Supporting Information for:

Long-Term Thermally Stable Nanoconfining Networks for Efficient Fully Conjugated Semicrystalline/Amorphous Diblock Copolymer Photovoltaics

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1. Synthesis of 1,4-dihexyloxybenzene.

1-Bromohexane (47.0 mL, 336 mmol) was added to a mixture of hydroquinone (15.0 g, 136 mmol) and K_2CO_3 (75.0 g, 543 mmol) in dry acetone (363 mL), and the reaction mixture was stirred at reflux for 3 days. After reaction complete, the mixture was extracted with distilled water and Et_2O. 10% aqueous $Na_2S_2O_3$ and water was used to wash the organic layer and dried over anhydrous $MgSO_4$. The solid content were removed by filtration and the white powder were obtained via evaporation, the residue was purified by recrystallization from MeOH to give a plate form of white crystals (35.1 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.82 (*s*, 4H), 3.89 (*t*, *J*=6.5 Hz, 4H), 1.74 (*q*, *J*=7.1 Hz, 4H), 1.46-1.42 (*m*, 4H), 1.35-1.31 (*m*, 8H), 0.91 (*t*, *J*=7.0 Hz, 6H).

2. Synthesis of 1,4-dibromo-2,5-dihexyloxybenzene (M1).

A $CHCl_3$ (250 ml) solution of Br_2 (19.4 ml, 366 mmol) was added dropwise with stirring to a solution of **1,4-dihexyloxybenzene** (34.0 g, 122 mmol) in $CHCl_3$ (50 ml) at 0-5^{o}C. The reaction mixture was stirred at room temperature for 4 hours. The resulting solution was washed with 10% $Na_2S_2O_3$, 10% KOH, and water to remove bromine. The residual organic layer was dried over anhydrous Na_2SO_4, the sodium sulfate powder was separated by filtration then removing the solvent. 1,4-dibromo-2,5-bis(hexyloxy)benzene was obtained as white crystalline needles by recrystallizing from ethanol. 53.0 g, 88% yield.–^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.06 (*s*, 2H), 3.93 (*t*, *J*=6.5 Hz, 4H), 1.78 (*q*, *J*=7.0 Hz, 4H), 1.53-1.46 (*m*, 4H), 1.34-1.32 (*m*, 8H), 0.89 (*t*, *J*=7.0 Hz 6H).

3. Synthesis of 3-butylthiophene.

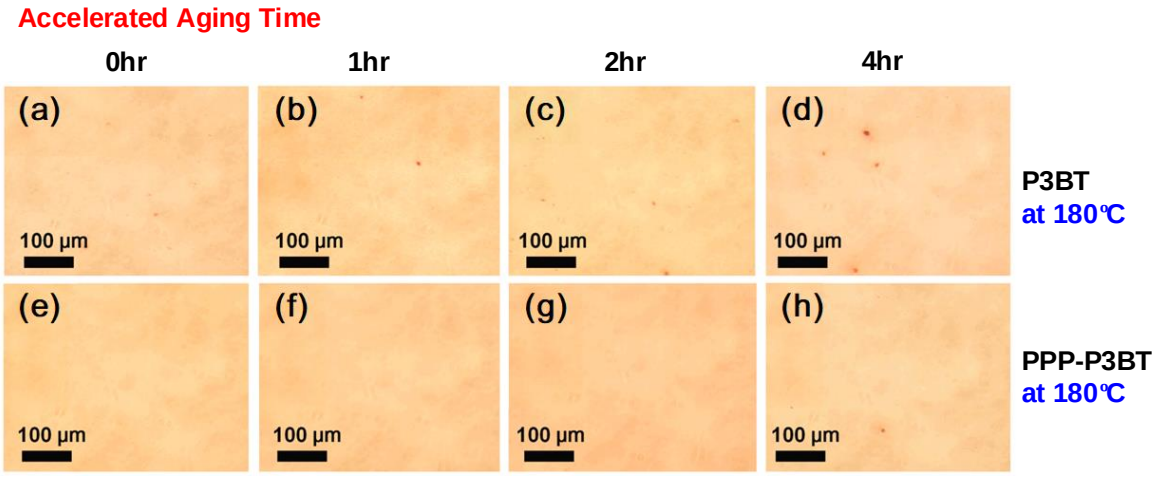
Magnesium turnings were added to a two-neck round bottom flask with dried ether. After mixing, 1-bromobutane was dropped slowly into the flask, and the blend solution was stirred under dry nitrogenous conditions at 0℃ for 1 h. The resulting solution was then transferred

into another flask with 3-bromothiophene and Ni(dppp)Cl_2 in dried ether, and the mixture was reacted at 40℃ for 12 hours. After reaction complete, 1M sodium chloride aqueous solution was used to extract the organic layer. The organic layer was then dried using sodium sulfate and, once the $MgSO_4$ was filtered out, the remaining ether evaporated by rotary evaporator. The crude product was further distilled under reduced pressure (65-70℃ (0.28 torr)). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.33-7.01 (*m*, 3H), 2.75 (*t*, *J*=15 Hz, 2H), 1.73 (*q*, *J*=15 Hz, 2H), 1.49-1.47 (*m*, 2H), 1.01 (*t*, *J*=13 Hz, 3H).

4. Synthesis of 2,5-dibromo-3-butylthiophene (M2).

Freshly distilled **3-butylthiophene** (13.0 g, 93 mmol) and anhydrous THF (100 mL) was charged into dry 250-mL three-neck round bottom flask which flushed with N_2 then NBS (27.4 g, 154 mmol) was added to the solution over a period of 5 minutes. After addition complete, the reaction mixture was stirred at room temperature for 8 hours. In the period of reaction, the color of solution changed from light yellow to orange. The resulting residue was washed with hexanes and the rotary evaporation was used to remove the solvent. After filtration, the oil product was further purified by using a silica gel chromatography column with hexanes as the eluent phase. The compound was dried under vacuum to yield 26.6 g (95%) of slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.80 (*s*, 1H), 2.54 (*t*, *J*=15 Hz, 2H), 1.56 (*q*, *J*=15 Hz, 2H), 1.39-1.37 (*m*, 2H), 0.96 (*t*, *J*=13 Hz, 3H).

5. Optical microscope images of (a-d) P3BT/PCBM and (e-h) PPP-P3BT/PCBM blends as a function of different accelerated aging times at 180℃.



It can be found from the above optical images that for homopolymer P3BT and copolymer PPP-P3BT films after 4hr of annealing at 180℃, there appears no PCBM aggregations for both devices.

6. The hole mobility measurements of PPP-P3BT/PCBM, P3BT/PCBM and PPP-P3HT/PCBM based device.

The characteristics of the three polymers is shown as follows.

		Molecular weight
1. Materials used in the current study	P3BT-PPP	44,000-4,000
	P3BT	50,000
2. Benchmark Material	P3HT-PPP	27,000-6,000

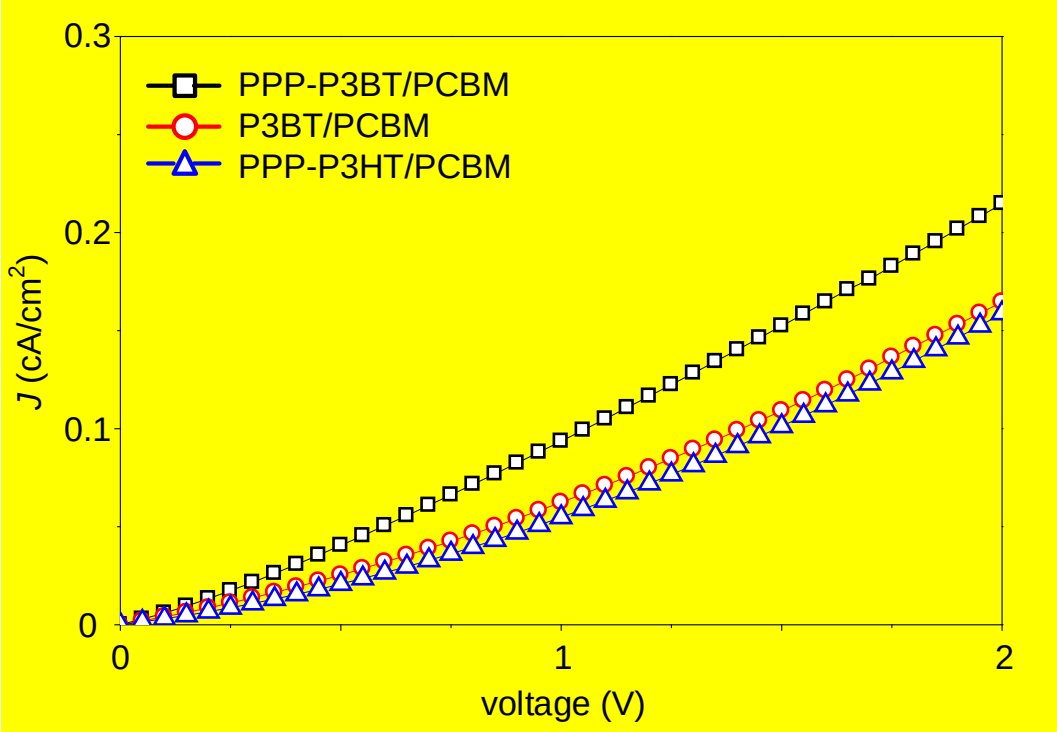
The hole mobility was measured with the device structure (ITO/PEDOT:PSS/polymer:PCBM/Au). The (ITO/PEDOT:PSS/polymer) device was first annealed at 120 ℃ for 10 min before a gold electrode was deposited on the polymer surface by thermal evaporation.

On the basis of SCLC model, the current density, J, of a solar cell device can be expressed as

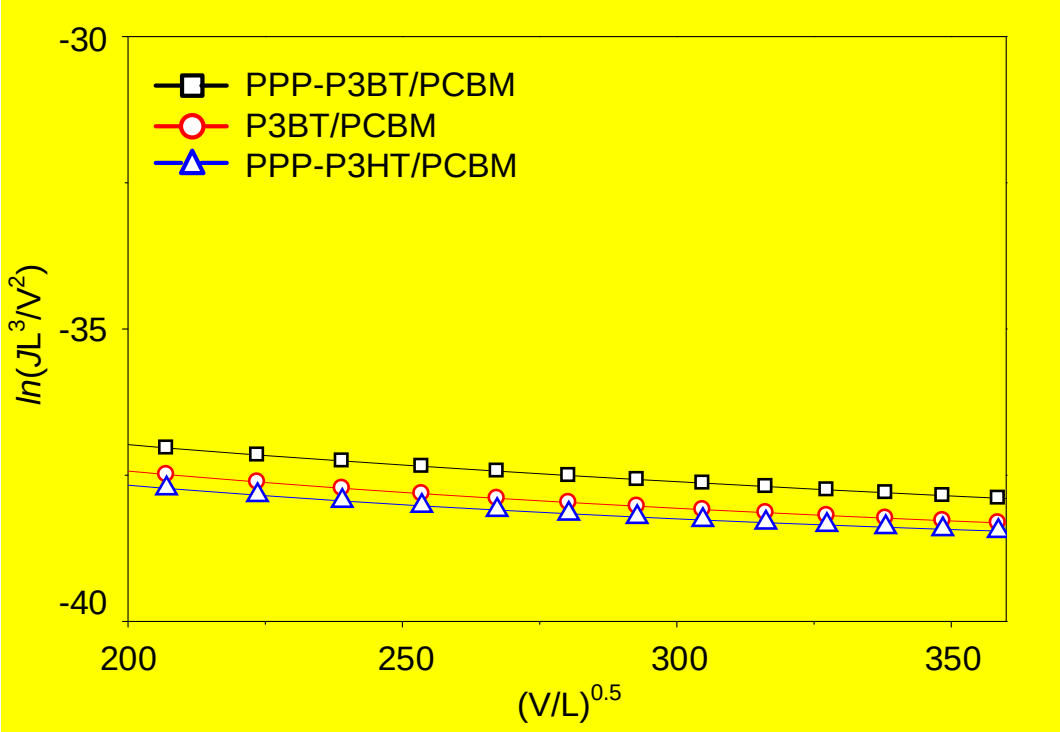
$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu_0\frac{V^2}{L^3}\exp\left(0.89\sqrt{\frac{V}{E_0 L}}\right) \quad (1)$$

where J is the current density, V is the applied bias, ε_r is the dielectric constant of the organic molecule under investigation, ε_0 is the permittivity of the vacuum, μ_0 is the

mobility of the charge carrier under no electric field, E_0 is the applied electric field.



Therefore, the mobility of the hole mobility of the three polymers can be obtained from the plot of $\ln\left(JL^3/V^2\right)$ vs $\left(V/L\right)^{0.5}$ with results shown as follows.



From the above plot, we can deduce the hole mobility for the three polymers with values listed below.

	hole mobility ($cm^2 V^{-1} s^{-1}$)

P3BT-PPP/PCBM	8.37×10^{-4}
P3BT/PCBM	4.95×10^{-4}
P3HT-PPP/PCBM	3.43×10^{-4}