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Electronic Supporting Information for

## Pt Complex Based Terpolymer Acceptors Linked Through Ancillary Ligand for All-Polymer

## **Solar Cells**

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Figure S1. EDS elemental analysis spectrum of P(dbm)PtPyTPA1.



Figure S2. EDS elemental analysis spectrum of P(dbm)PtPyTPA2.



Figure S3. EDS elemental analysis spectrum of P(dbm)PtPyTPA5.



Figure S4. <sup>1</sup>H NMR spectra of PNDIT2.



Figure S5. <sup>1</sup>H NMR spectra of P(dbm)PtPyTPA1.



Figure S6. <sup>1</sup>H NMR spectra of P(dbm)PtPyTPA2.



Figure S7. <sup>1</sup>H NMR spectra of P(dbm)PtPyTPA5.



Figure S8. Thermogravimetric analysis (TGA) curves for polymer acceptors.



Figure S9. Cyclic voltammogram of PTB7-Th.



Figure S10. J-V curves of different batches of PNDIT2.



**Figure S11.** *J-V* curves of PBDB-T:P(dbm)PtPyTPAx (x=0, 1, 2 and 5) in conventional device structure.



Figure S12. EQE spectra of PBDB-T:P(dbm)PtPyTPAx (x=0, 1, 2 and 5).



**Figure S13.** *J-V* curves of neat polymer acceptor in electron-only device structure under dark condition.

nalumar accentor	theoretical values values measured by E	
polymer acceptor	(wt%)	(wt%)
P(dbm)PtPyTPA1	0.20	0.17
P(dbm)PtPyTPA2	0.39	0.34
P(dbm)PtPyTPA5	0.98	0.64

**Table S1.** Theoretical weight ratio of Pt element in P(dbm)PtPyTPAx (x = 1, 2, 5) and the practical values measured by EDS.

**Table S2.** The key photovoltaic parameters of conventional devices based on PBDB-T:P(dbm)PtPyTPAx (x = 0, 1, 2 and 5) with average PCE collected from over 10 devices.

Active Layer	V <sub>oc</sub>	J <sub>sc</sub>	FF	$PCE_{max}$	$PCE_{ave}$
	[V]	[mA cm <sup>2</sup> ]	[%]	[%]	[%]
PBDB-T:	0.86	6.47	67.93	2 70	267
PNDIT2	(0.86±0)	(6.17±0.30)	(68.06±0.44)	5.79	5.02
PBDB-T:	0.86	10.84(10.57±0.5	65.99	C 10	6.01
P(dbm)PtPyTPA1	(0.86±0)	5)	(65.71±1.52)	0.10	0.01
PBDB-T:	0.86	9.41	67.02	5.64	5 5 7
P(dbm)PtPyTPA2	(0.86±0)	(9.23±0.18)	(69.35±2.33)	5.04	5.57
PBDB-T:	0.87	6.63	70.19	4.02	2 07
P(dbm)PtPyTPA5	(0.87±0)	(6.54±0.22)	(69.87±1.90)	4.02	5.97

**Table S3.** Charge mobilities of polymer acceptor neat film and PTB7-Th:P(dbm)PtPyTPAx (x=0, 1, 2 and 5) blends, data achieved by an average of 6 devices.

	$\mu_h$	$\mu_e$
	[cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	[cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]
PNDIT2	-	1.98×10 <sup>-5</sup>
P(dbm)PtPyTPA1	-	2.35×10 <sup>-5</sup>
P(dbm)PtPyTPA2	-	2.55×10 <sup>-5</sup>
P(dbm)PtPyTPA5	-	3.29×10 <sup>-5</sup>
PTB7-Th: PNDIT2	2.49×10 <sup>-4</sup>	3.30×10 <sup>-5</sup>
PTB7-Th: P(dbm)PtPyTPA1	3.61×10 <sup>-4</sup>	4.29×10 <sup>-5</sup>
PTB7-Th: P(dbm)PtPyTPA2	5.07×10 <sup>-4</sup>	4.98×10 <sup>-5</sup>
PTB7-Th: P(dbm)PtPyTPA5	6.25×10 <sup>-4</sup>	5.61×10 <sup>-5</sup>