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**Triisopropylsilylethynyl-functionalized dibenzo[def,mno]chrysene: a solution-processed small molecule for bulk heterojunction solar cells†**Lei Zhang,<sup>a</sup> Bright Walker,<sup>b</sup> Feng Liu,<sup>a</sup> Nicholas S. Colella,<sup>a</sup> Stefan C. B. Mannsfeld,<sup>c</sup> James J. Watkins,<sup>a</sup> Thuc-Quyen Nguyen<sup>b</sup> and Alejandro L. Briseno<sup>\*a</sup>

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**This communication reports the synthesis of a new polycyclic aromatic hydrocarbon and its unique packing motif. This molecule is shown to be an efficient electron donor in organic bulk heterojunction solar cells, exhibiting a power conversion efficiency of ~2.0%.**

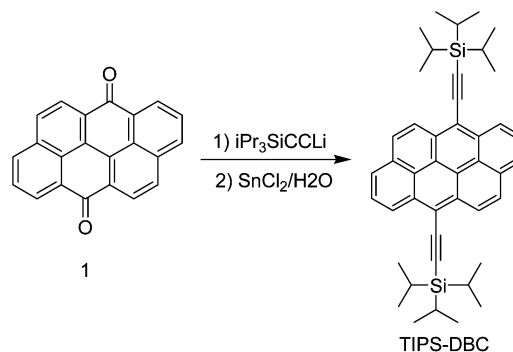
Organic solar cells are attractive due to their low cost, light weight, roll-to-roll processability and compatibility with flexible substrates.<sup>1</sup> Significant progress has been made in the development of new polymer-based materials for high-performance bulk heterojunction (BHJ) solar cells over the past few years. Among these materials, “push–pull” conjugated polymers with low band gaps that match the solar spectrum are important representative systems.<sup>2</sup> Some polymer-based BHJ solar cells have demonstrated power conversion efficiencies (PCEs) in excess of 7%.<sup>3</sup>

Compared to polymer-based BHJ solar cells, solution processed small molecule-based BHJ solar cells have received relatively little attention due to the non-bicontinuous, less interpenetrating phases of donors and acceptors, and the consequently reduced interfacial area between the donor and acceptor materials, which in turn limits the device's efficiency.<sup>4</sup> As a result, the development of small molecules for BHJ solar cells has lagged behind their polymer counterparts. However, by contrast, small molecules are easier to synthesize, to purify, and characterize. Furthermore, small molecule BHJ solar cells may be more suitable to investigate the fundamental relationships between the packing motif, morphology, and device performance due to the more precise molecular compositions and well-defined molecular structures. Small molecule BHJ solar cells based on oligothiophenes, soluble acenes, donor–acceptor chromophores, and organic dyes have been reported with promising results.<sup>5</sup> Recently,

PCEs of over 4% have been achieved in solar cells based on diketopyrrolopyrrole derivatives, and star-shaped triphenylamine.<sup>6</sup>

In this communication, we report a new soluble polycyclic aromatic hydrocarbon, 6,12-bis(triisopropylsilylethynyl)dibenzo[def,mno]chrysene (TIPS-DBC), and its applications for organic solar cells. In BHJ solar cells, it is possible to control the morphology by tuning the crystal packing of the donor to enhance transport in the active layer, thus improving device performance. Compared to linear acenes, polycyclic aromatic hydrocarbons with larger conjugated cores form one-dimensional stacks more easily due to the strong  $\pi$ – $\pi$  interactions.<sup>7</sup> This large orbital overlap has been shown to be favorable for high efficiency solar cells.<sup>8</sup> In addition, this molecule can be synthesized in a single step from a commercially available material, with very high yield. These advantages make this new material a promising candidate for organic electronic applications.

The synthesis of TIPS-DBC is described in Scheme 1. Anthanthrone (compound **1**) was reacted with lithium triisopropylsilylacetylide in THF to form a homogeneous solution. To this mixture, a solution of saturated SnCl<sub>2</sub> in 10% HCl was added to form the alcohol derivative, followed by dehydration and aromatization, affording the desired product in a very high yield (82%), which was unambiguously characterized by <sup>1</sup>H-NMR, MS and elemental analysis (see the ESI†). From the inexpensive starting material, the compound was easily prepared on a large, multigram scale. The compound is soluble in common solvents, such as THF, chloroform, toluene, and dichloromethane, and is easily purified by recrystallization from hexane.



**Scheme 1** The synthesis of 6,12-bis(triisopropylsilylethynyl)dibenzo[def,mno]chrysene (TIPS-DBC).

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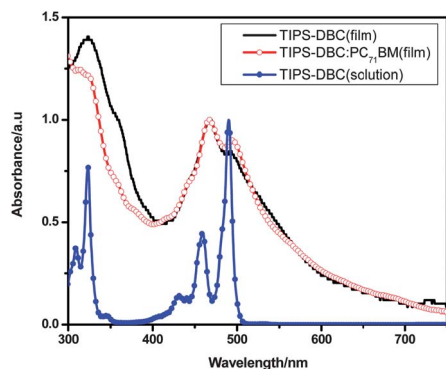
† Electronic supplementary information (ESI) available: Material synthesis, experimental details, CV, DSC. CCDC reference number 839641. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2jm14998b/

The UV-vis spectra of TIPS-DBC were measured in chloroform solution and from a spin-coated thin film on quartz (Fig. 1). There is a small red shift with a broadening in the solid state spectra compared to the solution spectra, partially due to multiple intermolecular interactions in the solid state.<sup>9</sup> The HOMO and LUMO energy levels were determined by cyclic voltammetry to be  $-5.46$  V and  $-3.60$  V, respectively. This yields an electrochemical band gap of  $1.86$  eV, while the optical band gap from UV-vis was estimated at  $1.90$  eV. The relatively low-lying HOMO level indicates that the molecule has good oxidative stability.<sup>10</sup> Based on these observed energy levels, the compound is suitable as a donor material for organic BHJ solar cells.<sup>11</sup>

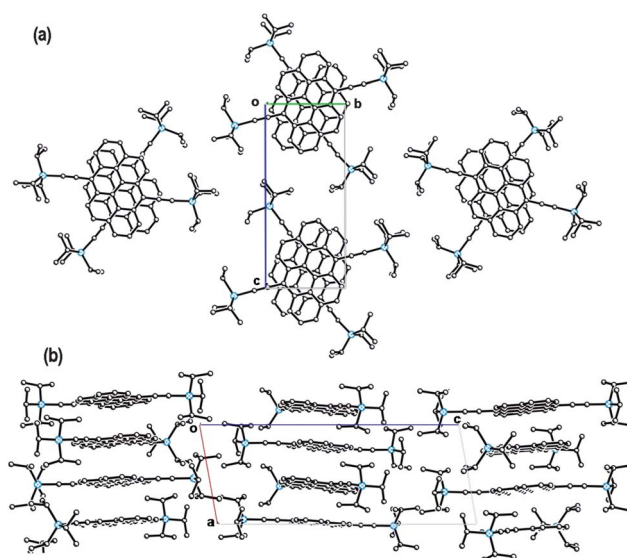
A single crystal suitable for X-ray structure analysis was obtained by slow evaporation of TIPS-DBC in hexane at room temperature.<sup>‡</sup> As shown in Fig. 2, the molecule exhibited a nearly planar core, with characteristic  $\pi$ - $\pi$  stacking between molecules along the  $a$ -axis. The  $\pi$ - $\pi$  distance between two molecules is  $3.41$  Å, which is similar to the sum of van der Waals radii ( $3.40$  Å) of carbon.<sup>12</sup> Compared to linear analogues, TIPS-DBC has an elliptical  $\pi$ -surface, which precludes slipped  $\pi$ - $\pi$  stacks along the long axis of the linear acenes (e.g., “brick-layer” motif),<sup>13,14</sup> leading to an excellent  $\pi$ -surface overlap and resulting in strong intermolecular interactions within each stack. In particular, the triisopropylsilyl groups of adjacent molecules along the  $a$ -axis stack are arranged at nearly  $90^\circ$  to each other to minimize steric interactions (see Fig. 2a). This crystal packing is favorable for forming efficient one-dimensional stacks, allowing facile charge transport along the  $\pi$ -stack direction.

In order to determine whether a potential Diels–Alder cycloaddition reaction occurs between TIPS-DBC and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) at different temperatures, which probably results in aromaticity loss of the donor, a 1 : 1 mixture at room temperature and the annealed film at  $150^\circ\text{C}$  in deuterated chloroform were characterized *via*  $^1\text{H-NMR}$  spectroscopy. The aromatic and alkyl protons from the TIPS-DBC and PCBM, respectively, were clearly identified in the spectrum and no new peaks were observed even after several days, confirming that no reaction had occurred between the two compounds (see the ESI<sup>†</sup>). This lack of reactivity is in stark contrast to the linear acenes (*i.e.* TIPS-pentacene), which readily undergoes a Diels–Alder reaction with fullerene derivatives in solution.<sup>15</sup>

The photovoltaic properties of TIPS-DBC were measured in BHJ solar cells with TIPS-DBC as the donor and PCBM or PC<sub>71</sub>BM as the acceptor. The device structure was ITO/PEDOT:PSS/TIPS-DBC:PCBM/Al (see the ESI<sup>†</sup>). The current density–voltage ( $J$ - $V$ ) characteristics of the solar cells under simulated AM 1.5 solar



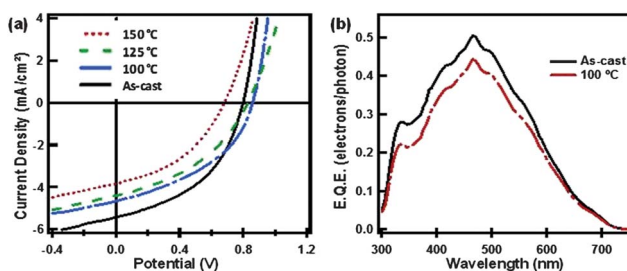
**Fig. 1** UV-vis spectra of TIPS-DBC in the solid state (black), TIPS-DBC/PC<sub>71</sub>BM (red), and TIPS-DBC in solution (blue).



**Fig. 2** (a) View down the crystallographic  $a$ -axis. (b) View down the crystallographic  $b$ -axis. Hydrogen atoms were omitted for clarity.

illuminations at  $100\text{ mW cm}^{-2}$  light intensity are shown in Fig. 3a. The BHJ solar cells were initially fabricated by spin coating a solution of TIPS-DBC and PCBM in chloroform, resulting in an active layer with a thickness about  $100\text{ nm}$ . These devices exhibited an open-circuit voltage ( $V_{oc}$ ) of  $0.70$  V, a short-circuit current density ( $J_{sc}$ ) of  $3.75\text{ mA cm}^{-2}$ , a fill factor of  $0.41$ , and a PCE of  $1.1\%$ . In contrast, the devices based on the blend of TIPS-DBC:PC<sub>71</sub>BM delivered a better performance with a  $V_{oc}$  of  $0.80$  V, a  $J_{sc}$  of  $5.41\text{ mA cm}^{-2}$ , and a fill factor of  $0.45$ , thus improving the PCE to  $\sim 2\%$ . The solar cell data are summarized in Table 1. The as-cast devices showed a  $V_{oc}$  of  $0.80$  V, which is much higher than the  $V_{oc}$  typically observed for P3HT:PCBM, and a value which itself is relatively high compared to other organic solar cells.<sup>16</sup> This is due to the low HOMO energy level of TIPS-DBC. Thermal annealing of the devices at moderate temperatures ( $100$ – $125^\circ\text{C}$ ) leads to a small increase in  $V_{oc}$  (up to  $0.86$  V) concurrent with a decrease in the  $J_{sc}$  which drops to  $4.64$  and  $4.39\text{ mA cm}^{-2}$  after annealing at  $100$  and  $125^\circ\text{C}$ , respectively. Annealing at higher temperatures ( $150^\circ\text{C}$ ) was found to cause a decrease in all device parameters. The changes in  $V_{oc}$  could be ascribed to thermally induced changes in the packing of the material and shifts in the HOMO band of the material after annealing.<sup>17</sup>

The external quantum efficiency (EQE) spectra of the blend as a function of incident light wavelength before and after annealing are



**Fig. 3** (a)  $J$ - $V$  characteristics of solar cells based on the blend of TIPS-DBC:PC<sub>71</sub>BM ( $50 : 50$ , w/w) (black: as cast; blue: annealed at  $100^\circ\text{C}$ ; green: annealed at  $125^\circ\text{C}$ ; red: annealed at  $150^\circ\text{C}$ ). (b) EQE spectra of the as-cast and annealed TIPS-DBC:PC<sub>71</sub>BM blends.

**Table 1** The optimized performance of selected solar cells based on the blend of TIPS-DBC/PC<sub>71</sub>BM (1 : 1, w/w)

	As-cast	100 °C	125 °C	150 °C
$J_{sc}/\text{mA cm}^{-2}$	5.41	4.64	4.39	3.82
$V_{oc}/\text{V}$	0.80	0.86	0.83	0.68
FF (%)	0.45	0.42	0.40	0.41
PCE (%)	1.95	1.70	1.45	1.06

shown in Fig. 3b. The spectra exhibit an appreciable EQE response in the 400–600 nm wavelength range, with a maximum of 50% at 450 nm. The spectral shape is not affected by thermal annealing, though the overall quantum efficiency is found to decrease. This decrease in  $J_{sc}$  and efficiency after annealing at high temperatures can be rationalized by changes in film morphology. Atomic force microscope images (see the ESI†) show a significant increase in the surface roughness of the films along with the growth of crystal-like features over 100 nm high and several microns in breadth after annealing at 150 °C. It appears that this increase in feature size reduces the donor–acceptor interfacial area, leading to a decrease in the photocurrent generating capacity of the blend due to exciton recombination.<sup>18</sup>

Synchrotron grazing incidence X-ray diffraction (GIXD) was performed to further elucidate the blend morphology. GIXD images of the TIPS-DBC:PC<sub>71</sub>BM blend (ESI†) show powder-diffraction signatures of micrometre-sized TIPS-DBC crystallites and PC<sub>71</sub>BM nanocrystals that are about 2 nm in size. The TIPS-DBC diffraction lines were successfully indexed consistent with the TIPS-DBC bulk unit cell shown in Fig. 2. The occurrence of additional, but faint TIPS-DBC Bragg rods suggests that close to the substrate surface the TIPS-DBC crystallites are not completely randomly oriented but have their basal plane aligned with the substrate surface (2D powder).

In summary, we present a new polycyclic aromatic hydrocarbon which possesses an extraordinary one-dimensional packing with strong  $\pi$ – $\pi$  interactions along the *a*-axis. The BHJ solar cell consisting of TIPS-DBC blended with PC<sub>71</sub>BM shows very promising results with a PCE of up to ~2.0%. We anticipate that the device performance can be further improved by careful optimization of the fabrication process to control the morphology of the film. Furthermore, our results provide a platform for the development of high performance small molecule semiconductors from inexpensive materials *via* control of their packing motifs.

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## Notes and references

† Crystal data for TIPS-DBC: C<sub>44</sub>H<sub>52</sub>Si<sub>2</sub>: 637.04, space group *P*-1, *a* = 13.8921(10) Å, *b* = 15.1742(12) Å, *c* = 35.4560(3) Å,  $\alpha$  = 88.906(6)°,

$\beta$  = 79.711(5)°,  $\gamma$  = 84.143(5)°, *V* = 7315.6(10) Å<sup>3</sup>, *Z* = 8.25 869 reflections collected, 14 127 unique, the final *R* was 0.1081, and *wR* was 0.2889.

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