Supporting information for

## Highly Sensitive Evaluation of Density of States in Molecular Semiconductors by Photoelectron Yield Spectroscopy in Air

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**Materials:** We used materials without further purification. The molecular structures and the suppliers of these materials are summarized in Table S1.

Short	Long name	Supplier	Molecular structure	
name				
rr-P3HT	Regioregular poly(3- hexylthiophene-2,5-diyl)	TCI, P2513	$ \begin{array}{c} \left\{ \begin{array}{c} \mathbf{S} \\ \mathbf{C}_{6} \mathbf{H}_{13} \end{array} \right\}_{n} \\ \mathbf{C}_{6} \mathbf{H}_{13} \end{array} $	
ran-	Regiorandom poly(3-	Sigma-	√s,]	
P3HT	hexylthiophene-2,5-diyl)	Aldrich,		
		510823	Ċ <sub>6</sub> H <sub>13</sub>	
PBTTT-	Poly[2,5-bis(3-	Sigma-	_ C <sub>14</sub> H <sub>29</sub>	
C <sub>14</sub>	tetradecylthiophen-2-	Aldrich,	s s	
	yl)thieno[3,2-	753971	s s	
	b]thiophene]		C <sub>14</sub> H <sub>29</sub>	
rr-	Regioregular poly(3-	Sigma-	√sJ	
P3DDT	dodecylthiophene-2,5-	Aldrich,	L\(J <sub>n</sub>	
	diyl)	682780	C <sub>12</sub> H <sub>25</sub>	
PTB7	poly({4,8-bis[(2-	1-Material,		
	ethylhexyl)oxy]benzo[1,	OS0007		
	2-b:4,5-b']dithiophene-			
	2,6-diyl} {3-fluoro-2-[(2-		s s	
	ethylhexyl)carbonyl]thie			
	no[3,4-b]thiophenediyl})		° "	
			ſ	
C <sub>60</sub>	-	TCI, B1641		
PCBM	[6,6]-phenyl C61 butyric	Solenne		
	acid methyl ester			

**Table S1.** Summary of the molecular structures and the suppliers for the semiconducting materials used in this study.

Y6	2,2'-((2Z,2'Z)-((12,13-	Derthon	$\langle \rangle$
	bis(2-ethylhexyl)-3,9-	OPV, S6755	
	diundecyl-12,13-dihydro-		
	[1,2,5]thiadiazolo[3,4-		N S N S
	e]thieno[2",3":4',5']		
	thieno[2',3':4,5]pyrrolo[3		F F F
	,2-		
	g]thieno[2',3':4,5]thieno[		
	3,2-b]indole-2,10-		
	diyl)bis(methanylylidene		
	))bis(5,6-difluoro-3-oxo-		
	2,3-dihydro-1H-indene-		
	2,1-		
	diylidene))dimalononitril		
	е		
IDT-BT	-	Derthon	H <sub>33</sub> C <sub>16</sub> C <sub>16</sub> H <sub>33</sub> N S N
		OPV, P3300	
			KI 's J <sub>n</sub>
			H <sub>33</sub> C <sub>16</sub> C <sub>16</sub> H <sub>33</sub>
PVK	Poly(9-vinylcarbazole)	Sigma-	<u>г</u> ,
		Aldrich,	1 Pn N
		368350	

**Preparation of substrate:** A glass substrate with an indium tin oxide (ITO) electrode was cleaned by sequential ultrasonication in detergent solution, water, 2-propanol, and acetone, followed by O<sub>2</sub> plasma treatment. This cleaning procedure was also used for field-effect transistor (FET) fabrication.

**Preparation of samples for photoelectron yield spectroscopy:** For film top samples, materials were directly spin-coated onto a pre-cleaned glass/ITO substrate at various solution concentrations (Table S2). For film bottom samples, we spin-coated materials onto both a pre-cleaned bare glass substrate and a pre-cleaned ITO substrate at half the solution concentrations of the film top samples. Then, the film on the glass substrate was transferred onto the film on the ITO substrate, making a film/substrate interface the sample surface. The total thicknesses of the directly spin-coated sample and transferred sample were the same. In previous reports, we used poly(sodium 4-styrenesulfonate) (PSSNa) in the contact film transfer method to speed up the detachment of the film from the glass substrate. A small amount of PSSNa remained on the sample surface after the film transfer, leading to a slight shift in the vacuum level. Therefore, in this study we did not use PSSNa for the transfer process, sacrificing the speed of the transfer.

Ultraviolet photoemission spectroscopy measurements: Ultraviolet photoemission spectroscopy (UPS) was performed with a photoelectron spectroscopy system (PHI5000 VersaProbe II, ULVAC-PHI Inc.) with He I excitation (21.2 eV). For all UPS measurements, a -5.0 V bias was applied to the sample. The measurement was conducted in a vacuum chamber with pressure of approximately  $1 \times 10^{-6}$  Pa.

**Photoelectron yield spectroscopy measurements:** Photoelectron yield spectroscopy (PYS) was performed with photoemission yield spectroscopy in air systems (AC-2 and AC-3, RIKEN KEIKI) with a monochromated D2 lamp. The overall energy resolution

was 0.27 eV evaluated with the Ag Fermi edge. Before the measurements, the samples were kept in air for more than three hours to eliminate the time dependence of photoemission yield. Just after taking the sample from the glovebox filled with N2, the photoemission yield had time-dependence; the yield decreased as time went by. After three hours, the yield became stable, and the multiple measurements confirmed the reproducibility of the results. Note that these systems rely on the counting of radical anions of oxygen molecules that are generated by photoelectrons emitted from a sample; thus, they require that the samples are measured in dry air. The counting time for the photoelectrons was 60 s for each energy. We measured the irradiated photon flux three times and used the average of the measurements (Figure S1b). The photoelectron flux was divided by the average photon flux, giving a photoelectron emission yield. We calculated the density of states (DOS) by calculating the central differential of the yield with energy. For measurements in an energy range from 3.4 to 5.3 eV, UV cut filters (FGUV5S and FGUV11S, Thorlabs) were placed between the D2 lamp and monochromator to eliminate stray light with higher energy. The effect of stray light is shown in Figure S2. For comparison, the obtained DOS was normalized to the area of the Gaussian fitted to the DOS edge.

**FET device fabrication and characterization:** The surface of the pre-cleaned n<sup>+</sup>Si substrates (0.2–0.6  $\Omega$  cm) with a 300 nm SiO<sub>2</sub> insulating layer (E&M) was covered with a benzocyclobutene (BCB; DOW Chemical Company) insulating layer to eliminate the charge traps in SiO<sub>2</sub>. A 5 vol % BCB solution diluted with mesitylene was spin-coated at 3000 rpm to produce an approximately 22-nm-thick passivation layer. The BCB film was thermally annealed at 250 °C for 3 h in the glovebox. The total capacitance of the SiO<sub>2</sub> and BCB layer was 9.7 nF/cm<sup>2</sup> (Figure S10). Approximately 20-nm-thick polymer films

were directly spin-coated onto BCB or spin-coated onto a glass substrate and transferred onto BCB using the contact film transfer method. After the formation of the semiconductor films, 15-nm-thick Au and 30-nm-thick Ag top-contact electrodes were formed sequentially by thermal evaporation through a metal shadow mask under a pressure of  $10^{-4}$  Pa. The channel width and length were 1000 and 200 µm, respectively. Source meters were used to measure the source-drain current (6430, Keithley) and gate leakage current (2400, Keithley). FET measurements were conducted in a vacuum of ~ $10^{-2}$  Pa.

**X-ray diffraction measurements:** X-ray diffraction was performed with an X-ray diffractometer (Smartlab, Rigaku). Monochromatized Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) was generated at 45 kV and 200 mA. Films were prepared on a Si/SiO<sub>2</sub> substrate using the same spin-coating conditions as the PYS measurements.

**Atomic force microscopy:** Atomic force microscopy (AFM) images were obtained with a scanning probe microscope (5400, Agilent Technologies) in tapping mode.

Table S2. Summary of spin-coating conditions, annealing conditions, and film thicknesses of organic semiconductor films. Annealing was conducted in a glovebox filled with dry  $N_2$ . Film thickness was measured by X-ray reflectivity, using films prepared on a Si substrate.

	Use	Solvent	Concentration	Rotation	Annealing	Thickness
			$(mg mL^{-1})$	speed (rpm)	(°C, min)	(nm)
rr-	PYS,	CB	5.0	1000	-	22
P3HT	FET					
ran-	PYS,	CB	4.0	1000	-	14
P3HT	FET					
rr-	PYS	CB	4.0	1000	-	16
P3DDT	FET					
PTB7	PYS	CB	8.0	1000	-	43
PTB7	FET	CB	4.0	1000	-	16
C <sub>60</sub>	PYS	Evapor	-	-	-	35
		ation				
PCBM	PYS	CB	10.0	600	-	35
Y6	PYS	CF	1.5	1000	-	13
PBTTT	PYS,	CB	3.0	1000	-	~15
<b>-</b> C <sub>14</sub>	FET					
IDT-BT	PYS	CB	8.0	1000	100, 30	68
IDT-BT	FET	CB	5.0	1000	100, 30	37
PVK	PYS	CB	8.0	1000	-	29

CB: chlorobenzene; CF: chloroform. -: not applicable.



**Figure S1.** (a) Photoelectron flux of rr-P3HT film with different counting times. For a counting time of 10 s (blue triangles), the flux at high energies varied in each scan. Increasing the counting time to 60 s (red squares) gave a flux identical to the average of five scans with a counting time of 10 s, indicating the variation was suppressed. (b) Three irradiated photon flux measurements (red squares). We used the average of these measurements (black line), although the variation in them was small.



**Figure S2.** Central differential of photoelectron emission yield of rr-P3HT film with and without using UV cut filters. Without the filters, the background signal level was two to three orders of magnitude higher than with the filter, limiting the gap states that could be investigated.



**Figure S3.** UPS spectra of the PCBM film plotted on a logarithmic scale. The purple line shows experimental raw data. Photons with an energy of 21.22 eV are the main irradiation from excited He, contributing to more than 97% of the signal. Other unnecessary high-energy radiation does not make a large contribution to the main peak, but in the energy region below the ionization energy, this small amount of radiation caused a large background signal. Assuming contributions of 2.0% and 0.36% from 23.09 and 23.74 eV photons, the background signal is quantitatively explained (dashed lines).



**Figure S4.** UPS spectra of rr-P3HT, PTB7, PCBM, and Y6. (a) Secondary electron cutoff region and (b) HOMO region. The binding energy is the value with respect to the Fermi level ( $E_F = 0$  eV). Cutoff energy was evaluated using the intersection of the fitting line. We fitted a single Gaussian to the edge of the occupied DOS. The ionization energy was systematically evaluated as Gaussian peak energy –  $2\sigma$ , where  $\sigma$  is the width of the Gaussian. The ionization energy evaluated by this Gaussian fit agreed well with the onset of the UPS signal.

## (a) PCBM



(b) Y6





**Figure S5.** Molecular orbital calculations of (a) PCBM, (b) Y6, (c) rr-P3HT, and (d) PTB7. Structural optimization and molecular orbital (MO) calculations were performed by using the Gaussian03 package with the B3LYP exchange-correlation function and 6-31G\* basis set. Ten and four monomer units were used for calculating rr-P3HT and PTB7, respectively. The alkyl side chains were replaced with a methyl group for the calculations. The simulated DOS was obtained by convoluting delta functions at MO energies with a Gaussian function with a full width at half-maximum of 0.542 eV ( $\sigma$  = 0.230 eV) by using GaussSum 3.0.



**Figure S6.** AFM topographic images of the film top and film bottom side of (a), (b) rr-P3HT, (c), (d) PBTTT-C<sub>14</sub>, and (e), (f) IDT-BT films. Image size:  $5 \times 5 \mu m$ . Bottom panels show line profiles at the positions indicated by dashed lines in the image. RMS: root mean square.



**Figure S7.** XRD out-of-plane diffraction patterns of polymer semiconductor films. (a) rr-P3HT, (b) PBTTT-C<sub>14</sub>, (c) IDT-BT, and (d) PTB7. Arrows indicate the diffraction peak positions.



**Figure S8.** DOS of (a) ran-P3HT, (b) rr-P3DDT, (c) PTB7, and (d) PVK spin-coated films. The DOS distribution of the film top and bottom are compared.



**Figure S9.** Transfer characteristics of bottom-gated, top-contact FETs of (a) ran-P3HT, (b) rr-P3DDT, and (c) PTB7. Four results in the forward and backward scan directions are plotted. Top and bottom mean that the FET channel was the film top and film bottom, respectively.



**Figure S10.** Total capacitance of  $SiO_2$  (300 nm)/BCB (22 nm) insulating layer measured by impedance spectroscopy. We used an n<sup>+</sup>Si substate and evaporated a 100-nm-Al onto the BCB layer as the electrodes. The capacitance was 9.7 nF/cm<sup>2</sup>.