#### **Supporting Information**

# Semi-crystalline random conjugated copolymers with panchromatic absorption for highly efficient polymer solar cells

Jae Woong Jung<sup>a</sup>, Feng Liu<sup>b</sup>, Thomas P. Russell<sup>b</sup>, and Won Ho Jo<sup>\*a</sup>

<sup>a</sup>WCU Hybrid Materials Program and Department of Materials Science and Engineering, Seoul National University, San 56–1, Shillim–dong, Kwanak–ku, Seoul 151–744, Korea. Fax: +82 2 876 6086; Tel: +82 2 880 7192; E-mail: whjpoly@snu.ac.kr

<sup>b</sup>Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, United States. E-mail: russell@mail.pse.umass.edu

Energy & Environmental Science



Fig. S1 UV-Vis absorption spectra of PR2 and a mixture of PIT and PDPP3T in film state.

Energy & Environmental Science



Fig. S2 Cyclic voltammetry curves of PIT, PDPP3T and random copolymers.



Fig. S3 J-V curves of PSCs of random copolymers fabricated under different conditions.

active layer	solvent	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	FF	PCE <sub>Max</sub> (%)	PCE <sub>Average</sub> (%)
PR1:PC71BM	CB	0.77	6.20	0.58	2.77	2.68
	CB/DIO	0.78	7.84	0.57	3.49	3.30
PR2:PC71BM	CB	0.76	6.99	0.61	3.24	3.11
	CB/DIO	0.77	13.52	0.58	6.04	5.88
PR3:PC71BM	CB	0.67	6.32	0.51	2.16	2.12
	CB/DIO	0.69.	12.35	0.57	4.86	4.75

#### Table S1 Photovoltaic properties of PSCs based on random copolymer and PC71BM



Fig. S4 SCLC hole mobilities of PIT, PDPP3T and random copolymers.



Fig. S5 DSC curves of PDPP3T, PIT and random copolymers.



Fig. S6 2-D images of GIWAXS of random copolymer thin films.



**Figure S7.** 2-D images of GIWAXS of PR2/PC<sub>71</sub>BM thin films cast from CB without and with DIO.

## Energy & Environmental Science



Fig. S8 TEM images of active layers from  $PR1/PC_{71}BM$  and  $PR3/PC_{71}BM$  under optimized condition.

Energy & **Environmental Science** 2 ф 0 -O- PR2 (first batch) Current Density [mA/cm<sup>2</sup>] -2 - PR2 (second batch) -4 -6 -8 -10 <del>₽₽₽₿₿₽₽₽₽₽</del>₽₽₽₽ -12 -14 0.2 0.4 0.6 0.8 1.0 -0.2 0.0 Bias [V]

Fig. S9 J-V curves of polymer solar cells made of first and second batches of PR2, respectively.

# Energy & Environmental Science

Table S2 Performance details of PSC devices based on different batches of PR2..

PR2	Mn (kDa)	PDI	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	FF	PCE (%)
first batch	25.3	1.17	0.77	13.52	0.58	6.04
second batch	22.7	1.26	0.74	13.67	0.58	5.87





**Fig. S10** <sup>1</sup>H NMR spectrum of PR1 in CDCl<sub>3</sub>.





Fig. S11 <sup>1</sup>H NMR spectrum of PR2 in CDCl<sub>3</sub>.





Fig. S12 <sup>1</sup>H NMR spectrum of PR3 in CDCl<sub>3</sub>.

**Table S3** Comparison of feed ratio and composition of DPP to isoindigo of random copolymer

polymer	feed ratio of DPP to Isoindigo (DPP/isoindigo)	composition in random copolymer (DPP/isoindigo)
PR1	3:7 (0.43)	0.41
PR2	5:5 (1.00)	0.96
PR3	7:3 (2.33)	2.31