SHORT COMMUNICATION

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A chlorinated lactone polymer donor featuring high performance and low cost

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The development of low-bandgap nonfullerene acceptors and wide-bandgap polymer donors speeds up the advance of organic solar cells (OSCs)[1–17]. Wide-bandgap copolymers based on fused-ring acceptor units are ideal donor materials due to their low-lying HOMO levels, high hole mobilities and complementary light absorption to nonfullerene acceptors[18–25]. Currently, high-performance donors with 18% power conversion efficiencies (PCEs) belong to this type. Fig. 1(a) summarizes these donors. They are D18-series copolymers based on dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c]-[1,2,5]thiadiazole (DTBT) unit[15, 16, 26], PBQx-TF and PBQx-TCl based on dithieno[3,2-f:2',3'-h]quinoxaline (DTQx) unit[17, 25], and PM6 based on benzo[1,2-c:4,5-c']dithiophene-4,8-dione (BDD) unit[27]. However, the above building units require tedious synthetic routes, thus increasing the cost. Efficient yet low-cost copolymer donors are highly desired[13, 28, 29]. The fused-ring lactone unit, dithieno[3,2-b:2',3'-d]pyran-5-one (DTP), is a commercially available building block, which can be obtained *via* a few synthetic steps from cheap starting materials[30]. Previously, our group first reported lactone copolymer donors L1, L2 and L3 based on DTP unit[20, 31]. PCEs up to 17.81% was achieved from L3-based ternary solar cells, demonstrating the great potential of lactone copolymer donors. In this work, copolymerizing a cost-effective monomer (4,8-bis(4-chloro-5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (ClBDT-Sn)[32] with DTP monomer produced a new lactone copolymer L4. Ternary OSCs with L4 as the donor and N3[33] and $PC_{61}BM$ as the acceptors offered a PCE of 18.10% (certified 17.7%).

L4 was synthesized *via* Stille copolymerization and the details can be found in the Supporting Information. The number-average molecular weight (M_n) and polydispersity index (PDI) are 51.8 kDa and 1.58, respectively. The absorption spectra for L4 in chloroform and as a film are shown in Fig. S2. For film, L4 shows an absorption onset at 645 nm, corresponding to an optical bandgap of 1.92 eV. The light absorption of L4 is complementary to that of N3. Cyclic voltammetry (CV) measurements were employed to estimate the energy levels (Fig. S3). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels are –5.52 and –2.95 eV for L4, respectively.

Solar cells with a structure of ITO/PEDOT:PSS/active layer/PDIN/Ag were made to assess the performance of L4. The D/A ratio, active layer thickness and diphenyl ether (DPE) additive content were optimized for L4:N3 cells (Tables S1–S3). The cells gave the highest PCE of 17.16%, with an open-circuit voltage (V_{oc}) of 0.844 V, a short-circuit current density (J_{sc}) of 26.43 mA/cm^2 and a fill factor (FF) of 76.9% (Fig. 1(b)). These cells have a D/A ratio of 1 : 1.4, an active layer thickness of 110 nm and 0.5 vol% DPE as the additive. Adding small amount of $PC_{61}BM$ into L4:N3 blend improved V_{oc}, J_{sc} and FF simultaneously (Table S4). The L4:N3:$PC_{61}BM$ (1 : 1.4 : 0.2) ternary cells gave the highest PCE of 18.10%, with a V_{oc} of 0.850 V, a J_{sc} of 27.07 mA/cm^2 and an FF of 78.7%. The best ternary cells were also measured at the National Institute of Metrology (NIM), and a certified PCE of 17.7% (V_{oc}, 0.856 V; J_{sc}, 26.43 mA/cm^2; FF, 78.4%; effective area, 2.580 mm^2) was recorded (Fig. S4). The external quantum efficiency (EQE) spectra indicate that after the addition of $PC_{61}BM$, the EQE at 455–600 nm and 650–820 nm increased. The EQE maximum increased from 82% for binary cells to 88% for ternary cells (Fig. 1(c)). The integrated photocurrent densities are 25.13 and 26.13 mA/cm^2, respectively, consisting with J_{sc}. The enhancement in J_{sc} and FF for ternary cells suggests the improved charge transport in the active layer. Hole and electron mobilities (μ_h and μ_e) were measured by using the space charge limited current (SCLC) method (Fig. S5 and S6)[34–42]. From binary to ternary blend films, μ_h increased from 7.91×10^{-4} to 9.23×10^{-4} cm^2/(V·s), μ_e increased from 5.58×10^{-4} to 7.48×10^{-4} cm^2/(V·s), and the μ_h/μ_e decreased from 1.42 to 1.23 (Table S5). The enhanced charge carrier mobilities and the more balanced charge transport benefit J_{sc} and FF for ternary cells. The active layer morphology was studied by using atomic force microscope (AFM) (Fig. S7). L4:N3:$PC_{61}BM$ (1 : 1.4 : 0.2) blend film is smoother than L4:N3 (1 : 1.4) film, as the root-mean-square roughnesses (R_{rms}) are 1.49 and 1.88 nm, respectively. Both blend films present typical nanofibers (diameter, ~20 nm) and fiber bundles.

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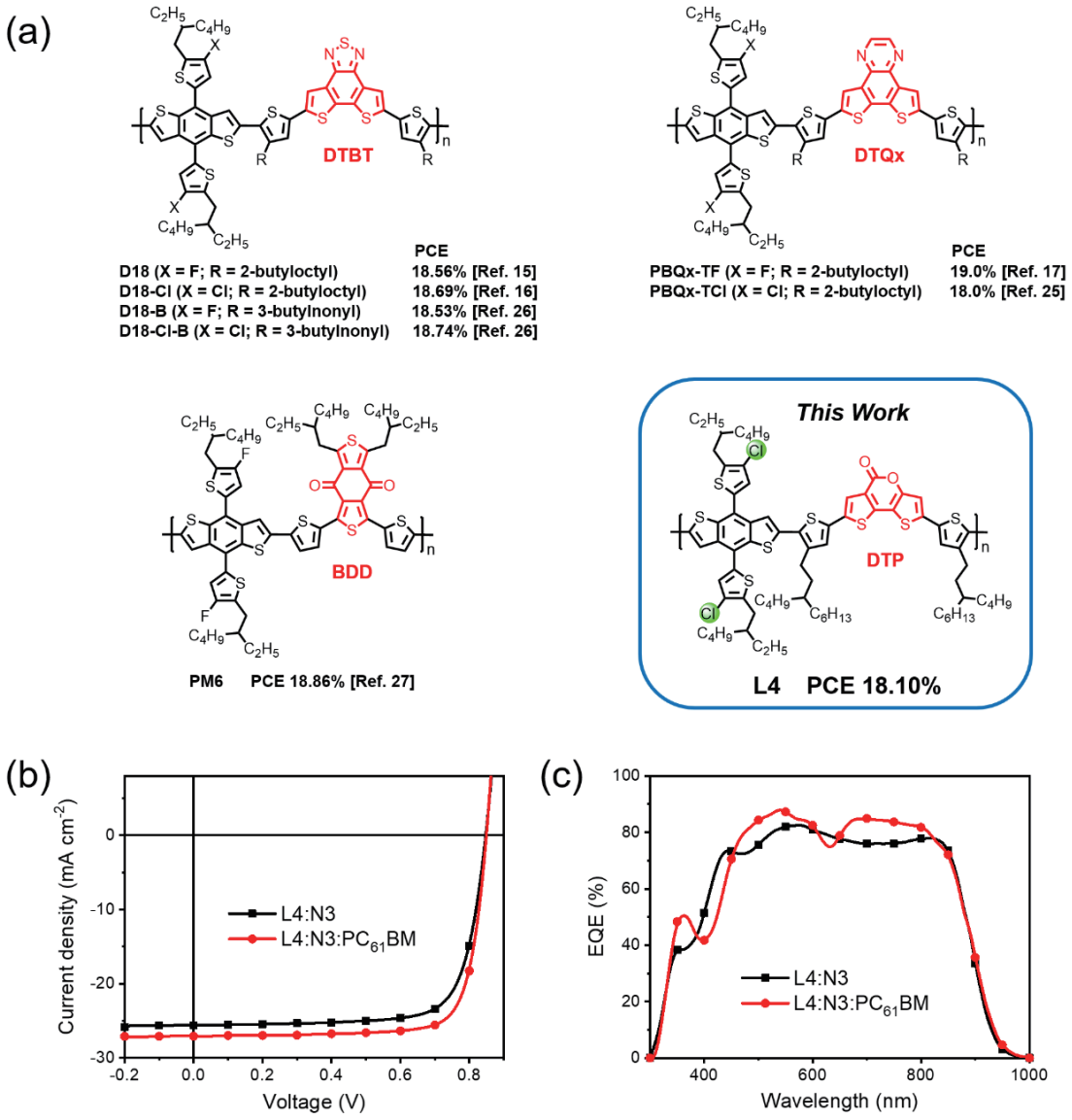

Fig. 1. (Color online) (a) Polymer donors offering PCEs over 18%. (b) *J*–*V* curves for L4:N3 and L4:N3:$PC_{61}BM$ solar cells. (c) EQE spectra for L4:N3 and L4:N3:$PC_{61}BM$ solar cells.

In short, by using a cost-effective lactone acceptor unit and a cost-effective chlorinated donor unit, we developed an efficient wide-bandgap polymer donor L4. L4 is a rare donor, featuring high performance (>18% PCE) and low cost. Lactone polymer donors hold promise for solar cells.

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Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1088/1674-4926/43/5/050501.

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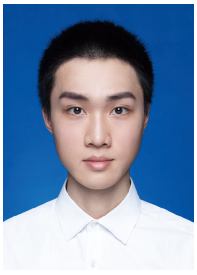

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