

### Electronic Supplementary Information

#### Synthesis of 4,7-bis(2-(1-(2-ethylhexyl)-4,5-dicyano-imidazol-2-yl)vinyl)benzo[c][1,2,5]thiadiazole (EV-BT)

1.00 g of Vinazene (6.9 mmol), 1.43 g of  $K_2CO_3$  (10.4 mmol), 2.50 g of 2-ethylhexyl iodide and 10 mL of DMF were added to a round-bottom flask. The reaction mixture was stirred at 80 °C for 48 h. This was followed by further adding 0.61 g of 4,7-dibromo-2,1,3-benzothiadiazole (2.1 mmol), 0.98 mL of *N,N*-dicyclohexylmethylamine (4.6 mmol) and 43 mg of  $Pd[P(t-Bu)_3]_2$  (0.08 mmol) and then stirring for another 48 h at 80 °C. At the end of the reaction, the mixture was concentrated, and the subsequent extraction was carried out using ethyl acetate and de-ionised water. The organic layer was dried using anhydrous  $MgSO_4$  and filtered. The filtrate was concentrated on a rotary evaporator to give a deep red solid. Column chromatography was performed on silica gel with  $CH_2Cl_2$  as the solvent. A bright green solution was obtained, followed by an orange solid after rotary evaporation. 0.833 g of the final product (62% yield) was isolated by re-crystallization from THF/EtOH at 4 °C.

Using differential scanning calorimetry, the glass transition temperature and melting point of EV-BT were determined to be 83 °C and 166 °C, respectively, compatible with processing on flexible plastic substrates.

$^1H$  NMR ( $CDCl_3$ ):  $\delta$ , [ppm] 0.91 (t, 6 H,  $J = 6.8$  Hz), 1.01 (t, 6 H,  $J = 7.4$  Hz), 1.39 (unresolved m, 16 H), 1.95 (septet, 2 H,  $J = 6.2$  Hz), 4.17 (dd, 4 H,  $J = 7.2, 5.6$  Hz), 7.73 (s, 2 H), 8.05 (d, 2 H,  $J = 15.6$  Hz), 8.36 (d, 2 H,  $J = 15.6$  Hz).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$ , [ppm] 11.0, 14.4, 23.3, 24.2, 28.9, 30.8, 41.6, 51.0, 109.0, 112.2, 113.5, 117.9, 123.2, 129.5, 133.0, 135.5, 150.7, 153.9. Anal. Calcd for  $C_{36}H_{40}N_{10}S$ : C, 67.05; H, 6.25; N, 21.72; S, 4.97. Found: C,

67.02; H, 6.26; N, 21.65; S, 4.83. MALDI-TOF-MS (dithranol)  $m/z$ : 645 (M + H); calcd. for CHNS = 644.

### **Determining the LUMO level of EV-BT with cyclic voltammetry (CV)**

CV measurements were performed with EV-BT in  $\text{CH}_2\text{Cl}_2$  with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte at room temperature at a scan rate of 100 mV/s. A conventional three-electrode configuration was used, consisting of a platinum wire working electrode, a gold counter electrode, and an Ag/AgCl in 3 M KCl reference electrode. The LUMO was estimated to be -3.6 eV based on a reduction onset potential of -0.8 V versus the standard calomel electrode (-4.4 eV versus vacuum), (see Fig. SI1).

### **Fabrication of bulk heterojunction solar cells**

BHJ solar cells of the form ITO / PEDOT:PSS / PCz:EVBT / Ca / Ag were fabricated by spin-coating PEDOT:PSS (Baytron P VP Al 4083) onto clean, patterned ITO-coated glass substrates. The active blend layer was subsequently spin-coated from a mixed solution of PCz and EV-BT in chloroform (10 mg/ml total concentration) under a dry nitrogen atmosphere. If required, this was followed by heating on a hotplate for 10 min to thermally anneal the organic film. The metal top electrode was deposited by the thermal evaporation of calcium (~30 nm) in a vacuum chamber, and subsequently followed by an additional protective layer of silver (~150 nm).

A K. H. S. metal halide solar simulator (with AM1.5 global filter) was used to simulate 100 mW/cm<sup>2</sup> of sunlight, with the intensity monitored by an Ophir Nova II thermopile power meter. The current-voltage response of the solar cells under illumination was measured using a Keithley 2400 source-measure unit. To obtain IPCE spectra, the mechanically-chopped (237 Hz) and monochromated output of a 150 W Xe lamp was directed onto the solar cells by means of a broadband optical fiber. The resulting modulated photocurrent was converted to a

voltage signal using a 50  $\Omega$  resistor and detected by a Stanford Research 830 lock-in amplifier. All spectra were corrected for the intensity of the incident light.

### Figure Caption for ESI

**Fig. S11** A cyclic voltammogram for EV-BT showing a reduction onset potential at -0.8 V relative to the standard calomel electrode (SCE). Assuming an absolute SCE potential of -4.4 eV, this implies a LUMO level of approximately -3.6 eV.

# Figure S11

