_{12}H_{21}BO_3]^+$; HRMS (EI): *m/z* calcd for $C_{28}H_{32}{}^{10}B_2O_4$: 452.2554 $[M]^+$; found: 452.2555; elemental analysis calcd (%) for $C_{28}H_{32}B_2O_4$: C 74.05, H 7.10; found: C 73.78, H 7.22.

4,4,5,5-Tetramethyl-2-pyren-2-yl-[1,3,2]dioxaborolane [2-(Bpin)pyrene] (2):[10,20] In a nitrogen-filled glove box, [{Ir(μ-OMe)cod}$_2$] (0.060 g, 0.09 mmol), dtbpy (0.048 g, 0.18 mmol), and B_2pin_2 (0.10 g, 0.39 mmol) were dissolved in hexane (5 mL). The mixture was added to a Young's tube containing pyrene (2.00 g, 9.89 mmol) and B_2pin_2 (2.79 g, 11.0 mmol). Hexane (10 mL) was added and the tube was sealed. Then, the reaction mixture was stirred at 80 °C for 16 h, at which time no B_2pin_2 was observed by GC-MS. The reaction mixture was passed through a silica plug (eluent: CH_2Cl_2) and the solvent was removed under reduced pressure. Purification of the residue by column chromatography (silica gel, hexane/CH_2Cl_2 1:1) and subsequent recrystallization from hexane afforded **2** (2.10 g, 65 %) as a white solid. M.p. 127–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.64$ (s, 2H), 8.17 (d, $J=8$ Hz, 2H), 8.11 (d, $J=9$ Hz, 2H), 8.06 (d, $J=9$ Hz, 2H), 8.02 (t, $J=8$ Hz, 1H), 1.47 ppm (s, 12H); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): $\delta=132.0$, 131.6, 130.7, 128.1, 127.6, 126.8, 126.6, 125.3, 124.9, 84.6, 25.2 ppm (*C*–B not observed); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): $\delta=31.4$ ppm; MS (EI): *m/z*: 328 $[M]^+$, 313 $[M-CH_3]^+$, 255 $[M-C_4H_9O]^+$, 242 $[M-C_5H_{10}O]^+$, 228 $[M-C_6H_{12}O]^+$, 202 $[M-\text{Bpin}]^+$; HRMS (EI): *m/z* calcd for $C_{22}H_{21}{}^{10}BO_2$: 327.1665 $[M]^+$; found: 327.1662; elemental analysis calcd (%) for $C_{22}H_{21}BO_2$: C 80.51, H 6.45; found: C 80.32, H 6.48.

Pyrene-2,7-bis(trifluoroborate) dipotassium salt (3): Compound **1** (1.50 g, 3.30 mmol) was dissolved in THF (30 mL). To this solution, KHF_2 (3.10 g, 39.7 mmol) in H_2O (10 mL) was added and the mixture was stirred at room temperature for 16 h. Then, the mixture was concentrated under reduced pressure. The precipitate was collected by filtration and washed with H_2O (10 mL) and hexane (50 mL) to give **3** (1.08 g, 79 %) as a white solid. NMR (500 MHz, [D$_6$]DMSO): $\delta=8.13$ (s, 4H), 7.90 ppm (s, 4H); ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]DMSO): $\delta=129.0$, 128.1, 126.3, 123.3 ppm (*C*–B not observed); ^{11}B{^{1}H} NMR (128 MHz, [D$_6$]DMSO): $\delta=3.6$ ppm; ^{19}F{^{1}H} NMR (376 MHz, [D$_6$]DMSO): $\delta=-138.2$ ppm.

[K$_2$([18]crown-6)$_{1.5}$] [pyrene-2,7-bis(trifluoroborate)] (3b): Compound **1** (0.10 g, 0.22 mmol) and [18]crown-6 (0.35 g, 1.3 mmol) were dissolved in THF (20 mL). To this solution, KHF_2 (0.10 g, 1.3 mmol) in H_2O (20 mL) was added and the mixture was stirred at room temperature for 16 h. The precipitate was collected by filtration and washed with acetone (3×10 mL), affording **3b** (0.13 g, 70 %) as a white solid. M.p. 286–288 °C; ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta=8.12$ (s, 4H), 7.90 (s, 4H), 3.54 ppm (s, 36H); ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]DMSO): $\delta=129.0$, 128.1, 126.3, 123.3, 69.4 ppm (*C*–B not observed); ^{11}B{^{1}H} NMR (128 MHz, [D$_6$]DMSO): $\delta=4.0$ ppm; ^{19}F{^{1}H} NMR (376 MHz, [D$_6$]DMSO): $\delta=-137.9$ ppm; MS (MALDI-TOF, positive ion mode): *m/z*: 303 [K([18]crown-6)]$^+$; (negative ion mode) *m/z*: 789 $[C_{16}H_8B_2F_6K_2+C_{16}H_8B_2F_6K]^-$, 375 $[C_{16}H_8B_2F_6K]^-$, 317 $[C_{16}H_8B_2F_5]^-$; elemental analysis calcd (%) for $C_{34}H_{44}B_2F_6K_2O_9$: C 50.38, H 5.47; found: C 50.63, H 5.92.

2,7-Dibromopyrene (4)[16b]

Method 1: Compound **1** (0.70 g, 1.5 mmol) was dissolved in THF (5 mL) and MeOH (15 mL), then $CuBr_2$ (2.07 g, 9.27 mmol) in H_2O (15 mL) was added. The mixture was heated at 90 °C for 16 h and then concentrated under reduced pressure. H_2O (50 mL) was added and the white precipitate was collected by filtration and washed with H_2O (2×50 mL), Et_2O (30 mL), and hexane (3×50 mL). The product was extracted into hot toluene (3×30 mL) and the solvent was removed under reduced pressure to give **4** (0.39 g, 70 %) as an off-white solid. Pure samples were obtained after recrystallization from acetone.

Method 2—one-pot C–H borylation/bromination: In a nitrogen-filled glove box, [{Ir((μ-OMe)cod}$_2$] (0.02 g, 0.03 mmol), dtbpy (0.02 g, 0.07 mmol), and B_2pin_2 (0.10 g, 0.39 mmol) were dissolved in THF (5 mL). The mixture was added to a Young's tube containing pyrene (0.71 g, 3.5 mmol) and B_2pin_2 (1.95 g, 7.68 mmol). After addition of THF (10 mL), the tube was sealed and the reaction mixture was stirred at 80 °C for 16 h. The mixture was transferred to a round-bottomed flask and THF/MeOH (1:1, 60 mL) was added, followed by $CuBr_2$ (4.42 g, 19.8 mmol) in H_2O (30 mL). The mixture was heated at 90 °C for 16 h and then concentrated under reduced pressure. H_2O (50 mL) was added and the white precipitate was collected by filtration and washed with H_2O (2×50 mL), Et_2O (30 mL), and hexane (3×50 mL). The product was extracted into hot toluene (3×30 mL), and the solvent was removed under reduced pressure to give **4** (0.89 g, 70 %) as an off-white solid. M.p. 320–321 °C [lit. >230 °C (chlorobenzene)];[16b] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.31$ (s, 4H), 8.01 ppm (s, 4H); ^{13}C{^{1}H} NMR (125 MHz, [D$_2$]1,1,2,2-tetrachloroethane, 80 °C): $\delta=132.3$, 127.8, 127.4, 122.8, 120.2 ppm; MS (EI): *m/z*: 360 $[M^+]$; HRMS (EI): *m/z* calcd for $C_{16}H_8{}^{79}Br_2$: 357.8987 $[M]^+$; found: 357.8993; elemental analysis calcd (%) for $C_{16}H_8Br_2$: C 53.37, H 2.24; found: C 53.06, H 2.24.

2,7-Dihydroxypyrene (5):[40] Compound **1** (0.50 g, 1.1 mmol) and NaOH (0.26 g, 6.5 mmol) were dissolved in THF (50 mL) and an aqueous solution of H_2O_2 (0.66 g, 6.5 mmol, 35 wt %) was added to this mixture. After stirring at room temperature for 4 h, the solution was acidified to pH 1–2 by using 1 M HCl. The product was extracted into Et_2O (3×100 mL) and the organic fractions were dried over $MgSO_4$. (**Caution**: care must be taken to destroy all peroxides in the aqueous phase by stirring with aqueous H_2SO_4 and CuI.) The solvent volume was reduced to about 10 mL under reduced pressure and the product was precipitated by addition of hexane (200 mL). The light-brown solid product **5** (0.23 g, 89 %) was collected by filtration. M.p. 320–322 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=9.89$ (s, 2H), 7.93 (s, 4H), 7.59 ppm (s, 4H); ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]DMSO): $\delta=154.8$, 131.0, 126.9, 118.6, 111.9 ppm; MS (ESI): *m/z*: 233 $[M-H]^-$; HRMS (ESI): *m/z* calcd for $C_{16}H_9O_2$: 233.0608 $[M-H]^-$; found: 233.0606; elemental analysis calcd (%) for $C_{16}H_{10}O_2$: C 82.04, H 4.30; found: C 81.80, H 4.25.

Pyrene-2,7-bis(boronic acid) (6)[7c]

Method 1: Compound **1** (1.0 g, 2.2 mmol) was dissolved in THF/H_2O (4:1, 20 mL) and $NaIO_4$ (3.83 g, 17.9 mmol) was added. The suspension was stirred for 40 min, then 1 M HCl (3 mL) was added and the mixture was stirred for 48 h. The suspension was diluted with water (20 mL) and extracted with EtOAc (3×50 mL). The combined organic phases were washed with brine (50 mL) and H_2O (50 mL), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was washed with hexane (5×50 mL) and dried in vacuo to give **6** (0.50 g, 78 %) as a light-brown solid.

Method 2: Compound **3** (1.23 g, 2.97 mmol) was suspended in THF (100 mL). LiOH·H_2O (2.24 g, 53.4 mmol) in H_2O (20 mL) was added to this suspension and the mixture was stirred for 16 h. The solvent was removed under reduced pressure, then aqueous ammonium chloride (80 mL) and 1 M HCl (20 mL) were added and the precipitate was collected by filtration. The residue was washed with H_2O (2×50 mL) and Et_2O (50 mL) to give **6** (0.77 g, 89 %) as an off-white solid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta=8.67$ (s, 4H), 8.42 (s, 4H), 8.14 ppm (s, 4H); ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]DMSO): $\delta=131.5$, 130.7, 128.1, 125.6 ppm (*C*–B not observed); MS (MALDI-TOF, negative ion mode): *m/z*: 291

$[M+H]^-$, 290 $[M]^-$; elemental analysis calcd (%) for $C_{16}H_{12}B_2O_4$: C 66.29, H 4.17; found: C 66.55, H 3.83.

Pyrene-2,7-bis(trifluoromethanesulfonate) (7): Under a nitrogen atmosphere, compound **5** (0.33 g, 1.4 mmol) was dissolved in dry pyridine (30 mL). After cooling to −10 °C, triflic anhydride (2.39 g, 8.47 mmol) in dry hexane (10 mL) was added dropwise over 30 min. The mixture was stirred at −10 °C for 1 h and allowed to warm to room temperature overnight. The solvent was removed in vacuo and H_2O (10 mL) was added to the residue. The reaction mixture was extracted with Et_2O (3×100 mL) and the organic fractions were dried over $MgSO_4$. After removal of the volatiles under reduced pressure, the residue was purified by column chromatography (silica gel, hexane/Et_2O 4:1) to give **7** (0.42 g, 60%) as a light-yellow solid. M.p. 192–194 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 4H), 8.15 ppm (s, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 147.6, 132.7, 128.8, 123.1, 119.1 (q, J(C,F) = 320 Hz), 117.9 ppm; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$): δ = −73.0 ppm; MS (EI): *m/z*: 498 $[M]^+$, 365 $[M-SO_2CF_3]^+$; HRMS (EI): *m/z* calcd for $C_{18}H_8F_6O_6S_2$: 497.9661 $[M]^+$; found: 497.9668; elemental analysis calcd (%) for $C_{18}H_8F_6O_6S_2$: C 43.38, H 1.62; found: C 43.22, H 1.58.

Pyrene-2,7-bis[4-(benzoic acid *n*-octyl ester)] (8): In a nitrogen-filled glove box, DMF (7 mL) and *n*-octyl 4-bromobenzoate (0.17 g, 0.54 mmol) were added to a Young's tube containing compound **6** (0.080 g, 0.28 mmol), [$PdCl_2$(dppf)] (0.014 g, 0.019 mmol), and anhydrous K_3PO_4 (0.30 g, 1.4 mmol). The tube was sealed and the reaction mixture was stirred at 80 °C for 72 h. Then, 1 M HCl (10 mL) was added to quench the reaction. The mixture was extracted into CH_2Cl_2 (3×30 mL) and the combined organic fractions were washed with brine (2×50 mL) and H_2O (50 mL), then dried over $MgSO_4$. The solution was passed through a 5 cm silica plug (eluent: CH_2Cl_2) and the solvent was removed under reduced pressure. The residue was purified by Kugelrohr distillation (140 °C at 1.4×10^{-2} mbar) to give **8** (0.14 g, 75%) as a yellow solid. M.p. 139–140 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.45 (s, 4H), 8.24 (d, J = 9 Hz, 4H), 8.19 (s, 4H), 7.97 (d, J = 9 Hz, 4H), 4.39 (t, J = 7 Hz, 4H), 1.84 (qn, J = 8 Hz, 4H), 1.45–1.55 (m, 4H), 1.24–1.44 (m, 16H), 0.91 ppm (t, J = 8 Hz, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 166.8, 145.9, 138.2, 131.8, 130.4, 129.6, 128.3, 128.1, 124.2, 109.1, 65.4, 31.9, 29.5, 29.4, 28.9, 26.3, 22.8, 14.3 ppm; MS (MALDI-TOF, positive ion mode): *m/z*: 666 $[M]^+$; HRMS (CI): *m/z* calcd for $C_{46}H_{50}O_4{\cdot}NH_4$: 684.4047 $[M+NH_4]^+$; found: 684.4047; elemental analysis calcd (%) for $C_{46}H_{50}O_4$: C 82.85, H 7.56; found: C 82.12, H 7.53.

2,7-Diphenylpyrene (9):[22b] Under a nitrogen atmosphere, compound **7** (0.080 g, 0.16 mmol), $PhB(OH)_2$ (0.040 g, 0.33 mmol), [$PdCl_2$(dppf)] (0.003 g, 0.004 mmol), and K_3PO_4 (0.10 g, 0.47 mmol) were dissolved in DMF (10 mL) and degassed H_2O (0.5 mL). The mixture was stirred at 80 °C for 16 h. Then, the reaction mixture was extracted with Et_2O (3× 50 mL). The combined organic fractions were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by elution through a 5 cm silica plug with hot toluene. Recrystallization from benzene gave **9** (0.045 g, 79%) as a white solid. M.p. 290 °C (dec.) [lit. 316 °C (CH_2Cl_2/toluene)];[22b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 4H), 8.16 (s, 4H), 7.90 (d, J = 7 Hz, 4H), 7.57 (t, J = 7 Hz, 4H), 7.45 ppm (t, J = 7 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 141.7, 139.1, 131.7, 129.1, 128.2, 128.1, 127.6, 124.1, 124.0 ppm; MS (MALDI-TOF, positive ion mode): *m/z*: 354 $[M]^+$; elemental analysis calcd (%) for $C_{28}H_{18}$: C 94.88, H 5.12; found: C 94.65, H 5.10.

2,7-Bis(phenylethynyl)pyrene (10): Under a nitrogen atmosphere, compound **7** (0.15 g, 0.30 mmol), [$PdCl_2(PPh_3)_2$] (0.006 g, 0.009 mmol), and CuI (0.0011 g, 0.006 mmol) were dissolved in dry DMF (10 mL). Phenylacetylene (0.061 g, 0.60 mmol) in Et_3N (5 mL) was then added. The mixture was stirred vigorously and then heated at 80 °C for 16 h. The reaction was quenched with 1 M HCl (10 mL) and then extracted with Et_2O (3×50 mL). The Et_2O fractions were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification of the residue by column chromatography (silica gel, hexane/Et_2O 4:1) gave **10** (0.06 g, 50%) as a light-yellow solid. M.p. 206–208 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.35 (s, 4H), 8.06 (s, 4H), 7.64–7.68 (m, 4H), 7.38–7.44 ppm (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 132.2, 131.7, 129.0, 128.9, 128.5, 128.1, 124.3, 123.6, 121.6, 90.5, 90.2 ppm; MS (MALDI-TOF, positive ion mode): *m/z*: 402 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{32}H_{18}$: 402.1403 $[M]^+$; found: 402.1406; elemental analysis calcd (%) for $C_{32}H_{18}$: C 95.49, H, 4.51; found: C 95.37, H 4.47.

2,7-Bis[4-(dimesitylboryl)phenylethynyl]pyrene (11): Under a nitrogen atmosphere, compound **7** (0.20 g, 0.40 mmol), [$PdCl_2(PPh_3)_2$] (0.009 g, 0.013 mmol), and CuI (0.002 g, 0.011 mmol) were dissolved in dry DMF (10 mL) and 1-ethynyl-4-(dimesitylboryl)benzene (0.28 g, 0.80 mmol) in Et_3N (5 mL) was then added. The mixture was stirred vigorously and then refluxed at 80 °C for 16 h. The reaction was quenched with 1 M HCl (10 mL) and extracted with Et_2O (3×50 mL). After drying of the organic fractions over $MgSO_4$, the volatiles were removed under reduced pressure. The residue was then purified by column chromatography (silica gel, hexane/Et_2O 4:1) to give **11** (0.11 g, 31%) as a yellow solid. M.p. 310 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (s, 4H), 8.05 (s, 4H), 7.62 (d, J = 8 Hz, 4H), 7.56 (d, J = 8 Hz, 4H), 6.85 (s, 8H), 2.33 (s, 12H), 2.03 ppm (s, 24H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 141.7 (br), 141.0, 139.0, 136.3, 131.4, 131.3, 128.4, 128.3, 127.8, 126.6, 124.2, 92.1, 90.7, 23.6, 21.6 ppm (one *C*–B not observed); MS (MALDI-TOF, positive ion mode): *m/z*: 898 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{68}H_{60}{}^{11}B_2$ $[M]^+$: 898.4876; found: 898.4879; elemental analysis calcd (%) for $C_{68}H_{60}B_2$: C 90.87, H 6.73; found: C 90.63, H 6.63.

2,7-Bis(trimethylsilylethynyl)pyrene (12)—method 1: Under a nitrogen atmosphere, compound **4** (0.070 g, 0.19 mmol), [$PdCl_2$(dppf)] (0.006 g, 0.008 mmol), and CuI (0.002 g, 0.008 mmol) were added to dry THF (2 mL). To this mixture, Et_3N (5 mL) and trimethylsilylacetylene (TMSA, 0.040 g, 0.41 mmol) were added and the reaction was refluxed for 16 h. The solvent was removed in vacuo and the reaction mixture was passed through a silica plug (eluent: hexane/Et_2O 3:2). The solvent was removed under reduced pressure. Recrystallization of the residue from hexane gave **12** (0.03 g, 44%) as a pale-yellow solid.

2,7-Bis(trimethylsilylethynyl)pyrene (12) and 2-(trifluoromethanesulfonyl)-7-(trimethylsilyl-ethynyl)pyrene (13)—method 2: Under a nitrogen atmosphere, compound **7** (0.10 g, 0.20 mmol), [$PdCl_2(PPh_3)_2$] (0.004 g, 0.006 mmol), and CuI (0.001 g, 0.005 mmol) were dissolved in dry DMF (10 mL). TMSA (0.040 g, 0.41 mmol) in Et_3N (5 mL) was then added. The mixture was stirred vigorously and then refluxed for 16 h. The reaction was quenched with 1 M HCl (10 mL) and extracted with Et_2O (3× 50 mL). The combined organic fractions were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexane/Et_2O 4:1). Recrystallization of the separated fractions from hexane gave **12** (0.04 g, 51%) and **13** (0.02 g, 22%) as white solids.

*Data for **12***: M.p. 178–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (s, 4H), 7.99 (s, 4H), 0.34 ppm (s, 18H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 131.3, 128.6, 127.7, 124.2, 121.2, 105.6, 95.2, 0.2 ppm; MS (EI): *m/z*: 394 $[M]^+$, 379 $[M-Me]^+$; HRMS (EI): *m/z* calcd for $C_{26}H_{26}Si_2$ $[M]^+$: 394.1568; found: 394.1561; elemental analysis calcd (%) for $C_{26}H_{26}Si_2$: C 79.13, H 6.64; found: C 78.83, H 6.60.

*Data for **13***: M.p. 136–138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 2H), 8.02–8.09 (m, 6H), 0.34 ppm (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 147.4, 133.0, 131.1, 129.4, 129.0, 127.3, 123.5, 123.4, 121.6, 119.1 (q, J(C,F) = 326 Hz), 117.0, 105.1, 95.8, 0.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −73.0 ppm; MS (EI): *m/z*: 446 $[M]^+$, 431 $[M-Me]^+$; HRMS (EI): *m/z* calcd for $C_{22}H_{17}F_3O_3SSi$: 446.0614 $[M]^+$; found: 446.0619; elemental analysis calcd (%) for $C_{22}H_{17}F_3O_3SSi$: C 59.18, H 3.84; found: C 58.98, H 3.59.

2,7-Bis[4-(*N*,*N*-dimethylamino)phenylethynyl]pyrene (14): Under a nitrogen atmosphere, compound **7** (0.075 g, 0.15 mmol), 4-ethynyl-*N*,*N*-dimethylaniline (0.044 g, 0.30 mmol), [$PdCl_2(PPh_3)_2$] (0.004 g, 0.005 mmol), and CuI (0.001 g, 0.003 mmol) were added to dry Et_3N (2.5 mL). To this mixture, DMF (5 mL) was added and the mixture was heated at 80 °C for 16 h. The mixture was extracted with Et_2O (3×50 mL) and washed with copious amounts of water. After drying of the organic fractions over $MgSO_4$, the volatiles were removed under reduced pressure. The residue was added to the top of a 4 cm plug of basic alumina (Brockmann I grade) and eluted with copious amounts of CH_2Cl_2. The solvent was removed under reduced pressure to give **14** (0.029 g, 40%) as a bright-yellow solid. Pure samples were obtained after recrystallization from

CH_2Cl_2. M.p. 140–143 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.29$ (s, 4H), 8.01 (s, 4H), 7.53 (d, $J = 8$ Hz, 4H), 6.73 (d, $J = 8$ Hz, 4H), 3.03 ppm (s, 12H); ^{13}C{^{1}H} NMR (151 MHz, $[D_2]$1,1,2,2-tetrachloroethane, 80 °C): $\delta = 150.3$, 132.8, 131.0, 127.7, 127.4, 123.1, 122.1, 111.9, 110.0, 91.7, 88.0, 39.9 ppm; MS (MALDI-TOF, positive ion mode): *m/z*: 488 $[M]^+$; HRMS (MALDI): *m/z* calcd for $C_{36}H_{28}N_2$: 488.2252 $[M]^+$; found: 488.2231.

2,7-Diethynylpyrene (15):[42b] Compound **12** (0.11 g, 0.28 mmol) was added to a suspension of Na_2CO_3 (0.22 g, 2.1 mmol) in MeOH (30 mL) and H_2O (3 mL). After stirring for 16 h at room temperature, the mixture was diluted with H_2O (10 mL) and concentrated under reduced pressure. Then, it was extracted with Et_2O (3×50 mL) and the ether fractions were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by elution with hexane/EtOAc (4:1) over a 5 cm silica plug to give **15** (0.06 g, 86%) as a light-brown solid. M.p. >350 °C [lit. 211–214 °C];[42b] ^{1}H NMR (700 MHz, $CDCl_3$): $\delta = 8.30$ (s, 4H), 8.03 (s, 4H), 3.26 ppm (s, 2H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$): $\delta = 131.3$, 128.8, 127.8, 124.3, 120.2, 84.2, 78.1 ppm; MS (EI): *m/z*: 250 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{20}H_{10}$: 250.0777 $[M]^+$; found: 250.0776.

2,7-Bis[*N*-(4-methoxyphenyl)-*N*-phenylamino]pyrene (16): Under a nitrogen atmosphere, a solution of $[Pd_2(dba)_3]$ (0.008 g, 0.009 mmol) in toluene (3 mL), followed by a solution of *N*-(4-*m*ethoxyphenyl)-*N*-phenylamine (0.061 g, 0.31 mmol) in toluene (3 mL), were added to a Young's tube containing **4** (0.05 g, 0.14 mmol) and NaO*t*Bu (0.090 g, 0.94 mmol). To this mixture, a solution of P*t*Bu$_3$ in toluene (0.025 mL, 0.015 mmol, 12.2% w/v) was added. The tube was sealed and the reaction mixture was stirred at 110 °C for 4 h. After cooling to room temperature, H_2O (30 mL) was added. The mixture was extracted into CH_2Cl_2 (3×30 mL) and the combined organic fractions were dried over $MgSO_4$. Then, the solvent was removed under reduced pressure. The residue was placed on a 3 cm basic alumina plug and eluted with hexane/CH_2Cl_2 to give **16** (0.077 g, 92%) as a bright-yellow solid. Purer samples were obtained by recrystallization from hexane/$CHCl_3$. ^{1}H NMR (700 MHz, C_6D_6): $\delta = 7.92$ (s, 4H), 7.44 (s, 4H), 7.26 (d, $J = 8$ Hz, 4H), 7.08–7.12 (m, 8H), 6.90 (t, $J = 8$ Hz, 2H), 6.75 (d, $J = 8$ Hz, 4H), 3.32 ppm (s, 6H); ^{13}C{^{1}H} NMR (176 MHz, C_6D_6): $\delta = 156.9$, 149.3, 146.4, 141.8, 132.4, 129.7, 128.4, 128.3, 123.5, 122.4, 121.7, 120.5, 115.4, 55.1 ppm; MS (ASAP, positive ion mode) *m/z*: 597 $[M+H]^+$; HRMS (ASAP): *m/z* calcd for $C_{42}H_{32}N_2O_2$: 596.2464 $[M]^+$; found: 596.2453; elemental analysis calcd (%) for $C_{42}H_{32}N_2O_2 \cdot 0.67CHCl_3$: C 75.77, H 4.87, N 4.14; found: C 75.96, H 4.90, N 4.13.

Pyrene-2,7-dicarboxylic acid (17):[37] Compound **17** was synthesized from **4** as previously reported.[37] ^{1}H NMR (700 MHz, $[D_6]$DMSO): $\delta = 13.34$ (s, 2H), 8.90 (s, 4H), 8.39 ppm (s, 4H); ^{13}C{^{1}H} NMR (176 MHz, $[D_6]$DMSO): $\delta = 167.6$, 131.1, 129.2, 128.5, 125.9, 125.4 ppm.

2-(7-*tert*-Butylpyren-2-yl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (2-Bpin-7-*t*Bu-pyrene) (18): In a nitrogen-filled Schlenk flask, [{Ir(μ-OMe)cod}$_2$] (0.034 g, 0.051 mmol), dtbpy (0.027 g, 0.10 mmol), and B_2pin_2 (0.050 g, 0.20 mmol) were dissolved in hexane (2 mL). To this flask, 2-*tert*-butylpyrene (1.01 g, 3.91 mmol) and B_2pin_2 (1.27 g, 5.00 mmol) in hexane (10 mL) were added and the mixture was stirred at 80 °C for 16 h. The reaction mixture was passed through a silica pad (eluent: CH_2Cl_2) and the solvent was removed under reduced pressure. Purification of the residue by column chromatography (silica gel, hexane/CH_2Cl_2 5:1) and subsequent recrystallization from hexane gave **18** (1.27 g, 85%) as colorless crystals. M.p. 240–241 °C; ^{1}H NMR (700 MHz, $CDCl_3$): $\delta = 8.65$ (s, 2H), 8.23 (s, 2H), 8.10 (d, $J = 8$ Hz, 2H), 8.05 (d, $J = 8$ Hz, 2H), 1.59 (s, 9H), 1.46 ppm (s, 12H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$): $\delta = 149.7$, 131.6, 131.3, 130.4, 127.8, 127.6, 126.5, 123.0, 122.2, 84.2, 35.4, 32.1, 25.2 ppm (*C*–B not observed); ^{11}B{^{1}H} NMR (225 MHz, $CDCl_3$): $\delta = 31.4$ ppm; MS (EI): *m/z*: 384 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{26}H_{29}{}^{10}BO_2$: 383.2291 $[M]^+$; found: 383.2285; elemental analysis calcd (%) for $C_{26}H_{29}BO_2$: C 81.26, H 7.61; found: C 81.02, H 7.58.

Pyrene-2-trifluoroborate potassium salt (19): Compound **2** (0.33 g, 1.00 mmol) was dissolved in MeOH (10 mL). To this solution, KHF_2 (0.30 g, 3.8 mmol) in H_2O (5 mL) was added and the resulting white slurry was refluxed for 1 h. After cooling to ambient temperature, the white precipitate was collected by filtration and washed with hexane (30 mL) and water (30 mL). Recrystallization from EtOH gave **19** (0.29 g, 94%) as colorless crystals. M.p. 313–314 °C; ^{1}H NMR (500 MHz, $[D_6]$DMSO): $\delta = 8.33$ (s, 2H), 8.18 (d, $J = 8$ Hz, 2H), 8.12 (d, $J = 8$ Hz, 2H), 8.05 (d, $J = 8$ Hz, 2H), 7.96 ppm (t, $J = 8$ Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $[D_6]$DMSO): $\delta = 130.5$, 129.2, 129.1, 128.0, 125.7, 125.1, 124.4, 123.9, 122.8 ppm (*C*–B not observed); ^{19}F{^{1}H} NMR (376 MHz, $[D_6]$acetone): $\delta = -142.0$ ppm; MS (EI): *m/z*: 269 $[M-K]^+$; elemental analysis calcd (%) for $C_{16}H_9BF_3K$: C 62.36, H 2.94; found: C 61.70, H 2.99.

2-Bromopyrene (20)

Method 1:[15, 16c, 36] To a round-bottomed flask fitted with a condenser, compound **2** (0.24 g, 0.73 mmol) and $CuBr_2$ (0.49 g, 2.2 mmol), dissolved in MeOH/H_2O (15 mL, 1:1), were added. The mixture was heated at 90 °C for 16 h until consumption of the starting materials was observed by GC-MS and then cooled to room temperature. H_2O (25 mL) was added and a white precipitate was collected by filtration and washed with H_2O (2×30 mL). Recrystallization from hexane gave **20** (0.17 g, 83%) as a white solid. M.p. 125–126 °C [lit. 131–133 °C (hexane),[15] 126–128 °C (EtOH),[16c] 135.5–136.5 °C (EtOH/EtOAc 10:1)[36]]; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.24$ (s, 2H), 8.16 (d, $J = 8$ Hz, 2H), 8.05 (d, $J = 9$ Hz, 2H), 8.01 (t, $J = 8$ Hz, 1H), 7.92 ppm (d, $J = 9$ Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): $\delta = 132.8$, 130.9, 128.7, 127.1, 126.4, 126.3, 125.8, 124.4, 123.3, 120.0 ppm; MS (EI): *m/z*: 280, 282 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{16}H_9{}^{79}Br$: 279.9882 $[M]^+$; found: 279.9881; elemental analysis calcd (%) for $C_{16}H_9Br$: C 68.35, H 3.23; found: C 68.18, H 3.35.

Method 2—one-pot process: In a nitrogen-filled glove box, [{Ir(μ-OMe)cod}$_2$] (0.02 g, 0.03 mmol), dtbpy (0.02 g, 0.07 mmol), and B_2pin_2 (0.10 g, 0.39 mmol) were added to hexane (5 mL). The mixture was added to a Young's tube containing pyrene (0.62 g, 3.07 mmol) and B_2pin_2 (0.67 g, 2.6 mmol). After addition of hexane (10 mL), the tube was sealed and the reaction mixture was stirred at 80 °C for 16 h. The mixture was transferred to a round-bottomed flask and the solvent was removed under reduced pressure. MeOH (30 mL) was added, followed by $CuBr_2$ (2.04 g, 9.13 mmol) in H_2O (30 mL). The mixture was heated at 90 °C for 16 h and then concentrated under reduced pressure. H_2O (30 mL) was added and the white precipitate was collected by filtration and washed with H_2O (3×30 mL). The product was then extracted into hot hexane (50 mL) and the solvent was removed under reduced pressure to give a mixture of **20** and pyrene (0.53 g, about 1:1 by GC-MS).

2-Hydroxypyrene (21):[16c] Compound **2** (1.00 g, 3.05 mmol) and NaOH (0.36 g, 9.0 mmol) were dissolved in THF/H_2O (10:1, 110 mL). To this mixture, an aqueous solution of H_2O_2 (0.93 g, 9.1 mmol, 35 wt%) was added. After stirring for 4 h, the solution was acidified to pH 1–2 by using 1 M HCl. The reaction mixture was extracted with Et_2O (3×50 mL). The organic fractions were dried over $MgSO_4$ and the solvent was removed by slow evaporation. (**Caution**: care must be taken to destroy all peroxides in the aqueous phase by stirring with aqueous H_2SO_4 and CuI.) The residue was washed with hexane (3×20 mL) to yield **21** (0.56 g, 84%) as a light-brown solid. M.p. 202–203 °C [lit. 206–207 °C (dec.)];[16c] ^{1}H NMR (400 MHz, $[D_6]$DMSO): $\delta = 10.1$ (s, 1H), 8.20 (d, $J = 8$ Hz, 2H), 8.09 (d, $J = 8$ Hz, 2H), 8.03 (d, $J = 8$ Hz, 2H), 7.93 (t, $J = 8$ Hz, 1H), 7.69 ppm (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, $[D_6]$DMSO): $\delta = 156.0$, 132.3, 130.4, 127.6, 126.6, 125.7, 125.1, 124.0, 118.3, 111.9 ppm; MS (ESI): *m/z*: 217 $[M-H]^+$; HRMS (ESI): *m/z* calcd for $C_{16}H_9O$: 217.0659 $[M-H]^+$; found: 217.0660; elemental analysis calcd (%) for $C_{16}H_{10}O$: C 88.05, H 4.62; found: C 87.68, H 4.71.

Pyrene-2-boronic acid (22):

Method 1: Compound **2** (0.20 g, 0.61 mmol) was dissolved in THF/H_2O (20 mL, 4:1) and $NaIO_4$ (0.39 g, 1.82 mmol) was added. The suspension was stirred for 40 min, then 1 M HCl (0.61 mL) was added and the mixture was stirred for 48 h. The suspension was diluted with water (20 mL) and extracted with EtOAc (3×50 mL). The combined organic phases were washed with brine (50 mL) and H_2O (50 mL) and dried over $MgSO_4$. Then, the solvent was removed under reduced pressure. The residue was washed with hexane (5×50 mL) and dried in vacuo to give **22** (0.12 g, 80%) as a light brown solid.

Method 2: Compound **19** (0.62 g, 2.0 mmol) was dissolved in THF/H_2O (4:1, 20 mL) and LiOH·H_2O (0.17 g, 4.1 mmol) was added. The solution

was stirred at room temperature for 20 h and then acidified to pH 1–2 with saturated aqueous NH_4Cl (8 mL) and 1 M HCl (2 mL). The mixture was extracted with EtOAc (3×10 mL), the organic fractions were dried over $MgSO_4$, and the solvent was removed under reduced pressure to give **22** (0.42 g, 85%) as a light-brown solid. M.p. 131–132 °C; ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.69 (s, 2H), 8.45 (br s, 2H), 8.28 (d, J = 8 Hz, 2H), 8.17 (s, 4H), 8.07 ppm (t, J = 8 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]DMSO): δ = 131.1, 131.0, 129.7, 127.8, 127.0, 126.5, 124.9, 124.8, 123.9 ppm (*C*–B not observed); MS (MALDI-TOF, negative ion mode): *m/z*: 246 $[M]^-$ (higher mass condensation products were also observed); elemental analysis calcd (%) for $C_{16}H_{11}BO_2$: C 78.10, H 4.51; found: C 77.35, H 4.54.

2-[4-(Dimesitylboryl)phenyl]pyrene (23): Under a nitrogen atmosphere, compound **19** (0.31 g, 1.0 mmol), 1-iodo-4-(dimesitylboryl)benzene (0.45 g, 1.0 mmol), [PdCl$_2$(dppf)] (0.007 g, 0.01 mmol), and K_2CO_3 (0.28 g, 2.0 mmol) were dissolved in EtOH (5 mL). The mixture was heated at 80 °C for 16 h. The reaction was quenched with 1 M HCl (10 mL) and extracted with CH_2Cl_2 (3×20 mL). The combined organic fractions were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Recrystallization of the residue from hexane gave **23** (0.34 g, 65%) as a white solid. M.p. 216–218 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 2H), 8.20 (d, J = 8 Hz, 2H), 8.14 (d, J = 9 Hz, 2H), 8.11 (d, J = 9 Hz, 2H), 8.02 (t, J = 8 Hz, 1H), 7.90 (d, J = 8 Hz, 2H), 7.73 (d, J = 8 Hz, 2H), 6.90 (s, 4H), 2.37 (s, 6H), 2.12 ppm (s, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 144.9, 141.8, 141.0, 138.8, 138.5, 137.4, 131.7, 131.3, 128.4, 128.0, 127.7, 127.5, 126.1, 125.3, 124.7, 124.3, 123.9, 23.7, 21.4 ppm (one *C*–B not observed); MS (MALDI-TOF, positive ion mode): *m/z*: 526 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{40}H_{35}{}^{10}B$: 525.2863 $[M]^+$; found: 525.2858; elemental analysis calcd (%) for $C_{40}H_{35}B$: C 91.25, H 6.70; found: C 90.45, H 6.70.

2-(Dimesitylboryl)pyrene (24): Under a nitrogen atmosphere, compound **20** (0.28 g, 1.0 mmol) was dissolved in Et_2O (5 mL). The solution was cooled to −78 °C and a solution of *n*BuLi in hexanes (1.6 M, 0.8 mL, 1.3 mmol) was added dropwise by using a syringe. The reaction was warmed to room temperature and stirred for 1 h. Then, the system was cooled to −78 °C and a solution of dimesitylboron fluoride (0.27 g, 1.0 mmol) in Et_2O (5 mL) was added. The mixture was again warmed to room temperature and stirred overnight. The reaction was quenched with 1 M HCl (10 mL) and extracted with CH_2Cl_2 (3×20 mL). The organic fractions were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification of the residue by column chromatography (silica gel, hexane/CH_2Cl_2, 4:1) gave **24** (0.14 g, 31%) as a pale-yellow solid. M.p. 174–175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (s, 2H), 8.18 (d, J = 8 Hz, 2H), 8.02–8.09 (m, 5H), 6.92 (s, 4H), 2.40 (s, 6H), 2.04 ppm (s, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 143.5, 142.1, 141.2, 139.0, 133.0, 132.1, 130.8, 128.5 (2 overlapped signals), 127.3, 126.9, 126.8, 125.0, 124.8, 23.8, 21.4 ppm; MS (MALDI-TOF, positive ion mode): *m/z*: 450 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{34}H_{31}{}^{10}B$: 449.2550 $[M]^+$; found: 449.2544; elemental analysis calcd (%) for $C_{34}H_{31}B$: C 90.66, H 6.94; found: C 90.90, H 6.96.

Pyrene-2-trifluoromethanesulfonate (25): Under a nitrogen atmosphere, compound **21** (0.66 g, 3.0 mmol) was dissolved in dry pyridine (30 mL). After cooling to 0 °C, triflic anhydride (2.54 g, 9.0 mmol) was added. The mixture was stirred at 0 °C for 1 h and then allowed to warm to room temperature overnight. The reaction was quenched with H_2O (20 mL) and the mixture was extracted with CH_2Cl_2 (3×30 mL). The organic fractions were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification of the residue by column chromatography (silica gel, hexane/CH_2Cl_2, 4:1) gave **25** (0.72 g, 69%) as a pale-yellow solid. M.p. 143–145 °C; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 8.26 (d, J = 8 Hz, 2H), 8.17 (d, J = 9 Hz, 2H), 8.08 (t, J = 8 Hz, 1H), 8.05 (d, J = 9 Hz, 2H), 8.04 ppm (s, 2H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$): δ = 147.2, 132.9, 131.0, 129.6, 126.8, 126.7, 126.4, 124.1, 123.0, 119.1 (q, J(C,F) = 320 Hz), 116.5 ppm; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ = −73.0 ppm; MS (ESI): *m/z*: 350 $[M]^+$; HRMS (ESI): *m/z* calcd for $C_{17}H_9F_3O_3S$: 349.0152 $[M-H]^+$; found: 349.0151; elemental analysis calcd (%) for $C_{17}H_9F_3O_3S$: C 58.29, H 2.59; found: C 58.32, H 2.61.

2-Phenylethynylpyrene (26): Under a nitrogen atmosphere in a Young's tube, compound **25** (0.10 g, 0.29 mmol), phenylacetylene (0.045 g, 0.44 mmol), [PdCl$_2$(PPh$_3$)$_2$] (0.007 g, 0.01 mmol), and CuI (0.002 g, 0.01 mmol) were dissolved in Et_3N (2 mL) and DMF (5 mL). The tube was sealed and heated at 90 °C for 16 h. The reaction was quenched with 1 M HCl (10 mL) and extracted with CH_2Cl_2 (3×20 mL), then the CH_2Cl_2 fractions were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 4:1) to give **26** (0.068 g, 78%) as a pale-yellow solid. M.p. 135–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 2H), 8.19 (d, J = 8 Hz, 2H), 8.09 (d, J = 9 Hz, 2H), 8.05 (d, J = 9 Hz, 2H), 8.02 (t, J = 8 Hz, 1H), 7.63–7.66 (m, 2H), 7.37–7.43 ppm (m, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 131.9, 131.4, 131.2, 128.6, 128.5, 128.2, 127.9, 127.1, 126.5, 125.5, 124.5, 124.4, 123.5, 120.8. 90.2, 89.9 ppm; MS (EI): *m/z*: 302 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{24}H_{14}$: 302.1090 $[M]^+$; found: 302.1093; elemental analysis calcd (%) for $C_{24}H_{14}$: C 95.33, H 4.67. Found: C 94.65, H 4.69.

2-(Trimethylsilylethynyl)pyrene (27):[16f] Under a nitrogen atmosphere in a Young's tube, compound **25** (0.10 g, 0.29 mmol), TMSA (0.10 g, 1.0 mmol), [PdCl$_2$(PPh$_3$)$_2$] (0.007 g, 0.01 mmol), and CuI (0.002 g, 0.01 mmol) were dissolved in Et_3N (2 mL) and DMF (5 mL). The tube was sealed and heated at 80 °C for 16 h. The reaction was quenched with 1 M HCl (10 mL) and extracted with CH_2Cl_2 (3×20 mL). The organic fractions were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification of the residue by column chromatography (silica gel, hexane/CH_2Cl_2 4:1) gave **27** (0.065 g, 75%) as a pale-yellow solid. M.p. 107–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (s, 2H), 8.16 (d, J = 8 Hz, 2H), 8.06 (d, J = 8 Hz, 2H), 7.99–8.03 (m, 3H), 0.36 ppm (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 131.4, 131.1, 128.2, 128.1, 127.0, 126.5, 125.5, 124.5, 124.4, 120.6, 105.9, 94.8, 0.2 ppm; MS (MALDI-TOF, positive ion mode): *m/z*: 298 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{21}H_{18}Si$: 298.1172 $[M]^+$; found: 298.1171; elemental analysis calcd (%) for $C_{21}H_{18}Si$: C 84.51, H 6.08; found: C 84.21, H 6.11.

4-(Pyren-2-yl)benzoic acid methyl ester (28): Under a nitrogen atmosphere, compound **22** (0.10 g, 0.41 mmol), methyl 4-iodobenzoate (0.11 g, 0.42 mmol), [PdCl$_2$(dppf)] (0.007 g, 0.01 mmol), and K_3PO_4 (0.26 g, 1.2 mmol) were dissolved in DMF (5 mL) and heated at 80 °C for 16 h. The reaction was quenched with 1 M HCl (10 mL) and extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with brine (2×80 mL) and H_2O (80 mL), and dried over $MgSO_4$, then the solvent was removed under reduced pressure. Purification of the residue by column chromatography (silica gel, hexane/CH_2Cl_2, 4:1) afforded **28** (0.083 g, 60%) as a pale-yellow solid. M.p. 169–170 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.37 (s, 2H), 8.20 (d, J = 8 Hz, 2H), 8.18 (d, J = 8 Hz, 2H), 8.09 (s, 4H), 8.00 (t, J = 8 Hz, 1H), 7.92 (d, J = 8 Hz, 2H), 3.99 ppm (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 167.2, 146.1, 137.6, 131.7, 131.3, 130.4, 129.1, 128.1, 128.0, 127.6, 126.3, 125.4, 124.6, 124.4, 123.7, 52.3 ppm; MS (MALDI-TOF): *m/z*: 336 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{24}H_{16}O_2$: 336.1145 $[M]^+$; found: 336.1143; elemental analysis calcd (%) for $C_{24}H_{16}O_2$: C 85.69, H 4.79; found: C 84.73, H 4.92.

2-Ethynylpyrene (29):[11b,16f,42a,43] Compound **27** (0.11 g, 0.37 mmol) was added to a suspension of Na_2CO_3 (0.14 g, 1.3 mmol) in MeOH (30 mL) and H_2O (3 mL). After stirring for 16 h at room temperature, the mixture was diluted with H_2O (10 mL) and concentrated under reduced pressure. Then it was extracted with Et_2O (3×50 mL) and the Et_2O fractions were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified on a 5 cm silica plug eluting with hexane/Et_2O (4:1), yielding **29** (0.068 g, 81%) as a pale-yellow solid. M.p. 107–109 °C [lit. 103–104 °C,[16f], 110–112 °C (dec.,[42a]), 112–114 °C (EtOH,[11b])], 125–127 °C (EtOH,[43])]; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.30 (s, 2H), 8.20 (d, J = 8 Hz, 2H), 8.09 (d, J = 8 Hz, 2H), 7.99–8.04 (m, 3H), 3.25 ppm (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 131.7, 131.5, 128.6, 128.5, 127.2, 127.0, 125.9, 124.8, 124.6, 119.9, 84.5, 77.8 ppm; MS (EI): *m/z*: 226 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{18}H_{10}$: 226.0777 $[M]^+$; found: 226.0774.

4-(Pyren-2-yl)butyric acid methyl ester (30): Under a nitrogen atmosphere, Zn powder (0.27 g, 4.1 mmol) was added to a Young's tube. After heating the tube at 70 °C under vacuum for 45 min, I_2 (0.035 g, 0.14 mmol) in DMF (9 mL) was added and the mixture was stirred until

the red color had faded (about 5 min). Freshly distilled (80 °C, 200 mTorr) 4-bromobutyric acid methyl ester (0.50 g, 2.8 mmol) in DMF (1 mL) was added and the mixture was stirred at 70 °C for 16 h. Inside a nitrogen-filled glovebox, the stock solution containing the zinc reagent (1.56 mL, 0.43 mmol) was added to a Young's tube containing **20** (0.10 g, 0.36 mmol) and $[PdCl_2(PPh_3)_2]$ (0.005 g, 0.007 mmol). The mixture was stirred for 16 h at room temperature, then H_2O (300 mL) was added. The mixture was extracted into Et_2O (3×100 mL) and the combined organic fractions were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2, 1:1), followed by recrystallization from hexane to give **30** (0.08 g, 74%) as white needles. M.p. 61–62 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, J = 7 Hz, 2H), 8.06 (d, J = 9 Hz, 2H), 8.02 (d, J = 9 Hz, 2H), 8.00 (s, 2H), 7.98 (t, J = 7 Hz, 1H), 3.68 (s, 3H), 3.10 (t, J = 8 Hz, 2H), 2.43 (t, J = 8 Hz, 2H), 2.20 ppm (qn, J = 8 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 174.1, 139.4, 131.5, 131.1, 127.7, 127.4, 125.8, 125.3, 125.1, 124.8, 123.5, 51.8, 35.9, 33.7, 27.3 ppm; MS (EI): m/z: 302 $[M]^+$; HRMS (ASAP, positive ion mode): m/z calcd for $C_{21}H_{18}O_2$: 302.1307 $[M]^+$; found: 302.1317; elemental analysis calcd (%) for $C_{21}H_{18}O_2$: C 83.42, H 6.00; found: C 83.22, H 5.91.

4-(Pyren-2-yloxy)butyric acid methyl ester (31): A mixture of **21** (0.10 g, 0.46 mmol) and NaO*t*Bu (0.05 g, 0.52 mmol) in DMF (6 mL) was stirred for 1 h and then added dropwise over 30 min to a solution of 4-bromobutyric acid methyl ester (0.37 g, 2.0 mmol) in DMF (6 mL). The mixture was stirred at room temperature for 1 h, then at 40 °C for 1 h and then at 80 °C for 16 h. After cooling to room temperature, H_2O (300 mL) was added and the mixture was extracted into Et_2O (3×100 mL). The combined organic fractions were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, CH_2Cl_2), followed by recrystallization from hexane to give **31** (0.11 g, 75%) as off-white platelets. M.p. 81–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, J = 8 Hz, 2H), 8.03 (d, J = 8 Hz, 2H), 7.96 (d, J = 8 Hz, 2H), 7.91 (t, J = 8 Hz, 1H), 7.68 (s, 2H), 4.30 (t, J = 7 Hz, 2H), 3.70 (s, 3H), 2.64 (t, J = 7 Hz, 2H), 2.25 ppm (qn, J = 7 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 173.9, 157.2, 132.7, 130.3, 128.2, 127.0, 125.4, 125.0, 124.7, 120.3, 111.1, 67.1, 51.9, 30.8, 25.0 ppm; MS (ASAP, positive ion mode): m/z: 318 $[M]^+$; elemental analysis calcd (%) for $C_{21}H_{18}O_3$: C 79.22, H 5.70; found: C 79.35, H 5.80.

4-(Pyren-2-yl)butyric acid (32):[50] LiOH·H_2O (0.027 g, 0.64 mmol) in H_2O (2.5 mL) was added to a solution of **30** (0.080 g, 0.26 mmol) in THF (10 mL). The mixture was stirred for 16 h at room temperature and quenched with 1 M HCl (50 mL), then extracted into EtOAc (3×80 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was dissolved in hot acetone (10 mL). Then, the product was precipitated by the addition of hexane. Filtration and drying gave **32** (0.06 g, 80%) as a white solid. M.p. 199–200 °C [lit. 199–201.5 °C];[50] ^{1}H NMR (700 MHz, [D$_6$]DMSO): δ = 12.08 (br s, 1H), 8.27 (d, J = 8 Hz, 2H), 8.16 (d, J = 8 Hz, 2H), 8.15 (d, J = 8 Hz, 2H), 8.14 (s, 2H), 8.04 (t, J = 8 Hz, 1H), 3.06 (t, J = 8 Hz, 2H), 2.33 (t, J = 8 Hz, 2H), 2.05 ppm (qn, J = 8 Hz, 2H); ^{13}C{^{1}H} NMR (176 MHz, [D$_6$]DMSO): δ = 174.3, 139.8, 130.7, 130.3, 127.3, 127.1, 125.8, 125.1, 125.0, 123.8, 122.4, 34.9, 33.3, 26.8 ppm; MS (ESI, negative ion mode): m/z: 575 $[2M-H]^-$, 287 $[M-H]^-$; HRMS (ESI, negative ion mode): m/z calcd for $C_{20}H_{15}O_2$: 287.1072 $[M-H]^-$; found: 287.1091; elemental analysis calcd (%) for $C_{20}H_{16}O_2$·0.33 H_2O: C 81.61, H 5.71; found: C 81.31, H 5.54.

4-(Pyren-2-yloxy)butyric acid (33): LiOH·H_2O (0.026 g, 0.62 mmol) in H_2O (2.5 mL) was added to a solution of **31** (0.08 g, 0.25 mmol) in THF (10 mL). The mixture was stirred for 16 h at room temperature. The reaction was quenched with 1 M HCl (50 mL) and extracted into EtOAc (3× 80 mL), then dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was dissolved in hot acetone (10 mL). Then, the product was precipitated by the addition of hexane. Filtration and drying gave **33** (0.05 g, 66%) as an off-white solid. M.p. 185–186 °C; ^{1}H NMR (700 MHz, [D$_6$]DMSO): δ = 12.20 (br s, 1H), 8.25 (d, J = 8 Hz, 2H), 8.15 (d, J = 8 Hz, 2H), 8.10 (d, J = 8 Hz, 2H), 7.99 (t, J = 8 Hz, 1H), 7.89 (s, 2H), 4.30 (t, J = 7 Hz, 2H), 2.10 ppm (qn, J = 7 Hz, 2H) (the third CH_2 signal was obscured by the H_2O signal); ^{13}C{^{1}H} NMR (176 MHz, [D$_6$]DMSO): δ = 174.3, 156.9, 132.2, 129.6, 127.9, 126.8, 125.3, 125.2, 123.8, 119.1, 111.0, 79.2, 67.2, 30.7 ppm; MS (ESI, negative ion mode): m/z: 303 $[M-H]^-$, 607 $[2M-H]^-$; HRMS (ESI, negative ion mode): m/z calcd for $C_{20}H_{15}O_3$: 303.1021 $[M-H]^-$; found: 303.1023; elemental analysis calcd (%) for $C_{20}H_{16}O_3$·0.5 H_2O: C 76.66, H 5.47; found: C 76.65, H 5.67.

2-(12-Bromo-*n*-dodecyloxy)pyrene (34): A mixture of **21** (0.15 g, 0.69 mmol) and NaO*t*Bu (0.068 g, 0.71 mmol) in DMF (6 mL) was stirred for 1 h and then added dropwise over 30 min to a solution of 1,12-dibromododecane (1.13 g, 3.44 mmol) in DMF (5 mL). The mixture was stirred at room temperature for 2 h and then at 80 °C for 16 h. After cooling to room temperature, H_2O (400 mL) was added. The mixture was extracted into Et_2O (3×100 mL) and the combined organic fractions were dried over $MgSO_4$. Then, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 9:1), followed by recrystallization from hexane and $CHCl_3$, to give **34** (0.23 g, 72%) as a white solid. M.p. 80–81 °C; ^{1}H NMR (700 MHz, C_6D_6): δ = 7.94 (d, J = 8 Hz, 2H), 7.84 (d, J = 8 Hz, 2H), 7.80 (d, J = 8 Hz, 2H), 7.73 (t, J = 8 Hz, 1H), 7.72 (s, 2H), 3.96 (t, J = 7 Hz, 2H), 2.97 (t, J = 7 Hz, 2H), 1.80–1.84 (m, 2H), 1.48–1.54 (m, 4H), 1.21–1.38 (m, 8H), 1.16–1.20 (m, 4H), 1.07–1.11 ppm (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ = 158.1, 133.3, 130.8, 128.4, 127.2, 125.6, 125.4, 125.2, 120.7, 111.5, 68.4, 33.7, 33.0, 30.2, 30.1, 30.0, 29.9 (2 overlapped signals), 29.8, 29.1, 28.4, 26.6 ppm; MS (ASAP, positive ion mode): m/z: 466 $[M]^+$; elemental analysis calcd (%) for $C_{28}H_{33}BrO$: C 72.25, H 7.15; found: C 72.33, H 7.09.

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