# **Supporting Information**

### A four-directional non-fullerene acceptor based on tetraphenylethylene and diketopyrrolopyrrole functionalities for efficient photovoltaic devices with a high open-circuit voltage of 1.18 V

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#### Experimental

All reagents and chemicals used, unless otherwise specified, were purchased from Sigma-Aldrich Co. The solvents used for reactions were obtained from Merck Speciality Chemicals (Sydney, Australia) and were used as received.

Details of spectroscopic measurements, and device fabrication and characterization of photovoltaic devices were reported previously.<sup>S1</sup>



Scheme S1 Reaction strategy for the synthesis of 4D.

## Synthesisof1,1,2,2-tetrakis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene (2):

This compound was prepared following a literature procedure (Advanced Materials, 2015, 27(6), 1015–1020) with slight experimental modifications.

A mixture of 1,1,2,2-tetrakis(4-bromophenyl)ethene (1) (500 mg, 0.77 mmol), bis(pinacolato)diboron (986 mg, 3.88 mmol), Pd(dppf)Cl<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (46 mg, 0.036 mmol) and potassium acetate (609 mg, 6.21 mmol) in 1,4-dioxane (20.0 mL) was heated to 110 °C for 16 h under N<sub>2</sub> atmosphere. The reaction mixture was cooled to room temperature, diluted with water (40.0 mL) and diethyl ether (50.0 mL), and the organic layer was separated. The ethereal layer was washed twice with water followed by brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>

and concentrated under vacuum to get crude residue which was purified by flash column chromatography to get the titled product as an off-white solid (400 mg, 61%). All spectroscopic data matches with the literature values.

#### Synthesis of 6,6',6''-((ethene-1,1,2,2-tetrayltetrakis(benzene-4,1diyl))tetrakis(thiophene-5,2-diyl))tetrakis(2,5-bis(2-ethylhexyl)-3-(thiophen-2-yl)-2,5dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione) (4D):

To a stirred solution of 2 (0.080 g, 0.096 mmol) and 3-(5-bromothiophen-2-yl)-2,5-bis(2ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.35)g, 0.58 mmol) in degassed 1,2-dimethoxyethane (10.0 mL) was added 2M Na<sub>2</sub>CO<sub>3</sub> solution (2.50 mL) and the resultant reaction mixture was degassed for 15 min using nitrogen. Then Pd(PPh<sub>3</sub>)<sub>4</sub> (0.011 g, 0.010 mmol) was added and resultant reaction mixture was allowed to reflux for 16 h. Reaction progress was monitored by TLC analysis. After completion, the reaction mixture was quenched with water and extracted with DCM (3 x 10 mL). Combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum to get crude residue which was purified by flash column chromatography to afford 4D as a bluishblack powder (100 mg, 43%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.83 (dd, J = 12.9, 3.9 Hz, 8H), 7.55 (d, J = 5.3 Hz, 4H), 7.44 (d, J = 8.3 Hz, 8H), 7.38 (d, J = 3.9 Hz, 4H), 7.20 (d, J = 5.3Hz, 4H), 7.10 (d, J = 8.3 Hz, 8H), 3.97 (d, 16H), 1.82 (m, 8H), 1.21 (m, 64H), 0.93–0.58 (m, 48H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>) δ 161.60, 161.47, 149.04, 143.85, 139.91, 139.78, 136.62, 134.84, 132.25, 131.94, 131.78, 131.22, 131.15, 130.55, 130.02, 128.97, 128.22, 127.81, 125.54, 124.45, 108.12, 45.68, 39.25, 39.11, 31.92, 30.24, 29.68, 29.36, 28.53, 28.36, 23.61, 23.47, 23.06, 22.69, 13.83, 13.78, 10.28, 10.21; HRMS (MALDI-TOF, m/z): [M+H]<sup>+</sup> calculated for C<sub>146</sub>H<sub>173</sub>N<sub>8</sub>O<sub>8</sub>S<sub>8</sub>: 2422.1142, found: 2422.1668.

#### **Experimental spectra of 4D:**

#### <sup>1</sup>H NMR:



#### <sup>13</sup>C NMR:



#### MALDI-TOF





Theoretical energy levels - HOMO (left): -5.12 eV; LUMO (right): -3.01 eV; Eg: 2.11 eV

Fig. S1 Orbital density distribution for the frontier molecular orbitals of 4D. Density functional theory calculations were performed using the Gaussian 09 suite of programs and the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory.



**Fig S2** Torsional angle of ~20 ° between the thiophene ring planes (of DPP) and phenyl ring planes (of TPE) of **4D** from the minimum energy conformations calculated using the Gaussian 09 suite of programs and the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory.

| Excited | State | 1: | Singlet-A | 1.8840 | eV | 658.09 | nm | f=0.6572 | <s**2>=0.000</s**2> |
|---------|-------|----|-----------|--------|----|--------|----|----------|---------------------|
| Excited | State | 2: | Singlet-A | 1.9945 | eV | 621.62 | nm | f=0.2443 | <s**2>=0.000</s**2> |
| Excited | State | 3: | Singlet-A | 2.0009 | eV | 619.64 | nm | f=0.1084 | <s**2>=0.000</s**2> |
| Excited | State | 4: | Singlet-A | 2.0293 | eV | 610.96 | nm | f=0.0011 | <s**2>=0.000</s**2> |
| Excited | State | 5: | Singlet-A | 2.0464 | eV | 605.87 | nm | f=1.1266 | <s**2>=0.000</s**2> |
| Excited | State | 6: | Singlet-A | 2.0628 | eV | 601.06 | nm | f=0.2650 | <s**2>=0.000</s**2> |
| Excited | State | 7: | Singlet-A | 2.1168 | eV | 585.72 | nm | f=0.0148 | <s**2>=0.000</s**2> |
| Excited | State | 8: | Singlet-A | 2.1324 | eV | 581.42 | nm | f=0.1331 | <s**2>=0.000</s**2> |



Fig. S3 Theoretical optical absorption transitions and spectrum of 4D.



**Fig. S4** PESA spectrum of thin film of **4D**. The dashed-lines show the fits to extract ionisation potential (-5.53 eV) which corresponds to the HOMO energy level.



Fig. S5 TGA curve showing thermal stability of 4D.



Fig. S6 IPCE curve of the best BHJ device based on a blend of P3HT: 4D.

#### **References:**

**S1** D. Srivani, A. Gupta, A. M. Raynor, A. Bilic, J. Li, S. V. Bhosale and S. V. Bhosale, *RSC Adv.*, 2016, **6**, 38703.