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Supplementary Information

Suppressing Pre-Aggregation to Increase Polymer Solar Cell Ink Shelf Life

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Experimental Section

Materials

Polymers D18-Cl, PM6 and small molecule Y6 were purchased from eFlexPV Limited. Fullerenes $PC_{61}BM$ and $PC_{71}BM$ were purchased from American Dye Source Incorporation.

Device Fabrication

The D18-Cl-based solar cell devices were fabricated with conventional architecture of ITO/PEDOT:PSS/active-layer/PFN-Br/Ag. The effective device area is 0.075 cm^2 and the film thickness of the active layers is probed to be ~100 nm. The hole-transporting layer PEDOT:PSS (Al 4083) was spin-cast onto the ITO glass at 4000 rpm, and then thermally treated at 150 C° for 15 min. The inks for active layers were prepared in chloroform (CF) with a polymer concentration of 5 mg mL^{-1} and were stirred at 50 °C for 30 min to fully dissolve. The binary blend D18-Cl:Y6 weight ratio was at 1:1.6 and that for the ternary blends D18-Cl:Y6:PCBM was 1:1.6:0.2. After cooling down to room temperature, the inks of each blend were distributed into three glass vials respectively, two of which were sealed, wrapped with Al foil and stored in the glove box. For devices made from fresh ink, the ink was spin-cast on the PEDOT:PSS modified substrate at 3000 rpm (for binary) and 3200 rpm (for ternary). The samples were then put in a glass petri dish for solvent vapor annealing treatment. Around 50 μL CF was added into the petri dish and the samples was kept in for 5 min. Then the PFN-Br solution (1 mg mL^{-1} in methanol) was spin-cast onto the active layer as electron transporting layer at 3000 rpm. At last, 160 nm Ag was thermally evaporated to the samples with a rate of 1-2 Å s^{-1}, at ~2×10^{-6} Pa. For devices made from aged inks, the aged inks were stirred for another 20 min before spin-casting, and the recipe was kept the same. We note that no matter the aged inks were stirred at room temperature or at warmer condition (e.g. 40-50 °C), the devices performance was fairly similar. This is consistent with our former work with D18 polymer (which is harder to process), where the inks cannot be restored and reused.[S1]

Characterizations

The *J–V* characteristics were measured on a computer controlled Keithley 2400 source meter under illumination of an AM 1.5G solar simulator (Oriel Sol3A, Newport Corporation) with an intensity of 100 mW cm^{-2}, which was calibrated by a certified silicon reference cell. Device performance was averaged from 12 cells. The UV-vis absorption spectra were recorded using a Varian Cary 50 UV-vis spectrophotometer. Transmission visible light microscopic (VLM) images are acquired with a Nikon Labophot-2 microscope. The film thicknesses were measured using a KLA Tencor (Model P-7) stylus profilometer.

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS)

GIWAXS measurements were performed at beamline 7.3.3,[S2] Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL). The samples were measured in a helium environment to minimize air scattering using 10 keV energy X-rays, which was incident at a grazing angle of 0.12°. The scattered X-rays were detected using a Pilatus 2M photon counting detector. The sample to detector distance was calibrated from diffraction peaks of the Silver-Behenate.

Resonant Soft X-ray Scattering (R-SoXS)

R-SoXS measurements were performed at beamline 11.0.1.2,[S3] ALS, LBNL. The sample to detector distance was calibrated from diffraction peaks of polystyrene nanoparticles (diameter 300 nm) and beamline energy was calibrated by a fullerene-based sample. The beam size at the sample was ~100 µm × 200 µm, and 2D R-SoXS patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE) at –45 °C.

Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) and Bilayer Fabrication

The TOF-SIMS experiments were conducted using a TOF-SIMS V (IONTOF Incorporation) instrument equipped with a Bi^{3+} charge compensation. Cs^{+} was used as the sputter source with a 10 keV energy and 20 nA current. The sputter area was 50 × 50 µm and sputter rate was approximately 1 nm s^{-1}. The analysis chamber pressure was maintained below 5×10^{-9} mbar to avoid contamination of the surfaces. Small molecule layers and polymer layers were made separately for bilayer samples. The small molecule films were spin-cast to ZnO modified Si substrate, and polymer films were spin-cast to PSS modified substrates and then float onto small molecule layers in water. Samples were dried and then moved into a glove box for thermal or solvent vapor annealing treatment.

References

S1. Z. Wang, Z. Peng, Z. Xiao, D. Seyitliyev, K. Gundogdu, L. Ding and H. Ade, *Adv. Mater.*, 2020, **32**, 2005386.

S2. A. Hexemer, W. Bras, J. Glossinger, E. Schaible, E. Gann, R. Kirian, A. MacDowell, M. Church, B. Rude, H. Padmore, *J. Phys. Conf. Ser.* **2010**, 247, 012007.

S3. E. Gann, A. T. Young, B. A. Collins, H. Yan, J. Nasiatka, H. A. Padmore, H. Ade, A. Hexemer, C. Wang, *Rev. Sci. Instrum.* **2012**, 83, 045110.

Supplementary Figures

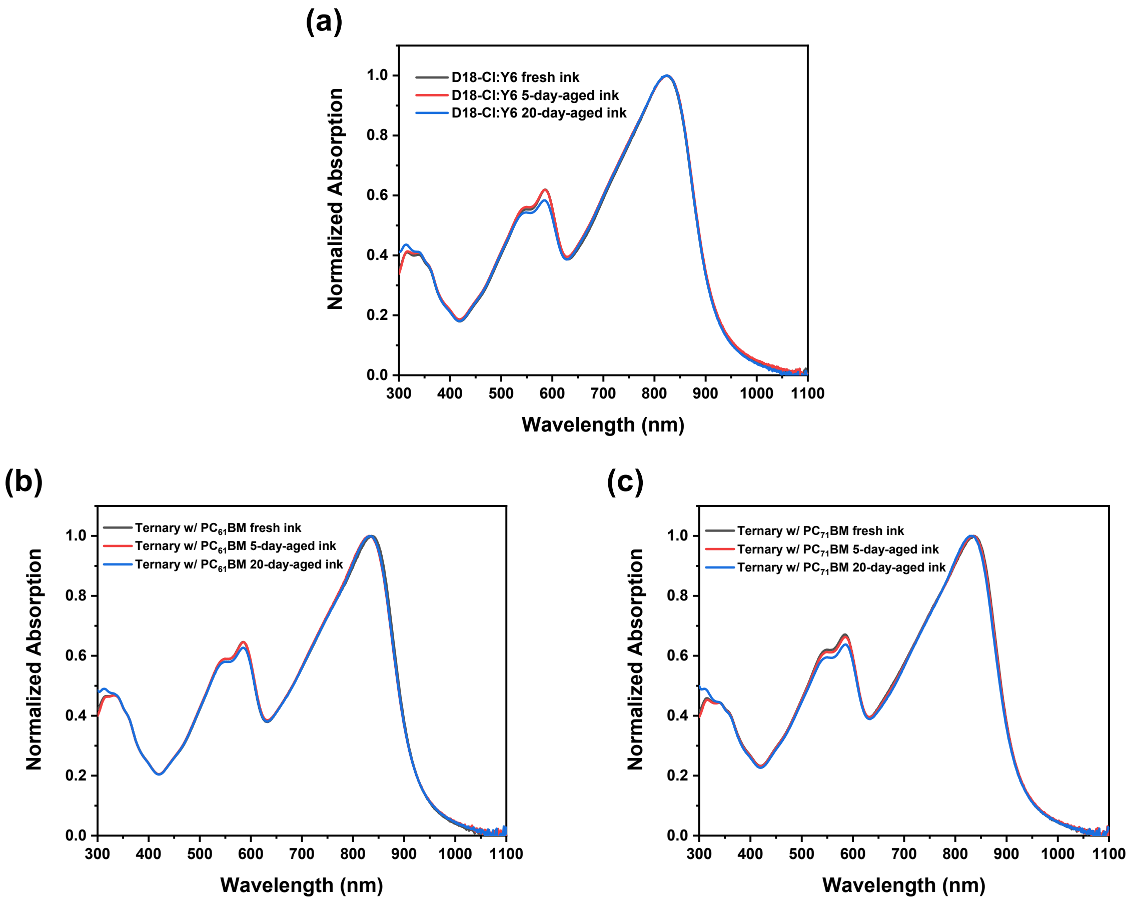

Figure S1. Normalized UV-vis absorption spectra of D18-Cl:Y6 (a), D18-Cl:Y6:$PC_{61}BM$ (b), and D18-Cl:Y6:$PC_{71}BM$ (c) blend films, cast from fresh, 5-day-aged and 20-day-aged inks, respectively.

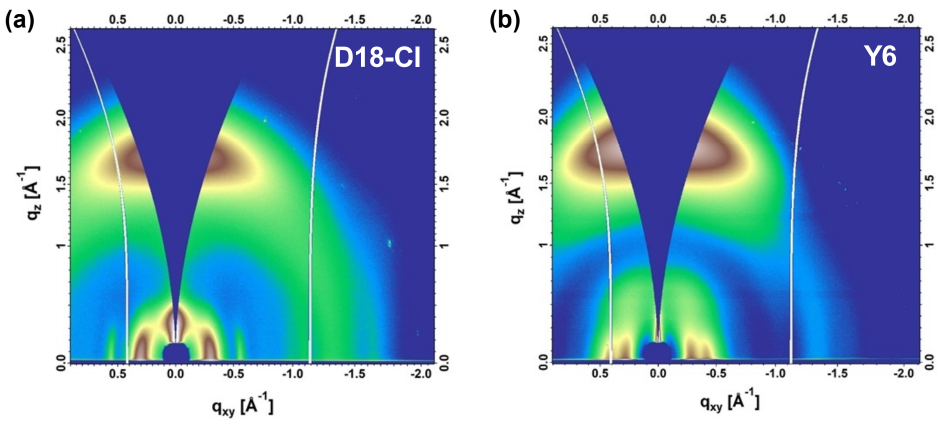

Figure S2. 2D GIWAXS patterns of neat D18-Cl and Y6 films.

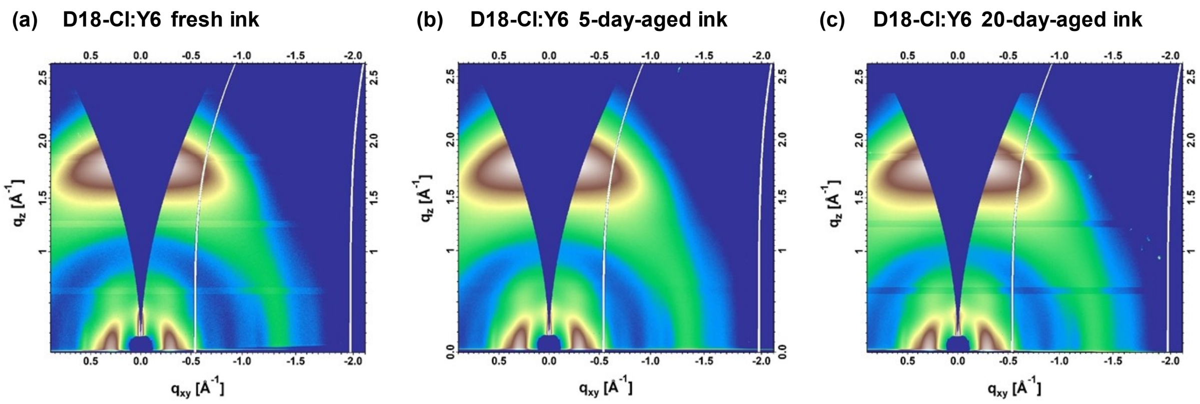

Figure S3. 2D GIWAXS patterns of D18-Cl:Y6 binary blend films, cast from fresh, 5-day-aged and 20-day-aged inks, respectively.

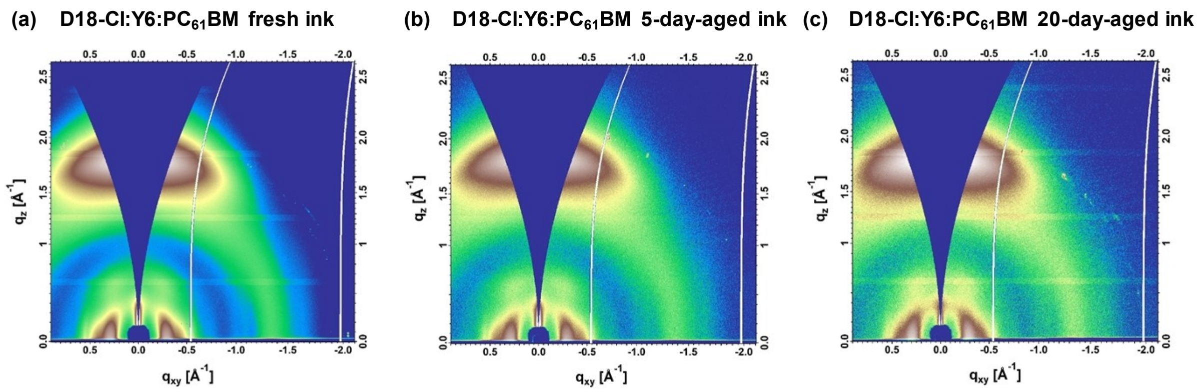

Figure S4. 2D GIWAXS patterns of D18-Cl:Y6:$PC_{61}BM$ ternary blend films, cast from fresh, 5-day-aged and 20-day-aged inks, respectively.

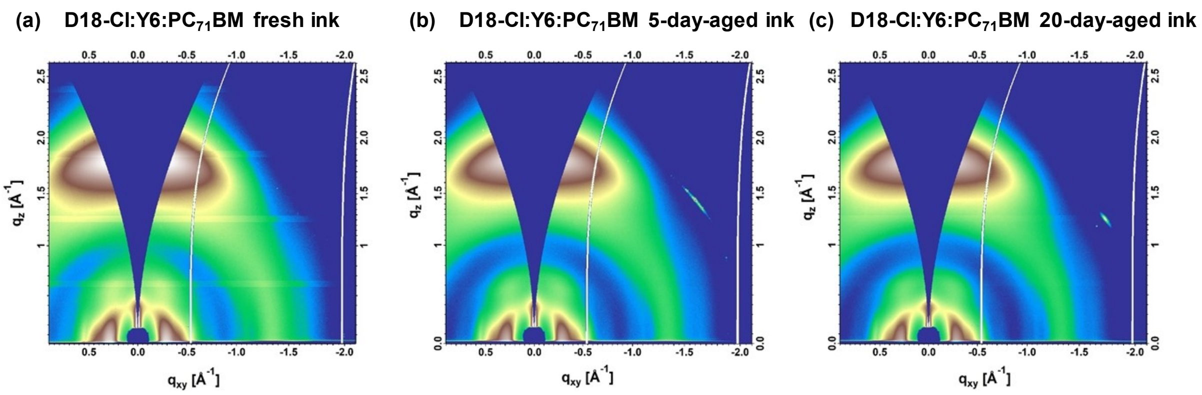

Figure S5. 2D GIWAXS patterns of D18-Cl:Y6:$PC_{71}BM$ ternary blend films, cast from fresh, 5-day-aged and 20-day-aged inks, respectively.

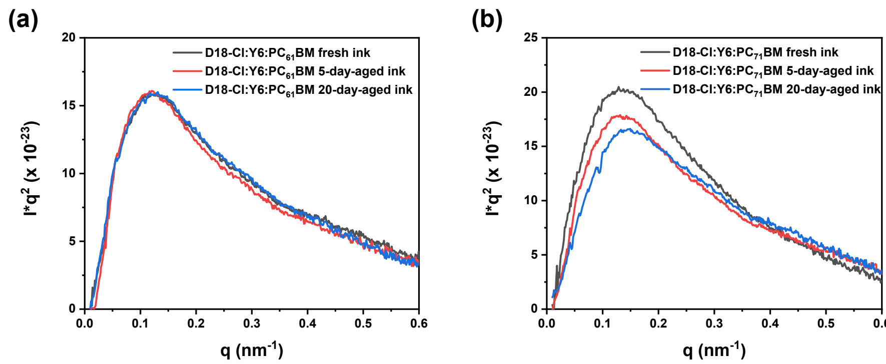

Figure S6. Lorentz-corrected thickness-normalized RSoXS profiles of films based D18-Cl:Y6:$PC_{61}BM$ (a) and D18-Cl:Y6:$PC_{71}BM$ (b) blends, cast from fresh, 5-day-aged, and 20-day-aged inks, acquired at 283.8 eV.

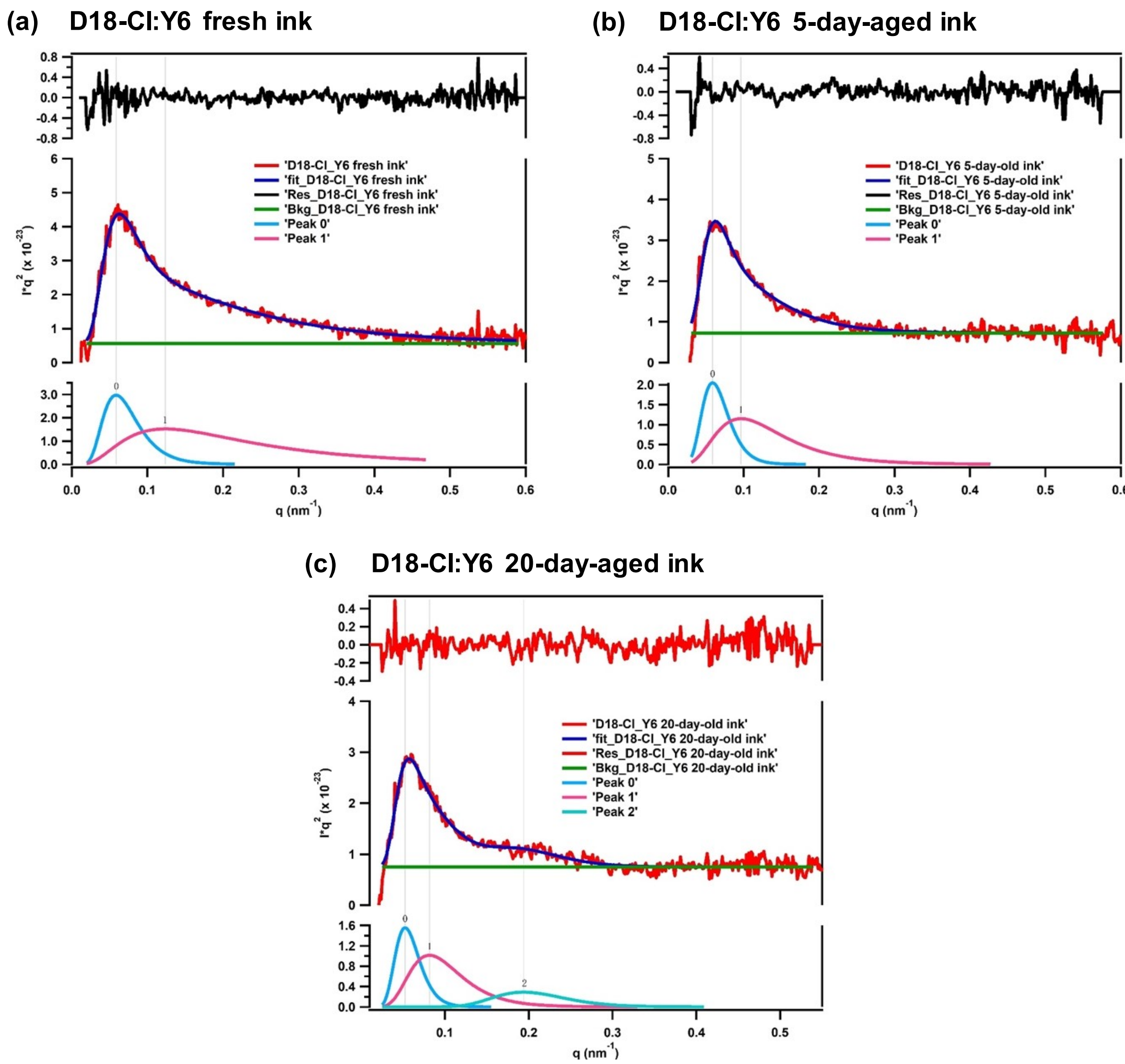

Figure S7. Lognormal fit of Lorentz-corrected RSoXS profiles of D18-Cl:Y6 binary blend films, cast from fresh, 5-day-aged and 20-day-aged inks, respectively, acquired at 283.8 eV.

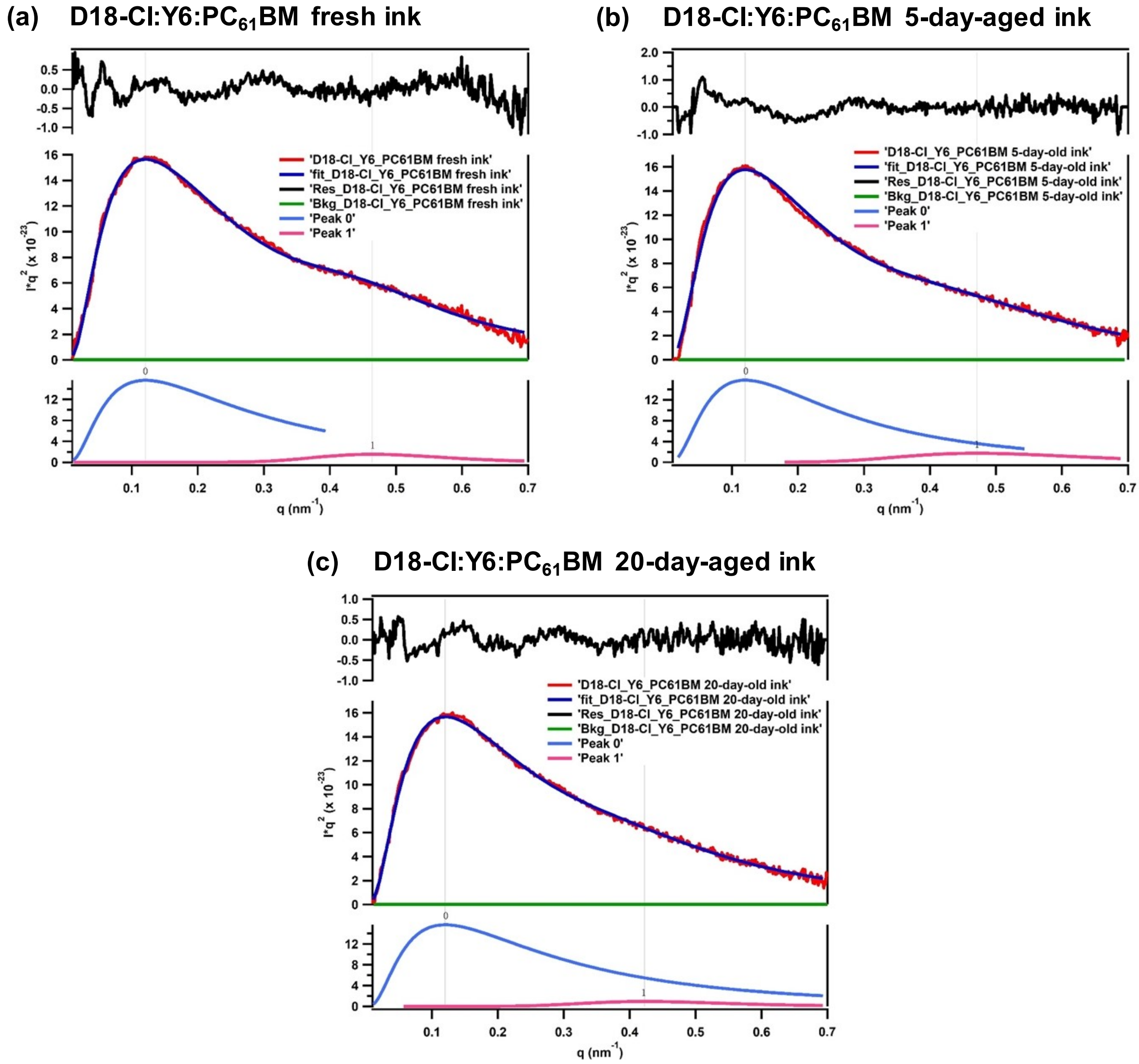

Figure S8. Lognormal fit of Lorentz-corrected RSoXS profiles of D18-Cl:Y6:PC$_{61}$BM ternary blend films, cast from fresh, 5-day-aged and 20-day-aged inks, respectively, acquired at 283.8 eV.

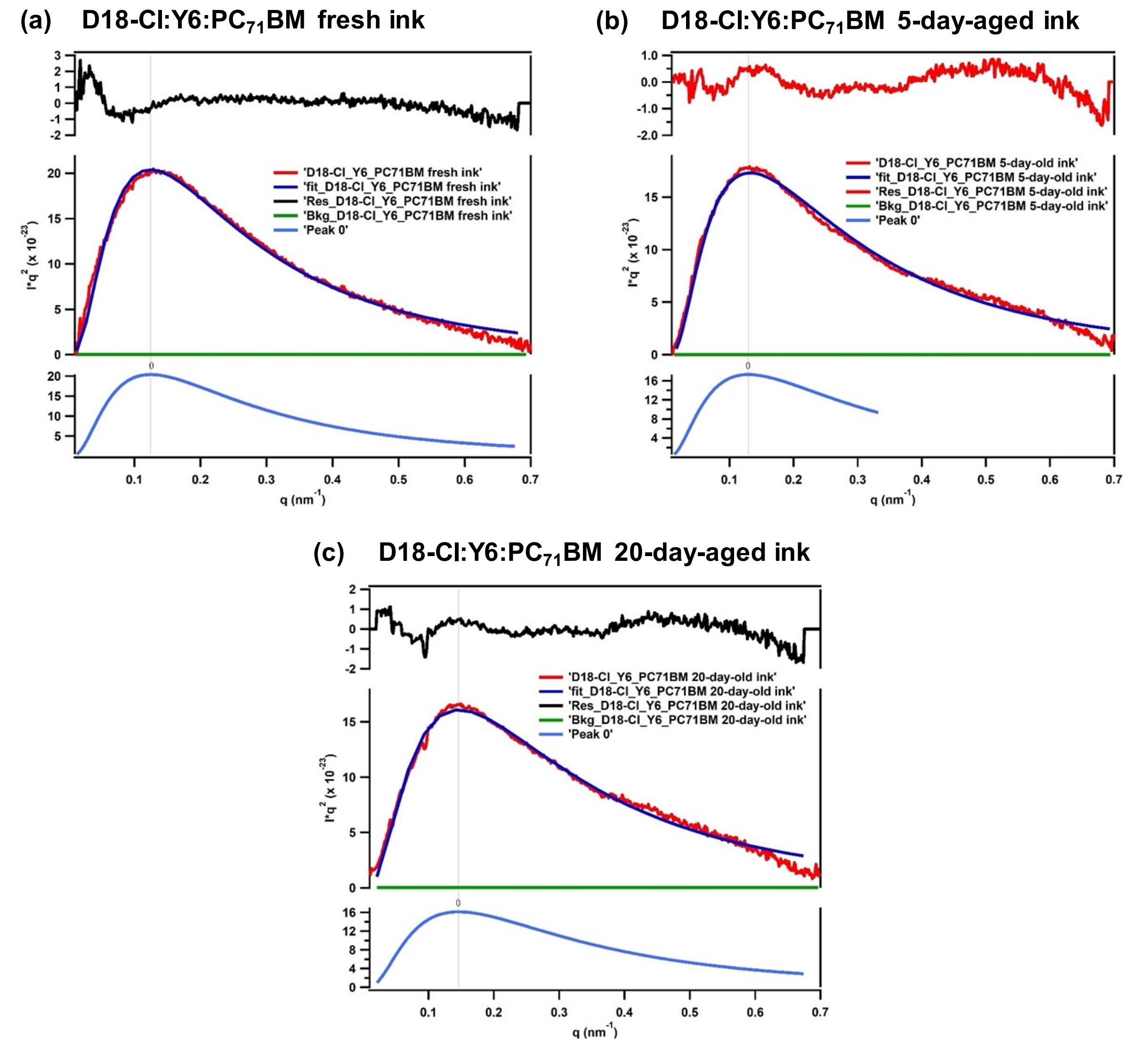

Figure S9. Lognormal fit of Lorentz-corrected RSoXS profiles of D18-Cl:Y6:$PC_{71}BM$ ternary blend films, cast from fresh, 5-day-aged and 20-day-aged inks, respectively, acquired at 283.8 eV.

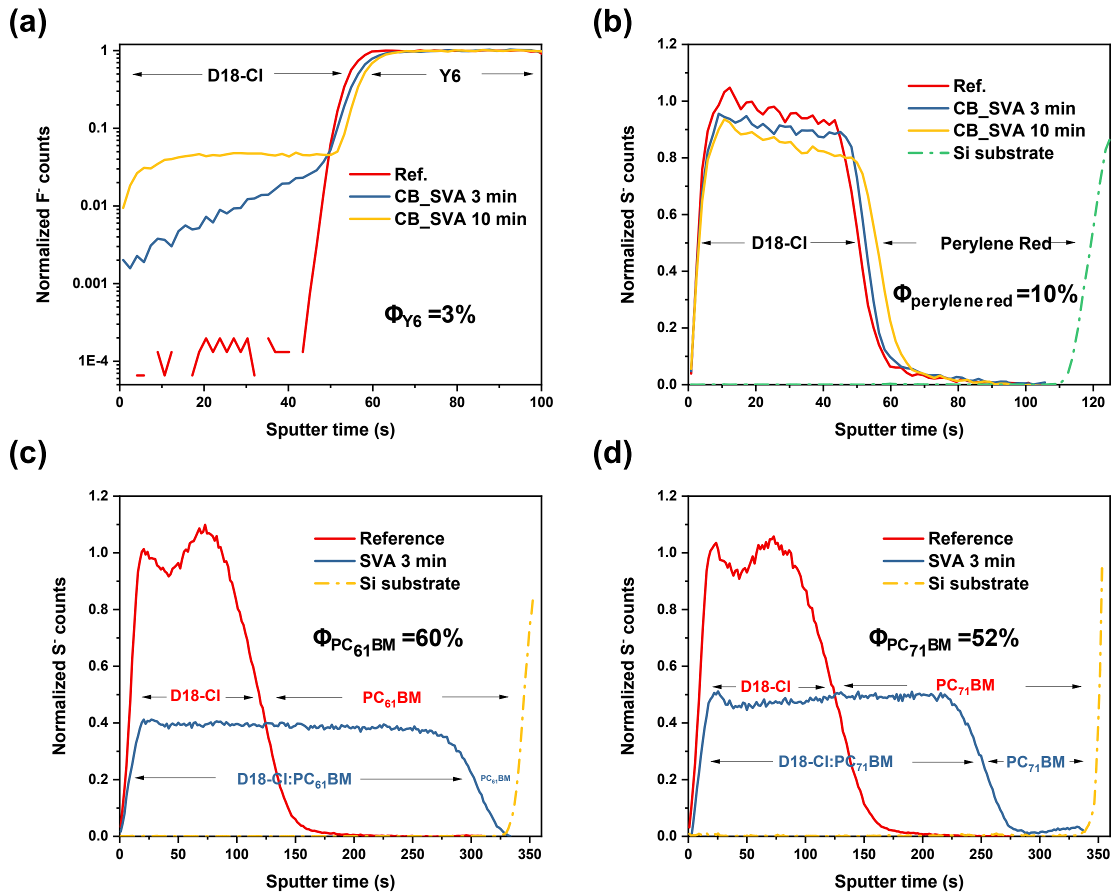

Figure 10. a) TOF-SIMS profiles of D18-Cl/Y6 bilayer samples annealed with CB vapor, tracking F^- ion of the acceptor. b) TOF-SIMS profiles of D18-Cl/Perylene Red bilayer samples annealed with CB vapor, tracking Cl^- ion of the polymer. c-d) TOF-SIMS profiles of D18-Cl/$PC_{61}BM$ (c) and D18-Cl/$PC_{71}BM$ (d) bilayers solvent vapor annealed, tracking S^- ion of the polymer.

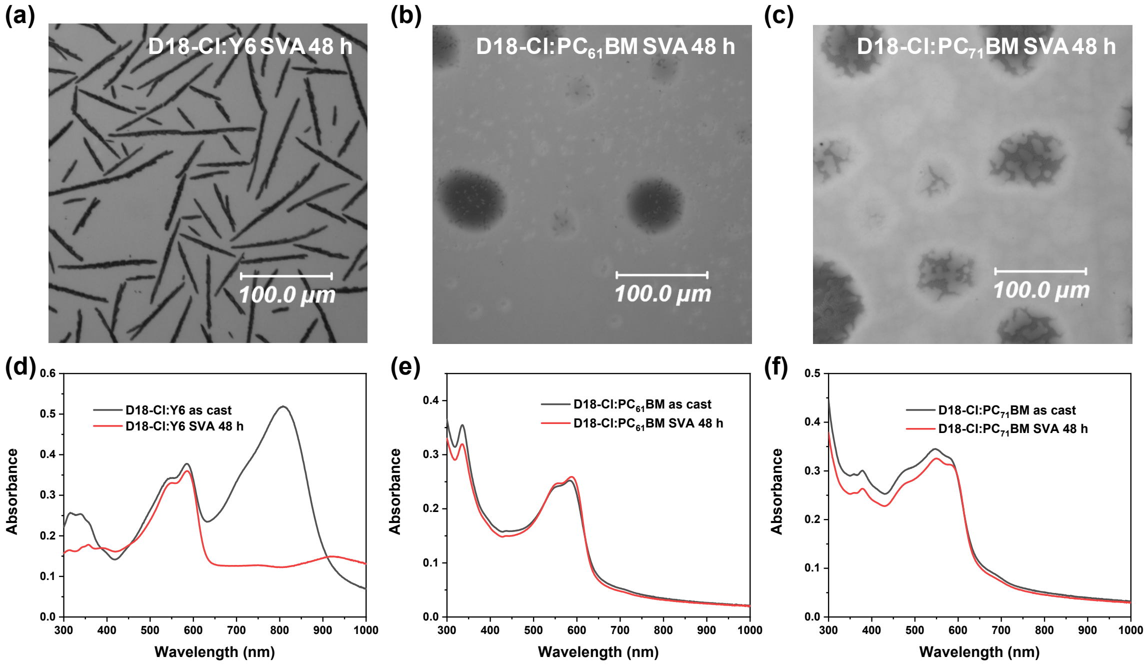

Figure S11. a-c) VLM images of D18-Cl:Y6, D18-Cl:$PC_{61}BM$, and D18-Cl:$PC_{71}BM$ blend films, SVA with chlorobenzene for 48 hrs. d-f) UV-vis absorption spectra of D18-Cl:Y6, D18-Cl:$PC_{61}BM$, and D18-Cl:$PC_{71}BM$ blend films, as-cast and SVA with chlorobenzene for 48 hrs.

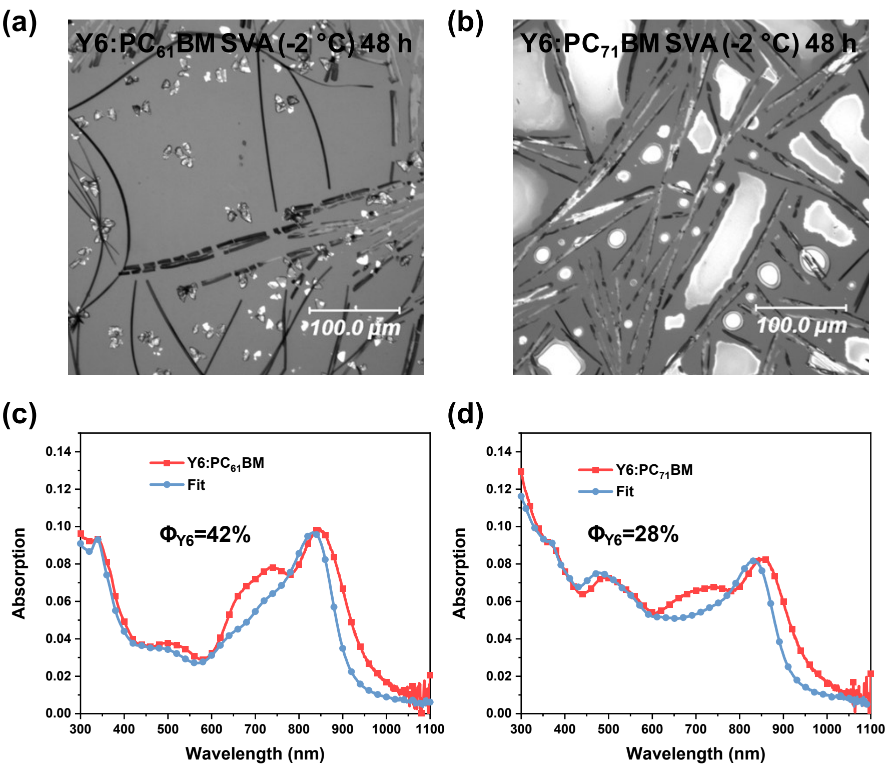

Figure S12. a-b) VLM images of Y6:$PC_{61}BM$, and Y6:$PC_{71}BM$ blend films, SVA with chlorobenzene for 48 h at –2 °C. c-d) UV-vis absorption spectra of Y6:$PC_{61}BM$, and Y6:$PC_{71}BM$ blend films, SVA with chlorobenzene for 48 h at –2 °C.

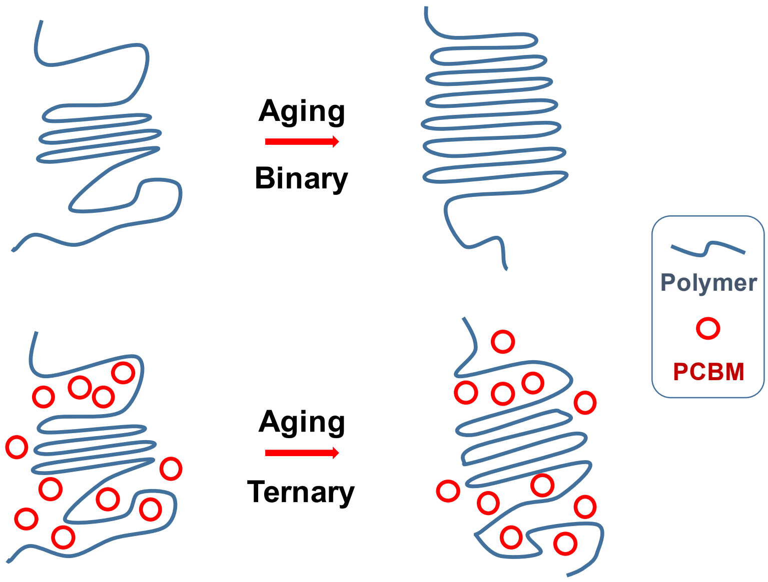

Figure 13. Schematic of PCBM suppressing the polymer pre-aggregation in the inks.

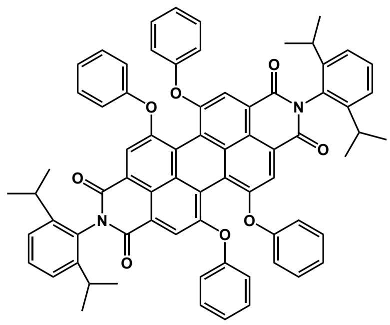

Figure 14. Molecular structures of Perylene Red.

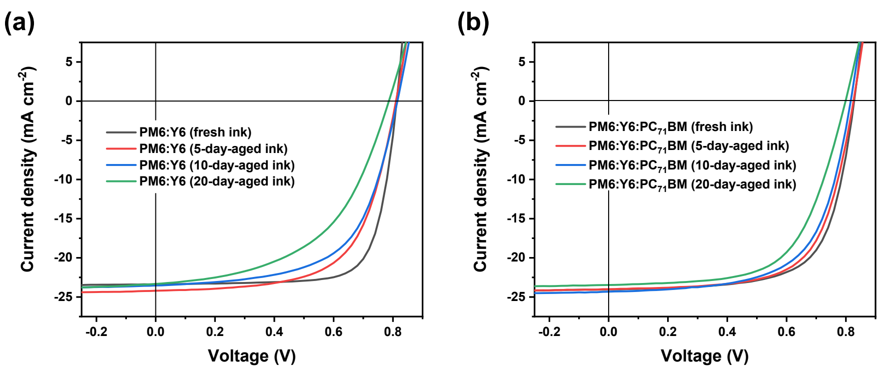

Figure S15. *J*–*V* curves of PM6:Y6 and PM6:Y6:$PC_{71}BM$ devices fabricated from fresh and aged inks.

Supplementary Tables

Table S1. Summary of the GIWAXS results (out-of-plane direction) for D18-Cl:Y6, D18-Cl:Y6:$PC_{61}BM$, and D18-Cl:Y6:$PC_{71}BM$ blend films, cast from fresh, 5-day-aged and 20-day-aged inks, respectively.

D18-Cl:Y6 fresh ink		
Peaks	(010) D18-Cl	(010)' Y6
q (Å^{-1})	1.69	1.79
L_C (Å)	13.8	23.6
g (%)	13.2	10.4
D18-Cl:Y6 5-day-aged ink		
Peaks	(010) D18-Cl	(010)' Y6
q (Å^{-1})	1.69	1.78
L_C (Å)	12.6	23.6
g (%)	13.9	10.4
D18-Cl:Y6 20-day-aged ink		
Peaks	(010) D18-Cl	(010)' Y6
q (Å^{-1})	1.69	1.77
L_C (Å)	11.8	25.7
g (%)	14.3	9.9
D18-Cl:Y6:$PC_{61}BM$ fresh ink		
Peaks	(010) D18-Cl	(010)' Y6
q (Å^{-1})	1.69	1.78
L_C (Å)	13.1	25.7
g (%)	13.6	10.0
D18-Cl:Y6:$PC_{61}BM$ 5-day-aged ink		
Peaks	(010) D18-Cl	(010)' Y6
q (Å^{-1})	1.69	1.80
L_C (Å)	13.1	25.7
g (%)	13.6	10.0
D18-Cl:Y6:$PC_{61}BM$ 20-day-aged ink		
Peaks	(010) D18-Cl	(010)' Y6
q (Å^{-1})	1.69	1.78
L_C (Å)	13.5	24.6
g (%)	13.4	10.2
D18-Cl:Y6:$PC_{71}BM$ fresh ink		
Peaks	(010) D18-Cl	(010)' Y6
q (Å^{-1})	1.69	1.79
L_C (Å)	12.6	25.7

g (%)	13.9	10.0
D18-Cl:Y6:PC_{71}BM 5-day-aged ink		
Peaks	(010) D18-Cl	(010)' Y6
q (Å^{-1})	1.69	1.79
L_C (Å)	12.8	25.7
g (%)	13.7	10.0
D18-Cl:Y6:PC_{71}BM 20-day-aged ink		
Peaks	(010) D18-Cl	(010)' Y6
q (Å^{-1})	1.69	1.79
L_C (Å)	12.6	26.9
g (%)	13.9	9.8

Table S2. Summary of photovoltaic performance of D18-Cl:Y6 and (D18-Cl:PC_{61}BM):Y6 devices where the donor, donor:PCBM and acceptor solutions were dissolved and aged separately and mixed together right before spin-casting.

Blends	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE_{avg} (%)
D18-Cl:Y6 fresh ink	0.867 ± 0.004	26.45 ± 0.62	67.3 ± 2.6	15.44 ± 0.95
D18-Cl:Y6 5-day-aged ink	0.843 ± 0.005	25.01 ± 0.49	58.8 ± 2.3	12.41 ± 0.76
D18-Cl:Y6 20-day-aged ink	0.850 ± 0.004	25.48 ± 0.47	51.9 ± 2.9	11.26 ± 0.85
(D18-Cl:PC_{61}BM):Y6 fresh ink	0.862 ± 0.004	26.38 ± 0.54	73.0 ± 1.6	16.61 ± 0.56
(D18-Cl:PC_{61}BM):Y6 5-day-aged ink	0.843 ± 0.006	24.59 ± 0.54	71.8 ± 4.8	14.91 ± 1.07
(D18-Cl:PC_{61}BM):Y6 20-day-aged ink	0.850 ± 0.007	26.18 ± 0.36	66.6 ± 2.5	14.84 ± 0.66

Table S3. Summary of photovoltaic performance of D18-Cl:Y6:Perylene Red devices fabricated from fresh and aged inks.

Blends	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE_{avg} (%)
D18-Cl:Y6:Perylene Red fresh ink	0.836 ± 0.010	22.12 ± 1.84	73.1 ± 1.6	13.54 ± 1.44
D18-Cl:Y6:Perylene Red 5-day-aged ink	0.822 ± 0.007	22.14 ± 0.10	63.2 ± 1.0	11.49 ± 0.20
D18-Cl:Y6:Perylene Red 20-day-aged ink	0.790 ± 0.009	21.77 ± 0.58	49.0 ± 0.7	8.43 ± 0.22

Table S4. Summary of photovoltaic performance of PM6:Y6 and PM6:Y6:PC_{71}BM devices fabricated from fresh and aged inks.

Blends	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE_{avg} (%)
PM6:Y6 fresh ink	0.810 ± 0.004	23.62 ± 0.13	74.5 ± 0.3	14.24 ± 0.11
PM6:Y6 5-day-aged ink	0.815 ± 0.005	24.00 ± 0.62	63.2 ± 0.9	12.36 ± 0.22
PM6:Y6 10-day-aged ink	0.816 ± 0.004	23.58 ± 0.24	60.5 ± 0.3	11.65 ± 0.16
PM6:Y6 20-day-aged ink	0.788 ± 0.004	22.96 ± 0.25	51.4 ± 0.6	9.30 ± 0.19

PM6:Y6:$PC_{71}BM$ fresh ink	0.827 ± 0.003	24.00 ± 0.18	67.5 ± 0.9	13.39 ± 0.22
PM6:Y6:$PC_{71}BM$ 5-day-aged ink	0.825 ± 0.006	23.52 ± 0.39	66.3 ± 0.4	12.86 ± 0.36
PM6:Y6:$PC_{71}BM$ 10-day-aged ink	0.810 ± 0.003	24.15 ± 0.25	63.6 ± 0.3	12.44 ± 0.15
PM6:Y6:$PC_{71}BM$ 20-day-aged ink	0.802 ± 0.003	23.22 ± 0.30	60.5 ± 1.5	11.28 ± 0.38

Table S5. Summary of photovoltaic performance of PTQ-10:Y6 and PTQ-10:Y6:$PC_{71}BM$ devices.

Blends	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE_{avg} (%)
PTQ-10:Y6 fresh ink	0.849 ± 0.002	24.74 ± 0.22	66.8 ± 0.7	14.04 ± 0.10
PTQ-10:Y6 5-day-aged ink	0.841 ± 0.002	23.12 ± 0.84	58.5 ± 1.2	11.39 ± 0.45
PTQ-10:Y6 10-day-aged ink	0.836 ± 0.011	22.03 ± 1.54	56.7 ± 4.3	10.46 ± 1.16
PTQ-10:Y6:$PC_{71}BM$ fresh ink	0.852 ± 0.003	25.50 ± 0 .17	64.2 ± 0.9	13.95 ± 0.22
PTQ-10:Y6:$PC_{71}BM$ 5-day-aged ink	0.852 ± 0.003	24.90 ± 0.33	60.9 ± 1.4	12.94 ± 0.19
PTQ-10:Y6:$PC_{71}BM$ 10-day-aged ink	0.848 ± 0.002	25.08 ± 0.13	60.0 ± 1.3	12.76 ± 0.29

Table S6. Summary of photovoltaic performance of PM6:N2200 and PM6:N2200:$PC_{71}BM$ devices processed with o-xylene.

Blends	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE_{avg} (%)
PM6:N2200 fresh ink	0.981 ± 0.002	8.97 ± 0.24	59.2 ± 0.5	5.21 ± 0.14
PM6:N2200 5-day-aged ink	0.976 ± 0.004	8.65 ± 0.20	55.7 ± 1.6	4.71 ± 0.26
PM6:N2200 20-day-aged ink	0.971 ± 0.003	8.49 ± 0.29	55.3 ± 1.4	4.56 ± 0.26
PM6:N2200:$PC_{71}BM$ fresh ink	0.974 ± 0.002	10.04 ± 0.25	61.8 ± 0.4	5.98 ± 0.15
PM6:N2200:$PC_{71}BM$ 5-day-aged ink	0.970 ± 0.003	10.05 ± 0.12	60.3 ± 0.8	5.88 ± 0.11
PM6:N2200:$PC_{71}BM$ 20-day-aged ink	0.965 ± 0.003	9.70 ± 0.24	59.2 ± 0.9	5.54 ± 0.20