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### First Synthesis of Diindeno[1,2-g:1',2'-s]rubicene **Derivatives and their Evaluation as Semiconductors**

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Solution-processable derivatives 4a-d of the novel diindeno[1,2-g:1',2'-s]rubicene ring system have been prepared in three steps from 1,5-dichloroanthraquinone. Charge extraction by linearly increasing voltage measurements indicates that 4a-d have bulk mobilities  $<10^{-7}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Consistent with these low mobility values, field-effect transistors fabricated from 4a-d show poor performance. X-ray crystallographic analyses indicate that in the crystalline state, molecules of compounds 4b-d pack in a manner that hinders  $\pi - \pi$  stacking, thus preventing strong electronic coupling between molecules that is essential for high charge mobility semiconductor performance.

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### Introduction

There is great interest in organic field-effect transistors (OFETs) due to their potential application in optoelectronic devices such as displays, organic radiofrequency identification (RFID) tags, biosensors and integrated circuits.<sup>[1]</sup> For example, OFETs are expected to enable the cost-effective production of flexible electronic components and fabrication of devices over large areas and on lightweight flexible substrates.<sup>[2]</sup> To fully realise the potential of OFETs in organic electronics, new semiconductor materials that display high charge mobility  $(>1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$  are required. These materials should be stable, solution processable and accessible in high purity from industrially scalable processes using readily available starting materials. There are several polycyclic aromatic semiconductors that have shown charge mobility  $(\mu) > 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  when fabricated into OFETs (Fig. 1), for example pentacene derivatives such as 1 and structurally related heteroaromatic analogues

such as  $2^{[3]}$  rubrene,<sup>[4]</sup> picene,<sup>[5]</sup> and dithieno[2,3-d:2'3'-d'] benzo[1,2-b:4,5-b'] dithiophene 3.<sup>[6]</sup>

A common attribute of each of these materials in the crystalline state is significant  $\pi$ - $\pi$  stacking between adjacent molecules, which enables strong electronic coupling between molecules, a necessary criterion for ensuring high charge mobility.<sup>[7]</sup> The recent report of the successful use of derivatives of the polycyclic aromatic hydrocarbon (PAH) rubicene<sup>[8]</sup> as p-type semiconductors in bilayer organic solar cells prompted us to consider the use of this little-explored PAH in the design of other polycyclic semiconductors.<sup>[9]</sup> In particular, we envisaged that annelation of indane rings to rubicene to form the 9,19dihydrodiindeno[1,2-g:1',2'-s]rubicene ring system would enable us to access soluble derivatives by means of attachment of appropriate substituents at positions 9 and 19, exemplified by compounds 4a-d in Scheme 1. Furthermore, as Wudl has shown rubicene derivatives crystallizing in columnar stacks and with



Fig. 1. Polycyclic aromatic semiconductors.

 $\pi$ - $\pi$  overlap between adjacent molecules in the stack,<sup>[10]</sup> we thought the planarity and extended  $\pi$  conjugation in this previously unreported 11-ring system could augur well for the discovery of diindeno[1,2-g:1',2'-s]rubicene derivatives with

Scheme 1. General synthesis of diindeno[1,2-g:1',2'-s]rubicene derivatives 4a-d.

crystal packing conducive to the high charge mobility required for effective semiconductor behaviour.

#### **Results and Discussion**

The synthetic route to our target compounds is shown in Scheme 1. Treatment of the 2-bromo-9,9-dialkylfluorenes 6a-d with n-butyl lithium, followed by reaction with 1,5dichloroanthraquinone 5 afforded the diol derivatives 7a-d. Reduction of compounds 7a-d with sodium hypophosphite hydrate/sodium iodide solution in acetic acid gave the 9,10-bis (2-fluorenyl)anthracenes 8a-d in good yield. In the final step, ring closure of 8a-d was achieved in N,N-dimethylacetamide, employing 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and bis (tricyclohexylphosphine)palladium(II) chloride<sup>[11]</sup> in a sealed ampoule at 140°C for 64 h, affording compounds 4a-d in good yield (63-81%). These compounds are the first reported derivatives of the diindeno[1,2-g:1',2'-s]rubicene ring system. The selectivity of this cyclization can be attributed to the increased steric hindrance in the palladium complex blocking the alternative cyclization at position 1'. The diindeno[1,2-g:1',2'-s]rubicene derivatives are magenta or dark purple crystalline solids that are stable in air. The structures of 4a-d were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, mass spectrometry and elemental analysis. Compounds 4a-d possess high thermal stability; thermal gravimetric analyses showed that compounds 4a-d are stable to 314, 340, 350 and 370°C with melting points of 205, 252, 345 and 421°C respectively.

Table 1 shows key data for the photophysical properties of the diindeno [1,2-g:1',2'-s] rubicene derivatives 4a-d. The UVvis absorption spectra for 4a-d show four significant maxima  $(\lambda_{abs})$  at 353, 488, 556 and 597 nm; compounds **4a–d** show an emission wavelength ( $\lambda_{em}$ ) at 705 nm. The absorption and photoluminescent spectra of 4a are shown in Fig. 2; 4b-d displayed almost identical spectra. Cyclic voltammetry (CV) was used to measure the HOMO and LUMO energy levels of 4a-d in dichloromethane referenced to the half-wave potential  $(E_{1/2})$  of the ferrocene/ferrocenium couple. They exhibited identical voltammograms with a reversible reduction, two reversible oxidations, and no sweep-rate dependence. The HOMO energy levels in films of 4a-b were measured using photoelectron spectroscopy in air (PESA). UV-vis spectroscopy was used to determine the band gap, thus enabling LUMO levels to be calculated. The small discrepancies between HOMO levels measured by PESA and CV can be explained by the difference in aggregation between molecules in solution v. the solid state. The LUMO was calculated to be -3.3 eV with a band gap of 2.0 eV for derivatives 4a-b, and the LUMO was calculated to be -3.2 eV with a band gap of 2.0 eV for derivatives 4c-d.

The photophysical properties of compounds 4a-d indicate that they are promising candidates for consideration as

| rubic it i notophysical properties of compounds in | Fable 1. | Photophysical | properties of | compounds 4a- | d |
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| 4 | $\lambda_{\rm abs}  [{\rm nm}]^{\rm A}$ | $\lambda_{\rm em}  [\rm nm]^{\rm A}$ | $E_{\text{onset}}^{\text{ox}}$ [V] | HOMO <sup>B,C</sup> [eV] | LUMO <sup>C</sup> [eV] | Band gap <sup>B</sup> [eV] |
|---|---|--------------------------------------|------------------------------------|--------------------------|------------------------|----------------------------|
| a | 353, 488, 556, 597                      | 705                                  | 0.55                               | -5.35 (-5.67)            | -3.33 (-3.75)          | 2.0                        |
| b | 353, 488, 556, 597                      | 705                                  | 0.53                               | -5.33 (-5.56)            | -3.32 (-3.64)          | 2.0                        |
| c | 353, 488, 556, 597                      | 705                                  | 0.53                               | -5.33                    | -3.23                  | 2.1                        |
| d | 353, 488, 556, 597                      | 705                                  | 0.46                               | -5.26                    | -3.20                  | 2.1                        |

<sup>A</sup>In CH<sub>2</sub>Cl<sub>2</sub> 10 mg in 1 mL.

<sup>B</sup>Electrochemical, referenced to  $E_{1/2}$  of the ferrocene/ferrocenium couple.

<sup>C</sup>Photoelectron spectroscopy in air (PESA); band gaps were determined from UV absorption.



semiconducting materials. The HOMO–LUMO energy levels and the band gap indicate that these compounds may have application as ambipolar semiconductors in transistors.

As a preliminary step to assessment of 4a-d in OFET devices, we attempted to measure the bulk mobility of these



Fig. 2. Absorption (solid) and photoluminescent (dashed) spectra of 4a at room temperature in CH<sub>2</sub>Cl<sub>2</sub>.

compounds using the (photo) charge extraction by linearly increasing voltage (CELIV) technique.<sup>[12]</sup> We were disappointed to observe that **4a–d** showed bulk mobilities  $<10^{-7}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which indicated that these particular compounds were unlikely to demonstrate sufficient charge mobility to enable high performance in transistor devices. Consistent with this view, we were unable to demonstrate transistor performance from OFET devices fabricated from **4a–d**.

In an effort to rationalize the poor semiconductor performance of these compounds, single-crystal X-ray crystallographic studies of **4b–d** were undertaken to determine crystal packing. The single crystal structures of 4b, 4c and 4d are presented in Figs. 3 and 4. The three structures each have a near-planar polycyclic core with the four alkyl chains lying approximately perpendicular to the plane. For both 4c and 4d, the molecules are sited on a crystallographic inversion centre that relates both halves of the molecule. In the case of 4c, the asymmetric unit comprises two half-molecules. The structure of 4b has two unique molecules, one located on an inversion centre and one complete molecule in the asymmetric unit. Most significantly, these X-ray crystallographic studies have shown that the molecular packing of these compounds hinders effective  $\pi - \pi$ stacking of the polycyclic aromatic cores. For example, in the structures of compounds 4b, 4c and 4d, adjacent molecules have their polycyclic core planes approximately perpendicular (interplanar angles: **4b**, 83.0(1)°; **4c**, 85.1(1)°; **4d**, 83.0(1)°) (Fig. 4). As a result, the aromatic core of each molecule is sandwiched between the alkyl chains of its two nearest neighbours; the closest contact between the aromatic cores being an edge-on



Fig. 3. Molecular diagrams of 4c and 4d as shown with 50% thermal ellipsoids and hydrogen atoms as spheres of arbitrary size; (a) side view; (b) top view. Only one of the two unique molecules of 4c is shown; the molecular diagrams of the second molecule, along with that of 4b, are shown in the Supplementary Material.



Fig. 4. Molecular packing of 4c, and 4d (above) and 4b (below) showing the polycyclic aromatic core surrounded by alkyl chains from adjacent molecules. Only the major components of disordered groups are shown. The interplanar separations of the aromatic cores are  $\sim$ 7.5 and 7.7 Å for 4c and 4d respectively, whereas in 4b, there is a closer contact between terminal C<sub>6</sub> rings of the parallel polycyclic ring planes of  $\sim$ 3.4 Å.

C-H...C type (H...C separation: 4b, 3.09 Å; 4c, 2.94 Å; 4d, 2.81 Å) between the terminal C6 ring and one of the central-ring C atoms. Furthermore, in 4c and 4d, the extended molecular packing shows layers of parallel molecules with an approximate interplanar separation of 7.5-7.7 Å (Fig. 4), which is too distant for any  $\pi$ - $\pi$  stacking interaction. However, there is a subtle difference in the packing of molecules in 4b, where the two perpendicular molecules are also individually arrayed into an offset stack (Fig. 4). The interplanar separation in this case is  $\sim$  3.4–3.6 Å but there is only a small amount of overlap between the edges of the terminal C<sub>6</sub> rings. The packing of these diindeno [1,2-g:1',2'-s]rubicene derivatives is unlike that of 5,13-di-tbutylrubicine,<sup>[13]</sup> which has an array of face-to-face  $\pi$ -stacked pairs of molecules. The packing is, however, similar to 3,3'dihexylsilylene-2,2':5,2":5',2"':5",2"":5",2""'-sexithiophene, with two Si-n-hexyl substituents. The molecular backbones of the Si-n-hexyl-substituted sexithiophene stack along the a axis in a slipped herringbone motif having a large minimum distance between the neighbouring backbones of 12.72 Å, indicating negligible  $\pi-\pi$  stacking interactions. Analogous

to **4a**–**d**, the long *n*-hexyl chains of the Si-*n*-hexyl-substituted sexithiophene occupy and create a large free volume between adjacent molecules; consistent with our results no field-effect transistor (FET) activity was observed.<sup>[14]</sup>

#### Conclusion

We have successfully established an efficient synthetic route to the previously unknown diindeno[1,2-g:1',2'-s]rubicene ring system. Compounds **4a**–**d**, derivatives of this novel polycyclic ring system have been prepared and demonstrate photophysical properties consistent with those required for a potential semiconductor. Unfortunately, CELIV measurements indicate that **4a**–**d** have very low bulk charge mobilities, which make them unsuitable for application in OFETs. X-ray crystallographic analyses indicate that in the crystalline state, molecules **4b**–**d** pack in a manner that hinders  $\pi$ – $\pi$  stacking, thus preventing strong electronic coupling between molecules that is essential for high charge mobility semiconductor performance. Further research on the use of diindeno[1,2-g:1',2'-s]rubicene derivatives as semiconductors will require structural modifications that enable the molecules to pack with effective  $\pi$ - $\pi$  stacking.

### **Methods and Materials**

Unless otherwise specified, all <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV400 spectrometer at 400 and 100.6 MHz respectively, or a Bruker AV200 spectrometer at 200 and 50 MHz respectively, using CDCl<sub>3</sub> solutions. Chemical shifts ( $\delta$ ) are measured in ppm, coupling constants (J) in Hz. TLC was performed on 0.25-mm thick plates precoated with Merck Kieselgel 60 F254 silica gel, and visualized by UV light (254 and 366 nm). Positive-ion EI mass spectra were measured on a ThermoQuest MAT95XL mass spectrometer using an ionization energy of 70 eV. Positive-ion electrospray mass spectra (ESIMS) were acquired with a Micromass Q-TOF II mass spectrometer using a cone voltage of 35 eV and a capillary voltage of 3.0 kV. High resolution positive-ion electrospray mass spectra (HR-ESIMS) were obtained with a resolution of 5000-10000 using perfluorokerosene (PFK) as the reference compound. The sample was introduced by direct infusion at a rate of  $5 \,\mu L \,\text{min}^{-1}$  using NaI as an internal calibrant. Microanalyses were performed by Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

Melting points were recorded on a Thermoscientific 9300 digital melting-point apparatus and a Mettler Toledo DSC821 and are uncorrected. UV-Vis spectra were recorded on a Hewlett Packard HP 8453 diode array UV-vis spectrometer. For films, the UV-vis absorptivity was calculated by dividing the measured absorbance by the film thickness. Fluorescence spectra were recorded on a Perkin Elmer LS50B fluorimeter. Thermal gravimetric analysis was carried out on a Mettler Toledo TGA/ SDTA851 and differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC821. Photo electron spectroscopy in air (PESA) measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.5. Samples for PESA were prepared on glass substrates. The electrochemistry measurements were carried out using a Powerlab ML160 potentiostat interfaced via a Powerlab 4/20 controller to a PC running Echem for Windows ver. 1.5.2. The measurements were run in nitrogenpurged dichloromethane with tetrabutylammonium hexafluorophosphate (0.2 M) as the supporting electrolyte. The voltammograms were recorded using a standard three-electrode configuration with a glassy carbon (2 mm diameter) working electrode, a platinum wire counter-electrode and a silver wire pseudo reference electrode. The silver wire was cleaned in concentrated nitric acid and then in concentrated hydrochloric acid to generate the Ag/Ag<sup>+</sup> reference. Voltammograms were recorded with a sweep rate of  $50-200 \,\mathrm{mV \, s^{-1}}$ . The sample concentration was 1 mM. All potentials were referenced to the  $E_{1/2}$  of the ferrocene/ferrocenium couple. Crystals of 4b, 4c and 4d suitable for X-ray crystallographic analysis were grown from CH<sub>2</sub>Cl<sub>2</sub>/hexane using vapour diffusion techniques. Alkyl fluorenes 6a-d were synthesized from literature procedures.<sup>[15]</sup>

### General Synthesis Procedure for 1,5-Dichloro-9,10-bis (9,9-dialkylfluoren-2-yl)-9,10-dihydroanthracene-9,10-diol **7a–d**

#### 1,5-Dichloro-9,10-bis(9,9-dioctylfluoren-2-yl)-9,10dihydroanthracene-9,10-diol **7a**

*n*-BuLi (1.6 M in hexanes, 3.6 mL, 5.8 mmol) was added to a solution of 2-bromo-9,9-dioctylfluorene **6a** (3.0 g, 6.4 mmol) in

THF (10 mL), under N<sub>2</sub> at  $-78^{\circ}$ C, the solution was stirred at  $-78^{\circ}$ C for 40 min and 1,5-dichloroanthraquinone 5 (0.57 g, 2.1 mmol) was added under a blanket of N<sub>2</sub>. The solution was slowly warmed to room temperature and stirred for 16 h. Hydrochloric acid (3 M, 10 mL) was slowly added and the solution stirred for 10 min. The reaction mixture was extracted with dichloromethane  $(2 \times 50 \text{ mL})$ . The combined organic phases were washed with water (50 mL  $\times$  3), the solvent removed under vacuum, the residue redissolved in dichloromethane and dried using a DryDisk<sup>®</sup>. Column chromatography of the residue (silica, 10% EtOAc/petroleum spirits 40–60°C) gave the title compound as pale yellow gum (1.8 g, 63 %). m/z(HR-ESIMS, CDCl<sub>3</sub>/MeOH) 1163.5388  $[M + Ag]^{+\bullet}$ . Calc. for C<sub>72</sub>H<sub>90</sub>O<sub>2</sub>Cl<sub>2</sub>107Ag 1163.5369. δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 7.92 (2H, m), 7.86 (2H, dd, J 8.0, 2.0), 7.58 (2H, d, J 8.0), 7.40-7.13 (12H, m), 4.43 (2H, s), 2.06 (8H, m), 1.31–1.12 (40H, m), 0.87 (12H, t, J 8.0), 0.68 (8H, m). δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>) 150.97, 150.91, 146.87, 142.24, 140.69, 140.08, 134.47, 132.77, 130.84, 129.25, 128.6, 127.11, 126.8, 124.85, 122.82, 120.38, 119.69, 119.45, 74.66, 55.25, 40.59, 40.51, 31.89, 31.85, 30.21, 30.18, 29.42, 29.34, 29.27, 23.96, 23.85, 22.65, 14.13.

The following compounds were prepared by the above procedure.

### 1,5-Dichloro-9,10-bis(9,9-dihexylfluoren-2-yl)-9,10dihydroanthracene-9,10-diol **7b**

Obtained as a pale yellow glassy solid after chromatography (silica, 10% EtOAc/petroleum spirits 40–60°C) (68%). *m/z* (HR-ESIMS, CDCl<sub>3</sub>/MeOH) 967.5013 [M + Na]<sup>+•</sup>. Calc. for C<sub>64</sub>H<sub>74</sub>Cl<sub>2</sub>O<sub>2</sub>Na 967.4964.  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 7.91 (1H, bs), 7.86 (2H, dd, *J* 2.4, 7.2), 7.67 (2H, m), 7.58 (1H, s), 7.56 (1H, s), 7.39–7.23 (10H, m), 7.13 (2H, bs), 4.41 (2H, s), 2.06 (8H, m), 1.14 (24H, m), 0.87–0.78 (12H, m), 0.66 (8H, m).  $\delta_{\rm C}$  (100 MHz, CDCl<sub>3</sub>) 150.96, 150.89, 146.86, 142.22, 140.67, 140.07, 134.45, 132.74, 130.84, 129.23, 128.58, 127.1, 126.79, 124.83, 122.8, 120.36, 119.68, 119.42, 74.65, 55.23, 40.57, 40.45, 31.61, 31.57, 29.79, 29.71, 23.80, 23.74, 22.57, 22.52, 14.07, 14.02.

### 1,5-Dichloro-9,10-bis(9,9-dipentylfluoren-2-yl)-9,10dihydroanthracene-9,10-diol **7**c

Obtained as a pale yellow glassy solid after chromatography (silica, 10% EtOAc/petroleum spirits 40–60°C) (88%). *m/z* (HR-ESIMS, CDCl<sub>3</sub>/MeOH) 911.4352 [M + Na]<sup>+•</sup>. Calc. for C<sub>60</sub>H<sub>66</sub>Cl<sub>2</sub>O<sub>2</sub>Na 911.4338.  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 7.87 (4H, m), 7.56 (2H, d, *J* 8.0), 7.38–7.21 (10H, m), 7.10 (2H, m), 4.35 (2H, s), 2.03 (8H, m), 1.10 (16H, m), 0.77–0.63 (20H, m).  $\delta_{\rm C}$  (100 MHz, CDCl<sub>3</sub>) 150.93, 150.88, 146.87, 142.16, 140.64, 140.06, 134.44, 132.70, 130.82, 129.25, 128.58, 127.09, 126.77, 124.79, 122.77, 120.34, 119.66, 119.41, 74.64, 55.20, 40.46, 40.33, 32.29, 32.21, 23.42, 23.4, 22.35, 22.29, 14.01, 13.95.

### 1,5-Dichloro-9,10-bis(9,9-dibutylfluoren-2-yl)-9,10dihydroanthracene-9,10-diol **7d**

Obtained as a white glassy solid after chromatography (silica, 10% EtOAc/petroleum spirits 40–60°C) (64%). *m/z* (HR-ESIMS, CDCl<sub>3</sub>/MeOH) 832.3808 [M + Na]<sup>+•</sup>. Calc. for C<sub>56</sub>H<sub>58</sub>Cl<sub>2</sub>O<sub>2</sub> 832.3814.  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 7.89–7.84 (4H, m), 7.65 (2H, m), 7.56 (2H, d, *J* 8), 7.38–7.23 (10H, m), 7.10 (2H, m), 4.34 (2H, s), 2.07 (8H, m), 1.13 (8H, m), 0.77–0.69 (20H, m).  $\delta_{\rm C}$  (50 MHz, CDCl<sub>3</sub>) 150.9, 146.9, 142.15, 140.64, 140.07, 134.43, 132.67, 130.83, 129.26, 128.59, 127.09, 126.78,

124.79, 122.81, 120.35, 119.66, 119.41, 74.64, 55.13, 40.25, 40.08, 26.01, 23.16, 23.02, 13.94, 13.88.

### General Synthesis Procedure for 1,5-Dichloro-9,10-bis (9,9-dialkylfluoren-2-yl)anthracene **8a–c**

1,5-Dichloro-9,10-bis(9,9-dioctylfluoren-2-yl) anthracene **8a** 

A mixture of potassium iodide (4.1 g, 27.3 mmol) and sodium hypophosphite hydrate (4.2 g, 47.6 mmol) in acetic acid (30 mL) was heated gently until the solids had dissolved. The hot solution was added to diol 7a (1.2 g, 2.2 mmol) and the resulting suspension heated at reflux for 4 h. The cooled suspension was filtered and the collected solid washed with water (100 mL) followed by MeOH (100 mL) to give the title compound as a yellow powder of sufficient purity for further reaction. mp 161-162°C. *m/z* (HR-ESIMS, CDCl<sub>3</sub>/MeOH) 1022.6282 [M]<sup>+•</sup> Calc. for C<sub>72</sub>H<sub>88</sub>Cl<sub>2</sub> 1022.6263. δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 7.83 (4H, dd, J 8.0, 2.4), 7.69 (4H, d, J 8.8), 7.50 (4H, d, J 6.8), 7.41-7.34 (10H, m), 7.14 (2H, dd, J7.2, 1.2), 2.0 (m, 8H), 1.22-1.08  $(m, 40H), 0.83 (m, 20H). \delta_{C} (100 \text{ MHz}, \text{CDCl}_{3}) 151.03, 151.01,$ 150.15, 150.12, 141.04, 140.66, 139.73, 137.85, 133.90, 131.68, 131.66, 130.07, 129.54, 127.57, 127.14, 126.88, 126.82, 126.29, 124.48, 122.81, 119.78, 118.91, 114.99, 55.19, 40.75, 40.55, 31.84, 30.11, 30.05, 29.38, 29.36, 29.25, 29.21, 24.01, 23.82, 22.61, 14.09.

The following compounds were prepared by the above procedure.

### 1,5-Dichloro-9,10-bis(9,9-dihexylfluoren-2-yl) anthracene **8b**

Obtained as a yellow powder (83 %). mp 202–203°C. m/z (HR-ESIMS, CDCl<sub>3</sub>/MeOH) 933.4947 [M + Na]<sup>+•</sup>. Calc. for C<sub>64</sub>H<sub>74</sub>Cl<sub>2</sub>Na 933.4909.  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 7.83 (4H, m), 7.68 (2H, M), 7.50 (2h, d, J6.8), 7.40–7.34 (10H, m), 7.14 (1H, d 7.2 J), 7.12 (1H, d, J 6.8), 1.99 (8H, m), 1.66–1.07 (24H, m), 0.79–0.65 (22H, m).  $\delta_{\rm C}$  (400 MHz, CDCl<sub>3</sub>) 151.02, 151.01, 150.16, 150.12, 141.05, 140.68, 139.74, 139.72, 137.85, 133.9, 131.67, 131.66, 130.1, 129.56, 127.57, 127.16, 126.91, 126.83, 126.28, 124.49, 122.81, 119.81, 119.79, 118.94, 118.92, 55.22, 55.19, 40.76, 31.62, 31.6, 29.74, 29.68, 29.64, 23.91, 23.76, 22.56, 22.51, 22.49, 14.03.

### 1,5-Dichloro-9,10-bis(9,9-dipentylfluoren-2-yl) anthracene **8c**

Obtained as a yellow powder (87%). mp 278–279°C. m/z (HR-ESIMS, CDCl<sub>3</sub>/MeOH) 877.4294 [M + Na]<sup>+•</sup>. Calc. for C<sub>60</sub>H<sub>64</sub>Cl<sub>2</sub>Na 877.4283.  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 7.83 (4H, m), 7.68 (2H, d, J 9.2), 7.50 (2H, d, J 6.8), 7.39–7.33 (10H, m), 7.14 (1H, d, J 8.8), 7.12 (1H, d, J 8.8), 2.0 (8H, m), 1.09 (16H, m), 0.86–0.65 (20H, m).  $\delta_{\rm C}$  (50 MHz, CDCl<sub>3</sub>) 150.99, 150.10, 150.06, 141.03, 140.65, 139.7, 137.81, 133.87, 131.61, 130.06, 129.54, 127.55, 127.13, 126.86, 126.8, 126.24, 124.45, 122.77, 119.77, 118.91, 55.19, 55.16, 40.68, 40.47, 32.3, 32.16, 32.14, 23.54, 23.46, 22.39, 22.33, 14.02, 13.94.

### 1,5-Dichloro-9,10-bis(9,9-dibutylfluoren-2-yl) anthracene **8d**

Obtained as a yellow powder (52%). mp 320–326°C. *m/z* (HR-ESIMS, CDCl<sub>3</sub>/MeOH) 821.36601 [M + Na]<sup>+•</sup>. Calc. for C<sub>56</sub>H<sub>56</sub>Cl<sub>2</sub>Na 821.36565.  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 7.85 (4H, m), 7.71 (2H, dd, *J* 1.2, 7.6), 7.53 (2H, d, *J* 6.8), 7.40 (10H, m), 7.18 (1H, d, *J* 7.2), 7.15 (1H, d, *J* 7.2), 2.03 (8H, m), 1.13 (8H, m),

0.85–0.67 (20H, m). Compound was not soluble enough for  $^{13}\mathrm{C}$  NMR.

General Synthesis Procedure for 9,9,19,19-Tetraalkyl-4,19dihydrodiindeno-[1,2-g:1',2'-s]rubicene **4a–d** 9,9,19,19-Tetraoctyl-9,19-dihydrodiindeno [1,2-g:1',2'-s]rubicene **4a** 

1,5-dichloro-9,10-bis(9,9-dioctylfluoren-2-yl)anthracene 7a (0.95 g, 0.93 mmol), bis(tricyclohexylphosphine)palladium(II) chloride (0.20 g, 0.27 mmol), 1,8-diazabicyclo[5.4.0]undec-7ene (10 mL) and N,N-dimethylacetamide (23 mL) were placed in an ampoule, with a stirring bead. The ampoule was degassed by three freeze-evacuate-thaw cycles, sealed under vacuum  $(\sim 0.05 \text{ mmHg})$  and then heated with stirring at 140°C for 65 h. The ampoule was cooled, opened and the solution poured into methanol (100 mL). The resulting red precipitate was collected by filtration and washed with methanol. Column chromatography (silica, 10% CH<sub>2</sub>Cl<sub>2</sub>/petroleum spirits 40-60°C) gave the title compound as a dark maroon powder (0.56 g, 64 %). mp 203–206°C. *m/z* (HR-ESIMS, CDCl<sub>3</sub>/MeOH) 950.6730 [M]<sup>+•</sup>. Calc. for C72H86 950.6764. Found: C 90.88, H 9.18. Calc.: C 90.89, H 9.11 %. δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 8.69 (2H, d, J 8.8), 8.20 (2H, s), 8.25 (2H, s), 8.12 (2H, d, J 6.8), 7.86 (4H, m), 7.43-7.33 (6H, m), 2.15 (8H, m), 1.10 (40H, m), 0.91-0.68 (20H, m). δ<sub>C</sub> (50 MHz, CDCl<sub>3</sub>) 151.41, 151.19, 141.12, 140.39, 139.51, 138.92, 138.46, 133.76, 133.69, 128.86, 126.98, 126.85, 125.39, 124.50, 122.86, 119.90, 119.56, 118.05, 113.04, 55.29, 40.73, 31.77, 30.10, 29.70, 29.22, 23.86, 22.54, 14.00.

The following compounds were prepared by the above procedure.

### *9,9,19,19-Tetrahexyl-9,19-dihydrodiindeno* [*1,2-g*:1',2'-s]*rubicene* **4***b*

Obtained as a dark rusty maroon powder following column chromatography (silica, 20% CH<sub>2</sub>Cl<sub>2</sub>/petroleum spirits 40–60°C) (67%). mp 249–252°C. *m/z* (HR-ESIMS, CDCl<sub>3</sub>/MeOH) 838.5488 [M]<sup>+•</sup>. Calc. for  $C_{64}H_{70}$  838.5478. Found C 91.45, H 8.41. Calc.: C 91.59, H 8.41%.  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 8.69 (2H, d, *J* 8.4), 8.30 (2H, s), 8.25 (2H, s), 8.11 (2H, d, *J* 6.9), 7.85 (4H, m), 7.43–7.33 (6H, m), 2.16 (8H, m), 1.10 (24H, m), 0.91–0.69 (20H, m).  $\delta_{\rm C}$  (50 MHz, CDCl<sub>3</sub>) 151.39, 151.17, 141.1, 140.37, 139.49, 138.9, 138.44, 133.73, 133.67, 128.86, 126.96, 126.84, 125.36, 124.48, 122.84, 119.89, 119.55, 118.02, 113.02, 55.26, 40.73, 31.49, 29.75, 23.81, 22.54, 13.93.

### *9,9,19,19-Tetrapentyl-9,19-dihydrodiindeno* [*1,2-g*:1',2'-s]*rubicene* **4***c*

Obtained as a dark purple solid following column chromatography (silica, 30 % CH<sub>2</sub>Cl<sub>2</sub>/petroleum spirits 40–60°C). mp 344–346°C. *m/z* (HR-ESIMS, CDCl<sub>3</sub>/MeOH) 782.4852 [M]<sup>+•</sup>. Calc. for C<sub>60</sub>H<sub>62</sub> 782.4821. Found C 92.02, H 7.98. Calc. C 92.13, H 7.90 %.  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 8.668 (2H, d, *J* 8.8), 8.30 (1H, s,), 8.25 (1H, s), 8.11 (1H, *J* 6.4), 7.85 (4H, m), 7.43–7.33 (6H, m), 2.15 (8H, m), 1.10 (16H, m), 0.89–0.68 (20H, m).  $\delta_{\rm C}$  (50 MHz, CDCl<sub>3</sub>) 151.38, 151.16, 141.1, 140.37, 139.5, 138.9, 138.43, 133.72, 133.66, 128.86, 126.97, 126.84, 125.36, 124.46, 122.83, 119.89, 119.55, 118.00, 113.03, 55.25, 40.69, 32.29, 23.53, 22.29, 13.95.

### *9,9,19,19-Tetrabutyl-9,19-dihydrodiindeno* [*1,2-g*:1',2'-s]*rubicene* **4d**

Obtained as a dark purple, almost black, solid following column chromatography (silica, 20% CH<sub>2</sub>Cl<sub>2</sub>/petroleum spirits

40–60°C). mp 420–422°C (DSC). *m/z* (HR-ESIMS, CDCl<sub>3</sub>/MeOH) 726.4222 [M]<sup>+•</sup>. Calc. for C<sub>56</sub>H<sub>54</sub> 726.4226. Found C 92.47, H 7.72. Calc.: C 92.51, H 7.49%.  $\delta_{\rm H}$  NMR (400 MHz, CDCl<sub>3</sub>) 8.70 (2H, d J 8.4), 8.31 (2H, s), 8.26 (2H, s), 8.12 (2H, d J 6.8), 7.87 (4H, m), 7.43–7.33 (6H, m), 2.16 (8H, m), 1.14 (8H, m), 0.85–0.67 (20H, m).  $\delta_{\rm C}$  (50 MHz, CDCl<sub>3</sub>) 151.38, 151.16, 141.11, 140.38, 139.5, 138.91, 138.44, 133.68, 128.89, 126.97, 126.84, 125.38, 124.49, 122.85, 119.98, 119.92, 119.55, 118.03, 113.03, 55.19, 40.55, 26.03, 23.11, 13.80.

# *X-Ray Crystal Structure Determinations for 9,9,19,19-Tetraalkyl-4,19-dihydrodiindeno- [1,2-g:1',2'-s]rubicene* **4b–d**

X-ray diffraction data were collected for representative crystals of 4b-d, covered in viscous oil and mounted onto a glass fibre, using a Bruker APEXII CCD diffractometer and MoKa radiation,  $\lambda = 0.71073$  Å, equipped with an Oxford Cryosystems 700 temperature controller. Data collection and data reduction were performed using the Bruker Apex2 v2.0 program suite.<sup>[16]</sup> A sphere or hemisphere of diffraction data  $(N_t)$  was collected to  $2\theta = 50^{\circ}$  using 0.5° correlated images and a combination of  $\phi$ and  $\omega$  scans. Data were corrected for absorption (SADABS<sup>[16]</sup>) and merged to N unique reflections ( $R_{int}$  as quoted) that were used for structure solution by direct methods and full matrix least-squares refinement using SHELX97<sup>[17]</sup> in conjunction with the X-SEED interface.<sup>[18]</sup> Hydrogen atoms were placed in calculated positions and refined using a riding model (C-H 0.954 Å,  $U_{iso}(H) = 1.5 \times U_{iso}(C)$  for CH<sub>3</sub> or  $U_{iso}(H) = 1.2 \times U_{iso}(H)$  $U_{iso}(C)$  for all other groups). Crystal and refinement details are listed below. In all cases, the samples appeared visually as wellformed crystals but gave problematic diffraction data. Several samples were measured for each compound under differing conditions, the presented data representing the best in each case. For compound 4c, several off-lattice reflections were observed in all samples. For the final dataset, two twin domains, related by 180° rotation about reciprocal axis 0 0 1, were identified using CELL\_NOW<sup>[16]</sup> and the images were processed using SAINT+/ TWINABS,<sup>[16]</sup> resulting in a total of 16463 reflections, of which 4059 were from domain 1, 4055 were from domain 2 and 8349 were composite. Successful refinement of the structure with HKLF5 gave a twin ratio 0.254.

### *9,9,19,19-Tetrahexyl-9,19-dihydrodiindeno* [*1,2-g:1',2'-s*]*rubicene* **4***b*

C<sub>64</sub>H<sub>70</sub>, FW 839.20. Cambridge Crystallographic Data Centre (CCDC) 842099. Red prism  $0.20 \times 0.13 \times 0.10$  mm, T = 173(1) K, monoclinic  $P2_1/n$ ; a = 13.070(4), b = 16.387(6),  $c = 34.727(13) \text{ Å}; \beta = 99.19(1)^\circ, V = 7342(4) \text{ Å}^3, Z = 6, \rho_{calc} = 1.139 \text{ g cm}^{-3}, \mu = 0.064 \text{ mm}^{-1}, T_{min}/T_{max} = 0.48, N_t = 32784,$ N = 12435 ( $R_{int} = 0.051$ ), R = 0.089, wR2 = 0.218 (for 7176 reflections with  $I > 2\sigma I$ , R = 0.145, wR2 = 0.260 (all data), GoF = 1.039. The maximum residual electron density peak of 0.54  $e\, {\rm \AA}^{-3}$  was located 0.96  ${\rm \AA}$  from C(92'). The structure contains 1.5 molecules in the asymmetric unit. After location and refinement of the aromatic components, four of the hexyl chains were partially located and the remaining two hexyl arms were poorly resolved. For the final refinement, two hexyl arms C(79-84) and C(91-96) were modelled as disordered over two positions (refined occupancies 0.54: 0.46 and 0.56: 0.44 respectively), with each component having restrained C-C bond lengths, C-C-C bond angles and anisotropic displacement parameters. For two further hexyl arms, the terminal C atoms C(30-32) and C(87-90) were also modelled as disordered (occupancies fixed at 0.50:0.50 and 0.60:0.40 respectively) with restrained C–C bond lengths, C–C–C bond angles and anisotropic displacement parameters.

### 9,9,19,19-Tetrapentyl-9,19-dihydrodiindeno [1,2-g:1',2'-s]rubicene **4**c

 $C_{60}H_{62}$ , FW 783.10. CCDC 842100. Red plate  $0.20 \times 0.18 \times 0.05 \text{ mm}$ , T = 123(1) K, triclinic P(-1); a = 9.883(2), b = 13.629(3), c = 17.419(3) Å;  $\alpha = 91.449(6)$ ,  $\beta = 94.875(9)$ ,  $\gamma = 109.933(6)^{\circ}$ ; V = 2194.(7) Å<sup>3</sup>, Z = 2,  $\rho_{calc} = 1.185 \text{ g cm}^{-3}$ ,  $\mu = 0.066 \text{ mm}^{-1}$ ,  $T_{min}/T_{max} = 0.68$ ,  $N_t = 16463$ , N = 8167 ( $R_{int} = 0.066$  (statistics for all single and composite reflections)), R = 0.078, wR2 = 0.191 (for 4212 reflections with  $I > 2\sigma I$ ), R = 0.141, wR2 = 0.251 (all data), GoF = 0.956.

## *9,9,19,19-Tetrabutyl-9,19-dihydrodiindeno* [*1,2-g*:1'*,2*'*-s*]*rubicene* **4d**

 $C_{56}H_{54}$ , FW 726.99. CCDC 842101. Red plate  $0.20 \times 0.17 \times 0.05 \text{ mm}$ , T = 123(1) K, monoclinic  $P2_1/c$ ; a = 9.7315(12), b = 15.945(2), c = 14.204(2) Å;  $\beta = 109.908(4)^\circ$ , V = 2072.2(4) Å<sup>3</sup>, Z = 2,  $\rho_{calc} = 1.165 \text{ g cm}^{-3}$ ,  $\mu = 0.065 \text{ mm}^{-1}$ ,  $T_{min}/T_{max} = 0.59$ ,  $N_t = 6032$ , N = 3591 ( $R_{int} = 0.079$ ), R = 0.071, wR2 = 0.140 (for 1453 reflections with  $I > 2\sigma I$ ), R = 0.199, wR2 = 0.193 (all data), GoF = 0.934. One of the butyl arms, C(25–28), was modelled as disordered with C(27) and C(28) refined in two positions (occupancies fixed at 0.60: 0.40 after trial refinement). The geometry of the minor component was restrained to be similar to that of the major component.

#### **Supplementary Material**

Supplementary material containing <sup>1</sup>H and <sup>13</sup>C NMR data for compounds, **7a–d**, **8a–d**, **4a** and additional crystallographic details of structures **4b–d** is available from the Journal's website.

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#### References

- (a) S. M. Goetz, C. M. Erlen, H. Grothe, B. Wolf, P. Lugli, G. Scarpa, *Org. Electron.* **2009**, *10*, 573. doi:10.1016/J.ORGEL.2009.02.011
   (b) D. M. de Leeuw, E. Cantatore, *Mater. Sci. Semicond. Process.* **2008**, *11*, 199. doi:10.1016/J.MSSP.2008.10.001
   (c) K. Myny, S. Steudel, S. Smout, P. Vicca, F. Furthner, B. van der Putten, A. K. Tripathi, G. H. Gelinck, J. Genoe, W. Dehaene, P. Heremans, *Org. Electron.* **2010**, *11*, 1176. doi:10.1016/J.ORGEL. 2010.04.013
- [2] (a) S. Allard, M. Forster, B. Souharce, H. Thiem, U. Scherf, *Angew. Chem. Int. Ed.* 2008, *47*, 4070. doi:10.1002/ANIE.200701920
  (b) Y. Yamashita, *Sci. Technol. Adv. Mater.* 2009, *10*, 024313. doi:10.1088/1468-6996/10/2/024313
- [3] (a) J. E. Anthony, Angew. Chem. Int. Ed. 2008, 47, 452. doi:10.1002/ ANIE.200604045

(b) M. M. Payne, S. A. Odom, S. R. Parkin, J. E. Anthony, *Org. Lett.* 2004, 6, 3325. doi:10.1021/OL048686D

(c) S. Subramanian, S. K. Park, S. R. Parkin, V. Podzorov, T. N. Jackson, J. E. Anthony, *J. Am. Chem. Soc.* **2008**, *130*, 2706. doi:10.1021/JA073235K

- [4] (a) O. Ostroverkhova, D. G. Cooke, F. A. Hegmann, J. E. Anthony, V. Podzorov, M. E. Gershenson, O. D. Jurchescu, T. T. M. Palstra, *Appl. Phys. Lett.* 2006, *88*, 162101. doi:10.1063/1.2193801
  (b) C. V. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, J. A. Rogers, *Science* 2004, *303*, 1644.
  (c) V. Podzorov, E. Menard, A. Borissov, V. Kiryukhin, J. A. Rogers, M. E. Gershenson, *Phys. Rev. Lett.* 2004, *93*, 086602. doi:10.1103/PHYSREVLETT.93.086602
  (d) V. Podzorov, E. Menard, J. A. Rogers, M. E. Gershenson, *Phys.*
  - (d) V. Podzorov, E. Menard, J. A. Rogers, M. E. Gersnenson, *Phys. Rev. Lett.* 2005, *95*, 226601. doi:10.1103/PHYSREVLETT.95.226601
    (e) J. Takeya, M. Yamagishi, Y. Tominari, R. Hirahara, Y. Nakazawa, T. Nishikawa, T. Kawase, T. Shimoda, S. Ogawa, *Appl. Phys. Lett.* 2007, *90*, 102120. doi:10.1063/1.2711393
- [5] H. Okamoto, N. Kawasaki, Y. Kaji, Y. Kubozono, A. Fujiwara, M. Yamaji, J. Am. Chem. Soc. 2008, 130, 10470. doi:10.1021/ JA803291A
- [6] P. Gao, D. Beckmann, H. N. Tsao, X. Feng, V. Enkelmann, M. Baumgarten, W. Pisula, K. Müllen, *Adv. Mater.* 2009, *21*, 213. doi:10.1002/ADMA.200802031
- [7] (a) H. Meng, F. Sun, M. B. Goldfinger, G. D. Jaycox, Z. Li, W. J. Marshall, G. S. Blackman, J. Am. Chem. Soc. 2005, 127, 2406. doi:10.1021/JA043189D

(b) H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara, T. Yui, J. Am. Chem. Soc. 2007, 129, 15732. doi:10.1021/JA0748411

(c) S. Subramanian, S. K. Park, S. R. Parkin, V. Podzorov, T. N. Jackson, J. E. Anthony, J. Am. Chem. Soc. 2008, 130, 2706. doi:10.1021/JA073235K

(d) G. R. Llorente, M.-B. Dufourg-Madec, D. J. Crouch, R. G. Pritchard, S. Ogier, S. G. Yeates, *Chem. Commun.* **2009**, 3059. doi:10.1039/B901448A

(e) M. M. Payne, S. R. Parkin, J. E. Anthony, C.-C. Kuo, T. N. Jackson, J. Am. Chem. Soc. 2005, 127, 4986.

(f) X.-C. Li, H. Sirringhaus, F. Garnier, A. B. Holmes, S. C. Moratti, N. Feeder, W. Clegg, S. J. Teat, R. H. Friend, *J. Am. Chem. Soc.* **1998**, *120*, 2206. doi:10.1021/JA9735968

- [8] R. G. Harvey, *Polycyclic Aromatic Hydrocarbons* 1997, p. 586 (Wiley/VCH: New York, NY).
- [9] H. Ikeda, R. Maeda, M. Matsuura, WO/2009/130991, PCT/JP2009/ 057044, 2009.
- [10] A. R. Mohebbi, F. Wudl, Chem. Eur. J. 2011, 17, 2642. doi:10.1002/ CHEM.201002608
- [11] (a) M. Smet, J. Dijk, W. Dehaen, *Synlett.* **1999**, 495.
  (b) L. Wang, P. B. Shevlin, *Org. Lett.* **2000**, *2*, 3703.
- [12] (a) G. Juška, K. Genevičius, K. Arlauskas, R. Österbacka, H. Stubb, *Macromol. Symp.* 2004, 212, 209. doi:10.1002/MASY.200450820
  (b) G. Dennler, A. J. Mozer, G. Juška, A. Pivrikas, R. Österbacka, A. Fuchsbauer, N. S. Sariciftci, *Org. Electron.* 2006, 7, 229. doi:10.1016/J.ORGEL.2006.02.004
  (c) A. J. Mozer, N. S. Sariciftci, A. Pivrikas, R. Österbacka, G. Juška, L. Brassat, H. Bässler, *Phys. Rev. B* 2005, 71, 035214. doi:10.1103/ PHYSREVB.71.035214
- [13] K. Peters, H. Langhals, G. Werner, Cryst. Struct. Commun. 1981, 10, 713.
- [14] H. Huang, J. Youn, R. P. Ortiz, Y. Zheng, A. Facchetti, T. Marks, *Chem. Mater.* 2011, 23, 2185. doi:10.1021/CM200009K
- [15] (a) S.-J. Liu, Q. Zhao, R.-F. Chen, Y. Deng, Q.-L. Fan, F.-Y. Li, L.-H. Wang, C.-H. Huang, W. Huang, *Chem – Eur. J.* 2006, *12*, 4351. doi:10.1002/CHEM.200501095
  (b) S. P. Dudek, M. Pouderoijen, R. Abbel, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* 2005, *127*, 11763. doi:10.1021/ JA052054K
  (c) Y. Geng, S. W. Culligan, A. Trajkovska, J. U. Wallace, S. H. Chen, *Chem. Mater.* 2003, *15*, 542. doi:10.1021/CM0208859
  (d) H. Li, M. S. Wong, Y. Tao, J. Lu, *Chem. – Eur. J.* 2005, *11*, 3285. doi:10.1002/CHEM.200401152
- [16] APEX2 v2.0, SAINT/SAINT+, SADABS, TWINABS, CELL\_NOW (Bruker AXS Inc.: Madison, WI).
- [17] G. M. Sheldrick, Acta Crystallogr. 2008, A64, 112.
- [18] L. J. Barbour, J. Supramol. Chem. 2001, 1, 189. doi:10.1016/S1472-7862(02)00030-8