Supporting Information

**Tuning the morphology of the active layer of organic solar cell by spin 1/2 radical**

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**Supporting experimental Characterization**

Grazing incidence small and wide angle X-ray scattering (GISAXS, GIWAXS) measurements were performed at the Shanghai Synchrotron Radiation Facility (SSRF) in the BL16B1 beamline using a photon energy of 10 keV with a sample to detector distance of approximately 1820mm. The incident angle was set to 0.3°. The NMR spectra (nuclear magnetic resonance) had been gathered using the Bruker ARX 400 NMR spectrometer. The BAS 100B was utilized for gathering the CV (cyclic voltammetry) results using room temperatures and scanning at a rate of 50mV/s. The
PerkinElmer Lambda 900 UV-VIS/NIR spectrometer was utilized for recording the UV-VIS spectra. The TA Instruments Model TGA Q500 thermogravimetric analyser was utilised for conducting the TGA (thermoravimetric analyses) with a heat rate of 10 °C per minute under N\textsubscript{2} flow (100 mL/minute). The atomic force microscopy (AFM) images were recorded on a nanoscope III A scanning probe microscope using the tapping mode. The morphologies of the hybrids were characterized by a field emission scanning electron microscope (FESEM, Hitachi S-4800, Japan). Time-resolved photoluminescence (PL) were carried out by using a femtosecond pump setup at 550 nm wavelength, the fluorescent light was directed to a spectrometer (Bruker Optics 250IS/SM) and detected by an intensified charge coupled device detector (Andor, lStar740) with time resolution of ~60 ps. The Electrochemical Workstation (Xe Lamp Oriel Sol3A™ Class AAA Solar Simulators 94023A, USA) was utilised for recording the curves of the J-V (photocurrent-voltage) with fabricated DSSCs, this was conducted using irradiation from solar light that was simulated with a 100W xenon arc lamp within an ambient environment.

**Information on Syntheses**

**4,7-dibromo-5,6-difluoro-2-(undecan-5-yl)-2H-benzo[d][1,2,3]triazole (M1).**

M1 was synthesized according to literature.\textsuperscript{1} \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400MHz, δ/ppm):

4.64(d, J=8, 2H), 1.55(s, 1H), 1.27(t, J=8, 16H), 0.86(t, J=6, 6H).

**4,7-dibromo-2-(heptadecan-9-yl)-2H-benzo[d][1,2,3]triazole (M2).**

M2 was synthesized according to literature.\textsuperscript{1} \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400MHz, δ/ppm):

7.43(S, 2H), 4.88(t, J=4, 1H), 2.21-2.14(m, 2H), 1.95(t, J=12, 2H), 1.55(s,10H),
1.23(d, J=24, 12H), 1.00(d, J=4, 2H), 0.88-0.83(m, 6H).

(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (M3). $^1$H NMR (CDCl$_3$, 400MHz, δ/ppm):

M3 was synthesized according to literature.$^{[2]}$ $^1$H NMR (CDCl$_3$, 400MHz, δ/ppm):

7.81(s, 2H), 7.28(s, 2H), 6.92(s, 2H), 2.94(s, 4H), 1.67(s, 2H), 1.59(d, J=8, 16H), 0.97(d, J=8, 12H), 0.60(t, J=10, 18H).

4,4-dioctyl-2,6-bis(trimethylstannyl)-4H-silolo[3,2-b:4,5-b'] dithiophene (M4).

M4 was synthesized according to literature.$^{[3]}$ $^1$H NMR (CDCl$_3$, 400MHz, δ/ppm):

1.53(s, 6H), 1.41(d, J=8, 4H), 1.27(d, J=8, 8H), 1.22(d, J=4, 2H), 0.90 (d, J=4, 12H), 0.86(t, J=6, 2H), 0.44(s, 4H), 0.37(t, J=4, 18H).

4-octyl-2,6-bis(trimethylstannyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (M5).

M5 was synthesized according to literature.$^{[4]}$ $^1$H NMR (CDCl$_3$, 400MHz, δ/ppm):

6.99(s, 3H), 4.17(t, J=8, 2H), 1.87(d, J=8, 2H), 1.52(s, 4H), 1.33(t, J=6, 6H), 1.29-1.25(m, 2H), 0.87 (t, J=6, 18H).

Synthesis of copolymers. Compounds M1 (0.6126mmol), M3 (0.6126mmol), Pd$_2$(dba)$_3$ (19.969mg), P(o-toly)$_3$ (26.481mg) and CuO (172.925mg) were stirred in 15mL toluene solution under N$_2$ protection at 110°C for 72 h. A yield of 75-87% of resultant was obtained.

P1: M1 (0.3236g, 0.6126mmol), M3 (0.6079g, 0.6126mmol), toluene (15ml), Pd$_2$(dba)$_3$ (19.696mg), P(o-toly)$_3$ (26.481mg) and CuO (172.925mg) were used, resulting in a yield of 79% reaction product. $^1$H NMR (CDCl$_3$, 400MHz, δ/ppm):

7.52(s, 1H), 7.02(d, 2H), 6.46(s, 1H), 5.35(s, 2H), 5.21(s, 2H), 5.06(t, 1H), 3.75(s,
1H), 2.98(s, 1H), 2.35(s, 2H), 2.22(t, 2H), 2.01(d, 3H), 1.85(s, 4H), 1.55(s, 126H), 1.43(s, 15H), 1.27(s, 49H), 1.01(s, 18H), 0.87(s, 19H).

**P2:** **M2** (0.3337g, 0.648mmol), **M3** (0.5862g, 0.648mmol), toluene (15ml), Pd$_2$(dba)$_3$ (19.256mg), P(o-toly)$_3$ (25.535mg) and CuO (166.743mg) were used, resulting in a yield of 82.5% reaction product. ¹H NMR (CDCl$_3$, 400MHz, δ/ppm): 8.83(s, 5H), 7.63(s, 2H), 7.52(s, 1H), 7.02(d, 2H), 6.86(s, 2H), 5.35(s, 2H), 5.18(s, 2H), 5.07(s, 1H), 4.99(s, 1H), 3.75(s, 1H), 3.02(s, 7H), 2.22(t, 2H), 2.01(s, 2H), 1.85(s, 1H), 1.55(s, 3H), 1.26(s, 107H), 0.88(s, 21H).

**P3:** **M1** (0.3911g, 0.8128mmol), **M4** (0.6050g, 0.8128mmol), toluene (15ml), Pd$_2$(dba)$_3$ (24.1528mg), P(o-toly)$_3$ (32.0289mg) and CuO (209.1413mg) were used, resulting in a yield of 87% reaction product. ¹H NMR (CDCl$_3$, 400MHz, δ/ppm): 8.30(s, 3H), 8.25(s, 1H), 7.51(s, 1H), 7.05(d, 2H), 5.30(s, 1H), 4.78(s, 5H), 4.64(d, 3H), 2.54(d, 1H), 2.32(s, 6H), 1.25(s, 321H), 0.92(t, 120H).

**P4:** **M2** (0.4003g, 0.7768mmol), **M4** (0.5782g, 0.7768mmol), toluene (15ml), Pd$_2$(dba)$_3$ (23.083mg), P(o-toly)$_3$ (33.579mg) and CuO (219.275mg) were used, resulting in a yield of 84.5% reaction product. ¹H NMR (CDCl$_3$, 400MHz, δ/ppm): 8.16(d, 1H), 8.04(d, 1H), 7.64-7.50(m, 2H), 7.36-7.31(m, 1H), 7.05-7.00(m, 1H), 5.30(s, 1H), 4.94(s, 2H), 2.73(d, 1H), 2.50(s, 4H), 2.24(d, 5H), 1.51(t, 147H), 1.04(d, 5H), 0.88-0.83(m, 51H).

**P5:** **M1** (0.4725g, 0.9821mmol), **M5** (0.6061g, 0.9821mmol), toluene (15ml), Pd$_2$(dba)$_3$ (29.1835mg), P(o-toly)$_3$ (38.7023mg) and CuO (252.7126mg) were used, resulting in a yield of 82% reaction product. ¹H NMR (CDCl$_3$, 400MHz, δ/ppm):
8.19(t, 1H), 7.51(s, 2H), 7.35-7.30(m, 1H), 7.03-6.99(m, 1H), 5.30(s, 4H), 4.80-4.63(m, 1H), 4.27(t, 4H), 2.33(d, 2H), 1.95(d, 3H), 1.60(s, 15H), 1.42(s, 16H), 1.24(s, 57H), 1.05-0.94(m, 36H).

**P6:** M2 (0.4793g, 0.9301mmol), M5 (0.5740g, 0.9301mmol), toluene (15ml), Pd$_2$(dba)$_3$ (27.6394mg), P(o-toly)$_3$ (36.6525mg) and CuO (239.3420mg) were used, resulting in a yield of 87% reaction product. $^1$H NMR (CDCl$_3$, 400MHz, $\delta$/ppm):

8.15(s, 2H), 7.43(t, 3H), 5.29(s, 1H), 4.93(s, 3H), 4.34(s, 2H), 2.22(s, 2H), 2.02(s, 14H), 1.67(s, 8H), 1.24(s, 3H), 1.20(d, 151H), 0.82(s, 50H).
Scheme S1. Synthetic Route for Polymers

Supporting Figures
Figure S1. TGA thermograms of all polymers measured in N\textsubscript{2} at a heating rate of 10\textdegree C/min

Figure S2. Cyclic voltammogram measurement of different polymers.
P1

HOMO = -4.55 eV
LUMO = -3.13 eV

P2

HOMO = -4.23 eV
LUMO = -2.72 eV
Figure S3. Optimized geometry and molecular orbital surfaces of the HOMO and LUMO of the model compounds, obtained by the DFT/B3LYP/6-31G* method. It was concluded that the bandgaps are around 1.42eV, 1.51eV, 1.36eV, 1.29eV, 1.63eV and 1.64eV, respectively.

Figure S4. Normalized UV-vis absorption spectra of pure galvinoxyl and PC$_{71}$BM.
Figure S5. AFM 3D structure of P$_x$:PC$_{71}$BM blend films prepared (a-f) without and (g-l) with addition of spin 1/2 to the chlorobenzene solution.
Figure S6. 2DGIWAXS patterns of Pₓ:PC₇₁BM blend films (a-f) without spin 1/2 radical and (g-l) with spin 1/2 radical.

Figure S7. I-V cures of solar cells made of Pₓ:PC₇₁BM without spin 1/2 radical.
Figure S8. I-V curves of solar cells made of $\text{P}_x:\text{PC}_{71}\text{BM}$ with and without spin $\frac{1}{2}$ radical.

Table S1. Molecular weights of polymers.

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