The Effects of Primary Structures on Photo-Induced Insolubilization of All-Cis Poly(*p*-phenylenevinylene)s in Thin Films

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All-cis poly(*p*-phenylenevinylene)s (PPVs) prepared by Suzuki–Miyaura-type polycondensation of (*Z*,*Z*)-1,4-bis(2-bromoethenyl)benzene with 2,5-dioctyloxybenzene-1,4-diboronic acid undergo photo-induced insolubilization in thin films, along with cis-to-trans isomerization of vinylene linkages to give all-trans PPVs. This phenomenon has been investigated using all-cis and all-trans PPVs with a range of molecular weights and terminal structures. The amounts of PPVs remaining on quartz substrates, after UV-irradiation on spin-coated films, followed by rinsing twice with $CHCl_3$, are dependent on the geometries of vinylene linkages, molecular weights, and terminal structures of the starting PPVs. It has been found that the all-cis configuration is of particular importance for insolubilization. The insolubilized films exhibit charge-carrier mobility (μ_{FET}) up to $1.6 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$.

π-Conjugated polymers are promising materials for the development of flexible optoelectronic devices such as organic field-effect transistors (OFETs) and organic light-emitting diodes (OLEDs).[1] Poly(*p*-phenylenevinylene)s (PPVs) are among the most studied.[2] A distinct advantage of polymeric materials is the accessibility of thin films by solution processes such as spin-coating and dip-coating, which enable easy and low-cost fabrication of devices. Since it is difficult to gain high device performance with a single component, most devices have multilayer structures. In this connection, several methods of insolubilizing thin films have been developed to avoid interfusion of polymer layers upon multi-coating; the establishment of well-defined interfacial boundaries of thin films is an essential requirement for achieving high device performance.[3] The most extensively investigated method is the use of photo- or thermal-cross-linkable polymers.[4–14] Alternatively, soluble precursors coated onto substrates are converted to insoluble polymers by thermal reactions.[2] Although insoluble films of PPVs are generally prepared by the latter method, it is known that the resulting polymers often involve structural defects due to incomplete reactions.[15]

We recently found that PPVs gain a unique film-forming property when the vinylene linkages are highly regulated to cis geometry.[16,17] All-cis PPV ($M_n = 4700$, $M_w/M_n = 1.92$) prepared by Suzuki–Miyaura-type polycondensation of (*Z*,*Z*)-1,4-bis(2-bromoethenyl)benzene with 2,5-dioctyloxybenzene-1,4-diboronic acid is highly soluble in organic solvents and forms an amorphous film by spin-coating.[16c] Interestingly, the resulting film becomes much less soluble under UV-irradiation, along with cis-to-trans isomerization of vinylene linkages to give all-trans PPV.[16a,18] Although one may assume that the photoisomerization giving all-trans PPV with a rigid framework causes this "photo-induced insolubilization" phenomenon, it has been observed that MEH-PPV as a commercial product with the all-trans configuration[21] remains soluble under UV light.

To clarify the factors governing this interesting phenomenon, we prepared in this study all-cis and all-trans PPVs with a range of molecular weights and end-group structures by Suzuki–Miyaura-type polycondensation, and examined their performance in photo-induced insolubilization by a quantitative method. As a result, the all-cis configuration has proven to be a particularly important factor. It has also been found that a 2-bromoethenyl group at the chain-end facilitates the photo-induced insolubilization to a notable extent.

Results and Discussion

Preparation of All-Cis and All-Trans PPVs. Table 1 lists the all-cis PPVs (**1a**–**1h** and **2a**–**2c**) and all-trans PPVs (**3a**–**3d**) employed in this study. Scheme 1 shows the synthetic routes to all-cis PPVs. We have already documented that polycondensation of (*Z*,*Z*)-1,4-bis(2-bromoethenyl)benzene (**4**) with 2,5-dioctyloxybenzene-1,4-diboronic acid (**5**) catalyzed by $Pd(PPh_3)_4$ forms two types of all-cis PPVs having different terminal structures (i.e., I and II in Scheme 1).[16b] Type I polymer bears a 4-(2-bromoethenyl)phenyl and 2,5-dioctyloxyphenyl group at each terminus, whereas type II polymer has a 2,5-dioctyloxyphenyl group at each end. The catalytic reaction affords a product mainly consisting of type I polymer. Compounds **1a**–**1h** are classified into this sort. The molecular weights may be controlled by catalytic conditions, especially by the amount of Bu_4NBr added to the system. The polymers with M_n of less than 3000 were synthesized in the absence of Bu_4NBr, whereas those with higher molecular weights were obtained in the presence of Bu_4NBr (1 equiv).

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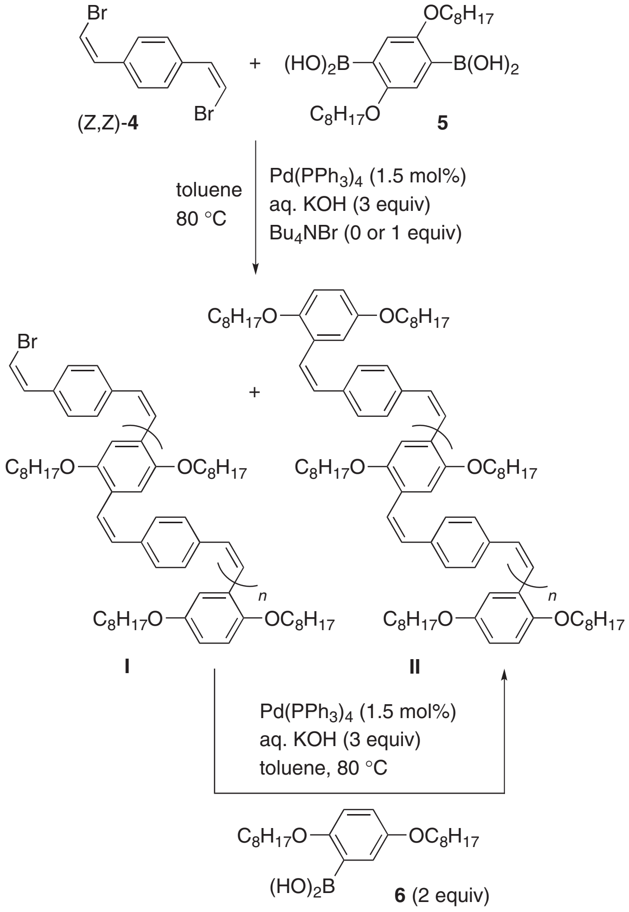
Table 1. List of PPVs and Their Performance in Photo-Induced Insolubilization

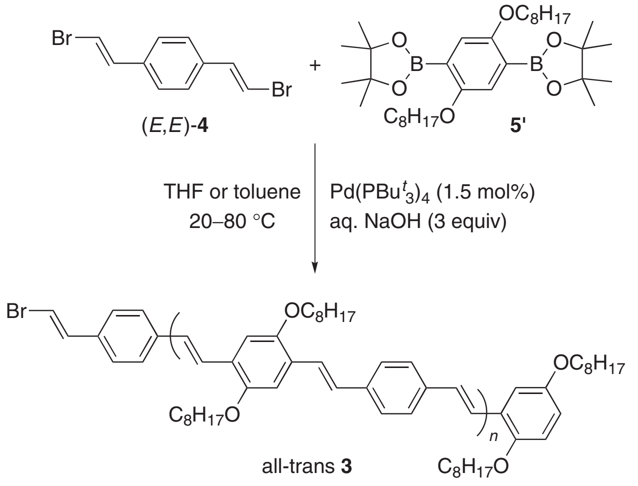
PPV (trans/cis)	M_n[a]	M_w/M_n[a]	Insolubilized PPV/%
1a (<1/99)	1800	1.39	36
1b (<1/99)	2800	1.55	33
1c (<1/99)	3500	1.55	59
1d (<1/99)	4700	2.79	56
1e (<1/99)	4800	2.20	64
1f (<1/99)	6600	3.14	85
1g (<1/99)	7000	2.69	84
1h (<1/99)	8100	3.93	89
2a (<1/99)	2400	1.24	2
2b (<1/99)[b]	5000	1.03	11
2c (<1/99)[b]	7700	1.11	35
3a (>99/1)	2200[c]	1.57	5
3b (>99/1)	3300[c]	1.44	10
3c (>99/1)	6100[c]	1.80	22
3d (>99/1)	7900[c]	1.96	43

a) Determined by GPC calibration based on polystyrene standards. b) Separated from **2a** by preparative GPC. c) Calibrated values to all-cis PPVs (see text).



Scheme 1. Synthetic routes to all-cis PPVs (**1** and **2**).

Type I polymer is converted to type II polymer by end-capping with 2,5-dioctyloxybenzeneboronic acid (**6**).[16b] This reaction was successful for the synthesis of **2a** with a relatively low molecular weight, but did not proceed well with higher molecular weight polymers. Thus, **2b** and **2c** in Table 1 were separated from **2a** by preparative GPC.



Scheme 2. Synthetic routes to all-trans PPVs (**3**).

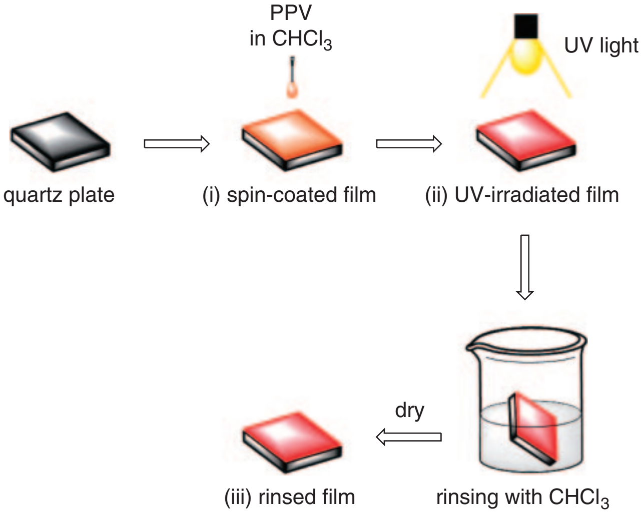


Figure 1. Experimental procedure for photo-induced insolubilization of PPVs.

All-trans PPVs (**3a–3d**) were synthesized by Suzuki–Miyaura-type polycondensation of (*E*,*E*)-**4** with the pinacolate ester of **5** (**5′**) in the presence of Pd(PBu$^t_3$)$_2$ as the catalyst (Scheme 2).[20] The resulting polymers bear the same end-group functionalities as type I polymers as confirmed by NMR spectroscopy. The M_n values given in Table 1 are calibrated to all-cis PPVs by using reference samples derived from all-cis PPVs by photoisomerization in solution, to avoid overestimation in GPC analysis arising from the rigid framework of all-trans PPVs.[22]

Photo-Induced Insolubilization of PPVs. Figure 1 illustrates the experimental procedure for photo-induced insolubilization. (i) A thin film of all-cis or all-trans PPV was prepared from a CHCl$_3$ solution (0.2 wt %) by spin-coating, and (ii) exposed to UV light (λ = 300–400 nm, 21.0 mW cm^{-2}) for 1 h at room temperature under vacuum. (iii) The irradiated film was rinsed twice with CHCl$_3$ and dried.

Figure 2 compares the UV–vis absorption spectra of the films at steps (i)–(iii) for all-cis PPV (**1g**). (i) The thin film of

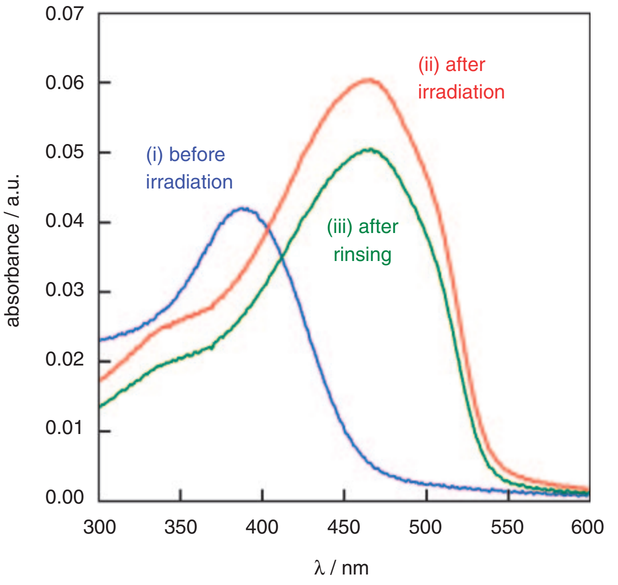


Figure 2. UV–vis absorption spectra of all-cis PPV (**1g**) in thin film, before and after UV-irradiation (i and ii), and after rinsing with $CHCl_3$ (iii).

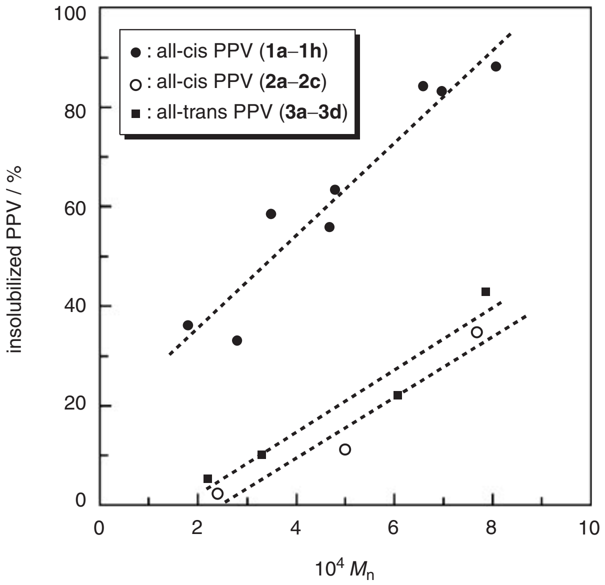


Figure 3. The relation between insolubilized PPV percentages and number-average molecular weights of PPVs.

1g exhibited a π–π^* transition at 388 nm. (ii) This absorption disappeared upon UV-irradiation, and a strong absorption assignable to the π–π^* transition of all-trans PPV appeared at 466 nm instead. (iii) The absorption remained after rinsing, though the intensity decreased to a certain extent. In the case of **1g**, 84% of the absorption intensity of spectrum (ii) was preserved in spectrum (iii). We employed this intensity ratio as the performance index of PPV in photo-induced insolubilization (i.e., insolubilized PPV (%) in Table 1).

Similar experiments were performed with all-cis PPVs (**1a**–**1f** and **1h**), end-capped all-cis PPVs (**2a**–**2c**), and all-trans PPVs (**3a**–**3d**). It was confirmed by UV–vis absorption spectroscopy that all-cis PPVs were entirely converted to all-trans isomers irrespective of the molecular weights and terminal structures during the UV-irradiation for 1 h at room temperature.[18] On the other hand, all-trans PPVs remained in the all-trans form under UV light.[20]

Figure 3 plots the insolubilized PPV percentages as a function of number-average molecular weights of the starting PPVs. All-cis PPVs (**1a**–**1h**) possess much higher performance than all-trans PPVs (**3a**–**3d**). It is also obvious that the higher molecular weight polymer tends to remain in the higher percentage. Moreover, end-capped polymers (**2a**–**2c**) are clearly less efficient than **1a**–**1h** having a 4-(2-bromoethenyl)-phenyl group at the chain-end.

There is a possibility that the insolubilization in thin films is caused by cross-linking of polymer chains via photochemical reactions such as [2 + 2] cycloaddition of vinylene units or radical addition of C–Br bonds to vinylene linkages. In any case, the shortening of effective π-conjugation length of PPV chain should occur to a considerable extent, but no notable blue shift was observed for insolubilized films. Accordingly, we presumed supramolecular interaction as an alternative driving force for insolubilization. We have already confirmed that all-cis PPV cast from a solution remains amorphous for a few hours.[16c] The amorphous all-cis PPV has a low T_g (ca. 0 °C) and is in the liquid state at room temperature. Thus, all-cis PPV molecules are expected to be highly mobile in thin films. In this situation, all-trans PPV molecules generated from all-cis PPVs by photoisomerization possibly form a highly aligned structure with the aid of π–π stacking between polymer chains, giving rise to the insolubilization phenomenon. On the other hand, it has been confirmed that PPVs prepared in the all-trans form from the beginning (i.e., **3a**–**3d**) have a higher T_g (ca. 50 °C) and are much less mobile in the solid state at room temperature,[16c] and this would be a prime reason for the much lower performance of **3a**–**3d**.

Although the above discussion is seemingly inconsistent with the low performance of the end-capped polymers (**2a**–**2c**), since halogen atoms on aromatic molecules are known to facilitate the formation of π-stacks,[23] it is possible that the photo-induced insolubilization is assisted by 4-(2-bromoethenyl)phenyl groups at the chain-end.

OFET Properties of Insolubilized PPVs. To gain experimental support for the occurrence of molecular alignment during the photo-induced insolubilization, charge-carrier mobility of PPV films was measured by using OFET devices fabricated in a top-contact configuration on Si/SiO_2 substrates. Molecular alignment of π-conjugated polymers has been known to be essential for the development of charge-carrier mobility.[24,25]

Table 2 summarizes the results. While all-cis PPVs simply coated on the substrates were insulators, they changed to semiconductors after UV-irradiation at room temperature for 1 h. The hole mobility was improved with increasing molecular weight of the staring polymer (Entries 1–4), and further by rinsing the film with toluene (Entry 4).[26] Interestingly, all-trans PPVs were totally insulators even after photoirradiation (Entries 5 and 6). Thus, these observations may be taken as another indication of the occurrence of molecular alignment during the photo-induced insolubilization of all-cis PPVs in thin films.

Table 2. Charge-Carrier Mobility of PPV Films before and after Photoirradiation

Entry	All-cis PPV		Mobility ($\mu_{\rm FET}$/cm^2 V^{-1} s^{-1})		
	$M_{\rm n}$[a]	$M_{\rm w}/M_{\rm n}$[a]	Spin-coated film	Irradiated film	Rinsed film
1	5900	3.61	$<10^{-6}$	1.0×10^{-6}	—[c]
2	7700	2.69	$<10^{-6}$	2.3×10^{-5}	—[c]
3	11200	2.66	$<10^{-6}$	5.0×10^{-5}	—[c]
4	34600[b]	1.47	$<10^{-6}$	5.0×10^{-5}	1.6×10^{-4}
5	6100	1.80	$<10^{-6}$	$<10^{-6}$	—[c]
6	7900	1.96	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$

a) Determined by GPC calibration based on polystyrene standards. b) Separated from all-cis PPV with $M_{\rm n} = 15700$ by recycle GPC. c) Not determined.

Conclusion

We confirmed that the all-cis configuration is of particular importance for photo-induced insolubilization of PPVs in thin films. The performance of all-cis PPVs is also dependent upon molecular weights and terminal structures. Thus, all-cis PPVs with $M_{\rm n} > 6600$ are insolubilized in 84–89% probability, when the polymers are equipped with a 4-(2-bromoethenyl)phenyl group at the chain-end. Although the insolubilization mechanism is not clear at present, the experimental observations reported in this paper include crucial information for designing poly(arylenevinylene)s that are insolubilized simply by UV-irradiation.

Experimental

General Considerations. All manipulations using organometallic compounds were carried out under a nitrogen or argon atmosphere using conventional Schlenk techniques. Nitrogen and argon gas were dried by passing through P_2O_5 (Merck, SICAPENT). Analytical GPC was carried out on a JASCO GPC assembly consisting of a model PU-980 precision pump, a model RI-1530 refractive index detector, and three polystyrene gel columns (Shodex KF-801, KF-803L, KF-805L). THF was used as the mobile phase with a flow rate of 1.0 mL min^{-1} at 40 °C. The columns were calibrated against 9 standard polystyrene samples (Shodex; $M_{\rm n} = 980$–1920000). Recycling preparative GPC was carried out on a JAI LC918U equipped with two preparative GPC columns (JAIGEL-1H-A and -2H-A). $CHCl_3$ was used as the mobile phase with a flow rate of 3.8 mL min^{-1}. ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C on a Varian Mercury 300 spectrometer, operating at 300.10 MHz. Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University. Spin-coating of PPV was performed with a Mikasa spin coater 1H-DX2. Photoirradiation was carried out at room temperature with an Asahi Spectra LAX-101 Xe lamp. UV–vis absorption spectra were recorded on a JASCO V-560 spectrometer.

Toluene was dried over sodium benzophenone ketyl, distilled, and stored over activated molecular sieves (MS4A). The following compounds were synthesized according to the literature: $Pd(PPh_3)_4$,[27] (*Z*,*Z*)-1,4-(2-bromoethenyl)benzene (**4**),[28] 2,5-dioctyloxybenzene-1,4-diboronic acid (**5**),[29] 2,5-dioctyloxybenzeneboronic acid (**6**),[30] and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dioctyloxybenzene.[16b] All-cis PPVs (**1a**–**1h** and **2a**)[16a,16b] and all-trans PPVs (**3a**–**3d**)[20] were prepared as previously reported. All other chemicals were obtained from commercial suppliers and used without further purification.

Photo-Induced Insolubilization of PPVs. A solution of PPV in $CHCl_3$ (0.2 wt %) was passed through a syringe filter (DISMIC-13 JP, PTFE 0.50 µm, Hydrophobic; ADVANTEC). A thin film of PPV was prepared by spin-coating on a quartz plate (1 cm^2); the filtrate (50 µL) was placed dropwise on a plate, and the plate was accelerated to 1200 rpm for 2 s, kept at this rate for 10 s, and then at 2000 rpm for 60 s. After drying under vacuum at room temperature for 30 min, the film was placed in a quartz cell under a nitrogen atmosphere, and analyzed by UV–vis absorption spectroscopy. Next, the film was placed in a stainless-steel holder with a quartz window, irradiated by a Xe lamp ($\lambda_{\rm max} = 365$ nm, 21.0 mW cm^{-2}) for 60 min under vacuum at room temperature, and analyzed. Finally, the film was rinsed twice in $CHCl_3$ (each 3 mL) with light shaking, dried under vacuum, and examined again by UV–vis absorption spectroscopy.

Preparation of All-Cis PPVs with High Molecular Weights (Entries 3 and 4 in Table 2). (*Z*,*Z*)-**1** (173 mg, 0.600 mmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dioctyloxybenzene (352 mg, 0.600 mmol) and methyltrioctylammonium chloride (Aliquat 336; 24.3 mg, 0.0600 mmol) were dissolved in toluene (3 mL), and aqueous Na_2CO_3 (2.0 M, 0.90 mL, 1.8 mmol) and $Pd(PPh_3)_4$ (10.4 mg, 9.00 µmol) were added. The mixture was vigorously stirred under reflux for 24 h in the dark. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (8 mL), washed with water, and then poured into vigorously stirred $MeOH/CH_2Cl_2$ (5/1, 180 mL). A yellow precipitate of all-cis PPV was collected by a membrane filter (0.5 µm), washed with MeOH, and dried under vacuum at room temperature overnight (254 mg, 92% yield, $M_{\rm n} = 11200$, $M_{\rm w}/M_{\rm n} = 2.66$). The polymer with $M_{\rm n} = 34600$ ($M_{\rm w}/M_{\rm n} = 1.47$) was obtained from this product by preparative GPC.

Measurement of Charge-Carrier Mobility. All manipulations were carried out in an argon-filled glove box. An OFET device was fabricated in a top-contact configuration on a p-type Si wafer as a gate electrode (one-side polished, <0.02 Ω resistance, Furuuchi Chemical Co.) with 3000-Å-thick SiO_2 ($C_{\rm i} = 11$ nF cm^{-2}) as a dielectric film. A plate was cut and washed in 2-propanol under ultrasonic wave and under boiling. A thin film of PPV (ca. 30-nm-thick) was deposited on the Si/SiO_2 substrate by spin-coating from a 0.1–0.5 wt % solution in $CHCl_3$ at 100–8000 rpm for 60 s, dried under vacuum at room temperature, and irradiated with a Xe lamp ($\lambda_{\rm max} = 365$ nm, 23.0 mW cm^{-2}) for 1 h. On the top of the thin film, gold films (30 nm) as source and drain electrodes were deposited through a mask. Drain–source channel length (*L*) and width (*W*) were 20 µm and 5 mm, respectively. Characteristics of OFET devices were evaluated at room temperature using two source meters (2400, Keithley Instruments Inc.). Charge-carrier mobility ($\mu_{\rm FET}$) was calculated in the saturation regime ($V_{\rm d} = 100$ V) of the $I_{\rm d}$ using the following equation,

$$I_{\rm d} = (WC_{\rm i}/2L)\mu_{\rm FET}(V_{\rm g} - V_{\rm t})_2 \tag{1}$$

where $C_{\rm i}$ is the capacitance of the SiO_2 insulator, and $V_{\rm g}$ and $V_{\rm t}$ are the gate and threshold voltages, respectively. In another case, the thin film of PPV was rinsed twice with toluene (1 mL) after UV-irradiation, and examined in a similar manner.

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