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Scholl Oxidative Coupling | *Very Important Paper* |

VIP

Insights into the Scholl Coupling Reaction: A Key Transformation of Relevance to the Synthesis of Graphenes and Related Systems

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Abstract: The Scholl-type reactions of 4,10-disubstituted chrysene derivatives proceeded by variegated and unexpected oxidation/coupling pathways. These observations serve as a cautionary note when attempting to employ the Scholl reaction in target-oriented materials synthesis.

Introduction

Polycyclic aromatics are ubiquitous structural motifs, which are to be found in a variety of materials such as organic electronics, OLEDS, sensors and graphenes.[1] Despite a flurry of interest in the development of "bottom-up" approaches to the synthesis of these systems, most strategies still rely upon the pre-fabrication of an oligo-aromatic scaffold followed by a late-stage intramolecular dehydrogenative or dehydrohalogenative coupling reaction in the pivotal planarisation step.[2] Both solution-[3] and surface-based[4] methodologies have been developed for this purpose, of which the Scholl reaction, first reported in 1910,[5] represents the most widely utilised.

The Scholl reaction, in its original form, enables the synthesis of biaryls, often in a reiterative sense, by the reaction between otherwise unactivated aromatic C–H bonds and aluminium chloride at elevated temperatures. Sequences involving inter-[6a] and intramolecular[6b] and a limited number of tandem inter-intramolecular[6c] coupling processes, are known, such that this protocol now represents a key transformation in the synthesis of extended polycyclic systems.[7] A common variant of this process involves the use of iron(III) chloride as oxidant.[8] Such reactions are typified by the use of an excess of this reagent to achieve acceptable levels of conversion, a constraint that often leads to complications in workup and product isolation. Here, the concomitant formation of halogenated byproducts[9a,9b] is not uncommon, and trace quantities of phenolic[9c] products have been reported. These particular reaction conditions may also promote rearrangement reactions,[10] which may detract from the potential of this particular procedure in target-orientated materials synthesis. To circumvent these experimental constraints, a metal-free variant of the Scholl reaction, as adumbrated by Rathore and co-workers,[11] has latterly found popular appeal.[12] Here, a high-potential quinone is used in conjunction with a protic/Brønsted acid to effect dehydrogenative biaryl formation. Although a full mechanistic understanding of this reaction remains elusive, it has been suggested that the formation of a radical cation[13] or arenium cation[14] precedes the crucial biaryl C–C bond-forming step. The incorporation of either activating or blocking groups into the substrate has been used to good effect in controlling the regiochemical outcome of these reactions,[15] although it is noteworthy that once more rearrangement reactions are not uncommon[16] and the formation of unexpected, oxygenated, byproducts have also been reported.[17a] Germane to this discussion is the recent report by Miao and co-workers concerning the concomitant oxygenation of aromatic substrates during the course of Scholl reactions promoted by methanesulfonic acid/DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone),[17b] a finding, which prompts us to present our observations in this area.

Results and Discussion

This study builds on our previous investigations concerned with the identification of new methodologies for the synthesis of polycyclic aromatics.[18] We presumed that readily available chrysene derivatives[18a] could be converted into tetrabenzo[*a*,*cd*,*h*,*jk*]pyrenes by using the ubiquitous Scholl-type oxidative coupling reaction (Scheme 1). In the event, the attempted cyclisation of **1a**, **2a** and **4a** (see the Supporting Information for details), by using either $FeCl_3$ or $MoCl_5$,[19] resulted in the generation of intractable reaction mixtures, whereas those

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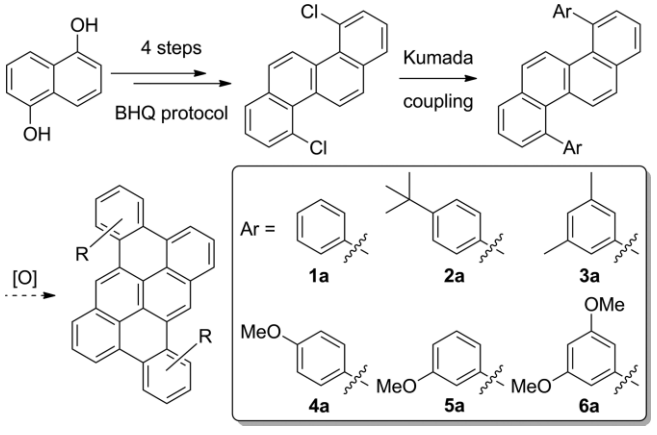
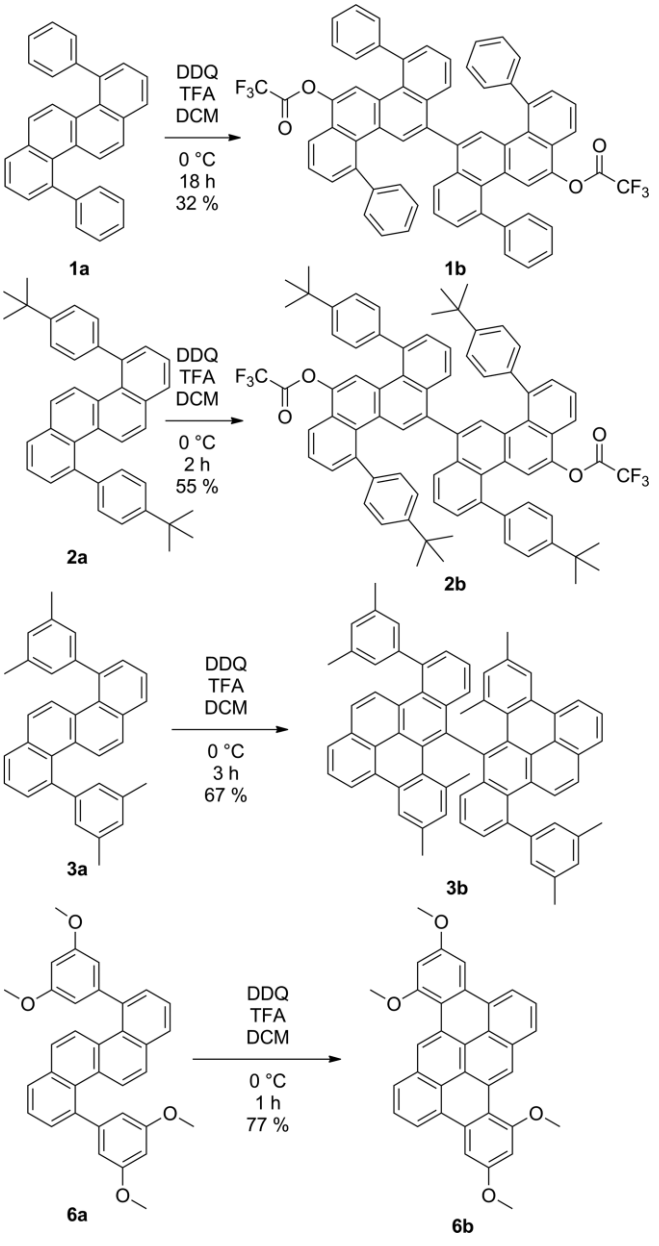
utilising DDQ/$MeSO_3H$[11] were much better behaved. Although this reagent combination apparently allowed the reaction to proceed with discrete C–C bond formation for substrates **1a** and **4a**, it was a process, which was again marred, in a practical sense, as product formation was also accompanied by irreproducible levels of mesylate incorporation.



Scheme 1. Proposed pathway to tetrabenzo[*a*,*cd*,*h*,*jk*]pyrenes by intramolecular coupling of 4,10-diarylchrysenes.

Eventually, it was determined that the use of the trifluoroacetic acid (TFA)/DDQ reagent combination[13a,20] was superior for the coupling reactions of these chrysene derivatives. However, the products of these reactions were not those expected based upon extensive literature analogy. Hence, the exposure of either **1a** or **2a** to DDQ (2.1 equiv.) and TFA (50 equiv.) in CH_2Cl_2 at 0–20 °C for up to 18 h led to the clean conversion (as monitored by ^{1}H NMR) into **1b** and **2b**, respectively, the products of a formal trifluoroacetoxylation/intermolecular coupling reaction (Scheme 2). The incorporation of the trifluoroacetate moieties was readily apparent from the ^{13}C NMR [for **1b**: C=O at δ = 156.1 ppm ($^3J_{C\text{-}F}$ = 43 Hz); CF_3 at δ = 114.6 ppm ($^1J_{C\text{-}F}$ = 285 Hz)] and ^{19}F NMR spectroscopic data (for **1b**: CF_3 at δ = –74.4 ppm). The structures of **1b** and **2b** were finally secured by single-crystal X-ray crystallography, which revealed that in the solid state both **1b** and **2b** adopt conformations (Figure 1) in which the two chrysene cores are essentially orthogonally disposed to each other (torsion angle of ca. 80°) and that the molecules are devoid of symmetry.

In solution, the structural assignments of **1b** and **2b** were somewhat complicated by NMR broadening due to hindered rotational interconversions on the NMR timescale.[21] At 25 °C, the ^{1}H NMR spectrum of **1b** shows a mixture of eight well-defined resonances together with several very broadened resonances, which on cooling to –38 °C are resolved into 18 discrete resonances in accordance with the proposed C-2 dimeric structure (Figure 2). We suggest that this dynamic picture involves at least two interconverting diastereoisomeric conformational states in which protons are shielded to varying extents by proximate aromatic systems. In onsonance with this analysis, we note that at 50 °C the ^{1}H NMR spectrum of **1b** shows seven



Scheme 2. Reactions of 4,10-disubstituted chrysenes with DDQ/TFA.

discrete multiplets. Attempted data acquisition at higher temperatures was thwarted by the decomposition of the substrate. Predictably, the trifluoroacetates **1b** and **2b** are susceptible to hydrolysis during aqueous workup or silica gel chromatography, which accounts for their diminished isolated yields (see the Supporting Information for a deacylation study of **2b**).

In the light of the above results, we were surprised to observe that the exposure of **3a** to the same reaction conditions resulted in the isolation of **3b**, which is devoid of trifluoroacetate groups and is presumably the result of a tandem intra-intermolecular coupling process.[6c] The X-ray crystallographic data of **3b** demonstrates the crowded environment around the central biaryl bond, which generates a chiral environment redolent of [7]helicene, an arrangement with an interfacial C–C distance

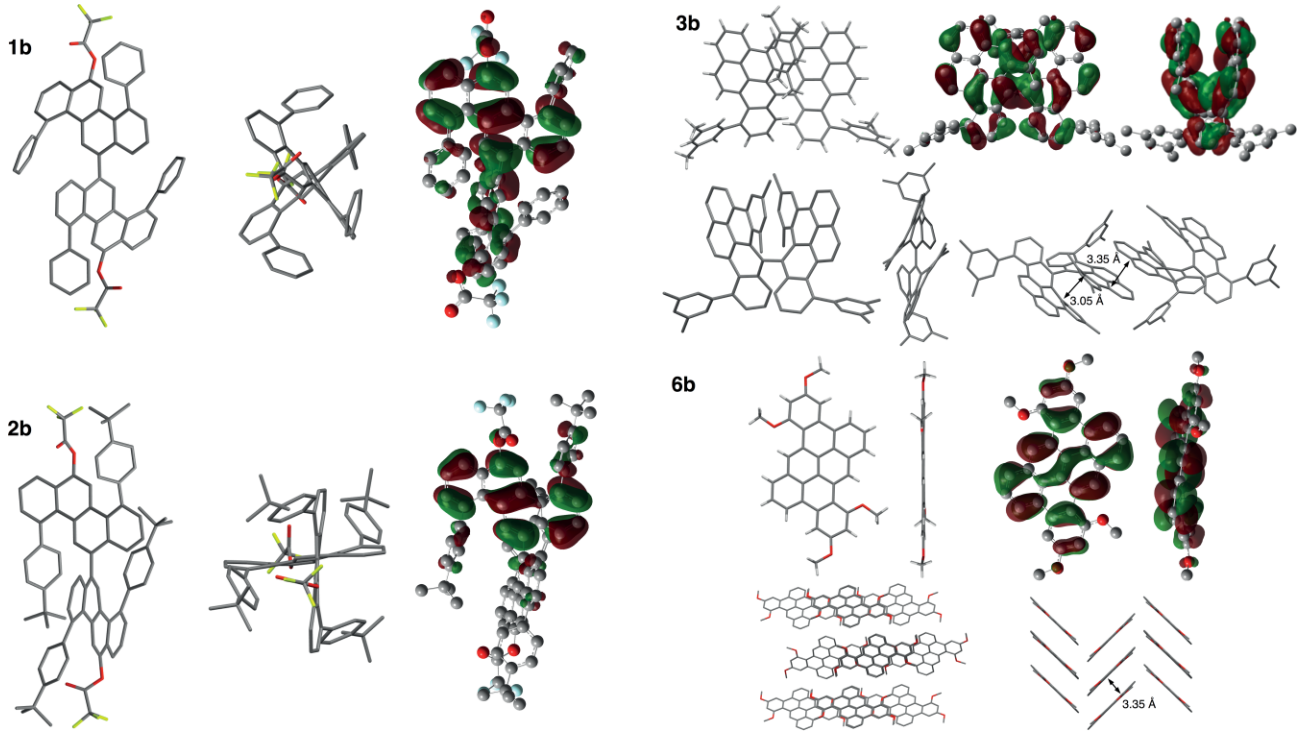


Figure 1. XRD structures and DFT [B3LYP/6-31G(d)] HOMO plots of the oxidative coupling products.

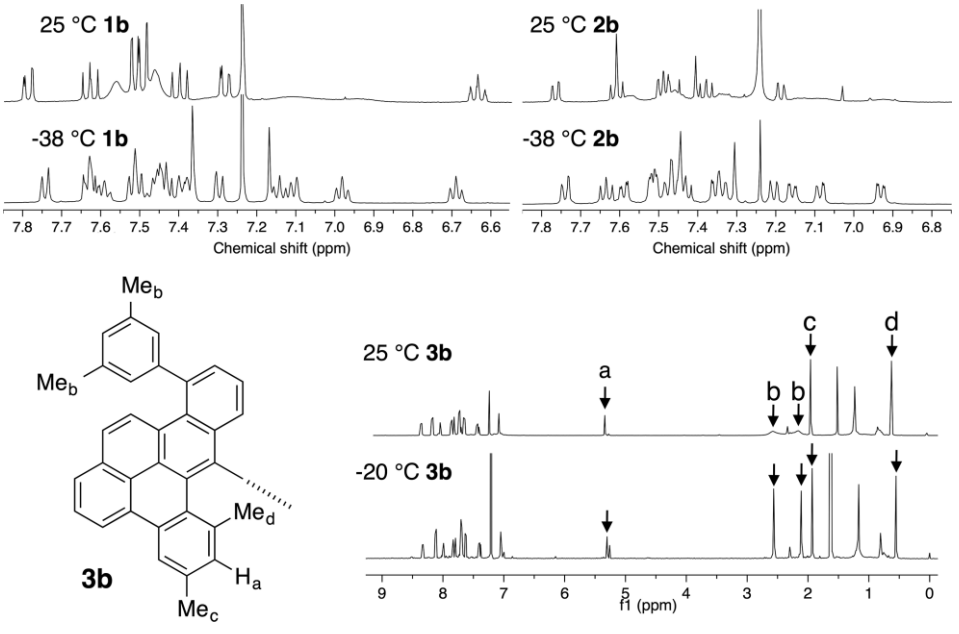


Figure 2. VT 500 MHz ^{1}H NMR spectra of **1b**, **2b** and **3b** (10 mM in $CDCl_3$).

of 3.05 Å (Figure 1). The yellow compound **3b** displays an intense fluorescence at 506 nm in natural sunlight, possibly due to an intramolecular charge-transfer state.[22] The ^{1}H NMR spectrum of **3b** again displays interesting behaviour: dynamic broadening of the resonances associated with the xylyl groups (Figure 2) is observed; H_a and Me_d signals also experience marked upfield shifts (appearing at δ = 5.2 and 0.5 ppm, respectively) due to the shielding environment of adjacent aromatic rings. Given that electron-donating groups both activate and direct oxidative aromatic coupling towards the *ortho* and *para* positions,[15] it is unsurprising that the oxidation of **4a** and **5a** afforded an intractable mixture of oligomeric material.[15a] We were pleased to observe, however, that the oxidation of **6a** with DDQ/TFA afforded the pyrene derivative **6b** in 77 % isolated yield. Also noteworthy is the observation that the conversion of **6a** into **6b** could also be replicated by using $FeCl_3$ without

the formation of chlorinated or oligomeric products. Indeed, **6b** exhibits a surprising degree of stability (even in $CDCl_3$) given its oxidation pattern and the relatively exposed C-5 position.

The identification of four competing, substrate-dependent, oxidation reactions by using the same oxidant deserves comment. Although the Scholl reaction has been reported to afford products arising from intermolecular,[11,13a,15a] intramolecular[13a] and, to a lesser extent, tandem processes,[6c] the incorporation of the acid component into the product, in a preparative sense, was until recently[17b] without precedent. It should also be noted that, although the hydroxylation of aromatics with DDQ has been reported, these reactions usually require photochemical activation.[23] Furthermore, although both the chemical (Mn^{III})[24] and enzyme-catalysed (P450)[25] hydroxylation of chrysenes have precedent, substrate dimerisation has not been observed in these cases.[26] Both radical-cation (Rathore and co-workers[13a]) and arenium mechanisms (King and co-workers[14a]) have been identified as likely pathways for Scholl reactions mediated by DDQ/acid. We suggest that the formation of hindered biaryls in the present study is indicative of the involvement of radical cations[27] during the key coupling processes (Scheme 3), a possibility that was probed through unrestricted DFT calculations.[28] For **1a**–**3a**, the loss of an electron affords radical cations in which the unpaired spin is concentrated at C-6 of the chrysene core (SOMOα and spin density of substrate cation radicals are depicted in Figure 3). Dimerisation at this locus initially leads to **1c**–**3c**. Subsequent oxidation of **1c**–**3c** affords a new radical-cation intermediate, which can be intercepted either externally by TFA[24a] (Route A) or internally by a neighbouring aromatic ring (Route B). This partitioning qualitatively follows the relative nucleophilicity of the *m*-xylyl and *p*-toluyl groups as reported by Mayr et al.[29] For **6a**$^{\bullet+}$,

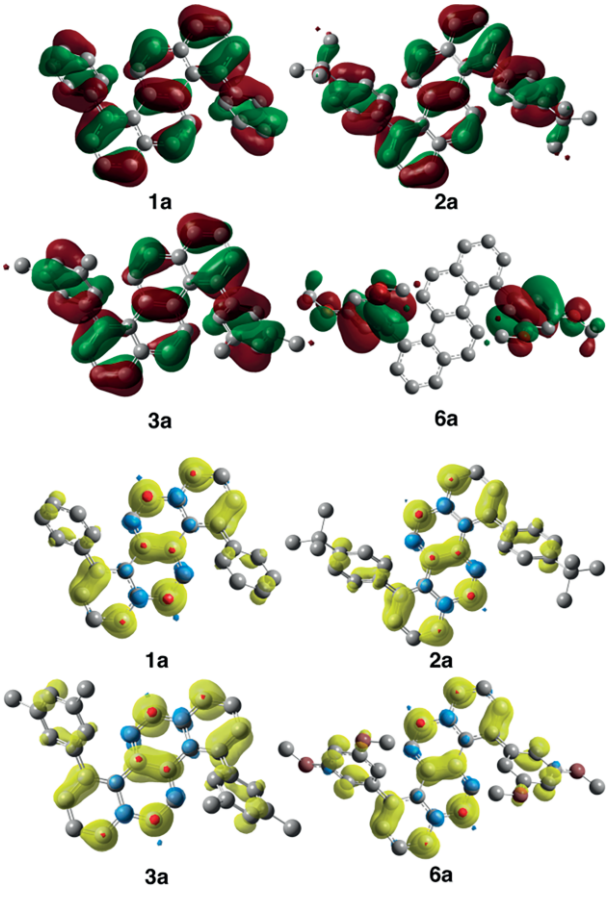
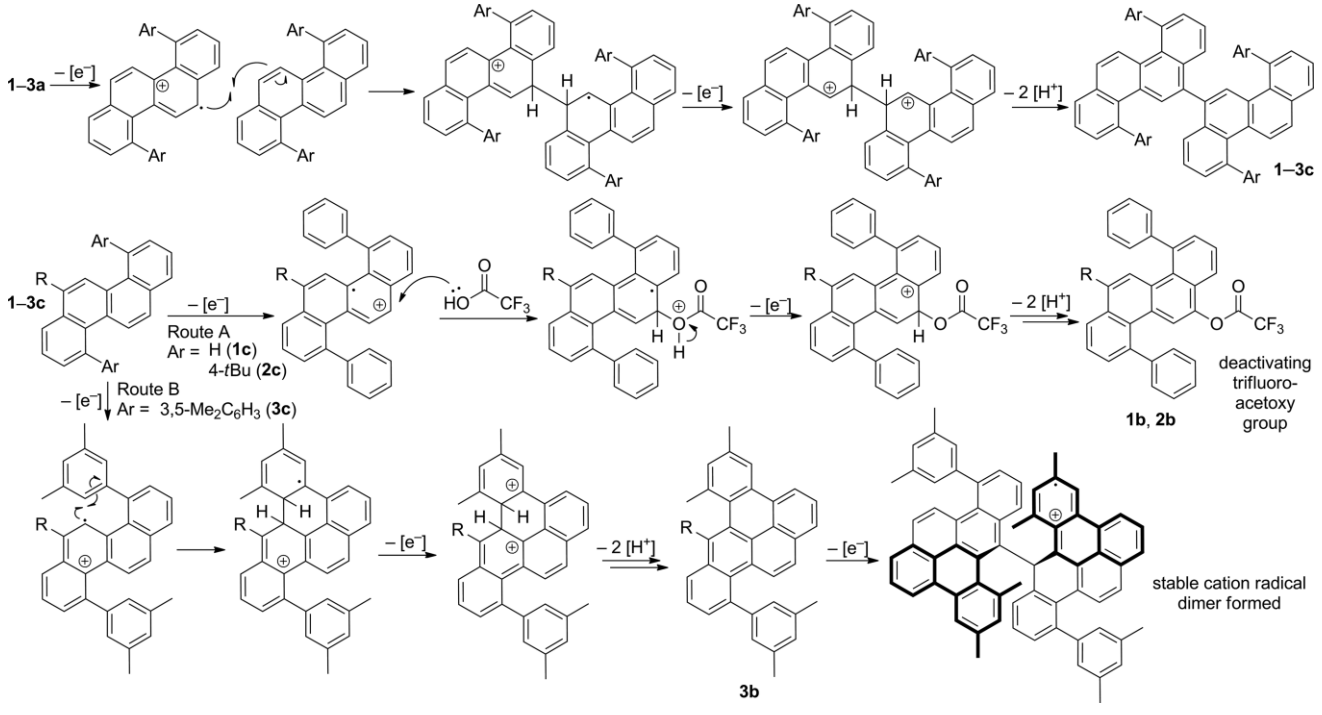


Figure 3. Top: unrestricted BL3LYP/6-31+G(d) DFT-calculated SOMOs for the corresponding cation radicals of oxidised substrates. Bottom: spin density isosurfaces (blue: –0.0015 Ha; yellow: 0.0015 Ha; red: 0.015 Ha).



Scheme 3. Proposed mechanisms for the reactions of **1a**–**3a** with DDQ/TFA detailing reactivity bifurcation after the initial dimerisation to **1c**–**3c**.

the predicted SOMOα (–0.3096 Ha) is confined solely to the dimethoxyphenyl substituents (in accordance with the observed cyclisation); however, the calculated spin density is a function of SOMO-2α (–0.31624 Ha), which allows resonance stabilisation throughout the core (see the Supporting Information). Preferential oxidation of the electron-rich dialkoxy-bearing aromatic rings[26a,30] in **6a** initiates an alternative mode of cyclisation leading ultimately to **6b**. It is clear therefore that the spin density within the radical cation and the (steric) protection of the coupling sites are controlling factors in determining the overall product distribution,[31] although it is not clear why the Scholl reaction of **3a** ultimately leads to **3b**, which is devoid of trifluoroacetate groups.

In principle the formation of dimers **1b**–**3b** necessitates only 1.5 equiv. of DDQ, but it was found that 2.1 equiv. were required for complete conversion of the starting material. This may be rationalised by the formation of a DDQ–product charge-transfer complex.[13a] The corresponding trimeric species were detectable by MALDI-MS, but as a very small fraction; for **1** and **2** it appears that the $OCOCF_3$ moiety acts as a blocking group, without which the substrate would undergo oligomerisation. The fused dimer **3b** may be deactivated by the formation of an intramolecular cation-radical dyad between the co-facial π-systems.[32] Materials **3b** and **6b** display some interesting electronic (Table 1 and the Supporting Information) and morphological characteristics in addition to being air-stable and solution-processable (see below). Compound **3b** is fluorescent (λ_{max} = 506 nm; Figure 4) and has electronic energy levels comparable to tetracene (Figure 5). Its X-ray structure exhibits considerable one-dimensional intermolecular π–π overlap at 3.35 Å (Figure 1). Compound **6b** possesses a high HOMO level ideal for hole injection from gold electrodes (–5.1 eV) while maintaining a reasonable optical gap [the energy levels compare favourably to sulfur-containing materials tetrathiafulvalene (TTF) and dinaphtho[2,3-*b*:20,30-*f*]thieno[3,2-*b*]thiophene (DNTT);[33] Figure 5]. In the solid state, **6b** adopts a two-dimensional brickwork herringbone structure with a π–π contact of 3.35 Å (Figure 1) and exhibits poor charge motilities (see the Supporting Information).

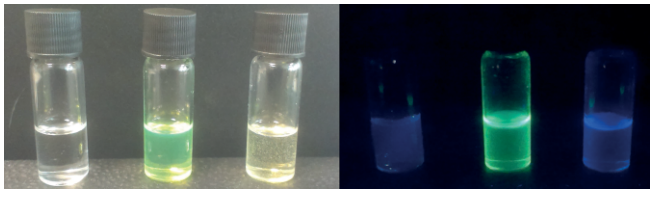


Figure 4. Solutions of **2b**, **3b** and **6b** in chloroform under ambient laboratory lighting (left) and illuminated by UV light at 365 nm (right).

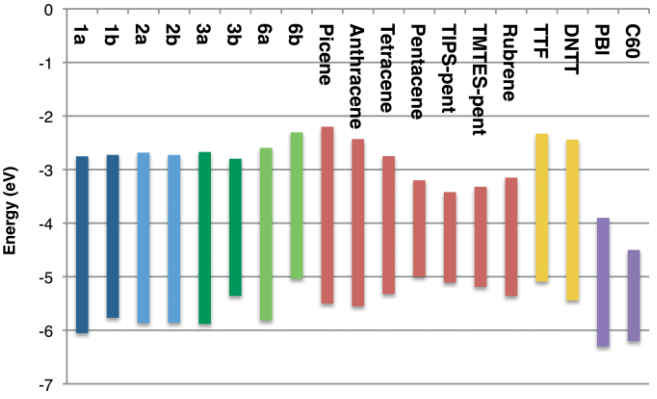


Figure 5. HOMO/LUMO energy levels of **1a**,**b**–**3a**,**b** and **6a**,**b** and popular p-type PAHs (red), thiophenes (yellow) and n-type organic semiconductor (OSC) materials (violet) for comparison.

Conclusions

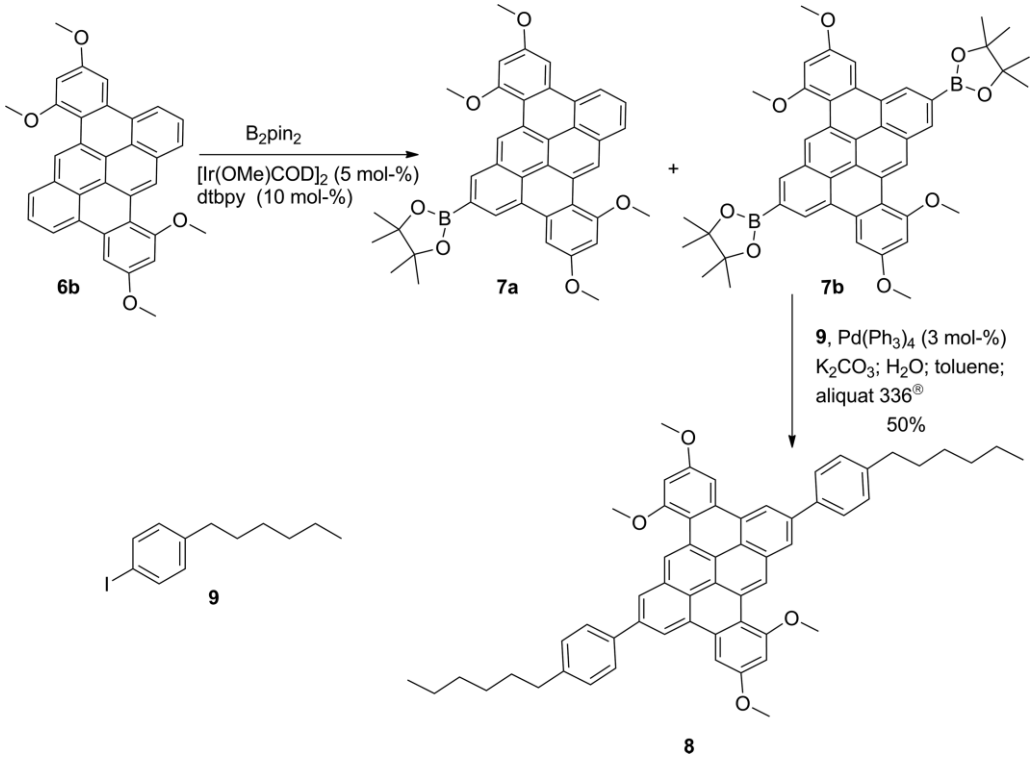
We have reported hitherto unrecognised oxidative coupling processes during dehydrogenative cyclisation reactions mediated by DDQ/TFA. The Rathore variant of the ubiquitous Scholl reaction should now be viewed with caution and product analysis carried out fastidiously when applied to the preparation of new organic materials. That these divergent modes of reaction have only now come to light suggests that unwanted products and side-reactions may have been previously overlooked or not reported.

In reality, the existence of these unexpected reaction pathways expands the potential synthetic utility of the Scholl reaction and could, if properly harnessed, enable the synthesis of new families of hindered biaryls[34] and peripherally functionalised graphene fragments. This study also illustrates that, by judicious choice of activating/protecting groups, access to tetrabenzo[*a*,*cd*,*h*,*jk*]pyrenes is possible from readily available chrysene derivatives. The tetrabenzo[*a*,*cd*,*h*,*jk*]pyrene **6b** is currently under investigation as a scaffold for the preparation of new

Table 1. Optical and electrochemical data from UV/Vis absorption, fluorescence and cyclic voltammetry measurements.

	λ_{MAX} (in CH_2Cl_2)		λ_{EDGE}		V_{OX} [V]			E_{HOMO}[a]	E_{LUMO}[b]	Fluorescence	
	[nm]	[eV]	[nm]	[eV]	obs.	wrt[c] V_{Fc}[d]	wrt[c] SCE	[eV]	[eV]	λ_{MAX} [nm]	[eV]
1a	288	4.31	376	3.30	1.574	1.253	1.689	–6.05	–2.75	385	3.22
1b	290	4.28	408	3.04	1.363	0.966	1.402	–5.77	–2.73	449	2.76
2a	291	4.26	390	3.18	1.498	1.063	1.499	–5.86	–2.68	387	3.20
2b	293	4.23	396	3.13	1.447	1.057	1.493	–5.86	–2.73	450	2.76
3a	288	4.31	386	3.21	1.511	1.081	1.517	–5.88	–2.67	385	3.22
3b	311	3.99	485	2.56	0.986	0.557	0.993	–5.36	–2.80	506	2.45
6a	285	4.35	385	3.22	1.404	1.014	1.45	–5.81	–2.59	385	3.22
6b	341	3.64	454	2.73	0.607	0.236	0.672	–5.04	–2.31	437	2.84

[a] E_{HOMO} estimated from V_{OX}. V_{Fc} = –4.8 V. [b] E_{LUMO} estimated from E_{HOMO} + $E_{\lambda MAX}$ (measured in CH_2Cl_2). [c] wrt = with respect to. [d] Oxidation potentials measured from the peak cathodic current relative to that of ferrocene.



Scheme 4. Functionalisation of scaffold **6b**.

materials.[35] In this regard, we have shown, in an exploratory study, that the borylation[18c] of **6b** proceeds in a regioselective manner to the mono- and bis-boranes **7a** and **7b**, which upon Suzuki reaction enables access to the alkylated derivative **8** in 30 % isolated yield (Scheme 4). Further work in this area is ongoing.

Experimental Section

General Experimental Procedures: All reactants and reagents were purchased from Sigma–Aldrich (UK) and were used without further purification. The solvents used were purified by standard methods. All reactions, unless otherwise noted, were carried out under N_2 gas using flame-dried glassware. NMR spectra were acquired with a B400 Bruker Avance III 400 MHz or B500 Bruker Avance II+ 500 MHz spectrometer using TMS as an internal standard (δ =0.00 ppm). Mass spectra were acquired with a Micromass Trio 200 spectrometer using electrospray (ES), atmospheric pressure chemical ionisation (APCI) or matrix-assisted laser desorption ionisation (MALDI) techniques, as stated. High-resolution mass spectra were recorded with a Kratos Concept IS spectrometer. UV/Vis spectra were recorded with a Varian Cary 50 spectrophotometer from solutions of DCM. Fluorescence spectra were recorded with a Varian Cary Eclipse spectrophotometer from solutions of DCM. Cyclic Voltammetry (CV) was performed with a BASi-Epsilon platform with a scan rate of 100 mV/s using solutions of 5–10 mM of analyte and 100 mM of tetrabutylammonium hexafluorophosphate in DCM. A Sanyo Gallenkamp melting point apparatus was used for melting point determinations. Infrared spectra were measured as films using a Bruker Alpha FT-IR spectrometer. CCDC 933452 (for **1a**), 1062056 (for **3a**), 1413513 (for **6a**), 1413514 (for **2a**), 1413515 (for **1b**), 1413516 (for **3b**) and 1413555 (for **6b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

4,10-Diphenylchrysene (1a): Bromobenzene (212 µL, 2.02 mmol) was added to a stirred mixture of magnesium ribbon (242 mg, 10.10 mmol) in anhydrous THF (5 mL) under N_2. Mechanical activation of the magnesium metal with a glass rod was followed by the exothermic generation of the Grignard reagent. The solution of phenylmagnesium bromide was then transferred by cannula to a stirred solution of 4,10-dichlorochrysene (200 mg, 0.68 mmol) and PEPPSI-IPr {[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]-(3-chloropyridyl)palladium(II) dichloride; 5 mol-%, 23 mg} in THF (5 mL) and the resultant orange mixture stirred for 30 min. The reaction was quenched by the addition of a satd. aqueous NH_4Cl solution (10 mL) and Et_2O (100 mL). The ethereal solution was washed with water (2 × 50 mL) and brine (50 mL), dried with Mg_2SO_4 and concentrated in vacuo. This crude product material was then quickly triturated with hot hexane and passed through a plug of silica with toluene to afford the title compound as colourless crystals (212 mg, 83 %). M.p. 204 °C. ^{1}H NMR (400 MHz, [D]-chloroform): δ = 7.80 (dd, J = 7.8, 1.5 Hz, 2 H), 7.72 (d, J = 9.1 Hz, 2 H), 7.59 (t, J = 7.3 Hz, 2 H), 7.38–7.54 (m, 14 H) ppm. ^{13}C NMR (101 MHz, [D]chloroform): δ = 145.0, 140.4, 133.0, 130.6, 130.6, 129.2, 129.0, 129.0, 127.7, 127.7, 127.0, 125.8, 124.4 ppm. MS (MALDI-Dithranol): m/z (%) = 380 (95) $[M]^+$. HRMS (EI^+): calcd. for $C_{30}H_{20}$ 380.1560; found 380.1565.

4,10-Bis(4-*tert*-butylphenyl)chrysene (2a): 1-Bromo-4-*tert*-butylbenzene (701 µL, 4.05 mmol) was added to a stirred mixture of magnesium ribbon (194 mg, 8.10 mmol) in anhydrous THF (5 mL) under N_2. Mechanical activation of the magnesium metal with a glass rod was followed by the exothermic generation of the Grignard reagent. The solution of 4-*tert*-butylphenylmagnesium bromide was then transferred by cannula to a stirred solution of 4,10-dichlorochrysene (200 mg, 0.68 mmol) and PEPPSI-IPr (5 mol-%,

23 mg) in THF (3 mL) and the resultant orange mixture stirred for 1 h. The reaction was quenched by the addition of a satd. aqueous NH_4Cl solution (10 mL) and Et_2O (100 mL). The ethereal solution was washed with water (2 × 50 mL) and brine (50 mL), dried with Mg_2SO_4 and concentrated in vacuo. The crude product was then triturated with hexane (10 mL), and the solids were recrystallised from hot toluene/hexane (1:9) to afford the title compound as colourless crystals (90 mg, 27 %). M.p. 267–268 °C. ^{1}H NMR (500 MHz, [D]chloroform): δ = 7.80 (dd, J = 7.9, 1.4 Hz, 2 H), 7.74 (d, J = 9.1 Hz, 2 H), 7.59 (t, J = 7.2 Hz, 2 H), 7.54 (dd, J = 7.2, 1.4 Hz, 2 H), 7.50 (d, J = 8.3 Hz, 4 H), 7.42 (d, J = 8.3 Hz, 4 H), 7.39 (d, J = 9.1 Hz, 2 H), 1.45 (s, 18 H) ppm. ^{13}C NMR (125 MHz, [D]chloroform): δ = 150.0, 142.0, 140.4, 133.0, 130.7, 130.4, 129.1, 128.7, 127.6, 127.4, 125.8, 125.7, 124.2, 34.6, 31.5 ppm. MS (MALDI-TCNQ$^+$): m/z (%) = 493 (100) [M]$^+$. HRMS (EI$^+$): calcd. for $C_{38}H_{36}$ 429.2817; found 429.2820.

4,10-Bis(3,5-dimethylphenyl)chrysene (3a): 1-Bromo-3,5-dimethylbenzene (229 µL, 1.69 mmol) was added to a stirred mixture of magnesium ribbon (81 mg, 3.38 mmol) in anhydrous THF (3 mL) under N_2. Mechanical activation of the magnesium metal with a glass rod was followed by the exothermic generation of the Grignard reagent. The solution of 3,5-dimethylphenylmagnesium bromide was then transferred by cannula to a stirred solution of 4,10-dichlorochrysene (100 mg, 0.34 mmol) and PEPPSI-IPr (5 mol-%, 11 mg) in THF (3 mL) and the resultant orange mixture stirred for 1 h. The reaction was quenched by the addition of a satd. aqueous NH_4Cl solution (10 mL) and Et_2O (100 mL). The ethereal solution was washed with water (2 × 50 mL) and brine (50 mL), dried with Mg_2SO_4 and concentrated in vacuo. The crude product mixture was then triturated with boiling hexane to afford the title compound as an off-white solid (72 mg, 49 %). M.p. 220 °C. ^{1}H NMR (500 MHz, [D]chloroform): δ = 7.74 (d, J = 9.0 Hz, 2 H), 7.71 (dd, J = 7.9, 1.3 Hz, 2 H), 7.49 (t, J = 7.6 Hz, 2 H), 7.42 (dd, J = 7.1, 1.5 Hz, 2 H), 7.34 (d, J = 9.2 Hz, 2 H), 2.29 (s, 12 H) ppm. ^{13}C NMR (125 MHz, [D]chloroform): δ = 145.0, 140.7, 139.4, 133.1, 130.6, 130.4, 129.0, 128.6, 127.6, 127.6, 126.9, 125.6, 124.4, 21.5 ppm. MS (MALDI-Dithranol): m/z (%) = 437 (100) [M + H]$^+$. HRMS (EI$^+$): calcd. for $C_{34}H_{29}$ 437.2269; found 437.2273.

4,10-Bis(4-methoxyphenyl)chrysene (4a): 4-Bromoanisole (338 µL, 2.70 mmol) was added to a stirred mixture of magnesium ribbon (328 mg, 13.52 mmol) in anhydrous THF (5 mL) under N_2. Mechanical activation of the magnesium metal with a glass rod was followed by the exothermic generation of the Grignard reagent. The solution of 4-methoxyphenylmagnesium bromide was then transferred by cannula to a stirred solution of 4,10-dichlorochrysene (200 mg, 0.68 mmol) and PEPPSI-IPr (2 mol-%, 9 mg) in THF (1 mL) and the resultant orange mixture stirred for 30 min. The reaction was quenched by the addition of a satd. aqueous NH_4Cl solution (10 mL) and Et_2O (100 mL). The ethereal solution was washed with water (2 × 50 mL) and brine (50 mL), dried with Mg_2SO_4 and concentrated in vacuo. This crude product material was then quickly triturated with hot hexane and passed through a plug of silica with toluene to afford the title compound as colourless crystals (207 mg, 69 %). M.p. 206 °C. ^{1}H NMR (400 MHz, [D]chloroform): δ = 7.70 (d, J = 8.8 Hz, 4 H), 7.48 (t, J = 7.5 Hz, 2 H), 7.42 (d, J = 7.1 Hz, 2 H), 7.32 (m, 3 H), 6.92 (d, J = 8.1 Hz, 4 H), 3.83 (s, 6 H) ppm. ^{13}C NMR (101 MHz, [D]chloroform): δ = 158.8, 140.0, 137.4, 133.1, 130.7, 130.5, 130.2, 129.1, 127.5, 127.4, 125.8, 124.3, 114.4, 55.4 ppm. MS (APCI): m/z (%) = 441 (100) [M + H]$^+$. HRMS (EI$^+$): calcd. for $C_{32}H_{24}O_2$ 440.1771; found 440.1753.

4,10-Bis(3-methoxyphenyl)chrysene (5a): 3-Bromoanisole (427 µL, 3.38 mmol) was added to a stirred mixture of magnesium ribbon (162 mg, 6.75 mmol) in anhydrous THF (5 mL) under N_2. Mechanical activation of the magnesium metal with a glass rod was followed by the exothermic generation of the Grignard reagent. The solution of 3-methoxyphenylmagnesium bromide was then transferred by cannula to a stirred solution of 4,10-dichlorochrysene (200 mg, 0.68 mmol) and PEPPSI-IPr (5 mol-%, 23 mg) in THF (5 mL) and the resultant orange mixture stirred for 1 h. The reaction was quenched by the addition of a satd. aqueous NH_4Cl solution (10 mL) and Et_2O (100 mL). The ethereal solution was washed with water (2 × 50 mL) and brine (50 mL), dried with Mg_2SO_4 and concentrated in vacuo. This crude product was then quickly triturated with hot hexane and passed through a plug of silica with toluene to afford the title compound as a white solid (259 mg, 87 %). (Extended heating of suspensions of this compound in contact with air causes the formation of a black oxidation product.) M.p. 222 °C. ^{1}H NMR (500 MHz, [D]chloroform, T = –40 °C): δ = 7.83 (d, J = 7.5 Hz, 2 H), 7.76 (d, J = 9.3 Hz, 2 H), 7.61 (t, J = 7.6 Hz, 2 H), 7.55 (d, J = 6.8 Hz, 2 H), 7.45 (d, J = 9.3 Hz, 2 H), 7.40 (t, J = 7.9 Hz, 1 H), 7.33 (t, J = 7.9 Hz, 1 H), 7.19 (s, 1 H), 7.08 (d, J = 7.4 Hz, 1 H), 7.05 (s, 1 H), 6.98 (d, J = 8.3 Hz, 2 H), 6.95 (d, J = 7.5 Hz, 1 H), 7.89 (s, 3 H), 7.80 (s, 3 H) ppm. ^{13}C NMR (125 MHz, [D]chloroform): δ = 160.0, 159.8, 146.3, 140.1, 132.9, 130.5, 130.2, 130.0, 128.9, 128.8, 128.0, 127.8, 127.8, 126.0, 124.6, 124.5, 122.2, 121.8, 114.5, 114.3, 112.4, 112.1, 55.6, 55.5 ppm. Low-temperature NMR spectroscopy shows the splitting of 3-$MeOC_6H_4$ signals. NMR spectra recorded at 20 °C show broadening of these signals. The compound is not stable at the higher temperatures required to resolve the signal average (>60 °C). MS (MALDI-TCNQ$^+$): m/z (%) = 440 (21) [M]$^+$. HRMS (EI$^+$): calcd. for $C_{32}H_{24}O_2$ 440.1771; found 440.1785.

4,10-Bis(3,5-dimethoxyphenyl)chrysene (6a): 1-Bromo-3,5-dimethoxybenzene (436 mg, 2.01 mmol) was added to a stirred mixture of magnesium ribbon (121 mg, 5.03 mmol) in anhydrous THF (5 mL) under N_2. Mechanical activation of the magnesium metal with a glass rod was followed by the exothermic generation of the Grignard reagent. The solution of 3,5-dimethoxyphenylmagnesium bromide was then transferred by cannula to a stirred solution of 4,10-dichlorochrysene (150 mg, 0.50 mmol) and PEPPSI-IPr (5 mol-%, 17 mg) in THF (5 mL) and the resultant orange mixture stirred for 1 h. The reaction was quenched by the addition of a satd. aqueous NH_4Cl solution (10 mL) and Et_2O (100 mL). The ethereal solution was washed with water (2 × 50 mL) and brine (50 mL), dried with Mg_2SO_4 and concentrated in vacuo. This crude product material was then dissolved in DCM (20 mL) and hexane 60 (mL), the DCM removed in vacuo and the precipitate collected and washed with hexane to afford the title compound as a white solid (150 mg, 60 %). M.p. 232 °C. ^{1}H NMR (400 MHz, [D]chloroform): δ = 7.85 (d, J = 9.0 Hz, 2 H, Ar-H_5), 7.80 (dd, J = 7.7, 1.3 Hz, 2 H), 7.85 (t, J = 7.5 Hz, 2 H, Ar-H_2), 7.51 (dd, J = 7.5, 1.3 Hz, 2 H), 7.45 (d, J = 9.0 Hz, 2 H, Ar-H_6), 6.61 (d, J = 2.2 Hz, 4 H, Ph-H_o), 6.52 (t, J = 2.2 Hz, 2 H, Ph-H_p), 3.76 (s, 12 H, CH_3O) ppm. ^{13}C NMR (101 MHz, [D]chloroform): δ = 161.2, 147.1, 140.2, 133.0, 130.4, 130.1, 128.8, 128.0, 127.5, 125.6, 124.7, 107.4, 99.1, 55.5 ppm. MS (MALDI-Dithranol): m/z (%) = 500 (100) [M]$^+$. HRMS (EI$^+$): calcd. for $C_{34}H_{28}O_4$ 500.1982; found 500.1970.

4,4′,10,10′-Tetraphenyl-6,6′-bichrysene-12,12′-diyl Bis(trifluoroacetate) (1b): Trifluoroacetic acid (0.5 mL) was added dropwise to a stirred solution of 4,10-diphenylchrysene (**1a**; 48 mg, 126 µmol) and DDQ (60 mg, 265 µmol) in DCM (5 mL) at 0 °C. Over the course of 18 h the reaction mixture was warmed to room temperature after which the reaction was quenched by the addition of a satd. $NaHCO_3$ solution (50 mL) and DCM (50 mL). The organic solution was then washed with $NaHCO_3$ solution (3 × 50 mL), water (2 × 50 mL) and brine (2 × 50 mL) and concentrated in vacuo to afford the crude product as an orange solid. This solid was then extracted

with hexane (200 mL), filtered through Celite® and the solution concentrated. This solid was then triturated with hexane (5 mL) to afford the title compound as an off-white solid (20 mg, 32 %). M.p. 301 °C. ^{1}H NMR (500 MHz, [D]chloroform, acquired at –40 °C): δ = 7.74 (d, J = 8.1 Hz, 2 H), 7.65–7.57 (m, 6 H), 7.52 (d, J = 7.5 Hz, 2 H), 7.51 (d, J = 7.2 Hz, 2 H), 7.49–7.37 (m, 10 H), 7.37 (s, 2 H), 7.30 (d, J = 8.1 Hz, 2 H), 7.17 (s, 2 H), 7.14 (t, J = 7.7 Hz, 2 H), 7.11 (d, J = 7.7 Hz, 2 H), 6.98 (t, J = 7.7 Hz, 2 H), 6.69 (t, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D]chloroform, acquired at –40 °C): δ = 156.1 [q, J = 43 Hz, ^3J(C-CF$_3$)], 144.0, 143.3, 141.0, 140.8, 140.0, 134.8, 132.6, 131.4, 130.4, 130.0, 129.7, 129.5, 129.3, 129.2, 129.2 (2 C), 128.9 (2 C), 128.9, 128.4, 128.2, 127.5, 127.1, 126.9, 126.4, 125.6, 119.7, 118.9, 114.6 [q, J = 285 Hz, ^2J(C-CF$_3$)] ppm. ^{19}F NMR (376 MHz, [D]chloroform): δ = –74.44 (s) ppm. MS (MALDI-TCNQ$^+$): m/z (%) = 982 (100) [M]$^+$. HRMS: calcd. for $C_{64}H_{37}F_6O_4$ 983.2596; found 983.2616.

4,4′,10,10′-Tetrakis(4-*tert*-butylphenyl)-6,6′-bichrysene-12,12′-diyl Bis(trifluoroacetate) (2b): Trifluoroacetic acid (1 mL) was added dropwise to a stirred solution of 4,10-bis(4-*tert*-butylphenyl)chrysene (**2a**; 200 mg, 407 μmol) and DDQ (203 mg, 894 μmol) in DCM (10 mL) at 0 °C. Over the course of 2 h the reaction mixture was warmed to room temperature after which the reaction was quenched by the addition of a satd. $NaHCO_3$ solution (50 mL) and DCM (50 mL). The organic solution was then washed with a $NaHCO_3$ solution (3 × 50 mL), water (2 × 50 mL) and brine (2 × 50 mL) and concentrated in vacuo to afford the crude product as a dark-violet solid. This material was then dissolved in diethyl ether/hexane (1:1; 50 mL) and stirred with activated charcoal (1 g) for 10 min. This suspension was then filtered, the solids were washed with diethyl ether/hexane (1:1; 50 mL), and the solution was concentrated to afford a pale-violet solid (136 mg, 55 %), pure as measured by ^{1}H NMR spectroscopy. Repeated trituration with hexane (ca. 5 mL) resulted in an incrementally less-coloured material until an off-white solid was obtained (30 mg, 12 %). M.p. 328 °C. ^{1}H NMR (500 MHz, [D]chloroform, acquired at –40 °C): δ = 7.73 (dd, J = 8.3, 1.0 Hz, 2 H), 7.63 (dd, J = 7.1, 8.1 Hz, 2 H), 7.58 (dd, J = 8.1, 2.0 Hz, 2 H), 7.52–7.49 (m, 4 H), 7.46 (dd, J = 8.1, 2.0 Hz, 2 H), 7.44–7.40 (m, 4 H), 7.34 (dd, J = 8.1, 2.1 Hz, 2 H), 7.33 (dd, J = 8.1, 2.1 Hz, 2 H), 7.29 (s, 2 H), 7.19 (dd, J = 8.2, 1.0 Hz, 2 H), 7.15 (dd, J = 7.9, 2.1 Hz, 2 H), 7.07 (d, J = 8.1, 2.0 Hz, 2 H), 6.92 (dd, J = 7.9, 2.1 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D]chloroform, acquired at –40 °C): δ = 155.4 [q, J = 43 Hz, ^3J(C-CF$_3$)], 155.2 [^2J(C-F$_3$)], 150.1, 149.5, 140.7, 140.5, 140.4, 140.0, 139.8, 134.6, 132.4, 131.5, 130.3, 129.5, 128.7, 128.0, 127.9, 127.5, 126.7, 126.7, 126.1, 125.9, 125.7, 125.7, 125.2, 125.2, 119.1, 118.4, 114.3 [q, J = 285 Hz, ^2J(C-CF$_3$)] ppm. ^{19}F NMR (376 MHz, [D]chloroform): δ = –74.38 (s) ppm.

4,4′,10,10′-Tetrakis(4-*tert*-butylphenyl)-12,12′-hydroxy-6,6′-bichrysene (2d): The trifluoroacetate **2b** (25 mg, 21 μmol) was dissolved in EtOH (10 mL) and the violet solution treated with a 2 M NaOH solution (10 mL) and stirred until a bright-green colour developed. This solution was then acidified with HCl (2 M, 12 mL), diluted with water (100 mL) and extracted with DCM (2 × 25 mL). This organic solution was then washed with water (2 × 50 mL) and brine (25 mL), dried with magnesium sulfate and concentrated to afford the hydrolysis product **2d** in quantitative yield. M.p. >350 °C. ^{1}H NMR (500 MHz, [D]chloroform, acquired at –40 °C): δ = 8.23 (d, J = 8.2 Hz, 2 H), 7.62–7.54 (m, 4 H), 7.50–7.44 (m, 6 H), 7.43–7.38 (m, 4 H), 7.36–7.32 (m, 4 H), 7.21 (s, 2 H), 7.20 (d, J = 8.2 Hz, 2 H), 7.14 (d, J = 8.0 Hz, 2 H), 7.11 (d, J = 8.0 Hz, 2 H), 6.92 (d, J = 8.0 Hz, 2 H), 6.88 (s, 2 H), 5.65 (br. s, 2 H, OH) ppm. ^{13}C NMR (125 MHz, [D]chloroform, acquired at –40 °C): δ = 207.6, 148.8, 148.2, 145.8, 141.1, 139.8, 138.9, 138.5, 132.0 130.8, 130.1, 129.4, 128.7 (2 C), 128.4, 127.6, 127.6 (2 C), 126.8, 126.4, 125.9, 124.7, 124.6 (2 C), 124.6, 124.3, 124.3, 123.8, 120.0, 108.1 ppm. MS (MALDI-TCNQ$^+$): m/z (%) = 1014 (100) [M]$^+$. HRMS (APCI$^+$): calcd. for $C_{76}H_{71}O_2$ 1015.5454; found 1015.5427.

8,8′-Bi[5,7-dimethyl-12-(3,5-dimethylphenyl)dibenzo[*a*,*e*]pyrene] (3b): Trifluoroacetic acid (1 mL) was added dropwise to a stirred solution of 4,10-bis(3,5-dimethylphenyl)chrysene (**3a**; 150 mg, 347 μmol) and DDQ (165 mg, 728 μmol) in DCM (10 mL) at 0 °C. Over the course of 3 h the reaction mixture was warmed to room temperature after which the reaction was quenched by the addition of a satd. $NaHCO_3$ solution (100 mL) and DCM (100 mL). The organic solution was then washed with $NaHCO_3$ solution (3 × 50 mL), water (2 × 50 mL) and brine (2 × 50 mL) and concentrated in vacuo to give the crude product, which was then purified by column chromatography (25 % toluene/hexane) to afford the title compound as fluorescent yellow crystals (101 mg, 67 %). M.p. >350 °C. ^{1}H NMR (500 MHz, [D]chloroform, acquired at –40 °C): δ = 8.36 (d, J = 7.5 Hz, 2 H), 8.18 (d, J = 9.1 Hz, 2 H), 8.06 (d, J = 8.3 Hz, 2 H), 7.86 (d, J = 7.5 Hz, 2 H), 7.82 (s, 2 H), 7.75–7.70 (m, 6 H), 7.65 (d, J = 9.1 Hz, 2 H), 7.43 (dd, J = 8.3, 7.5 Hz, 2 H), 7.08 (s, 2 H), 5.34 (s, 2 H), 2.60 (s, 6 H), 2.14 (s, 6 H), 1.96 (s, 6 H), 0.58 (s, 6 H) ppm. ^{13}C NMR (125 MHz, [D]chloroform, acquired at –40 °C): δ = 144.8, 139.4, 138.7, 138.3, 136.5, 135.6, 133.4, 132.8, 132.2, 130.7, 130.6, 130.4, 129.8, 129.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.0, 126.4, 126.2, 126.1, 125.9, 125.8, 125.4, 124.1, 123.9, 119.7, 119.4, 22.9, 22.1, 21.6, 21.3 ppm. MS (MALDI-TCNQ$^+$): m/z (%) = 866 (100) [M]$^+$. HRMS (EI$^+$): calcd. for $C_{68}H_{51}$ 867.3991; found 867.3986.

2,4,10,12-Tetramethoxytetrabenzo[*a*,*cd*,*h*,*jk*]pyrene (6b): Trifluoroacetic acid (2.5 mL) was added dropwise to a stirred solution of 4,10-bis(3,5-dimethoxyphenyl)chrysene (**6a**; 125 mg, 0.25 mmol) and DDQ (125 mg, 0.55 mmol) in DCM (25 mL) at 0 °C. Over the course of 1 h the reaction mixture was warmed to room temperature after which the reaction was quenched by the addition of a satd. $NaHCO_3$ solution (100 mL) and DCM (100 mL). The organic solution was then washed with a $NaHCO_3$ solution (3 × 50 mL), water (2 × 50 mL) and brine (2 × 50 mL) and concentrated in vacuo to give the crude product, which was then purified by column chromatography (DCM/hexane, 6:4) to afford the title compound as fluorescent yellow crystals (96 mg, 77 %). M.p. 285 °C. ^{1}H NMR (500 MHz, [D]chloroform): δ = 10.33 (s, 2 H, Ar-H$_5$), 8.76 (d, J = 7.5 Hz, 2 H), 8.46 (d, J = 7.6 Hz, 2 H), 8.05 (t, J = 7.6 Hz, 2 H, Ar-H$_7$), 7.91 (d, J = 2.4 Hz, 2 H, Ar-H^1), 6.90 (d, J = 2.4 Hz, 2 H, Ar-H^3), 4.22 (s, 6 H, CH_3O), 4.09 (s, 6 H, CH_3O) ppm. ^{13}C NMR (125 MHz, [D]chloroform): δ = 167.1, 159.3, 134.4, 131.1, 129.3, 128.1, 127.8, 126.0, 125.5, 122.8, 122.7, 119.7, 115.6, 99.9, 98.8, 56.1, 55.5 ppm. MS (MALDI-DCTB$^+$): m/z (%) = 496 (100) [M]$^+$. HRMS (EI$^+$): calcd. for $C_{34}H_{24}O_4$ 496.1663; found 496.1669.

7,15-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,4,10,12-tetramethoxytetrabenzo[*a*,*cd*,*h*,*jk*]pyrene (7b): 2,4,10,12-Tetramethoxytetrabenzo[*a*,*cd*,*h*,*jk*]pyrene (**6b**; 100 mg, 0.201 mmol), bis(pinacolato)diboron (102.1 mg, 0.402 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dtbpy; 7.2 mg, 0.03 mmol, 10 mol-%) and [Ir(OMe)(cod)]$_2$ (11.22 mg, 0.0169 mmol, 5 mol-%) were added to a 100 mL two-necked round-bottomed flask, which was then purged with N_2. 2-MeTHF (20 mL) was then added by syringe and the reaction mixture heated at reflux overnight. The reaction mixture was then concentrated in vacuo and recrystallised from acetone. Afterwards, the crude product was purified by column chromatography and eluted with a gradient solvent system of 20 % ethyl acetate/petroleum ether followed by 20 % methanol/DCM to afford 7,15-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,4,10,12-tetramethoxytetrabenzo[*a*,*cd*,*h*,*jk*]pyrene (**7b**; overall yield of 49.8 mg) as a yellow powder together with 2,4,10,12-tetramethoxytetrabenzo[*a*,*cd*,*h*,*jk*]pyrene (**6b**) and 7-(4,4,5,5-tetramethyl-1,3,2-dioxa-

borolan-2-yl)-2,4,10,12-tetramethoxytetrabenzo[*a*,*cd*,*h*,*jk*]pyrene (**7a**; ratio of **7b**/**7a**/**6b** = 1.18:1.02:1.0 by ^{1}H NMR spectroscopy). Unfortunately **7a**, **7b** and **6b** proved to be inseparable by column chromatography. Data for **7b**: M.p. 296–298 °C. ^{1}H NMR (400 MHz, [D]-chloroform): δ = 1.26 (s, 24 H, Me), 4.17 (s, 6 H, H 4-OCH_3), 4.27 (s, 6 H, 4-OCH_3), 6.95 (d, J = 2.26 Hz, 2 H, 3-H), 8.08 (s, 2 H, 1-H), 8.99 (s, 2 H, 8-H), 9.17 (s, 2 H, 6-H), 10.43 (s, 2 H, 5-H) ppm. ^{13}C NMR (101 MHz, [D]chloroform): δ = 134.8, 133.7, 131.9, 131.0, 130.8, 130.2, 128.6, 128.1, 128.0, 127.2, 127.0, 126.9, 126.8, 122.8, 121.3, 120.8, 120.7, 120.5 ppm. MS (MALDI-Dithranol): *m*/*z* (%) = 748.5 (98) $[M]^+$, 749.5 (45) $[M + H]^+$, 622 $[M + H - C_6H_{12}BO_2]^+$ HRMS (APCI$^+$): calcd. for $C_{46}H_{47}B_2O_8$ 749.3452 $[M + H]^+$; found 749.3461. IR: $\tilde{\nu}_{max}$ = 3127 and 2978 (Ar C–H), 2929 and 2851 (C–H), 1617 and 1606 (Ar C=C), 1332 (C–O–C), 1321 (br., O–B), 1044 (O–C–B), 1218 (C–B), 688 (B–O bending) cm^{-1}.

7,15-Bis(4-hexylphenyl)-2,4,10,12-tetramethoxytetrabenzo-[*a*,*cd*,*h*,*jk*]pyrene (8): An inseparable mixture of **7b**, **7a** and **6b** (ratio of **7b**/**7a**/**6b** = 1.18:1.02:1.0; 50 mg) was added to a 50 mL three-necked round-bottomed flask, which was then purged with N_2. Toluene (3 mL), 1-iodo-4-hexylbenzene (**9**; 67 mg, 0.233 mmol) and aliquat 336® (2 drops) were then added by syringe, and the solution was degassed with N_2 for 20 min with vigorous stirring. K_2CO_3 (415.0 g, 3.002 mmol) was then dissolved in water (1.5 mL) to form a 2 M solution, which, after degassing for 10 min with N_2, was added to the reaction mixture. The toluene/water biphasic mixture was then degassed for a further 10 min before a solution of $[Pd(PPh_3)_4]$ (0.4 mg, 3.4615 mmol, 3 mol-%) in toluene (ca. 1.5 mL) was added by syringe under N_2. The reaction mixture was then stirred at 80 °C overnight. The toluene layer was then collected and the water layer washed with toluene (10 mL). The combined organic layers were then washed with water (2 × 10 mL) and brine (2 × 10 mL) before drying with $MgSO_4$ and concentrating in vacuo to isolate the crude product. Purification was achieved by column chromatography using a 10–30 % ethyl acetate/petroleum ether solvent system to isolate the purified title compound (10 mg, 50 % yield) as a light-brown solid. ^{1}H NMR (400 MHz, [D]chloroform): δ = 10.38 (s, 1 H), 8.97 (s, 1 H), 8.64 (s, 1 H), 8.00 (s, 1 H), 7.93 (d, J = 8.33 Hz, 1 H), 7.44 (d, J = 8.33 Hz, 1 H), 6.95 (br. s, 1 H), 4.27 (s, 3 H), 4.13 (s, 3 H), 2.77 (br. t, J = 7.7 Hz, 2 H), 1.80–1.72 (m, 2 H), 1.40–1.50 (m, 6 H), 0.94 (m, 3 H) ppm. MS HRMS (APCI$^+$): calcd. for $C_{58}H_{56}O_4$ 817.4251 $[M]^+$; found 817.4249. IR: $\tilde{\nu}_{max}$ = 3110, 3074 and 3005 (Ar C–H), 2154 and 2014 (C–H), 1624 and 1565 (Ar C=C), 1390 (C–O–C) cm^{-1}.

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