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# An orthogonal C–H borylation – cross-coupling strategy for the preparation of tetrasubstituted “A<sub>2</sub>B<sub>2</sub>”-chrysene derivatives with tuneable photophysical properties†

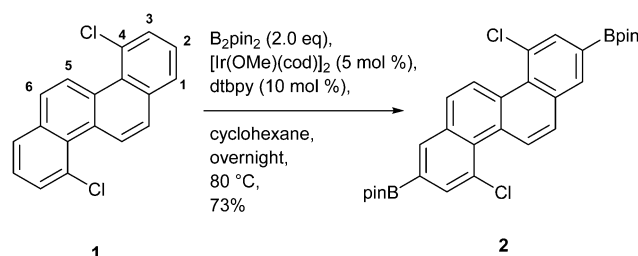
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The regioselective, orthogonal functionalisation of 4,10-dichlorochrysene enables the synthesis of a variety of 2,8,4,10-“A<sub>2</sub>B<sub>2</sub>”-tetrasubstituted chrysenes. Such compounds exhibit broadened UV-vis absorption spectra, decreased band gap and higher HOMO levels compared to the parent chrysene.

The field of organic electronics is a rapidly expanding area and in recent times, the syntheses of a plethora of polycyclic aromatic hydrocarbons (PAHs) have been performed in order to investigate their electronic properties.<sup>1a</sup> In this regard, although much effort has been devoted to the synthesis of pentacene and its analogues,<sup>1b–d</sup> it is only recently that the synthesis of non-linear acene analogues has come to the fore.<sup>1e</sup> The first synthesis of an “A<sub>4</sub>” tetra-substituted chrysene derivative was reported<sup>2</sup> in 2008 and a subsequent study in 2014 indicated that these chrysene derivatives possess promising photophysical properties.<sup>3</sup> A route to “A<sub>2</sub>B<sub>2</sub>” tetra-substituted chrysenes was recently reported by Isobe and co-workers which provides access to chrysenes bearing halogen substituents at either the 3,9- or 2,8-positions, although the substituents at the 6,12-positions are limited to alkyl groups.<sup>4</sup> In connection with our ongoing studies into atom transfer radical cyclisation (ATRC) reactions, we recently reported a new benzannulation reaction (the “BHQ reaction”)<sup>5a</sup> which provides an operationally simple route to halogenated aromatics including 4,10-dichlorochrysene (**1**). In addition we have shown that halide substitution in **1** proceeded cleanly with a variety of nucleophiles enabling a general route, for the first time, to 4,10-disubstituted chrysenes whose electronic and structural properties were examined in some detail.<sup>5b</sup> Given that our newly developed methodology affords ready access to 4,10-dichlorochrysene (**1**) it was envisaged that the halogen substituents in this substrate would serve as directing groups in the C–H borylation chemistry developed by Smith, Hartwig, Ishiyama and Miyaura.<sup>6</sup>

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Scheme 1 Borylation of 4,10-dichlorochrysene (**1**).

Diborylation of 4,10-dichlorochrysene (**1**) using Perutz’s standard reaction conditions<sup>7</sup> (Scheme 1) cleanly afforded 2,8-diborylated chrysene (**2**), as a single regioisomer, in 73% yield after purification by direct recrystallization from the reaction mixture.

By way of comparison it should be noted that the Ir-catalysed borylation of unsubstituted chrysene has been the subject of a previous study by Isobe and co-workers<sup>8</sup> who found the reaction to proceed with high levels of conversion for the di-borylated product (72% yield), but afforded a mixture of isomeric products (2,8- : 2,9- : 5,9- = 1 : 2.1 : 1.2), as shown in Fig. 1.

The present result is notable therefore in that it provides access to a single regioisomer of tetra-substituted chrysene derivative **2** without recourse to lengthy purification.<sup>9,10</sup>

The regiochemical outcome of this reaction requires some comment given the ongoing debate in the literature on this topic.<sup>11</sup> Whereas DFT calculations<sup>12</sup> suggest an order of C–H acidity as

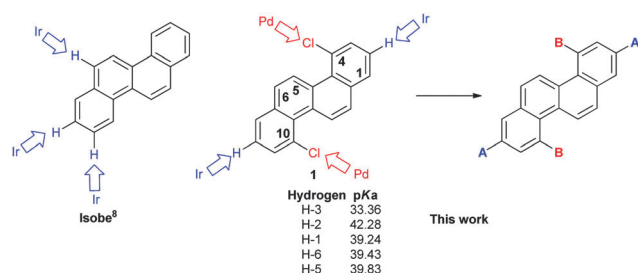
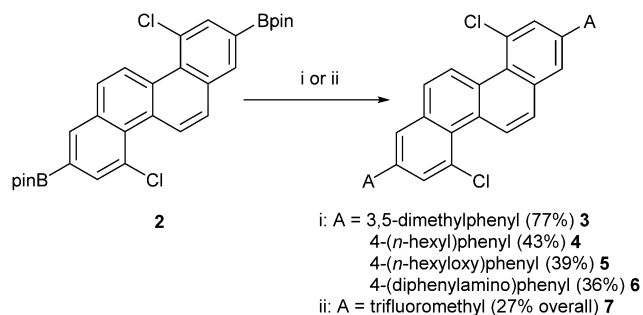


Fig. 1 Orthogonal functionalization of chrysene.



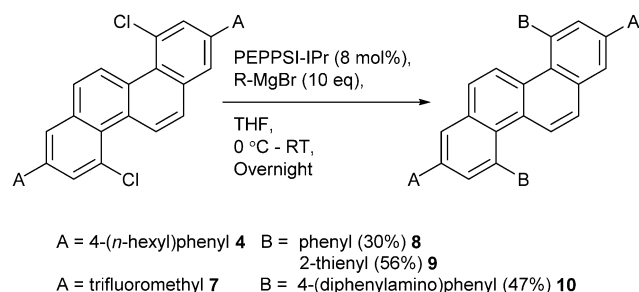
**Scheme 2** Substitution of the 2,8-positions of **2**. Methods: (i) I-A (2.2 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (3 mol%), K<sub>2</sub>CO<sub>3</sub>, aliquot 336, toluene–water, 80 °C overnight. (ii) (a) NaIO<sub>4</sub> (6.0 eq.), HCl (1.4 eq.), THF–water, room temperature, overnight; (b) sodium triflinate (6.0 eq.), CuCl (2.0 eq.), TBHP (10 eq.), MeOH–DCM–water, room temperature, overnight.

depicted in Fig. 1, the present experimental findings support the notion that steric effects play an important role in determining the regiochemical outcome of this borylation reaction.<sup>13</sup> In the present study the chlorine substituent impedes *ortho*-delivery of the catalyst to the most acidic C3-H/C9-H C–H bonds and directs the catalyst to the most accessible, but least acidic C2-H/C8-H centres.

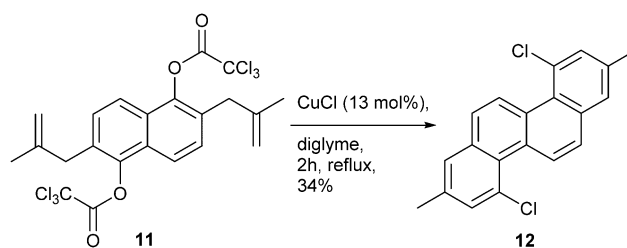
Having optimised the synthesis of the diboronic acid derivative **2** we next embarked upon a study of its functionalisation with the prospect that this would result in the regioselective synthesis of A<sub>2</sub>B<sub>2</sub> tetrasubstituted chrysenes. Encouragingly, the Suzuki reaction of **2** with aryl iodides proved to be chemoselective, affording the coupled products **3–6** in acceptable overall yields where the C–Cl moiety remained intact (Scheme 2).

Due to the extremely low solubility of the tetra-substituted chrysene derivative **3** in common organic solvents solubilising hexyl chains were introduced into the coupling partners during the preparation of **4** and **5**. An electron-withdrawing –CF<sub>3</sub> moiety was also successfully installed at the 2,8-positions of the chrysene core using the chemistry developed by Sanford and co-workers.<sup>14</sup> Here, prior conversion of the ester **2** to the corresponding boronic acid, as described by Hartwig,<sup>15</sup> followed by reaction with sodium triflinate in the presence of CuCl and TBHP afforded the bis-trifluoromethyl derivative **7**.

Further functionalisation at the C4- and C10-positions of **4** and **7** was possible from Kumada cross-coupling reactions with representative aryl Grignard reagents, leading to the preparation of **8** and **9** and the donor–acceptor system **10** (Scheme 3). Overall this strategy enables the orthogonal derivatisation<sup>16</sup> of readily available chrysenes, providing access to novel substitution patterns for further evaluation (Fig. 1).



**Scheme 3** Kumada coupling of 4,10-positions of **4** and **7**.



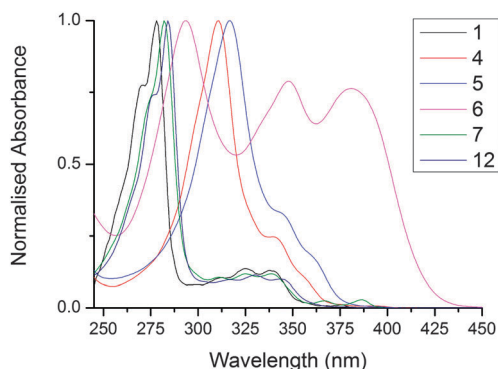
**Scheme 4** Synthesis of 4,10-dichloro-2,8-dimethylchrysene (**12**).

Access to 2,8-dialkylated chrysenes also becomes possible by judicious modification of the substrate employed in the initial BHQ reaction. Hence, the two-directional BHQ benzannulation reaction of the readily available bis-trichloroacetate **11** afforded 4,10-dichloro-2,8-dimethylchrysene **12** in a 34% yield (Scheme 4).

UV-vis data were obtained for compounds **4–10** and **12** in order to probe their electronic properties. In previous studies<sup>5b</sup> substitution of the parent chrysene **1** at the 4,10-positions results in a meagre bathochromic shift (up to 40 nm) of the observed  $\lambda_{\text{max}}$ . In contrast, introduction of even an unfunctionalised aromatic substituent at the C2- and C8-positions (**4**) results in a pronounced bathochromic shift (Fig. 2). This effect is accentuated by the introduction of electron-releasing substituents on the aryl substituent as in the case of the *n*-hexyloxyphenyl-substituted analogue **5**, a trend which becomes significant in the case of the (diphenyl)aminophenyl-substituted chrysene **6**. In this particular example two significant absorptions are now apparent and the tangent of the lowest energy transition (corresponding to the optical band gap) is shifted to 419 nm.

The UV-vis data for **8**, **9**, and **10** (Fig. 3) indicates that in this series only **8** experiences a noticeable bathochromic shift in its  $\lambda_{\text{max}}$  compared to **4**. It is apparent from these measurements that introduction of an aromatic substituent at the C2-/C8-positions of the chrysene core appears to have a significant impact on the UV-vis spectra compared to that resulting from C4-/C10-substitutions.

We were also fortunate in obtaining single crystal X-ray structures for **4**, **7** and **8** (Fig. 4). The crystal structure of **4** was well resolved about the central chrysene core and its aromatic substituents, although it is noted that the hexyl chains present in **4** produce a certain amount of conformational disorder that can be seen in Fig. 4. Similarly to **1**<sup>5b</sup> a torsion is seen across the bay region of the chrysene core of **4** (average of 23.1°). However, while **1** features a 2D lamellar  $\pi$ - $\pi$  stack with a minimum C–C



**Fig. 2** Normalised UV-vis spectra of **1** (lit),<sup>5b</sup> **4–7** and **12**.

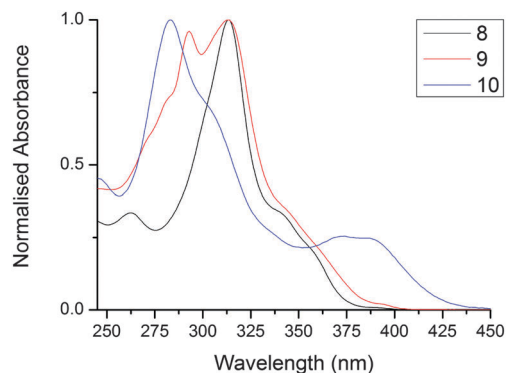


Fig. 3 Normalised UV-vis spectra of **8–10**.

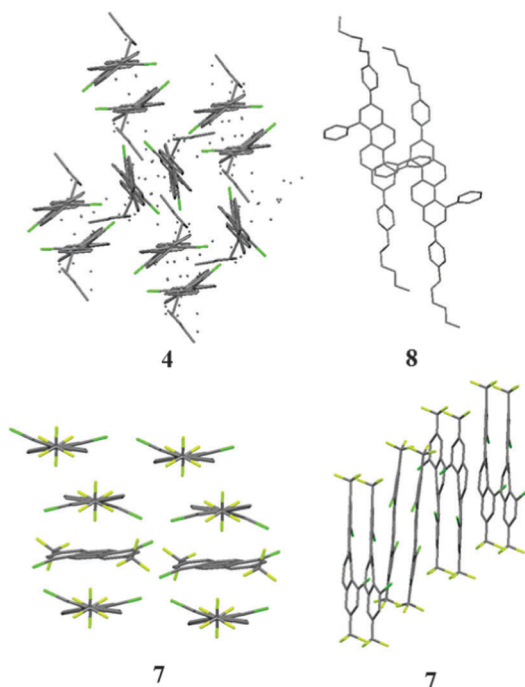


Fig. 4 Crystal structures of **4**, **8** and **7**.

distance of 3.48 Å, **4** features slipped  $\pi$ - $\pi$  stacking that arranges into a dimeric herringbone motif with the closest C-C distance in the  $\pi$ - $\pi$  stack between chrysene cores being 3.61 Å and 3.57 Å between the chrysene and the substituted phenyl ring. In contrast the crystal structure of **8** features no  $\pi$ - $\pi$  stacking. The dimeric structure is instead dominated by the C-H interactions between the 4,10-phenyl substituents and the chrysene core of the neighbouring molecule. By comparison, the structure of the  $\text{CF}_3$ -substituted chrysene (**7**) features a slipped  $\pi$ - $\pi$  stack with a minimum C-C distance of 3.26 Å.

Unusually, the crystal structure of **7** displays two modes of core twisting: one of near planarity (average torsion across the bay region of 5.7°) sandwiched between two twisted chrysenes (average torsion across the bay region of 20.5°). To further add to the complexity of this packing arrangement, the central planar chrysene is also rotated slightly about the stacking axis, giving a slightly off centre  $\pi$ - $\pi$  stack. It is also notable in the crystal structure of **7** that the stacking observed is not lamellar, with slipped stacking in two dimensions.

Analysis of the X-ray data for **4**, **7** and **8** also provides a plausible explanation for the differences in  $\lambda_{\text{max}}$  observed for the C2-/C8- and C4-/C10-substitution patterns. We conclude that the smaller torsion angle between the aryl substituents at C2-/C8- with respect to the chrysene core compared to that observed when substituents are introduced at the C4-/C10- positions (34° vs. 58°; see ESI†) results in a more efficient orbital overlap between the aromatic rings positioned about the biaryl axis, an arrangement which is reflected in the relative magnitude of the bathochromic shifts observed for these molecules.

The UV-vis data presented above also permitted the estimation of an optical band gap for the each of the derivatives synthesised, corresponding to the tangent of the lowest energy transition. Cyclic voltammetry (CV) (measured relative to the ferrocene  $\text{Fc}/\text{Fc}^+$  couple, taken to be -4.8 eV below vacuum) allows the estimation of the HOMO levels of each of the derivatives synthesised (the LUMO of each derivative was estimated by adding the optical band gap to the estimated HOMO), providing a critical insight into their electronic properties. The results are represented in Fig. 5 along with a selection of known semiconducting small molecules for comparison.

Based on this electronic data, it can be observed that relative to **1**, **4** has a slightly reduced band gap with a higher HOMO and a lower LUMO owing to increased conjugation. Both **5** and **6** have higher HOMOs and LUMOs and reduced band gaps, with **6** exhibiting the largest effect due to the electron-donating amino residue. Considering the C4-/C10-positions, the introduction of phenyl substituents, as in **8**, results in an increase in both the HOMO and LUMO relative to **4**, a feature which becomes more pronounced in **9** due to the presence of electron-rich thienyl substituents. Introduction of a powerfully electron-withdrawing  $-\text{CF}_3$  group as in **7**, lowers both the HOMO and LUMO, while the donor-acceptor chrysene **10** features the lowest band gap of all the derivatives, with a significantly increased HOMO compared to **7** and a slightly reduced LUMO compared to **6**. Materials **6**, **9** and **10** display electronics comparable to popular p-type materials tetracene

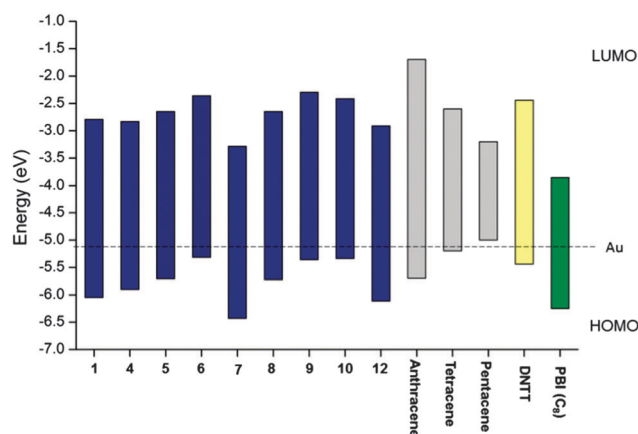


Fig. 5 Graphical representation of the estimated HOMO and LUMO levels of the chrysene derivatives synthesised compared to anthracene, tetracene, pentacene, DNIT, a  $\text{C}_8\text{H}_{17}$  substituted perylene bisimide and the work function of gold (-5.1 eV).<sup>17a-g</sup>

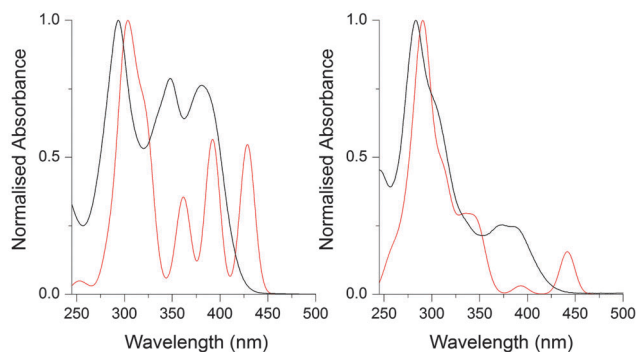


Fig. 6 Comparison of experimental (black) and predicted (red) normalised UV-vis spectra of **6** (left) and **10** (right).

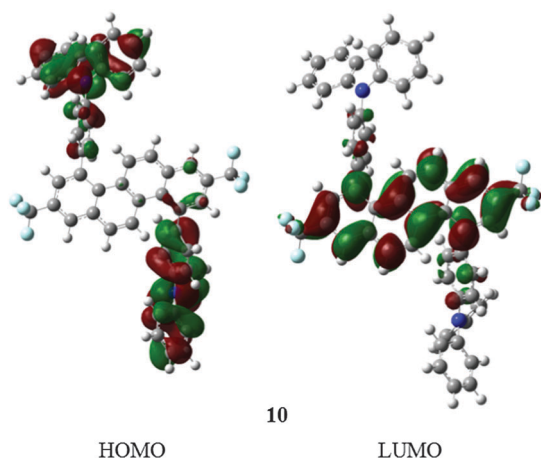


Fig. 7 Computationally predicted MOs of **10**.

and DNTT in terms of band gap, with the magnitude of the HOMO/LUMO levels suggesting applications as p-type materials.

Gas-phase UV-vis spectra were calculated by TD-DFT calculations (as exemplified by **6** and **10** in Fig. 6). Comparison with experimental spectra showed that the lowest energy transitions (HOMO to LUMO) are typically predicted to be too low by about 40–50 nm. In contrast predicted  $\lambda_{\text{max}}$  values, which usually arise from a mixture of HOMO – 1 to LUMO and HOMO to LUMO + 1 transitions, were in good agreement with experimental results.

The HOMO and LUMO of donor–acceptor chrysene **10** (Fig. 7) indicate a strong charge-transfer transition from the HOMO (localised on the electron-rich triphenylamine groups) to the LUMO (localised on the electron-deficient chrysene core), an observation which mirrors the behaviour observed in other donor–acceptor systems.<sup>18</sup> Such effective conjugation is in spite of the out of plane twisting of the substituents at the 4,10-positions, highlighting the effectiveness of this A<sub>2</sub>B<sub>2</sub> donor–acceptor substitution in increasing observed levels of conjugation.

In conclusion, the borylation of 4,10-dichlorochrysene proceeds in a highly regioselective manner enabling the orthogonal synthesis of “A<sub>2</sub>B<sub>2</sub>”-tetrasubstituted chrysenes. The synthetic utility of this methodology combined with the oxidative stability and observed tuneability of the HOMO and LUMO levels of the

core chrysene unit opens up new opportunities for utilisation in organic electronic applications such as p-type semiconductors or as tuneable emissive materials in OLED applications.

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