Supplementary Information (SI) for Journal of Materials Chemistry C.

Supplementary information

Chemical Structure and Processing Solvent of Cathode Interlayer Materials Affect Organic Solar Cells Performance

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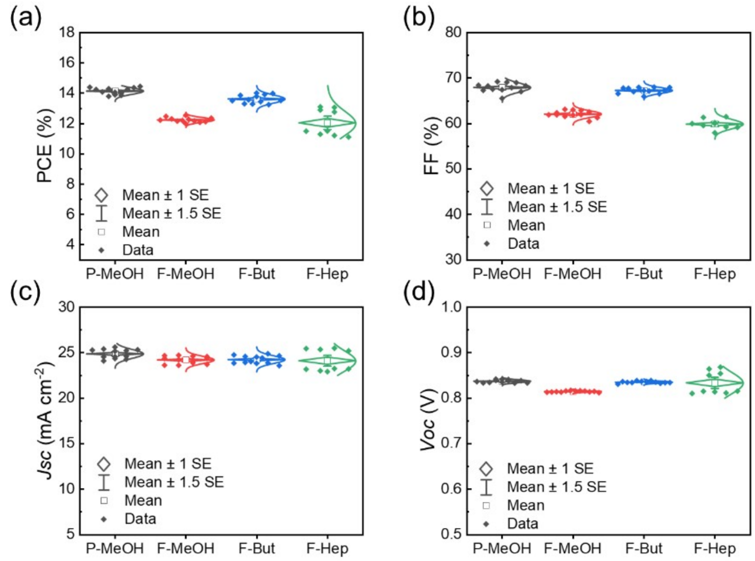


Figure S1. *J-V* parameter distribution of the PM6:Y6 OSCs with different CILs: (a) PCE, (b) FF, (c) *Jsc*, and (d) *Voc*, respectively.

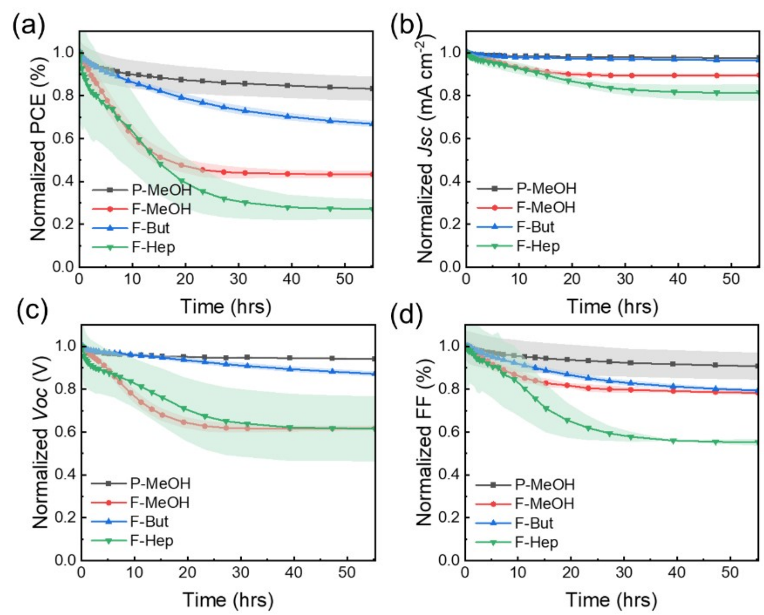


Figure S2. Photostability under N_2 environment for the unoptimized CIL devices for 60 hours showing (a) PCE, (b) *Jsc*, (c) *Voc*, and (d) FF. The deviation values are calculated for over 5 different devices each.

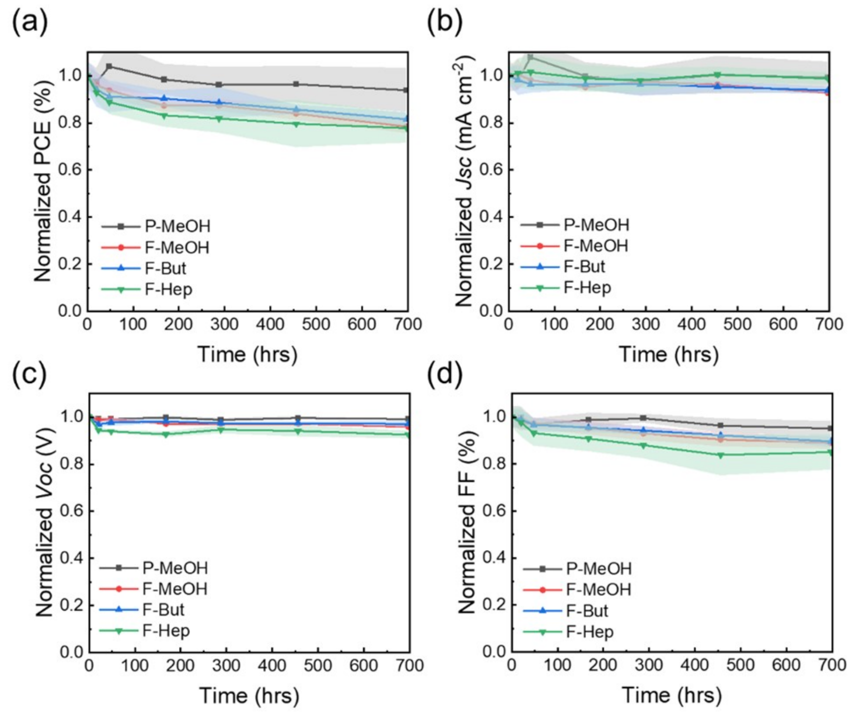


Figure S3. Shelf stability under N_2 environment for 700 hours showing (a) PCE, (b) *Jsc*, (c) *Voc*, and (d) FF. The deviation values are calculated for over 5 different devices each.

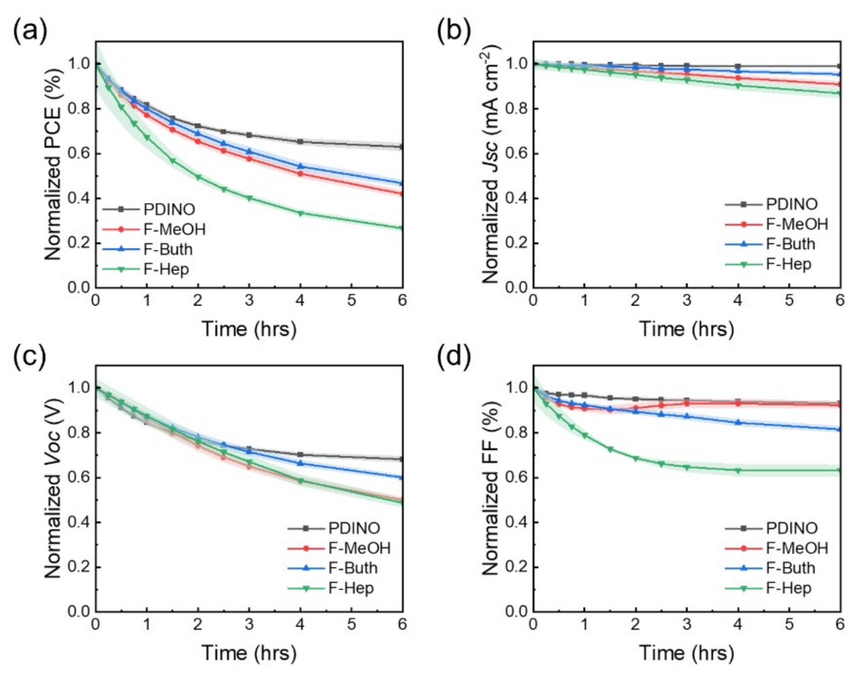


Figure S4. Shelf stability under an ambient environment for 6 hours showing (a) PCE, (b) *Jsc*, (c) *Voc*, and (d) FF. The deviation values are calculated for over 5 different devices each.

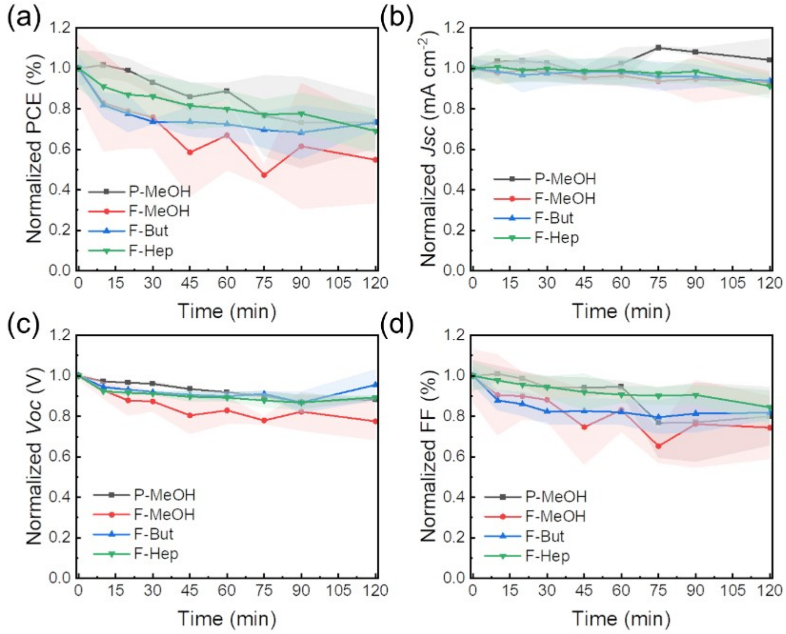


Figure S5. Thermal stability measurement at 85°C, following ISOS-T-1 protocol under N_2 environment for 2 hours: (a) PCE, (b) *Jsc*, (c) *Voc*, and (d) FF. The deviation values are calculated for over 5 different devices each.

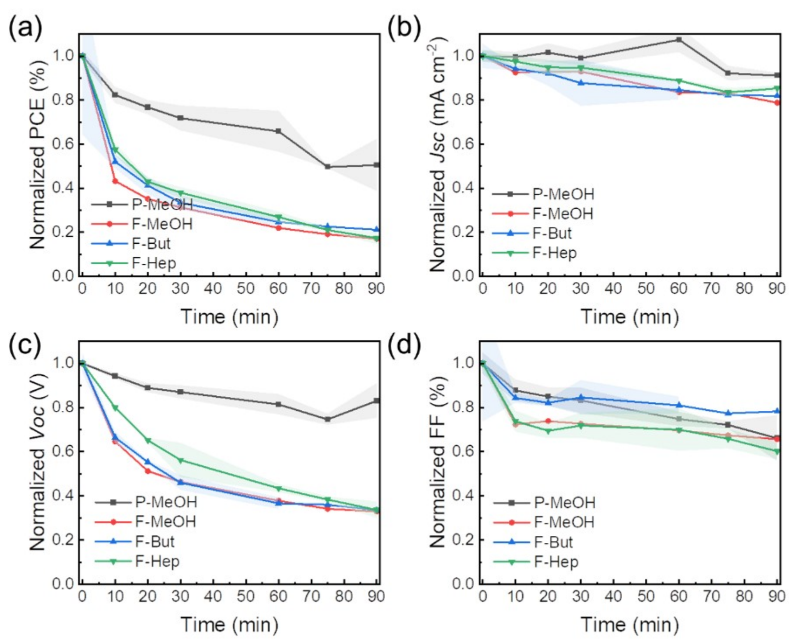


Figure S6. Thermal stability at 85°C, following ISOS-T-1 protocol in ambient environment for 90 minutes: (a) PCE, (b) *Jsc*, (c) *Voc*, and (d) FF. The deviation values are calculated for over 5 different devices each.

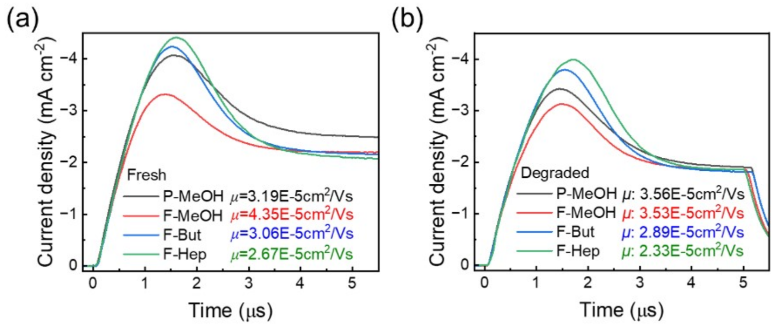


Figure S7. Photo-generated charge extraction by linear increasing voltage (photo-CELIV) data for OSC devices with different CILs under N_2 environment: (a) fresh and (b) degraded (under illumination with 100 mW/cm^2 for 55 hours).

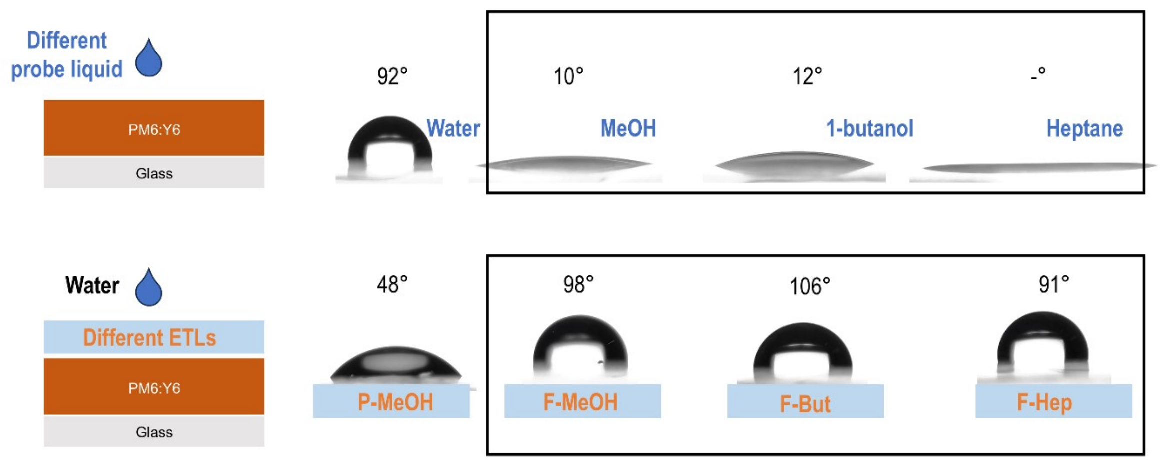
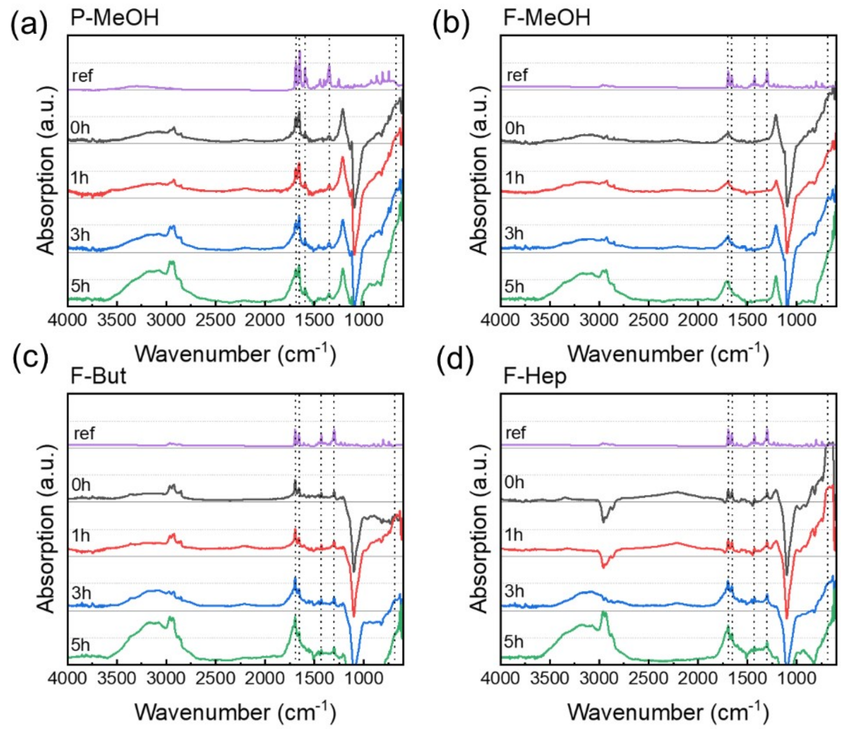


Figure S8. Contact angle measurement: Different probe liquids onto PM6:Y6 film (top row) and water onto different PM6:Y6/different CIL films (bottom row).

We probe the surface properties by measuring the contact angle between these green solvents and PM6:Y6 films and between water and CILs/PM6:Y6 films, as shown in **Figure S8.** F-PDIN-EH films show a higher contact angle than PDINO regardless of the solvent used, as shown in the bottom row. In the top row, PM6:Y6 film exhibits high hydrophobicity with a contact angle of 92° with water, while the contact angles of methanol, 1-butanol, and heptane are 10°, 12° and near 0°, respectively. This indicates better wettability between the solvents and PM6:Y6 films, with heptane showing the best wettability. The superior wettability of heptane might surprisingly contribute to the instability of F-Hep, either due to solvent residue or chemical interaction with PM6:Y6 underneath.

To explore solvent residue or chemical interaction with PM6:Y6 underneath, we conducted Fourier transform infrared spectroscopy (FTIR) on fresh, 3-day, and 6-day aged thin films under a nitrogen environment. However, it was difficult to detect any solvent residue or chemical interaction between PM6:Y6, CILs, and solvents for CILs through FTIR measurement.



3200-2700	Weak broad	O-H	alcohol	intramolecular bonded
3000-2840	medium	C-H	stretching	alkane
1870-1550	-	C=O	stretching	Esters, ketones, amides, carboxylic acids and their salts, acid anhydrides
1740-1670	-	C=O	stretching	Imide
1600-1450	-	C=C	Stretching	aromatic ring
2000-1650	weak	C-H	bending	aromatic compound
1400-1000	strong	C-F	stretching	fluoro compound
1380-1350	-	C-N	stretching	imide
1360–1290	medium	N-O	stretching	nitro compounds
1350-1200	-	C-N	stretching	aromatic C-N
1250-1000	-	C-N	stretching	aliphatic C-N
900-675	-	C-H	bending	Out-of-plane bending of aromatic C-H bonds

Figure S9. Fourier transform infrared spectroscopy (FT-IR) data of CIL films at different times stored under ambient shelf conditions up to 5 hours: (a) P-MeOH, (b) F-MeOH, (c) F-But, and (d) F-Hep. The references are measured using ATR-FTIR on PDINO and F-PDIN-EH powders. Spectra were baseline-corrected using a straight-line method, and sinusoidal interference from the silicon wafer was corrected within the Bruker OPUS software. The subtraction artifact from Si–O–Si at 1100 cm^{-1} was noted but is not presented in the main manuscript for clarity. All raw data are available upon request.

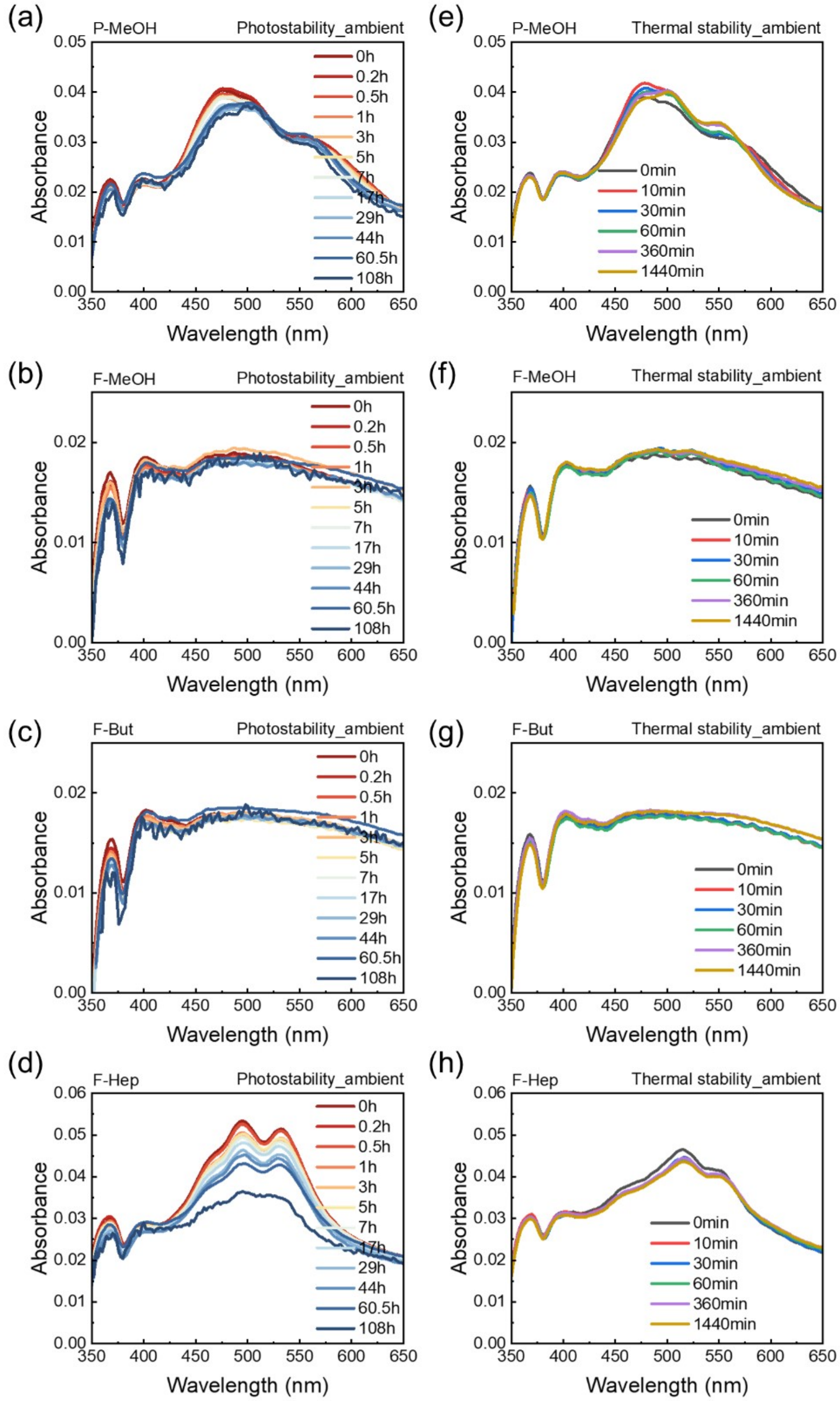


Figure S10. The absorbance of CIL films under continuous illumination in ambient for up to 108 hours: (a) P-MeOH, (b) F-MeOH, (c) F-But, and (d) F-Hep, and under heat treatment at 85°C in ambient conditions up to 1440 min: (d) P-MeOH, (b) F-MeOH, (c) F-But, and (d) F-Hep.

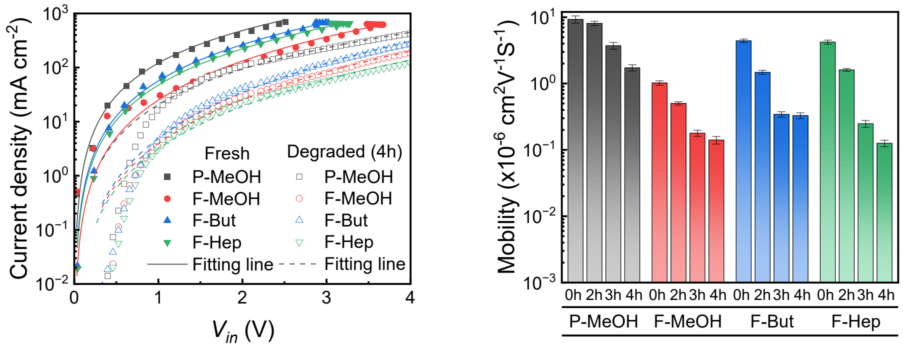


Figure S11. Extracted electron mobility from SCLC methods for (a) fresh and degraded devices (4 hours) and (b) comparison of electron mobility for each device type at 0, 1, 2, 3, and 4 hours.

Table S1. Summary of the transient photovoltage (TPV) parameters of the fresh and degraded devices with different CILs.

#	Samples	Fresh					Degraded (55hrs under illumination in N_2)				
		A_1	τ_1	A_2	τ_2	Weighted $\tau_{ave.}$	A_1	τ_1	A_2	τ2	Weighted $\tau_{ave.}$
1	P-MeOH	0.2	22.6	0.8	22.6	22.6	0.4	45.8	0.6	45.8	45.8
2	F-MeOH	0.6	24.8	0.3	24.8	24.9	0.9	15.9	0.1	77.8	20.5
3	F-But	0.8	25.1	0.2	51.6	30.8	0.5	31.2	0.5	31.2	31.2
4	F-Hep	0.1	5.2	1.0	30.5	28.5	0.9	15.6	0.1	95.9	23.5

* Bi-exponential equation: $y = y_0 + A_1 e^{-x/\tau_1} + A_1 e^{-x/\tau_2}$

* Weight average equation: $\tau_{ave.} = \dfrac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$

Table S2. Summary of the transient photocurrent (TPC) parameters of the fresh and degraded devices with different CILs.

#	Samples	Fresh			Degraded (55hrs under illumination in N_2)		
		τ_1	τ_2	Weighted $\tau_{ave.}$	τ_1	τ_2	Weighted $\tau_{ave.}$
1	P-MeOH	0.66	0.66	0.66	0.65	0.65	0.65
2	F-MeOH	0.80	0.82	0.61	0.84	0.83	0.83
3	F-But	0.63	0.63	0.63	0.85	0.86	0.85
4	F-Hep	0.39	3.93	0.57	0.60	4.19	1.07

Table S3. Summary of the impedance spectroscopy (EIS) parameters of the fresh and degraded devices with different CILs.

#	Samples	Fresh			Degraded (55hrs under illumination in N_2)		
		R_S (Ohm)	R_{Sh} (kOhm)	C (nF)	R_S (Ohm)	R_{Sh} (kOhm)	C (nF)
1	P-MeOH	14.75	319.94	5.41	10.85	43.15	4.59
2	F-MeOH	21.22	594.66	4.56	12.34	111.99	4.25
3	F-But	17.37	1437.81	4.48	16.90	1750.92	3.99
4	F-Hep	17.50	3963.94	4.31	11.02	1.68	3.76

Table S4. Summary of the mobility parameters of electron-only devices with different CILs at different times. The average values are calculated from 6 different devices.

Time (hours)	Mobility ($cm^2V^{-1}s^{-1}$)							
	P-MeOH		F-MeOH		F-But		F-Hep	
	Average μ	Average error	Average μ	Average error	Average μ	Average error	Average μ	Average error
0	1.01E-05	7.80E-07	2.09E-06	9.88E-08	1.09E-05	8.17E-06	1.40E-06	1.14E-07
1	5.00E-05	2.34E-05	1.34E-05	4.11E-06	1.19E-05	5.77E-07	1.83E-06	8.70E-08
3	9.98E-05	4.82E-05	2.14E-05	7.48E-06	1.22E-05	6.00E-07	7.25E-06	5.16E-07
6	1.86E-04	7.96E-05	4.24E-05	1.74E-05	5.53E-05	1.50E-05	1.85E-05	6.04E-06
12	2.29E-04	1.38E-04	1.01E-04	3.72E-05	1.10E-04	8.63E-05	4.77E-05	2.13E-05
24	2.57E-04	2.03E-04	1.68E-04	1.31E-04	1.43E-04	2.74E-05	1.21E-04	9.48E-05
44	2.51E-04	2.02E-04	2.02E-04	7.34E-05	1.75E-04	6.65E-05	1.56E-04	9.29E-05
84	2.34E-04	1.34E-04	1.71E-04	3.17E-05	1.69E-04	-	1.44E-04	5.45E-05
132	2.44E-04	9.59E-05	1.74E-04	-	1.72E-04	3.25E-05	1.48E-04	1.12E-04
172	2.26E-04	1.30E-04	1.72E-04	6.57E-05	1.73E-04	3.12E-05	1.47E-04	1.12E-04
220	2.24E-04	1.73E-04	1.70E-04	9.80E-05	1.71E-04	9.95E-05	1.43E-04	7.13E-05