Supporting Imformation

Effect of Alkyl-Chain Branching Position on Nanoscale Morphology

and Performance of All-polymer Solar Cells

1. Measurements of Electrochemical Cyclic Voltammetry: The electrochemical cyclic voltammetry (CV) was conducted with Pt disk, Pt plate, and Ag/AgCl electrode as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The polymer films were coated on a glassy carbon electrode from a DCB solution of polymer (~4 mg/mL). The potential of Ag/AgCl electrode is located at 4.4 eV. The energy levels of the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) were then calculated according to the equations:

$$\begin{split} E_{LUMO} &= -e(E_{red} + 4.4) \; (eV) \\ E_{HOMO} &= -e(E_{ox} + 4.4) \; (eV), \end{split}$$

where E_{red} is the onset reduction potential vs Ag/AgCl, and E_{ox} is the onset oxidation potential vs Ag/AgCl.

2. Measurements of the charge mobility by the space-charge limited current (SCLC) method: The hole mobility were carried out using the space charge limited current method (SCLC), employing a device architecture of ITO/PEDOT:PSS(30nm)/ PBDT-TT:polymer(~150 nm for C1 and 170nmfor C3)/Au(600nm) and ITO/TIPD (30nm)/PBDT-TT:polymer(~150 nm for C1 and 170nm for C3)/Au(600nm) for the hole and electron mobility, respectively. The active layers were spin-coated under the conditions that afford the best photovoltaic results. The following equation was applied to estimate the hole and electron mobilities:

$$J = 9/8\varepsilon\varepsilon_0\mu_h V^2/L^3 exp[0.89(V/E_0L)^{0.5}]$$
(1)

where ε is the average dielectric constant of the blended film (here, ε is taken as 3.0 typically for polymers), the permittivity of the vacuum, μ_h the zero-field mobility, E_0 the characteristic field, J the current density, L the thickness of the films, and V = Vappl- Vbi; Vappl the applied potential, and Vbi the built-in potential which results from the difference in the work function of the anode and thecathode (in this device structure, Vbi = 0.2 V). The results are plotted as $\ln(JL3/V2)$ vs (V/L)0.5. The charge mobility of the blending films was deduced from the intercept value of $\ln(9\varepsilon\varepsilon_0\mu_0/8)$.

3. Supporting Figure



Fig. S1 TGA curves of the polymers C1 and C3.



Fig. S2 Out-of-plane grazing incidence X-ray scattering pattern of both polymer films. Films were dropped on Si substrates.



Fig. S3 Plots of ln(JL3/V2) vs. (V/L)0.5 of blend films based on C1 and C3. Hole mobility (a) and electron mobility (b) characteristics extracted from the hole-only SCLC curves and electron-only SCLC devices in optimal conditions.



Fig. S4 AFM height (a-d) and phase (e-f) images of polymer C1(a, b, e, f) and C3(c, d, g, f) based devices with 0% (a, c, e, g), 1% (b, f), 3% (d, h) DIO used as the co-solvent. For all phase images, the phase shift is fixed from -5° to 5° for comparison.



Fig. S5 TEM images of blend films: donor:C3 with a D/A ratio of 2/1 (a) and 1/1 (b) without DIO. Polymer weight concentration of blend solution is 20 mg/mL.

From the TEM image in Figure S4a, the blend film of PBDTT-C-T:C3 with a D/A ratio of 2/1 showed two phase domains (dark domains and bright domains) and no obvious aggregation domains. However, a lot of aggregation domains were observed from the D/A ratio of 1/1 in Figure S4b. Moreover, the area of dark domains also increased in blend film with a D/A ratio of 1/1. The comparison clearly revealed that the obvious aggregation domains and dark domains observed in Figure S4b were from the acceptor, C3. In the same way, obvious aggregation domains and dark domains in blend film of PBDTT-C-T:C3 with a D/A ratio of 1/1 were from polymer C1. Therefore, the dark regions in the TEM image could be attributed to the acceptor (C1 or C3) domains, while the bright regions were attributed to the donor (PBDTTT-C-T) domains.



Fig. S6 Absorption spectra of thin film of donor PBDTTT-C-T, and its blend films with C1 and C3.

4. Supporting Table

Table S1 Photovoltaic performances of OSC devices based on the two copolymers with with DCB as the solvent and DIO as a processing additive

Active layer ^a	Solvent ^b (v/v)	PCE ^c (%)	J_{sc} (mA/cm ²)	$V_{oc}\left(\mathbf{V} ight)$	FF(%)
	100:0	1.21	3.08	0.81	48.5
PBDTTT-C-T/C1	99:1	1.68	3.64	0.81	56.9
	98:2	1.55	3.55	0.81	53.7
	100:0	1.27	3.27	0.78	50.0
	99:1	1.36	3.38	0.78	51.7
PBDTTT-C-T/C3	98:2	1.47	3.66	0.78	51.3
	97:3	1.92	4.70	0.79	51.7
	96:4	1.60	3.90	0.79	51.9

^aD:A=1:1; ^bDCB:DIO; ^cthe best PCE of devices.

Table S2 Photovoltaic performances of OSC devices based on polymer C1 with DCB as the solvent.

Device	PCE (%)	$J_{\rm sc}$ (mA/cm2)	$V_{ m oc}({ m V})$	FF (%)
1	1.21	3.08	0.81	48.5
2	1.02	2.83	0.80	45.2
3	1.10	2.82	0.80	48.8
4	1.09	2.8	0.81	48.0

Table S3 Photovoltaic performances of OSC devices based on polymer C1 with DCB as the solvent and 1% DIO as a processing additives.

Device	PCE (%)	$J_{\rm sc}$ (mA/cm2)	$V_{\rm oc}({ m V})$	FF (%)
1	1.68	3.64	0.81	56.9
2	1.63	3.53	0.81	57.0
3	1.62	3.52	0.81	56.9
4	1.55	3.55	0.81	53.7
5	1.53	3.53	0.81	53.4
6	1.51	3.53	0.81	52.9
7	1.54	3.58	0.81	53.1
8	1.64	3.60	0.81	56.4

Device	PCE (%)	$J_{\rm sc}$ (mA/cm2)	$V_{\rm oc}({ m V})$	FF (%)
1	1.27	3.27	0.78	50.0
2	1.26	3.22	0.78	50.3
3	1.21	3.09	0.77	51.0
4	1.24	3.10	0.78	51.3

Table S4 Photovoltaic performances of OSC devices based on polymer C3 with DCB as the solvent.

Table S5 Photovoltaic performances of OSC devices based on polymer C3 with DCB as the solvent and 3% DIO as a processing additive.

Device	PCE (%)	$J_{\rm sc}$ (mA/cm2)	$V_{\rm oc}({ m V})$	FF (%)
1	1.78	4.63	0.80	48.0
2	1.75	4.55	0.79	48.5
3	1.89	4.82	0.79	49.6
4	1.92	4.7	0.79	51.7
5	1.83	4.91	0.79	47.1
6	1.88	4.81	0.79	49.9
7	1.81	4.75	0.79	48.3
8	1.90	4.64	0.79	51.8
9	1.85	4.66	0.80	48.2
10	1.89	4.79	0.79	49.9
11	1.83	4.96	0.79	48.7
12	1.91	4.78	0.80	50.0
13	1.87	4.77	0.80	49.0
14	1.85	4.74	0.79	49.4