Supporting information

Switching from electron to hole transport in solution-processed organic blend field-effect transistors

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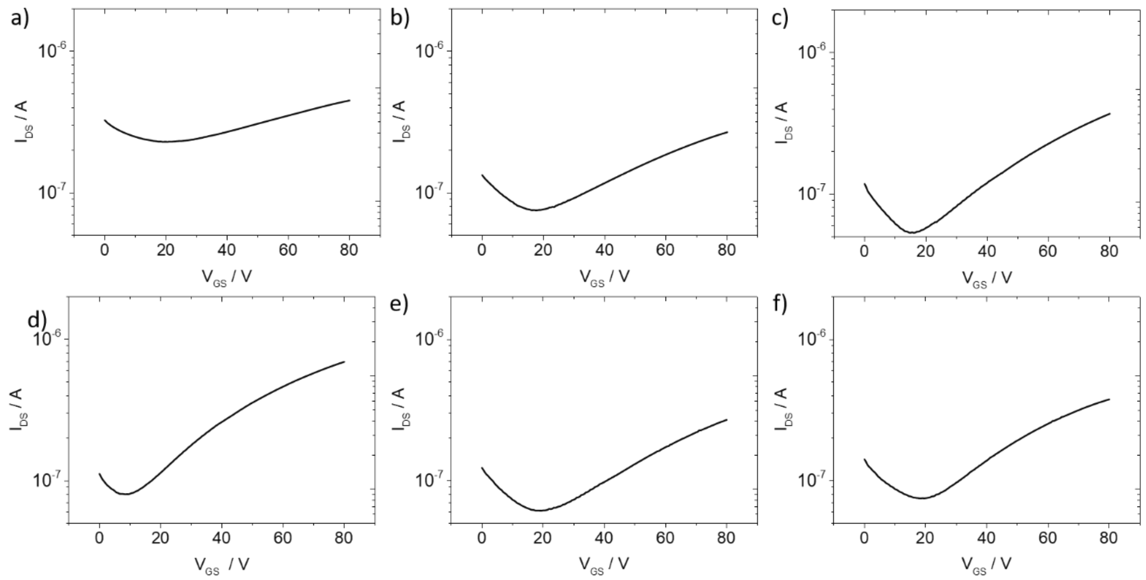

Figure S1. Transfer characteristics (V_{DS} = +80V) of OFETs based on PBTTT-C_{14}:PDI8-CN_2 composites obtained by spin-coating for 100 °C solution and: a) 1000 rpm, b) 2000 rpm, c) 3000 rpm, d) 4000 rpm, e) 5000 rpm, f) 6000 rpm rotation speeds

Table S1. Field-effect mobility values for PBTTT-C_{14}:PDI8-CN_2 composites obtained by spin-coating for 100 °C solution and different rotation speeds.

Rotation speed [RPM]	1000	2000	3000	4000	5000	6000
Thickness [nm]	80	68	42	55	53	38
Channel length [µm]	25	30	30	30	30	25
Field-effect mobility [10^{-4} $cm^2/(Vs)$]	0.8	1.0	2.1	2.3	1.3	1

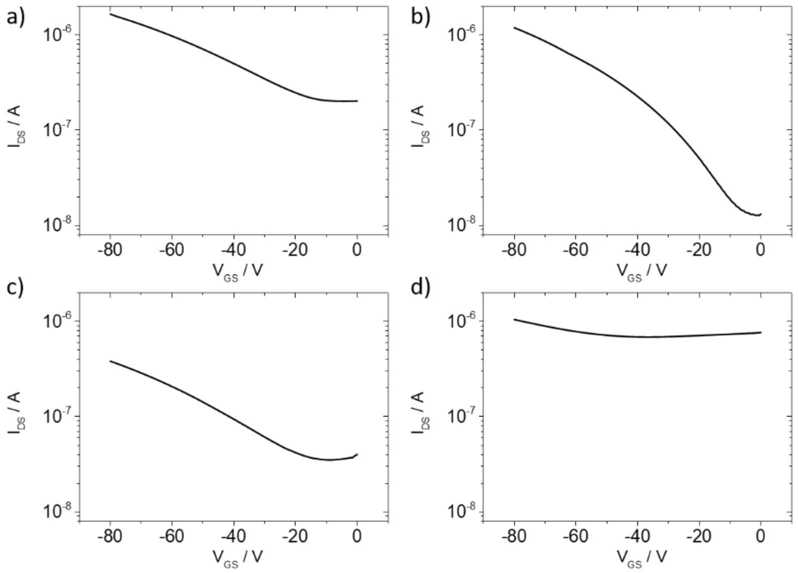

Figure S2. Transfer characteristic (V_{DS} = -80V) of OFETs based on PBTTT-C_{14}:PDI8-CN_2 composites fabricated with rotation speed of 4000 rpm and solutions at a) 80 °C , a) 100 °C , a) 120 °C , a) 140 °C.

Table S2. Field-effect mobility values for PBTTT-C_{14}:PDI8-CN_2 composites fabricated with rotation speed of 4000 rpm and different solution temperatures.

Solution temperature [°C]	80	100	120	140	160	180
Field-effect mobility [10^{-3}cm^2/(Vs)]	0.5	1.0	0.3	0.2	-	-

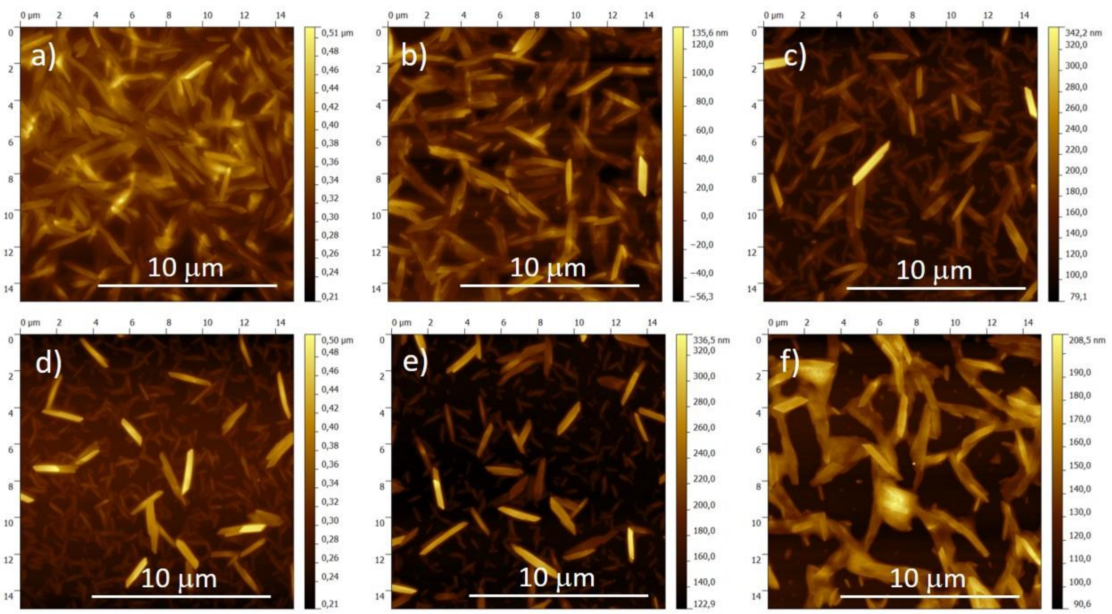

Figure S3. AFM images of solution temperature dependence for PBTTT-C_{14}:PDI8-CN_2 heterojunction composites additionally annealed at 200°C. PBTTT-C_{14}:PDI8-CN_2 films obtained at: a) 80 °C, b) 100 °C, c) 120 °C, d) 140 °C, e) 160 °C, f) 180 °C.

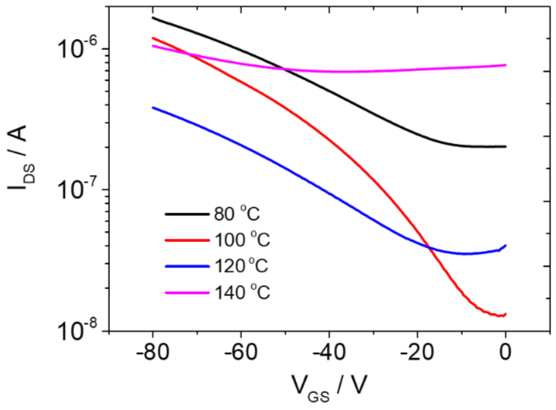

Figure S4. Transfer characteristic (V_{DS} = -80V) of OFETs based on PBTTT-C_{14}:PDI8-CN_2 composite with rotation speed of 3000 for various solution temperature after annealing at 140 °C

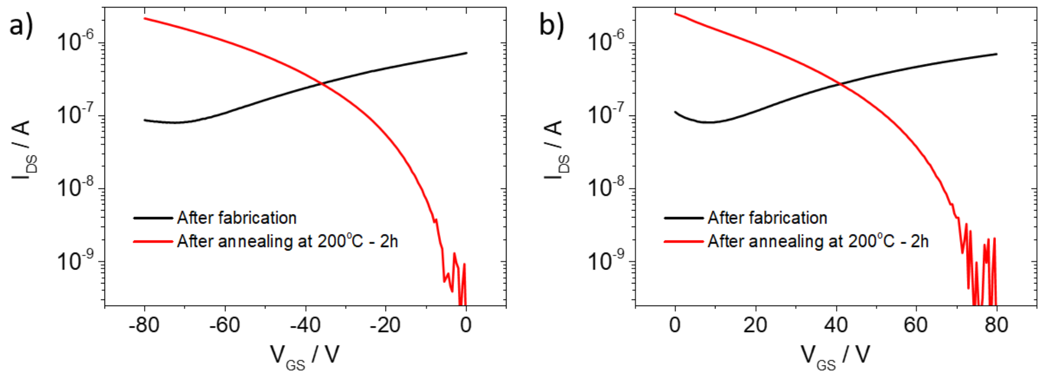

Figure S5. Transfer characteristic of OFETs based on PBTTT-C_{14}:PDI8-CN_2 composite with rotation speed of 4000 rpm a) *p-type* (V_{DS} = -80V) and b) *n-type* (V_{DS} = +80V) behavior.

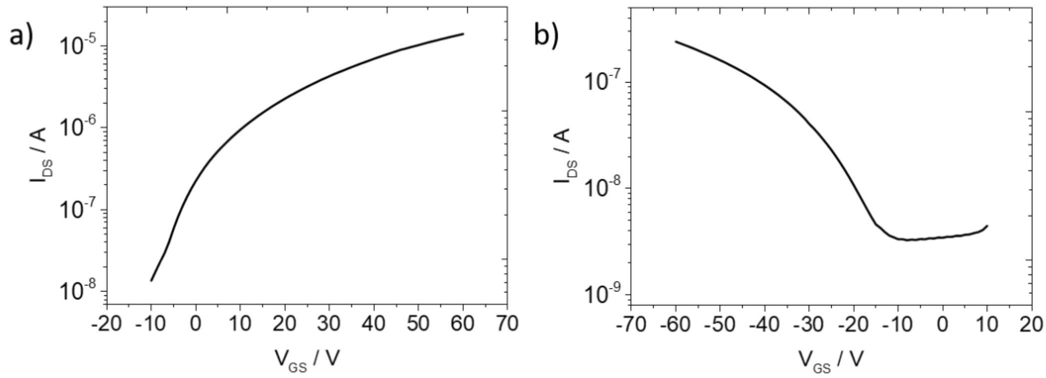

Figure S6. Transfer characteristic of OFETs based on PBTTT-C_{14}:PDI8-CN_2 composite fabricated with rotation speed of 4000 rpm on substrate modified by OTS; a) before annealing - *n*-type *type* (V_{DS} = +60V) b) annealed at 200 °C - *p-type* (V_{DS} = -60V)

Table S3. Field-effect mobility values for PBTTT-C_{14}:PDI8-CN_2 composites fabricated with rotation speed of 4000 rpm on substrate modified by OTS.

Thermal annealing	None		200°C/2h	
Transport type	*p-type*	*n-type*	*p-type*	*n-type*
Field-effect mobility [10^{-2} $cm^2/(Vs)$]	-	1.5	0.1	-

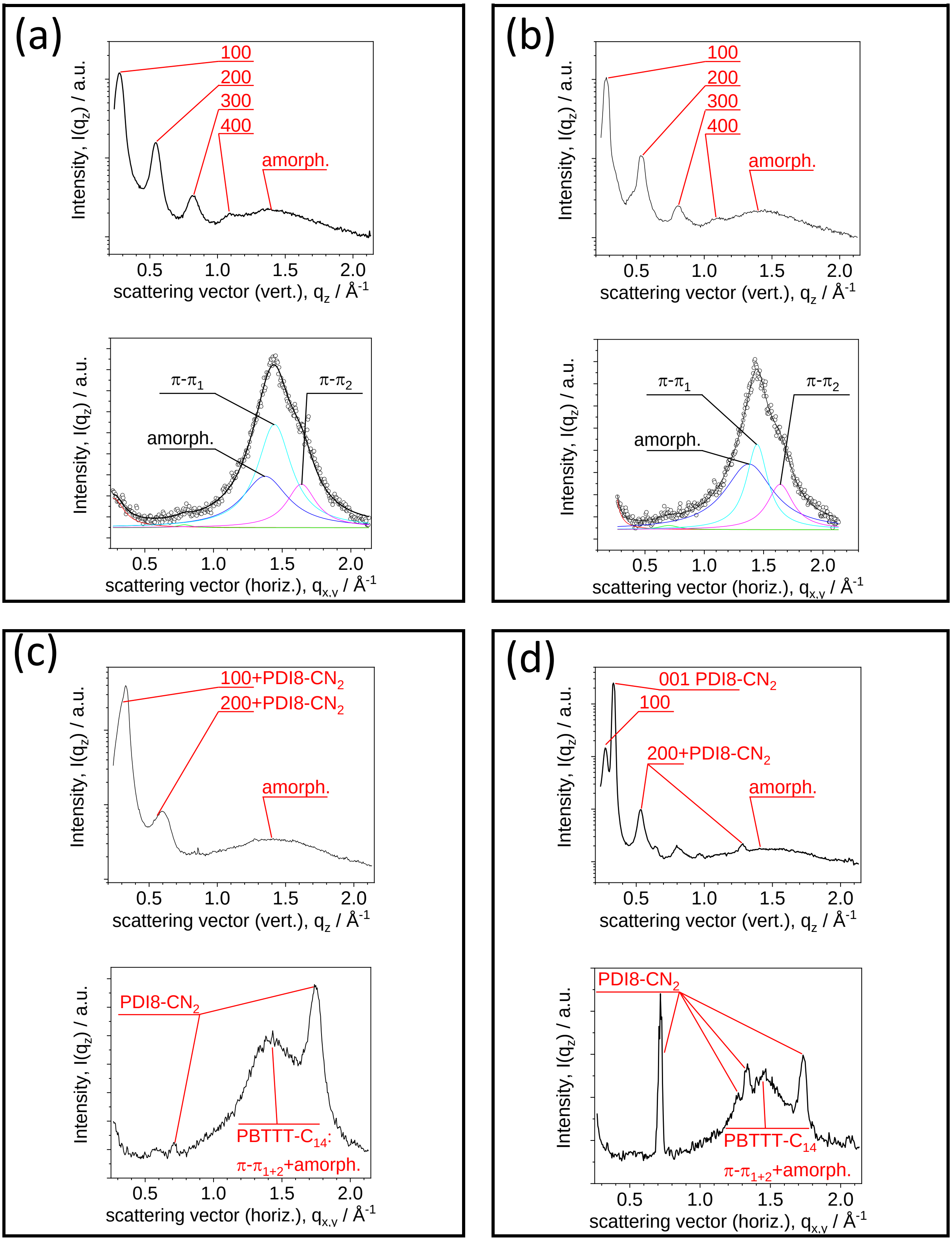

Figure S6. Vertical (q_z / vert. – upper plots) and horizontal ($q_{x,y}$, horiz. – lower plots) integrations of GIWAXS patterns shown in Figure 6 in the main part of the paper. The integrations correspond to PBTTT-C_{14} (a), annealed PBTTT-C_{14} (b), PBTTT-C_{14}:PDI8-CN_2 blend (c), and the annealed PBTTT-C_{14}:PDI8-CN_2 (d). In the horizontal integrations of PBTTT-C_{14} the deconvolution of patterns is included. Open points correspond to the experimental data, color lines show contributions of the π-π-stacking components and amorphous halos whereas black solid line correspond to the fitted data. If not specified otherwise Miller hkl indices correspond to crystal structure of PBTTT-C_{14}.

Table S4. PBTTT-C_{14} crystal structure parameters extracted from GIWAXS data shown in Figure SX. q_{max}, d, and t denote, respectively, peak position, interplanar spacing and crystal coherence length (Scherrer coherence) 100 and π-π subscripts correspond to 100 interplanar distance and π-π stacking distance. Since in PBTTT-C_{14} there are two distinct π-π systems (see main text for details) there are π-π_1 and π-π_2 symbols.

Crystal structure parameter	**System**			
	PBTTT-C_{14}	PBTTT-C_{14}, annealed	PBTTT-C_{14}:PDI8-CN_2	PBTTT-C_{14}:PDI8-CN_2 annealed
$q_{max\ (100)}$ / $Å^{-1}$	0.276	0.276	0.284	0.274
d_{100} / Å	22.8	22.8	22.2	22.9
t_{100} / Å	115	170	90.9	180
$q_{max\ (\pi-\pi_1)}$ / $Å^{-1}$	1.44	1.44	n/a	n/a
$d_{\pi-\pi1}$ / Å	4.4	4.4	n/a	n/a
$d_{\pi-\pi1}$/ Å	19.4	26.8	n/a	n/a
$q_{max\ (\pi-\pi_2)}$ / $Å^{-1}$	1.64	1.64	n/a	n/a
$d_{\pi-\pi2}$ / Å	3.8	3.8	n/a	n/a
$t_{\pi-\pi2}$ / Å	22.5	22.5	n/a	n/a