SHORT COMMUNICATION

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Side chain engineering on D18 polymers yields 18.74% power conversion efficiency

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Donor–acceptor (D–A) conjugated copolymers containing fused-ring acceptor units demonstrate outstanding performance in organic solar cells (OSCs)[1–13]. We have invented highly efficient D–A copolymer donors D18 and D18-Cl by using a fused-ring acceptor unit, dithieno [3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]thiadiazole (DTBT)[1, 2]. OSCs with D18 or D18-Cl gave power conversion efficiencies (PCEs) of 18.56% and 18.69%, respectively[3, 4]. Side chain engineering is an effective approach to improve the performance of conjugated polymers in optoelectronic devices[14–16]. The alkyl side chains not only determine polymers' solubility, but also influence their crystallinity and mobility. In this work, we develop two efficient donors D18-B and D18-Cl-B *via* side chain engineering on D18 polymers (Fig. 1(a)). These donors offer PCEs up to 18.74% (certified 18.2%) in ternary OSCs.

The structural difference between D18 and D18-B (or D18-Cl *vs* D18-Cl-B) polymers is the alkyl chains on thiophene bridge units. For D18 and D18-Cl, the side chain is 2-butyloctyl, and for D18-B and D18-Cl-B, the side chain is 3-butylnonyl. The synthesis details for D18-B and D18-Cl-B are given in the Supporting Information. To figure out the influence of molecular weight to photovoltaic performance of polymers, we prepared D18-B and D18-Cl-B samples with high, moderate and low molecular weights. Different molecular weights were achieved by adjusting the ratio between the donor and acceptor monomers during the polymerization. The well-studied D18-B and D18-Cl-B present moderate number-average molecular weights (M_n) of 47.2 and 60.6 kDa, respectively, with polydispersity indexes (PDI) of 1.89 and 1.95, respectively. D18-B and D18-Cl-B show similar absorption spectra in either solution or film, indicating that F or Cl substitution has negligible influence to the optical properties of the polymers (Fig. S7). The 0–1 transition peak intensifies in both polymer films, suggesting the H-aggregation in solid state[17, 18]. The optical bandgaps for D18-B and D18-Cl-B are 1.97 and 1.98 eV, respectively. Energy levels for D18-B and D18-Cl-B were estimated by cyclic voltammetry (CV) (Fig. S8). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels are –5.51 and –2.71 eV for D18-B, and –5.56 and –2.68 eV for D18-Cl-B, respectively. The hole mobilities (μ_h) from space-charge limited current (SCLC) measurements are 8.64×10^{-4} and 6.93×10^{-4} cm^2/(V·s) for D18-B and D18-Cl-B, respectively (Fig. S9). Ternary solar cells with D18-B or D18-Cl-B as the donor and N3[19]/$PC_{61}BM$ as the acceptors were made. Device fabrication conditions were optimized (Tables S1–S8). The best D18-B:N3:$PC_{61}BM$ (1 : 1.4 : 0.2) cells gave a PCE of 18.53%, with an open-circuit voltage (V_{oc}) of 0.823 V, a short-circuit current density (J_{sc}) of 28.50 mA/cm^2 and a fill factor (FF) of 79.0%. The best D18-Cl-B:N3:$PC_{61}BM$ (1 : 1.4 : 0.2) cells offered a PCE of 18.74%, with a V_{oc} of 0.836 V, a J_{sc} of 28.50 mA/cm^2 and a FF of 78.7% (Fig. 1(b), Table 1). D18-Cl-B:N3:$PC_{61}BM$ cells afforded the highest external quantum efficiency (EQE) of 90% at 550 nm (Fig. 1(c)). The addition of $PC_{61}BM$ enhanced J_{sc} and FF for both D18-B and D18-Cl-B ternary cells (Tables S2 and S5), suggesting that fullerene balances charge transport in the devices[20, 21]. The best D18-Cl-B devices were also measured at the National Institute of Metrology (NIM), and a certified PCE of 18.2% (V_{oc}, 0.835 V; J_{sc}, 27.64 mA/cm^2; FF, 78.9%; effective area, 2.580 mm^2) was recorded (Fig. S10). The active layer morphology was investigated by atomic force microscope (AFM). Both D18-B:N3:$PC_{61}BM$ and D18-Cl-B:N3:$PC_{61}BM$ blend films present typical nano-structures (Fig. S11). We also tested the performance of low-M_n and high-M_n D18-B or D18-Cl-B in ternary solar cells (Table 1). Low-M_n and high-M_n D18-B deliver 17.69% and 17.36% PCEs, respectively, while low-M_n and high-M_n D18-Cl-B give 17.87% and 17.39% PCEs, respectively. Optimizing the molecular weight of polymers is important for achieving the optimal performance.

In short, we create two polymer donors D18-B and D18-Cl-B *via* side chain engineering on D18 polymers. PCEs of 18.53% and 18.74% were achieved, respectively, demonstrating their potential in organic solar cells.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1088/1674-4926/42/10/100501.

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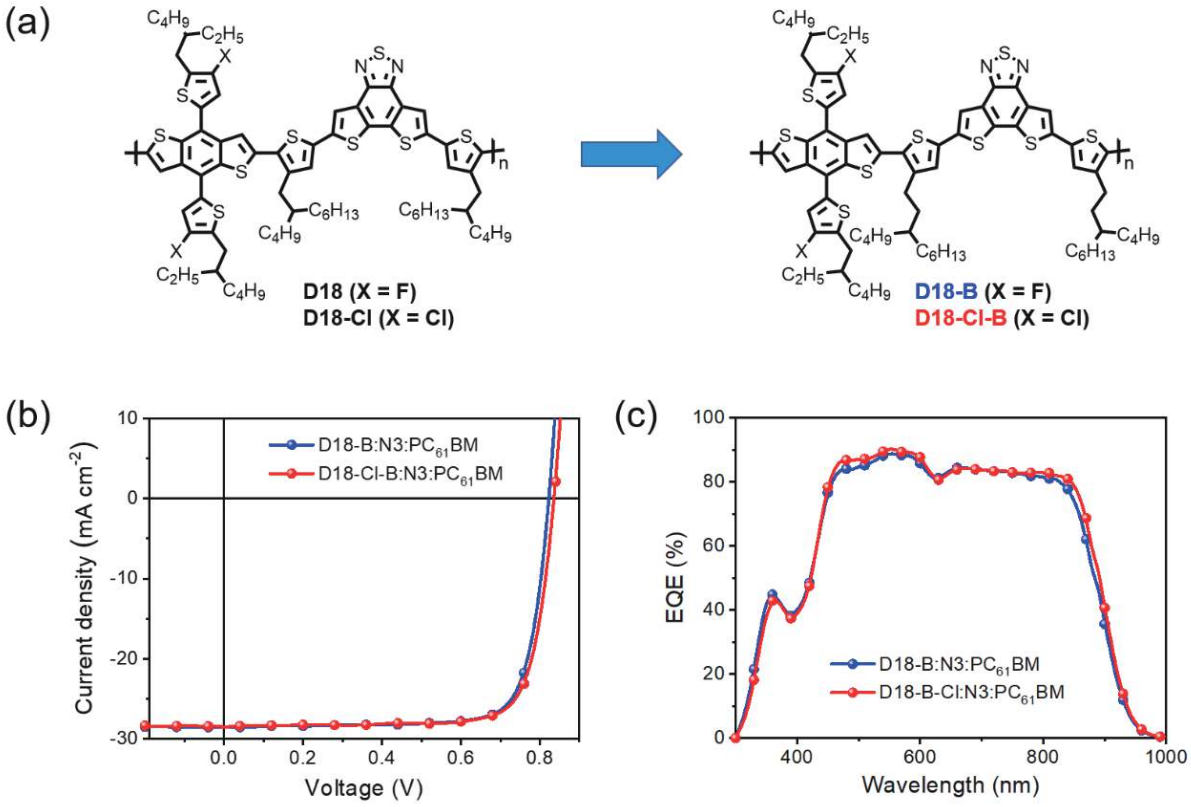

Fig. 1. (Color online) (a) Chemical structures. (b) *J*–*V* curves for D18-B:N3:$PC_{61}BM$ and D18-Cl-B:N3:$PC_{61}BM$ solar cells. (c) EQE spectra for D18-B:N3:$PC_{61}BM$ and D18-Cl-B:N3:$PC_{61}BM$ solar cells.

Table 1. Performance data for D18-B:N3:$PC_{61}BM$ (1 : 1.4 : 0.2) and D18-Cl-B:N3:$PC_{61}BM$ (1 : 1.4 : 0.2) solar cells.

Donor	M_n (kDa)	PDI	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
D18-B_L	33.0	1.84	0.825	27.31	78.6	17.69 (17.52)[a]
D18-B_M	**47.2**	**1.89**	**0.823**	**28.50**	**79.0**	**18.53 (18.40)**
D18-B_H	57.0	1.95	0.810	27.94	76.7	17.36 (17.18)
D18-Cl-B_L	38.1	1.98	0.832	27.68	77.6	17.87 (17.52)
D18-Cl-B_M	**60.6**	**1.95**	**0.836**	**28.50**	**78.7**	**18.74 (18.52)**
D18-Cl-B_H	68.6	2.06	0.821	27.45	77.2	17.39 (17.22)

[a]Data in parentheses stand for the average PCEs for 10 cells.

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