SI: Investigation of the role of acceptor molecule in bulk heterojunction photovoltaic cells using impedance spectroscopy

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S1. General

Commercially available reagents were used as received from Sigma Aldrich, and Alfa Aesar. The polymerization was carried out under anhydrous conditions in an inert atmosphere of argon in flame-dried glassware. Gel permeation chromatography (GPC) was performed using a Waters Associates GPCV2000 liquid chromatography with is internal differential refractive index detector at 40 °C, using two Waters Styragel HR-5E column (10 mm PD, 7.8 mm i.d., 300 mm length) with HPLC grade THF as the mobile phase at flow rate of 1.0 mL/min. The polymer was dissolved in THF (1 mg/mL), and allowed to solubilize for 24-48 hour period, in which the solution was filtered through a Millipore 0.5 μm filter. Injections of ~200 μL were performed and retention times were calibrated against narrow molecular weight polystyrene standards. Absorption spectra were recorded in a double-beam Varian Cary 5000 UV-Vis-NIR spectrophotometer.

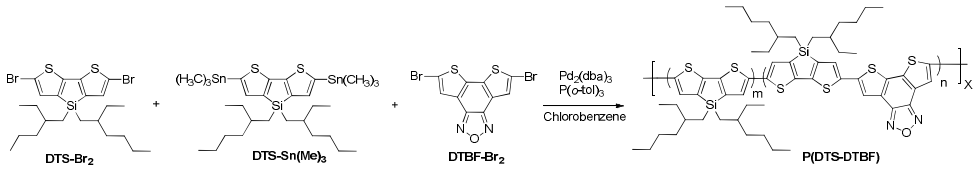
S2. Synthetic Procedures and Characterization of Products

S2.1. Materials

The **DTS-Br$_2$** and **DTS-Sn(Me)$_3$** monomers were synthesized according previously reported methods.[1] The **DTBF** (**Dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c]furazan)** monomer was synthesized according to previously reported methods.[2] The synthesis of **P-DTS-TPD** and **P-DTG-TPD** were synthesized according to previously reported methods.[3]

S2.2. Polymerization Procedures

Synthesis of Poly(DTS-DTBF)

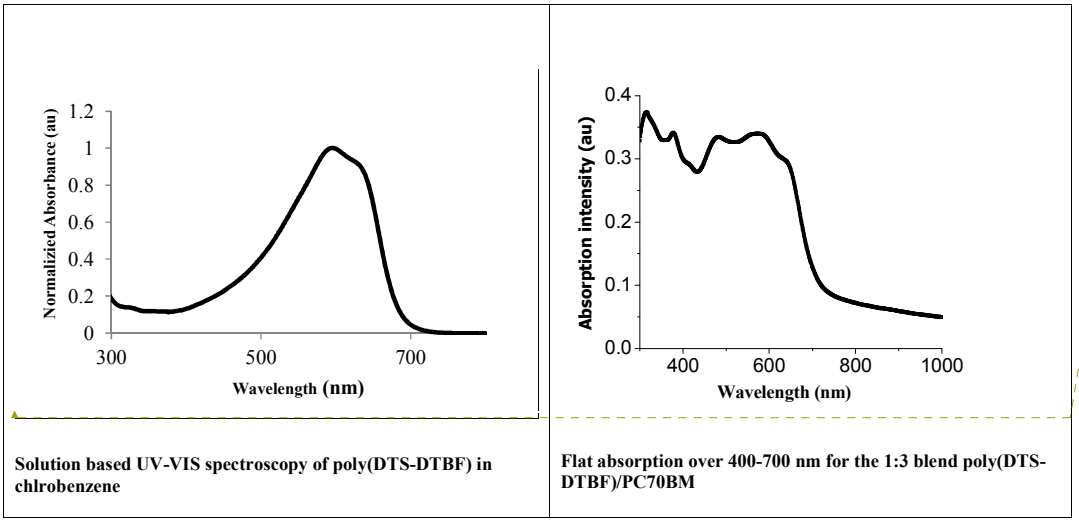


Ratio: 1:2:1

To a 25-mL Schlenk flask argon flushed , containing a stir bar and argon atmosphere, was added 0.13 mmol of **Br$_2$-DTBF**, using a ratio 1:2:1 of **Br$_2$-DTS**:**(Me$_3$Sn)$_2$-DTS**:**Br$_2$-DTBF**, and Pd2(dba)$_3$ (1 mol%), P(o-tol)$_3$ (3 mol%), and chlorobenzene (7 mL). The reaction was run for 7 days at 115 °C, then, 5 mL of chlorobenzene, and a scoop of diethylammonium diethyldithiocarbamate were added. The mixture was stirred for 15 minutes and added dropwise into 300 mL of MeOH. The resulting solid was filtered (osmotics, nylon membrane, 20 um), and washed with acetone. The resulting solid was transferred to a cellulose thimble and purified by Soxhlet extraction, using MeOH (12 hours), acetone (12h), hexanes (6h), DCM (6h), and chlorobenzene. The resulting chlorobenzene solution was concentrated to ~15 mL and then precipitated dropwise into 200 mL of methanol. The resulting solid was filtered (osmotics, nylon membrane, 20 um), air-dried for 5 minutes, and dried under vacuum overnight. Elemental analysis calculated for $C_{82}H_{110}N_2OS_8Si_3$: C (66.52%), H (7.49%), N (1.89%). Found: C (65.08%), H (7.8%), N (1.43%). GPC Analysis, M_n = 20,200 Da, PDI = 3.1

S3. Supporting Figures

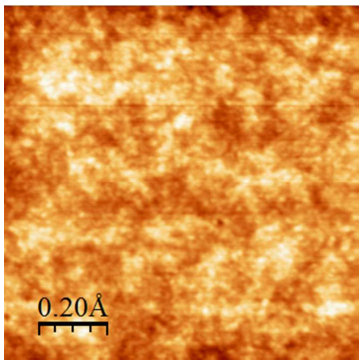
S3.1. Solution and Thin Film Based UV-VIS Spectroscopy of Poly(DTS-DTBF):



Solution based UV-VIS spectroscopy of poly(DTS-DTBF) in chlrobenzene

Flat absorption over 400-700 nm for the 1:3 blend poly(DTS-DTBF)/PC70BM

S3.2. Thin Film morphology (AFM):



AFM morphology image measured in tapping mode of a thin film of active layer on ITO/PEDOT. The films had very low roughness.

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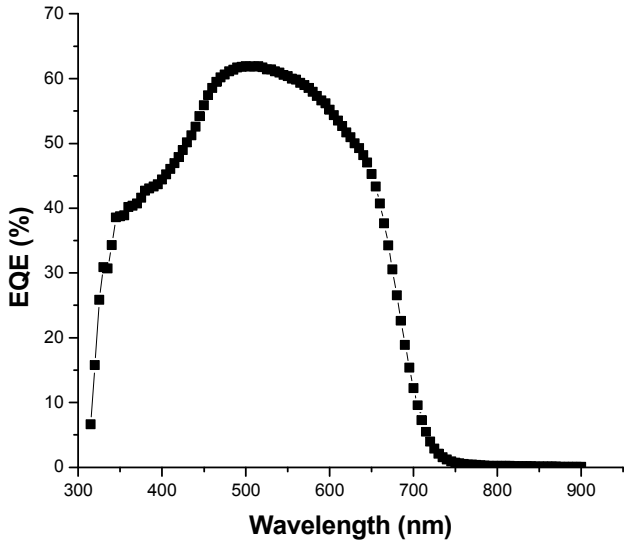
S3.2. Device Performance:



External quantum efficiency (EQE) of pDTS-DTBF) device.

S4. References

1) F. A. Arroyave, C. A. Richard, and J. R. Reynolds *Org. Lett.* **2012,** *14* (24), 6138-6141

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3) C. M. Amb, S. Chen, K. R. Graham, J. Subbiah, C. E. Small, F. So, and J. R. Reynolds *J. Am. Chem. Soc.* **2011** *133* (26), 10062-10065