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Dibenzo[*b*,*def*]chrysene Derivatives: Solution-Processable Small Molecules that Deliver High Power-Conversion Efficiencies in Bulk Heterojunction Solar Cells

Kevin N. Winzenberg,[†] Peter Kemppinen,[†]
Giovanni Fanchini,[†] Mark Bown,[†] Gavin E. Collis,[†]
Craig M. Forsyth,[‡] Katalin Hegedus,[†]
Th. Birendra Singh,[†] and Scott E. Watkins*,[†]

[†]*Ian Wark Laboratory, CSIRO Molecular and Health Technologies, Clayton South, Victoria 3169, Australia and*
[‡]*School of Chemistry, Monash University, Clayton, Victoria 3800, Australia*

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Organic solar cells offer the promise of low-cost electricity and the design of new materials to deliver on this promise is an area of intense research. To date, the most successful active (light absorbing) materials have been based on thiophene-based polymers blended with soluble, small molecule fullerenes.[1−3] Recently, reports of high power conversion efficiencies from devices based on small molecule−small molecule blends have raised the prospect of a distinct shift in approach toward the design and selection of materials for organic solar cells.[4−10] The choice of small molecule−small molecule blends over polymer-based blends offers advantages in terms of cost and purity of materials and affords the opportunity to develop a new understanding of device performance-morphology correlations. In this communication, we report the first examples of a new class of organic semiconductor based on the polycyclic aromatic hydrocarbon dibenzo[*b*,*def*]chrysene (DBC). By contrast with other well-studied small molecules, such as pentacenes,[11] we show that DBC derivatives do not undergo cycloaddition reactions with fullerenes. We demonstrate that soluble DBCs can deliver power conversion efficiencies in bulk heterojunction solar cells of 2.25%. We also show that the efficiencies of these small molecule-based devices are highly dependent on the morphology of the active layer and provide a correlation between solution processing conditions, film morphology, and device efficiency.

Through almost 10 years of research into materials for organic solar cells, the specific combination of the electron donor regioregular poly(3-hexylthiophene) (P3HT) and electron acceptor [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) continues to attract a great deal of research interest, with device power conversion efficiencies having increased to around 5.1%.[1] New polymers, which have delivered higher device efficiencies, are still based around thiophene derivatives.[12−14] Another type of organic semiconductor that has been actively investigated in the area of organic electronics are small molecules.[4−11,15−17] In particular, acenes are a class of small molecule that has delivered particularly impressive results in organic field-effect transistors.[11] However, the use of the most widely studied acene, pentacene, in bulk heterojunction (BHJ) solar cells (where the interface between the donor and acceptor materials is maximized by distribution throughout a single active layer) has been limited by the propensity of pentacenes to undergo cycloaddition reactions with dienophilic fullerenes.[11,18] This reactivity has restricted the development of solution processed solar cells based on pentacene to planar devices; even then the reported power conversion efficiencies are low, in the range of 0.1−0.5%.[19]

In recent years, solution processed, small molecule-based devices, using anthradithiophene,[5] squaraine,[6] merocyanine,[7] or dendritic thiophene[8] derivatives with improved device power conversion efficiencies of up to 1.7% have been reported. Very recently, even higher device efficiencies have been reported using a combination of $PC_{71}BM$ and oligothiophenes with diketopyrrolopyrrole[9,10] cores. By contrast with polymers, the synthesis and purification of small molecules is generally easier as the exact molecular composition of the

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*Corresponding author. Tel: +61 (0)3 95452618. Fax: +61 (0)3 95452446. E-mail: scott.watkins@csiro.au.

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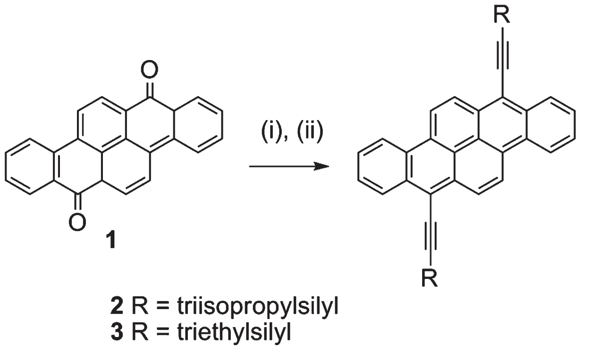
Scheme 1. Synthesis of Compounds 2 and 3



Reagents and conditions: (i) (i-Pr)$_3$SiCCLi (for 2), or (Et)$_3$SiCCLi (for 3), THF, −78 °C, then 25 °C; (ii) SnCl$_2$, 0−25 °C. Overall yield 70% for 2 and 81% for 3.

compounds can be unambiguously identified. This minimizes issues with batch-to-batch reproducibility that can pose problems with polymers.[12] However, despite these apparent benefits, in order for the production of organic photovoltaics to be scaled-up and printed on large-area plastic substrates, a continued focus on the development of new photoactive molecular systems that can be synthesized in simple, industrially scalable processes from cheap, widely available precursors is required. Moreover, a greater variety of chemical templates will also enable the creation of systems with optimized energy levels to deliver even higher device power conversion efficiencies.[20]

Toward this aim, we identified the polycyclic aromatic template, dibenzo[*b*,*def*]chrysene, as a promising candidate for use in organic electronic devices. The synthesis of solution processable DBC derivatives was readily achieved following the approach used for pentacenes,[11] beginning with the commercial dyestuff dibenzo[*b*,*def*]-chrysene-7,14-dione (Vat Yellow 4) **1** (Scheme 1). The reaction of **1** with the appropriate lithium acetylides followed by treatment with SnCl$_2$ gave the new DBCs **2** and **3** in high yield. In our laboratories, we have reproducibly prepared 50 g batches of **1** and 5 g batches of **2**. Notably, preliminary investigations have also indicated a surprisingly high tolerance of DBC-based impurities in devices. Material having a purity of less than 92% still gives devices with power conversion efficiencies of around 1.4%. Nearly all of these impurities have been traced to the industrial dyestuff used as the starting material.

The DBC derivatives **2** and **3** are both red, crystalline materials. The X-ray crystal structure of **2** shows that the DBC units adopt a 1-D stack (see Figure 1 and the Supporting Information), an arrangement that Anthony has previously suggested is optimal for solar cells.[5,11]

The UV−vis and photoluminescence spectra of the compounds as thin films (see the Supporting Information) are similar. The photoluminescence of **3** is shifted to slightly lower energy compared with **2**. The origin of this shift may be due to the reduction in the steric bulk of the alkyl substituents, which may allow closer interactions between molecules of **3** compared with **2**. Cyclic voltammetry was used to estimate the HOMO/LUMO energy levels of **2** and **3** in solution. Both derivatives exhibit reversible reductions and quasi-reversible oxidations. Notably, neither couple exhibits any sweep rate dependence (see the Supporting Information). The HOMO and LUMO energy levels in films were estimated using a combination of photoelectron spectroscopy in air (PESA) and UV−vis spectroscopy (see the Supporting Information). For both derivatives, the HOMO is estimated at −5.1 and the LUMO at −2.9 to −3.0 eV, with the band gap being slightly larger in **2** and slightly increased in the solutions. These considerations confirmed that soluble DBCs were suitable electron donors for fullerene-based BHJ solar cells. The luminescence of the DBCs in thin films ($\lambda_{\max}$ = 600 and 620 nm for **2** and **3**, respectively, see the Supporting Information) is totally quenched on blending with PCBM at a ratio of 1:1 w/w, indicative of efficient charge separation, see the Supporting Information.

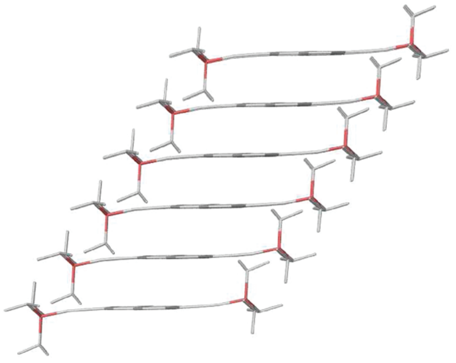


Figure 1. Molecular diagram of the X-ray crystal structure of **2** (hydrogen atoms omitted) as viewed down the longer molecular axis showing that individual molecules pack into canted infinite stacks with an interlayer spacing of ca. 3.44 Å.

The absence of a reaction between the DBCs and fullerenes was demonstrated by dissolving equimolar amounts of **2** and PCBM in chloroform under ambient conditions and monitoring the solution by NMR. After 3 days in solution, the NMR spectrum of the mixture was unchanged. By contrast, evidence for the reaction between 6,13-bis(triisopropylsilylethynyl)pentacene and PCBM is clear within minutes (see the Supporting Information), consistent with previous reports of the propensity of pentacene derivatives to undergo reaction with fullerene derivatives.[11,19] BHJ solar cells were prepared by spin coating blends of **2** or **3** and PCBM using both high- and low-boiling point solvents, such as chlorobenzene (PhCl) and chloroform (CHCl$_3$) respectively. The UVVis spectra of films of these blends (see the Supporting Information) are almost identical to those of the pristine DBCs. The effects of tuning the morphology of the films on device performance are shown in Table 1 and Figure 2. Microstructured films are typically obtained from high-boiling solvents (Figure 2a), whereas low-boiling solvents generally lead to nanostructured DBC:PCBM films (Figure 2b−d).

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Table 1. BHJ Solar Cell Parameters for Optimized Thickness and DBC: PCBM Ratios

	device			
	a	b	c	d
donor material	3	3	3	2
DBC: PCBM (mg: mg)	10:10	10:10	20:20	10:10
solvent (1 mL)	PhCl	$CHCl_3$	$CHCl_3$	$CHCl_3$
optimum spin speed (rpm)	3000	4000	8500	4500
optimum thickness (nm)	150	90	85	75
V_{OC} (V)	0.26	0.78	0.83	0.91
J_{SC} (mA/cm^2)	0.003	4.73	6.55	5.19
fill factor	0.28	0.41	0.41	0.47
optimized efficiency, η (%)	0.005	1.51	2.25	2.22

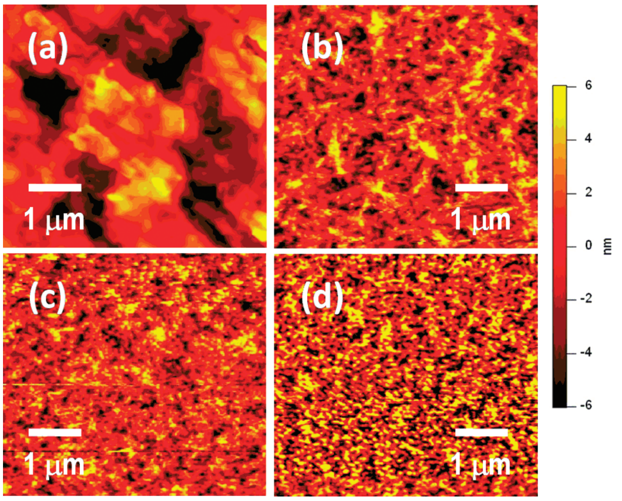

Figure 2. AFM images of the active layer of photovoltaic devices based on **2** and **3**. Devices are (a) 10:10 (mg) **3**:PCBM 150 nm, from 1 mL PhCl; (b) 10:10 (mg) **3**:PCBM 90 nm, from 1 mL $CHCl_3$; (c) 20:20 (mg) **3**:PCBM 85 nm, from 1 mL $CHCl_3$; and (d) 10:10 (mg) **2**:PCBM 75 nm, from 1 mL $CHCl_3$.

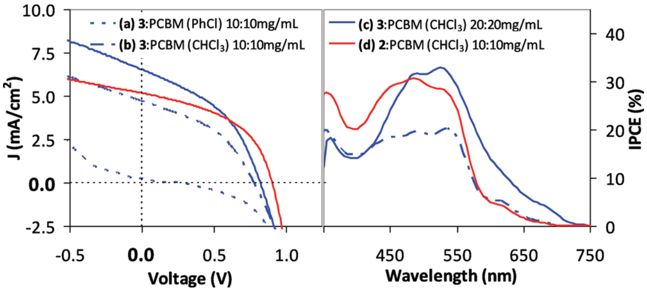

Figure 3. Left: AM1.5 photovoltaic characteristics of devices a−d in Table 1. Right: Incident photon conversion efficiencies (IPCE) of the same devices, except device a, which showed negligible photocurrent.

Higher power conversion efficiencies were measured for devices made from the nanostructured films (Figure 3); these films are expected to display better intermixing of the DBC and fullerene phases at the nanoscale, consistent with the view that such morphologies allow more efficient dissociation of the photogenerated excitons and collection of separated charges. Preliminary studies of the effects of thermal annealing of devices at 90 °C showed that this had no effect on device performance.

Moreover, for films spun from $CHCl_3$, it can be observed that the higher the concentration of the solution, the smaller the size of voids and the higher the device power conversion efficiency (e.g., devices b and c in Figures 2 and 3). This finding is consistent with the view that differences in phase separation and the nature of grain boundaries in the films are likely to lead to a positive correlation between smoother, more intimately mixed films and device efficiencies.

The measured open circuit voltage (V_{OC}) of all devices is around 0.3 V greater than typically seen for devices based on P3HT:PCBM.[1] This correlates with the fact that in films, the HOMO of the DBCs is around 0.4 eV deeper than P3HT measured under the same conditions (see the Supporting Information). Devices based on **3**:PCBM tend to possess higher short-circuit currents (J_{SC}), possibly as a consequence of the higher optical absorption tails in the near-infrared, leading to a better exploitation of the AM1.5 illumination in that spectral region.

The attainment of high power conversion efficiencies in devices based on DBCs is a significant result. These compounds do not contain thiophene substituents which shows that good performance from materials based on other aromatic templates is achievable. The demonstration that, unlike pentacene, DBCs are nonreactive toward fullerenes presents an opportunity to develop even larger, nonacene-based, polycyclic systems with greater functionality and optimized spectroscopic and electronic properties. The large, delocalized, conjugated network in a polycyclic aromatic system, compared with simpler heteroaryl templates such as thiophene, also provides greater scope for variation of chemical structure.

In summary, solution processable electroactive dibenzo[*b*,*def*]chrysene derivatives have been prepared in high yield from the quinone **1**. These compounds are stable under ambient laboratory conditions and unreactive toward PCBM. BHJ solar cells made from compound **3** reach a PCE of 2.25%, which makes them one of the highest performing solution-processed small molecule photovoltaic cells to date. In combination, these findings strongly encourage investigation of the use of other previously unexplored polycyclic aromatic compounds in solution-processable bulk heterojunction solar cells.

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Supporting Information Available: Full experimental and characterization details for compounds **1**, **2**, and **3**; X-ray structural information on **2**; NMR stability data and optimization data for devices (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.