Supporting Information

Enhanced Photovoltaic Performance of Tetrazine-Based Small Molecules with Conjugated Side Chain

Chen Wang, Chang Li, Shanpeng Wen, Pengfei Ma, Ge Wang, Changhao Wang, Huayang Li, Liang Shen, Wenbin Guo and Shengping Ruan*

Methods:

The thermal stability of two synthesized SMs is investigated by thermogravimetric analysis (TGA). The TGA was performed on a Perkin Elmer Pyris 1 analyzer under a nitrogen atmosphere (100 mL min^{-1}) at a heating rate of 10 °C min^{-1}. The temperatures with 5% loss for TBDT(TTzT)2 and TBDT(TTz2T)2 are 315 ℃ and 320 ℃, respectively.

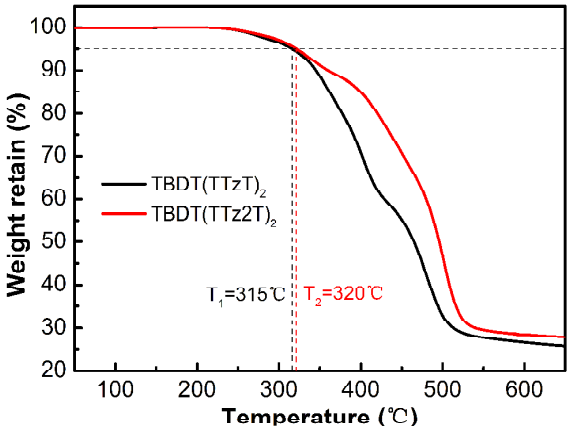


Figure S1.TGA plots of $TBDT(TTzT)_2$ and $TBDT(TTz2T)_2$ small molecules.

Transmission electron microscopy (TEM) test was carried out towards four SM:$PC_{71}BM$ blend films to investigate the morphology across the active layers. TEM was conducted using a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD camera.

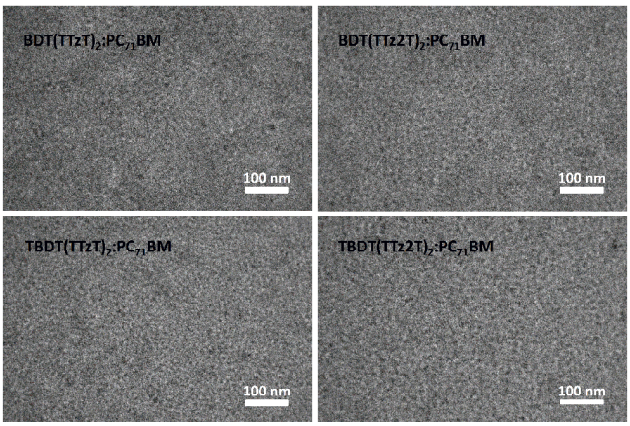


Figure S2.TEM images of blend film morphology of four SMs.

In this work, hole mobilities (μ_h) are determined using space-charge-limited-current (SCLC) method, with a hole only device structure of ITO/PEDOT:PSS/Sample films/Au. Sample films include pure SM films and SM:$PC_{71}BM$ blend films. The dark *J-V* curves were recorded and fitted to a space charge limited form, where the SCLC is described by the Equation of

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_h\frac{(V - V_{bi} - V_r)^2}{L^3}.$$

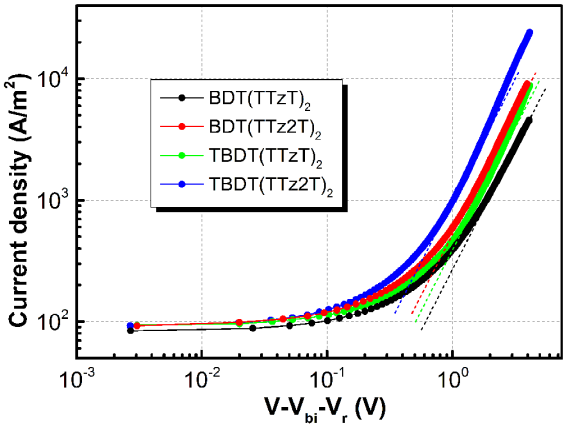


Figure S3. *J*-V characteristics of the hole-only device based on pure SM films.

Table S1. The derived μ_h values of four small molecules in pure films.

	$BDT(TTzT)_2$	$BDT(TTz2T)_2$	$TBDT(TTzT)_2$	$TBDT(TTz2T)_2$
μ_h (cm^2/Vs)	1.28×10^{-4}	2.54×10^{-4}	1.65×10^{-4}	5.01×10^{-4}

Table S2. The dihedral angles of four SMs determined through DFT calculations.

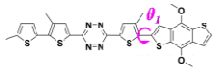
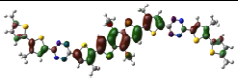
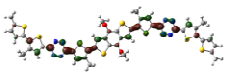
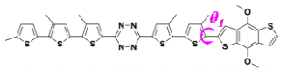
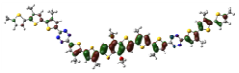
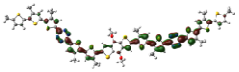
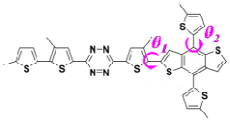
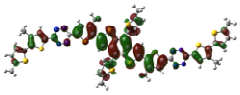
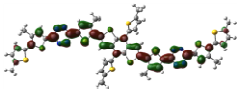
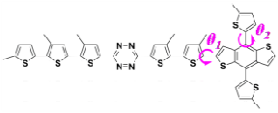
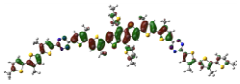
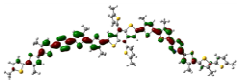
Small molecule	Structure	θ_1 (°)	θ_2 (°)	HOMO orbital	LUMO orbital
$BDT(TTzT)_2$		2.8	-		
$BDT(TTz2T)_2$		5.1	-		
$TBDT(TTzT)_2$		4.6	56.8		
$TBDT(TTz2T)_2$		6.9	57.0		

Table S3. Photovoltaic parameters based on different photoactive layer and D/A weight ratio under similar film thickness.

Photoactive layer	Weight ratio	Film thickness (nm)	V_{oc}(V)	J_{sc} (mAcm^{-2})	FF(%)	PCE (%)
TBDT(TTzT)$_2$: PC$_{71}$BM	2:1	70	1.00	4.83	47.0	2.27
	1.5:1	75	1.03	5.10	52.0	2.73
	1:1	73	1.01	4.62	50.7	2.34
	1:1.5	78	1.01	4.21	43.4	1.85
TBDT(TTz2T)$_2$: PC$_{71}$BM	2:1	76	0.89	5.02	46.1	2.06
	1.5:1	79	0.93	5.41	51.6	2.60
	1:1	81	0.96	6.10	53.1	3.11
	1:1.5	80	0.95	5.78	49.4	2.71