Supporting Information

Solution-processed anthradithiophene-PCBM p-n junction photovoltaic cells fabricated by using the p photoprecursor method

Hiroko Yamada*^{a,d}, Yuji Yamaguchi^b, Ryuta Katoh^c, Takao Motoyama^b, Tatsuya Aotake^a, Daiki Kuzuhara^a, Mitsuharu Suzuki^a, Tetsuo Okujima^c, Hidemitsu Uno^c, Naoki Aratani^a, and Ken-ichi Nakayama*^{b,d}

^aGraduate School of Materials Science, Nara Institute of Science and Technology, 8916-5, Ikoma, Nara 630-0192, Japan. Fax: +81-743-72-6042; Tel: +81-743-72-6041; E-mail: hyamada@ms.naist.jp

^b Department of Organic Device Engineeing, Graduate School of Science and Engineering, Yamagata University, Yonezawa 992-8510, (Japan), Fax: (+81)238-26-3713, E-mail: nakayama@yz.yamagata-u.ac.jp

^cGraduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan ^dCREST, JST, Chiyoda-Ku, Tokyo 102-0075, Japan

Experimenatal

General ¹H NMR and ¹³C NMR spectra were recorded on a JEOL JNM-AL 400 and JNM-WCX400 spectrometer using tetramethylsilane as an internal standard. FAB and ESI mass spectra were measured on a JEOL JMS-MS 700V spectrometer. UV-vis spectra were measured on JASCO UV/VIS/NIR Spectrophotometer V-570. Elemental analyses were performed on a Yanaco MT-5 elemental analyzer. All solvents and chemicals were reagent grade quality, obtained commercially and used without further purification except as noted. Thin-layer chromatography (TLC) and column chromatography were performed on Art. 5554 (Merck KGaA) and Silica Gel 60N (Kanto Chemical Co.), respectively.

The current density-voltage curves were measured using a Keithley 2400 source measure unit. The photocurrent was measured under AM 1.5G illumination at an intensity of 100 mW cm⁻² using a solar simulator (Bunko-keiki, CEP-2000). IPCE spectra were measured with a Xe lamp and monochromator using a CEP-2000 integrated system by Bunko-keiki Co.

Ionization potential was determined by atmospheric photoelectron spectroscopy (Riken Keiki, AC-3). UV-vis absorption spectra of thin films were recorded in air using a JASCO V-650 spectrometer. ATR-FTIR spectra of films on Si substrates were recorded in air using a Shimadzu IRPrestige-21 spectrometer. Thin film structures were characterized by XRD measurements in out-of-plane and in-plane configuration using a Rigaku SmarLab diffractometer equipped with rotating anode (Cu K α radiation, λ =1.5418 Å).

Photochemical reactions The photocleavage reactions were carried out in a quartz UV cell which was irradiated by monochromatic excitation light through a monochrometor (Ritsu MC-10N) by a 500 W xenon lamp (Ushio XB-50102AA-A) and monitored by OCEAN OPTICS high resolution spectrometer system HR-4000 with light source DH-2000-BAL.

Film preparation The typical spin-coated p-n junction devices of acenes and PC₆₁BM [ITO / PEDOT:PSS (30 nm) / acene (40 nm) / PC₆₁BM (40 nm) / Ca (10 nm) / Al (80 nm)] were fabricated as follows; ITO-coated glass substrates were cleaned stepwisely in Semico clean 56, water, acetone, and isopropyl alcohol under ultrasonication for 10 min each. After the UV/O₃ treatment for 20 min, PEDOT:PSS (Clevios, AI4083) was spin-coated onto a cleaned ITO surface. After being baked in air at 120 °C for 20 min, the substrate were transferred into a nitrogen filled glove box (< 0.5 ppm O₂ and H₂O). **PDK** or **ADT-DK** (5 mg ml⁻¹, 250 µl) in CHCl₃ spin-coated at 800 rpm for 30 sec in a glove box, then irradiated by blue LED (200 mW cm⁻²) at rt for 30 min. Then PC₆₁BM (10 mg ml⁻¹) in CHCl₃ was spin-coated at 800 rpm for 30 s in grove box, followed by the continuous vacuum deposition of Ca (10 nm) and Al (80 nm). The device was then tested in air after the encapsulation in the glove box.

The **ADT-DK** film for IR was prepared on ITO by spin coating of **ADT-DK** (5 mg ml⁻¹, 250 μ l) in CHCl₃ at 800 rpm for 30 sec in a glove box. The conversion from **ADT-DK** film to **ADT** films were performed by irradiation by blue LED (200 mW cm⁻²) at rt for 30 min. The pentacene and **ADT** films for XRD measurements were prepared by the same procedure as that for OPV device preparation but with the deposition of PCBM, Ca, and Al layers omitted. The p-n junction films for UV-vis measurements were prepared by the same procedure as that for OPV device preparation of Ca and Al layers omitted.

Synthesis



A solution of **ADT** (0.78 g, 2.7 mmol) and vinylene carbonate (2.5 mL, 39 mmol) in xylene (100 mL) was heated at 180 °C in an autoclave for 3 days. After removal of the solvent in *vacuo*, the residue was purified with recrystallization from CHCl₃/MeOH to give **1** as a white powder (0.82 g, 2.2 mmol, 81%). ¹H NMR (400 MHz, CDCl₃, Mixture of isomers) δ 7.89 (s, 2H), 7.83 (s, 2H) 7.46 (d, *J* = 5.4 Hz, 2H), 7.46 (d, *J* = 5.5 Hz, 1H), 7.42 (d, *J* = 5.0 Hz, 1H), 7.28 (m, 2H), 4.99 (m, 2H), 4.84 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, Some peaks overlaped because isomers were mixed.) δ 154.09, 139.13, 139.09, 138.98, 134.13, 134.02, 133. 90, 133.77, 132.62, 132.60, 132.39, 132.37, 127.42, 127.41, 126.93, 126.91, 123.57, 123.55, 123.51, 123.49, 121.58, 121.55, 120.56, 120.53, 120.50, 119.59, 119.56, 76.41, 76.39, 76.37, 76.35, 47.88, 47.86; MS (FAB) *m*/*z* 377 (M⁺+1); Anal. Calculated for C₂₁H₁₂O₃S₂: C, 67.00; H, 3.21. Found: C, 66.78; H, 3.40.



1 (0.70 g, 1.9 mmol) was added to a mixture of 4 M NaOH aq. (5.6 mL) and THF (21 mL). The resulting mixture was refluxed for 2 h. The reaction mixture was cooled to rt, poured into water and then extracted with $CHCl_3$. The combined organic layer was washed with water and brine over Na_2SO_4 . The solvent was removed under reduced pressure. The residue was washed with diethyl ether to give 2 as a white powder (0.49 g, 1.4 mmol, 74%).

¹H NMR (400 MHz, DMSO, Mixture of isomers) δ 7.97 (s × 2, 1H), 7.90 (s × 2, 1H), 7.84 (s × 2, 1H), 7.79 (s × 2, 1H) 7.67 (d, *J* = 5.5 Hz, 1H), 7.64 (d, *J* = 5.5 Hz, 2H), 7.37 (m, 2H), 4.71 (m, 2H), 4.51 (m, 2H), 3.98 (s, 2H, -OH); ¹³C NMR (100 MHz, DMSO, Some peaks overlaped because isomers were

mixed.) δ ; 137.76, 137.64, 137.55, 137.38, 137.31, 137.17, 136.87, 136.79, 136.63, 136.60, 136.36, 126.78, 126.09, 123.66, 123.62, 120.80, 119.66, 119.30, 118.31, 67.12, 67.09, 51.15, 51.13; MS (ESI) m/z 373 (M⁺+Na); (HR-ESI) m/z = 373.03334, calcd for C₂₀H₁₄NaO₂S₂ = 373.03329 [M+Na]⁺



Trifluoroacetic anhydride (1.4 mL, 20 mmol) was added dropwise to a mixture of *dry*-DMSO (1.4 mL, 252 mmol) and *dry*-CH₂Cl₂ (5.0 mL) at -60 °C under argon. After stirring for 10 min, **2** (0.20 g, 0.57 mmol) dissolved in a mixture of *dry*-DMSO (3.0 mL) and dry-CH₂Cl₂ (3.0 mL) was added dropwise. After stirring for 90 min, *N*,*N*-diisopropylethylamine (3.5 mL, 20 mmol) was added dropwise to the reaction mixture. The solution was stirred at -60 °C for 60 min and warmed to rt before 1 M HCl (86 mL) was added to the mixture. The mixture was extracted with CH₂Cl₂, and the combined organic layers were washed with water and brine, and dried with Na₂SO₄. After removal of the solvent in *vacuo*, the residue was purified by column chromatography on silica gel with CH₂Cl₂ and recrystallized from toluene to give **ADT-DK** as yellow crystals (0.16 g, 0.46 mmol, 81 %).

¹H NMR (400 MHz, CDCl₃, Mixture of isomers) δ 7.96 (s, 2H), 7.89 (s, 2H), 7.52 (d, J = 5.4 Hz, 2H), 7.33 (d, J = 5.4 Hz, 2H), 5.16 (s, 2H); ¹³C NMR (100 MHz, CDCl₃, Mixture of isomer) δ 184.57, 184.50, 184.42, 140.73, 140.33, 131.36, 131.14, 131.11, 130.90, 128.20, 128.17, 123.53, 123.51, 121.13, 121.11 120.19, 120.17, 60.27, 60.26, 60.24; MS (ESI) m/z 369 (M⁺+Na); Anal. Calculated for C₂₀H₁₄O₂S₂: C, 69.34; H, 2.91. Found: C, 69.34; H, 3.20.

Film structure	Concentration of the spin-coating solution / mg ml ⁻¹		Thickness of total film / nm	Thickness of acene / nm	Thickness of PCBM / nm
	precursors	РСВМ			
ITO / PEN	5	-	42	42	-
ITO / PEN / PC ₆₁ BM	5	10	82	42	40
ITO / PEN / PC ₇₁ BM	5	10	83	42	41
ITO / ADT	5	-	46	46	-
ITO / ADT / PC ₆₁ BM	5	10	83	46	37
ITO / ADT / PC ₇₁ BM	5	5	59	46	13
ITO / ADT / PC ₇₁ BM	5	10	85	46	39
ITO / ADT / PC ₇₁ BM	5	15	141	46	95
ITO / ADT / PC ₇₁ BM	5	20	162	46	116

Table S1 Film thickness of spin-coated films of acene and PCBM

Experimental condition: The thickness of the acene films was measured for [ITO / PEN] and [ITO / ADT] prepared by spin coating and photoirradiation, using Veeco Dektak8 stylus profiler. The thickness of PCBM films were obtained by the subtraction of [ITO / acene / PCBM] and [ITO / acene] films.



Figure 1. X-ray crystal structure of ADT-DK. Crystals are syn-anti isomeric mixtures.



Figure S2 UV-vis spectra of **ADT-DK** (dotted line) and **ADT** (solid line) in toluene. Inset: Change of UV-vis absorption spectra of **ADT-DK** to **ADT** during irraditaion monochromatic excitation light through a monochrometor (Ritsu MC-10N) by a 500 W xenon lamp ($\lambda_{EX} = 468$ nm; 14.9 mW cm⁻²) in toluene. Spectra were measured every 2.5 min.



Figure S3 IR spectra of **ADT-DK** before (black line) and after (red line) the irraditaion by blue LED (200 mA cm⁻², rt, 30 min) in a glove box.



Figure S4 Measurement of ionization potential of ADT film by photoelectron spectroscopy, AC-3.



Figure S5 XRD patterns of pentacene (black) and **ADT** (red) films prepared by the photoconversion of precursors. Peaks over 20 degrees belongs to the ITO substrates.



Figure S6 Space charge limited current (SCLC) of (a) [ITO/MoO₃ (5 nm)/ **ADT** (85 nm)/ MoO₃ (5 nm) / Al (80 nm)] and (b) [ITO/MoO₃ (5 nm)/ **PEN** (77 nm)/ MoO₃ (5 nm) / Al (80 nm)], measured by using an Agilent HP4155C semiconductor parameter analyzer. Active layers were prepared by the precursor method.

Characterization of compounds

¹H NMR spectrum (CDCl₃) of **1**





 $^1\mathrm{H}$ NMR spectrum (CDCl₃) of ADT-DK



¹³C NMR spectrum (CDCl₃) of **ADT-DK**

