

Supporting Information

Intrinsically Stretchable and Efficient Cross-linked Small Molecular Emitter for Flexible Organic Light-emitting Diodes

Ning Sun,[†] Xiang An,[‡] Jianye Gong,[†] Yingying Zheng,[‡] Lubing Bai,[‡] Huaqiang Gong,[‡] Yahui Zhang,[‡] Mingjian Ni,[‡] Zhiqiang Zhuo,[‡] Chuanxin Wei,[§] Man Xu,[§] Jianguo Wang,^{*†} Yamin Han,^{*‡} Jinyi Lin,^{*‡} Wei Huang^{†,‡,§}

[†]Country College of Chemistry and Chemical Engineering, Inner Mongolia Key Laboratory of Fine Organic Synthesis, Inner Mongolia University, Hohhot 010021, China.

[‡]State Key Laboratory of Organic Electronics and Information Displays, Nanjing University of Posts and Telecommunications, Nanjing 210023, China.

[§]Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Nanjing Tech University (NanjingTech), Nanjing 211816, China.

Keywords: Intrinsically stretchable films, Side-chain crosslinked strategy, Small molecular semiconductor, Mechanical property, Flexible organic light-emitting diodes

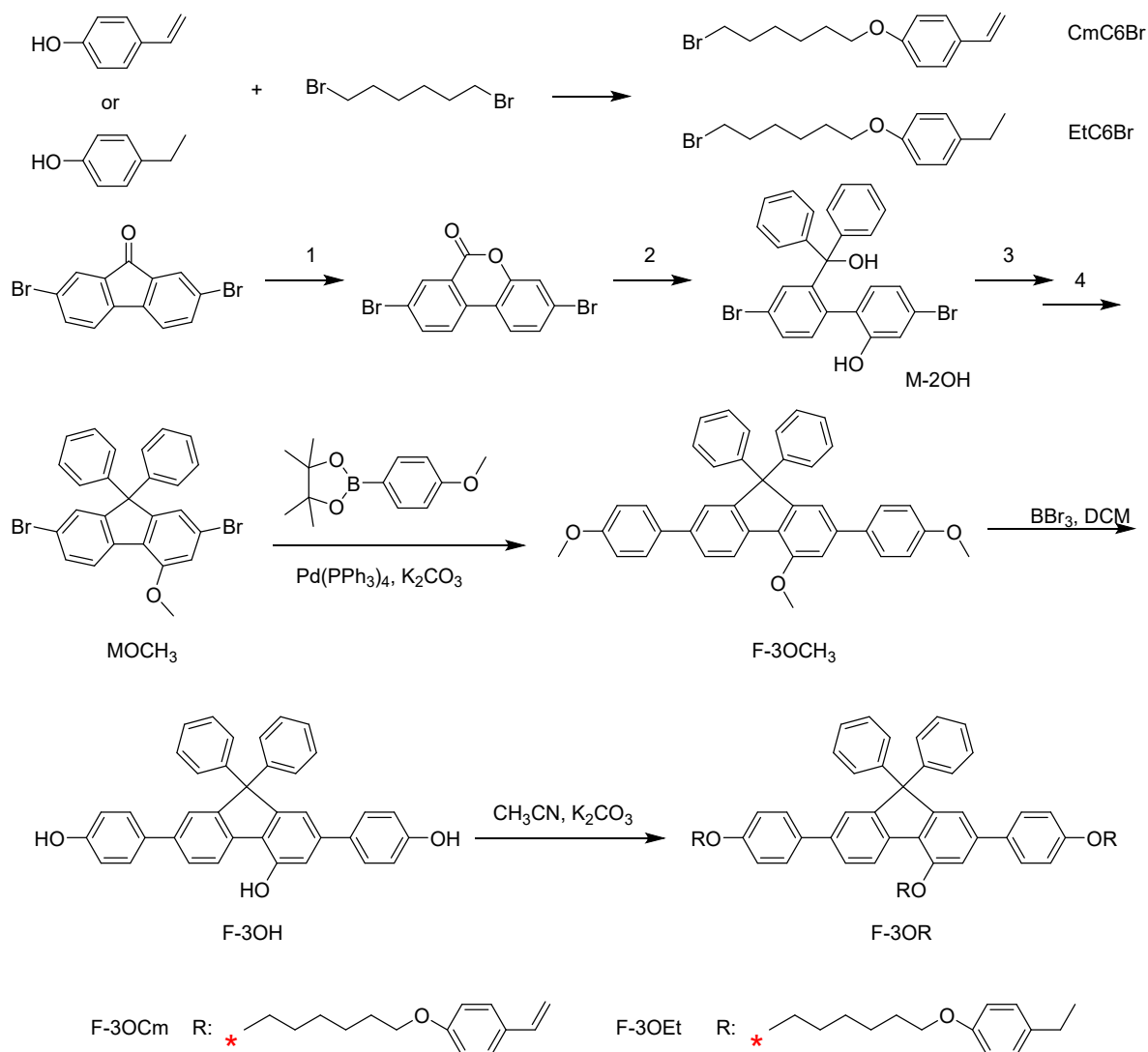
Experimental Section

Chemicals. All reagents from commercial sources were used without further purification, unless otherwise noted. All dry reactions were performed with glassware that was flamed under high vacuum and backfilled with N₂.

Characterization. ¹H- and ¹³C-NMR spectrum was recorded on JOEL NMR spectrometer (JNM-ECZ400S, 400 MHz Japan) in CDCl₃ with tetramethylsilane (TMS) as the interval standard. Thermogravimetric analyses (TGA) were conducted by Shimadzu DTG-60H and DSC test was acquired using Shimadzu Instruments DSC-60A. The UV-vis absorption spectra were obtained by Shimadzu UV-1750. Steady-state fluorescence spectra were measured using Hitachi F-4600. The PLQY was measured using Edinburgh FLS 980 time-correlated single photon-counting (TCSPC) fluorescence spectrophotometer equipped with xenon arc lamp (Xe900). The film morphologies of compounds were recorded with Bruker's Dimension Icon AFM in tapping mode (Bruker's Sb/Si probe tip with resonant frequency 320 kHz and the spring constant 42 Nm⁻¹). Cyclic voltammetric (CV) studies were conducted using CHI660C Electrochemical Work station in typical three-electrode cell with platinum sheet working electrode, platinum wire counter electrode, and silver/silver chloride (Ag/Ag⁺) reference electrode.

OLEDs devices fabrication. The OLEDs devices were fabricated onto prepatterned indium-tin oxide (ITO) whose sheet resistance is 10 Ω per square. The structure of device is ITO / PEDOT: PSS / Emission materials / TPBI / LiF / Al. Thin hole-injection layer (20 nm) of PEDOT: PSS was spin-coated on the transparent conductive ITO at spin speed of 3000 rpm for 78 s. After thermal annealed in air for 15 minutes, the emissive layer was spin-coated on the top of the PEDOT: PSS layer. The cross-linking condition of the emissive layers were annealed at 140°C or 180°C for 10 min. The background pressure of the chamber was under 10⁻⁶ Torr during the deposition process. EL spectra and CIE coordinates of the devices were used Spectra Scan PR655 spectra radiometer to measure. All the devices were characterized without encapsulation under ambient condition. The device's current-voltage luminescence characteristics were recorded by Keithley source meter (model 2602) and PR655 spectra radiometer.

Synthesis



The detailed synthesis procedure for target molecules.

CmC6Br:

To the solution of K₂CO₃ (0.41 g, 3 mmol) and 1,6-dibromohexane (0.96 g, 4 mmol) in acetone (20 mL) was added dropwise 4-vinylphenol (0.24 g, 2 mmol). The mixture was heated to 40°C for 24 h in the dark. The mixture was extracted with distilled water and dichloromethane organic layer was dehydrated with dried over Na₂SO₄. After the removal of the solvent, the residue was purified by column chromatography on silica gel to afford CmC6Br (0.36 g, yield 63%). ¹H NMR (400 MHz, Chloroform-d, ppm) δ: 7.36-7.32 (m, 2 H), 6.87-6.83 (m, 2 H), 6.70-6.62 (m, 1 H), 5.64-5.58 (d, 1 H), 5.14-5.10 (d, 1 H), 3.98-3.94 (t, 2 H), 3.45-3.41 (t, 2 H), 1.94-1.86 (m, 2 H), 1.84-1.76 (m, 2 H), 1.55-1.47 (m, 4 H). ¹³C NMR (125 MHz, Chloroform-d, ppm) δ: 158.79, 136.19, 130.25, 127.33, 114.41, 111.45, 67.69, 33.82, 32.64, 29.05, 27.89, 25.26.

EtC6Br:

To the solution of K_2CO_3 (0.41 g, 3 mmol) and 1,6-dibromohexane (0.96 g, 4 mmol) in acetone (20 mL) was added dropwise 4-ethylphenol (0.24 g, 2 mmol). The mixture was heated to 40°C for 24 h. The mixture was extracted with distilled water and dichloromethane organic layer was dehydrated with dried over Na_2SO_4 . After the removal of the solvent, the residue was purified by column chromatography on silica gel to afford EtC6Br (0.41 g, yield 72%). 1H NMR (400 MHz, Chloroform-d, ppm) δ : 7.21-7.16 (d, 2 H), 6.93-6.88 (d, 2 H), 4.03-3.97 (d, 2 H), 3.50-3.45 (d, 2 H), 2.72-2.64 (m, 2 H), 2.00-1.91 (m, 2 H), 1.90-1.82 (m, 2 H), 1.62-1.53 (m, 4 H), 1.34-1.27 (m, 3 H). ^{13}C NMR (125 MHz, Chloroform-d, ppm) δ : 157.01, 136.27, 128.65, 114.29, 67.69, 33.84, 32.67, 29.13, 27.94, 27.91, 25.30, 15.89.

The synthetic route 1 and 2 refer to the published literature.

MOCH₃:

In clean and dry round-bottom flask, M-2OH (1 g, 1.96 mmol) was dissolved in mixture of K_2CO_3 (0.5 g) and acetone (20 mL), then CH_3I (0.55 g, 3.92 mmol) was dropwise added into the flask, and the reaction was stirred under room temperature for 24 h. After this reaction completed, acetone was removed under reduced pressure before DCM (20 mL) adding into the flask, and followed by adding $BF_3 \cdot Et_2O$ (0.5 mL). The mixture was reacted under room temperature for 12 h, then it was poured into water and extracted with DCM for three times. After the organic phase dried with anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the crude product was purified with silica gel column chromatography (PE:DCM=4:1) to give the target monomer as a white power (0.79 g, yield of 80%). 1H NMR (400 MHz, Chloroform-d) δ (ppm): 7.96-7.94 (d, 1 H), 7.48-7.44 (m, 2 H), 7.26-7.23 (m, 6 H), 7.16-7.12 (m, 5 H), 7.01-6.99 (d, 1 H), 4.01-3.98 (s, 3 H). ^{13}C NMR (100 MHz, Chloroform-d) δ (ppm): 155.99, 154.03, 152.37, 144.42, 137.48, 130.76, 128.69, 128.47, 128.03, 127.09, 126.29, 125.34, 122.08, 121.54, 120.91, 113.26, 65.90, 55.75.

F-3OCH₃:

2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.84 g, 7.88 mmol) and $MOCH_3$ (1 g, 1.97 mmol) were dissolved in mixed solvent of THF/distilled water (25 mL). To the mixture, 1.4 g potassium carbonate aqueous solution (5 mL) and tetrakis(triphenylphosphine)palladium(0) (0.1 g) were added slowly and refluxed 36 h under nitrogen atmosphere. The mixture was extracted with distilled water and dichloromethane organic layer was dehydrated with dried over Na_2SO_4 . After the removal of the solvent, the residue was purified by column chromatography on silica gel to afford F-3OCH₃ (0.57 g, yield 52%). 1H NMR (400 MHz, Chloroform-d) δ (ppm): 8.21-8.18 (d, 1 H), 7.59-7.56 (m, 2

H), 7.54-7.51 (m, 4 H), 7.34-7.31 (m, 4 H), 7.28-7.26 (m, 2 H), 7.25-7.22 (m, 5 H), 7.07-7.06 (d, 1 H), 6.98-6.95 (m, 4 H), 4.11-4.09 (s, 3 H), 3.85-3.84 (s, 6 H). ¹³C NMR (100 MHz, Chloroform-d) δ (ppm): 159.29, 159.09, 155.99, 153.76, 151.53, 146.13, 141.65, 139.26, 138.01, 134.21, 134.14, 128.45, 128.39, 128.36, 128.25, 126.77, 126.70, 126.23, 124.18, 123.98, 117.12, 114.23, 108.34, 66.01, 55.46.

F-3OH:

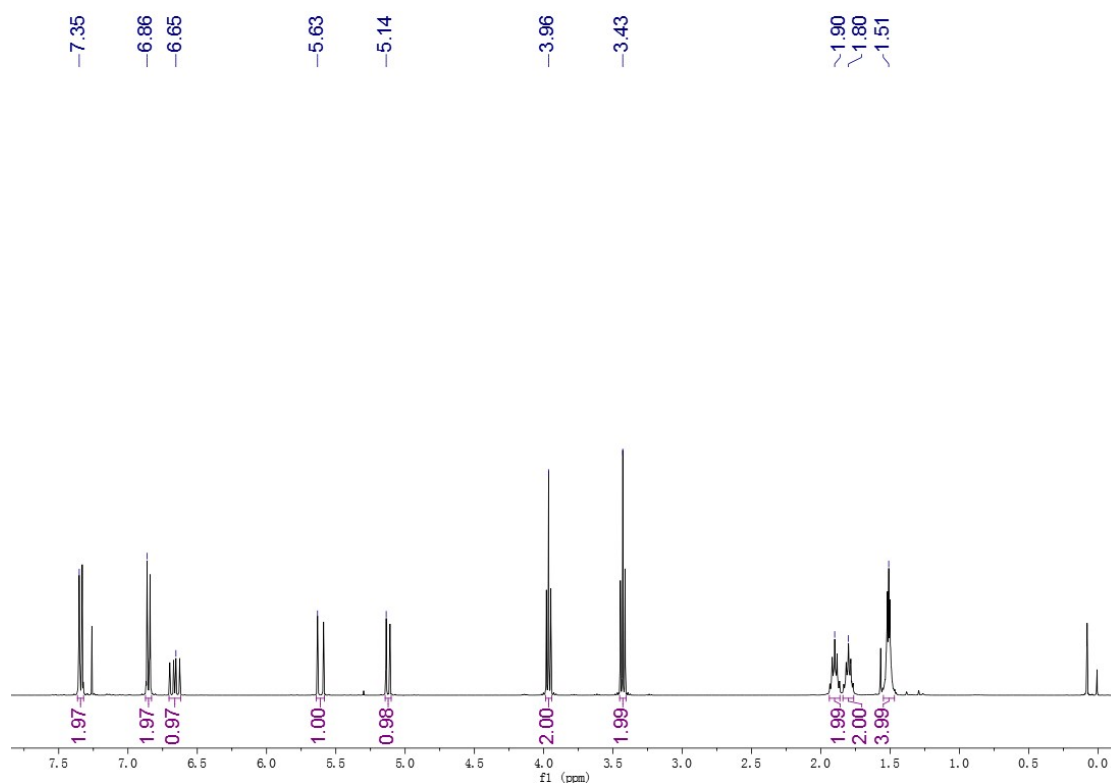
Added F-3OCH₃ (1 g, 1.78 mmol) into 100 mL round-bottomed flask, sealed the device, pumped vacuum and filled with nitrogen, kept nitrogen atmosphere in the reaction flask, and placed the device in ice water bath and stir. Added BBr₃ (1.12 g, 4.5 mmol) and reacted for 12 h. The mixture was extracted with distilled water and dichloromethane organic layer was dehydrated with dried over Na₂SO₄. After the removal of the solvent, the residue was purified by column chromatography on silica gel to afford F-3OH (0.37 g, yield 40%). ¹H NMR (400 MHz, Chloroform-d) δ (ppm): 10.31-10.28 (s, 1 H), 9.56-9.52 (d, 2 H), 8.09-8.06 (d, 1 H), 7.61-7.57 (m, 1 H), 7.53-7.51 (d, 1 H), 7.43-7.40 (d, 2 H), 7.35-7.32 (d, 2 H), 7.30-7.25 (m, 4 H), 7.23-7.19 (m, 6 H), 7.04-7.01 (m, 2 H), 6.84-6.79 (d, 4 H). ¹³C NMR (100 MHz, Chloroform-d) δ (ppm): 157.71, 157.57, 154.18, 153.83, 151.35, 146.45, 141.44, 138.86, 138.04, 131.50, 128.94, 128.39, 128.21, 127.12, 126.03, 124.84, 124.09, 123.31, 116.29, 115.02, 112.63, 65.87, 55.45.

F-3OCm:

To solution of K₂CO₃ (0.97 g, 7 mmol) and F-3OH (1 g, 1.93 mmol) in CH₃CN (20 mL) was added CmC6Br (3.3 g, 11.58 mmol). The mixture was heated to 60°C in the dark for 24 h. The mixture was extracted with distilled water and dichloromethane organic layer was dehydrated with dried over Na₂SO₄. After the removal of the solvent, the residue was purified by column chromatography on silica gel to afford F-3OCm (0.65 g, yield 30%). ¹H NMR (400 MHz, Chloroform-d, ppm) δ: 8.18-8.15 (d, 1 H), 7.56-7.52 (m, 2 H), 7.49-7.45 (d, 4 H), 7.36-7.32 (m, 5 H), 7.31-7.28 (m, 5 H), 7.25-7.18 (m, 7 H), 7.04-7.02 (d, 1 H), 6.94-6.91 (d, 4 H), 6.87-6.84 (m, 6 H), 6.70-6.61 (m, 3 H), 5.63-5.56 (m, 3 H), 5.14-5.09 (m, 3 H), 4.28-4.24 (t, 2 H), 4.03-3.96 (m, 10 H), 2.09-2.01 (m, 2 H), 1.91-1.79 (m, 10 H), 1.76-1.63 (m, 4 H), 1.58-1.56 (m, 3 H), 1.56-1.53 (m, 5 H). ¹³C NMR (100 MHz, Chloroform-d) δ (ppm): 158.84, 158.44, 155.28, 153.58, 151.38, 146.02, 141.49, 139.08, 137.94, 130.20, 128.32, 128.04, 127.32, 126.53, 126.07, 123.90, 116.78, 114.64, 114.41, 111.38, 108.77, 67.78, 65.81, 29.35, 29.16, 26.11, 25.83.

F-3OEt:

To the solution of K_2CO_3 (0.97 g, 7 mmol) and F-3OH (1 g, 1.93 mmol) in CH_3CN (20 mL) was added EtC6Br (3.3 g, 11.58 mmol). The mixture was heated to $50^\circ C$ for 24 h. The mixture was extracted with distilled water and dichloromethane organic layer was dehydrated with dried over Na_2SO_4 . After the removal of the solvent, the residue was purified by column chromatography on silica gel to afford F-3OEt (0.61 g, yield 28%). 1H NMR (400 MHz, Chloroform-d, ppm) δ : 8.188-8.157 (d, 1 H), 7.57-7.54 (m, 2 H), 7.50-7.46 (m, 4 H), 7.32-7.28 (m, 4 H), 7.26-7.18 (m, 7 H), 7.12-7.08 (m, 6 H), 7.04-7.03 (d, 1 H), 6.95-6.91 (m, 4 H), 6.85-6.82 (m, 6 H), 4.29-4.23 (t, 2 H), 4.02-3.94 (m, 10 H), 2.62-2.55 (m, 6 H), 2.09-2.02 (m, 2 H), 1.86-1.794(m, 8 H), 1.75-1.63 (m, 4 H), 1.58-1.52 (m, 10 H), 1.24-1.19 (m, 9 H). ^{13}C NMR (100 MHz, Chloroform-d) δ (ppm):158.63, 158.44, 157.06, 157.05, 155.29, 153.57, 151.37, 146.03, 141.50, 139.08, 137.95, 136.20, 133.91, 128.64, 128.19, 126.53, 126.09, 123.81, 116.77, 114.63, 114.29,108.78, 67.76, 65.81, 29.38, 29.29, 29.25, 29.18, 27.94, 27.93, 26.11, 25.92, 25.87, 25.85, 15.90, 15.88.



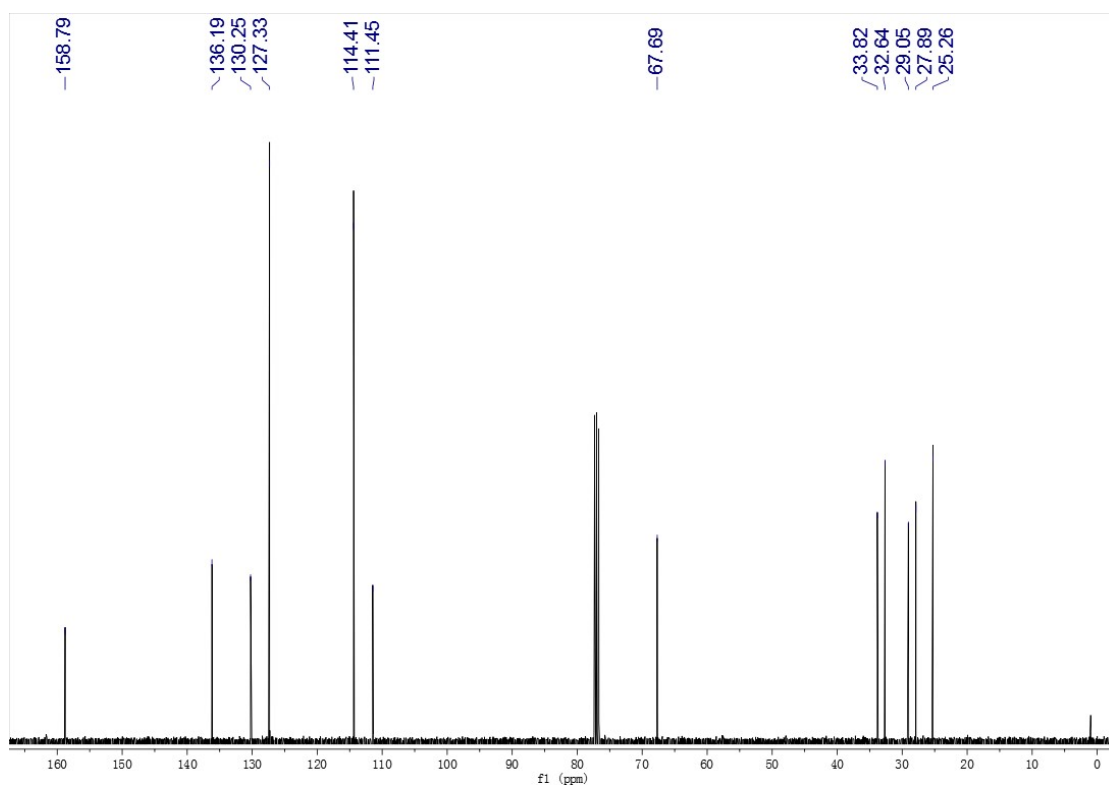
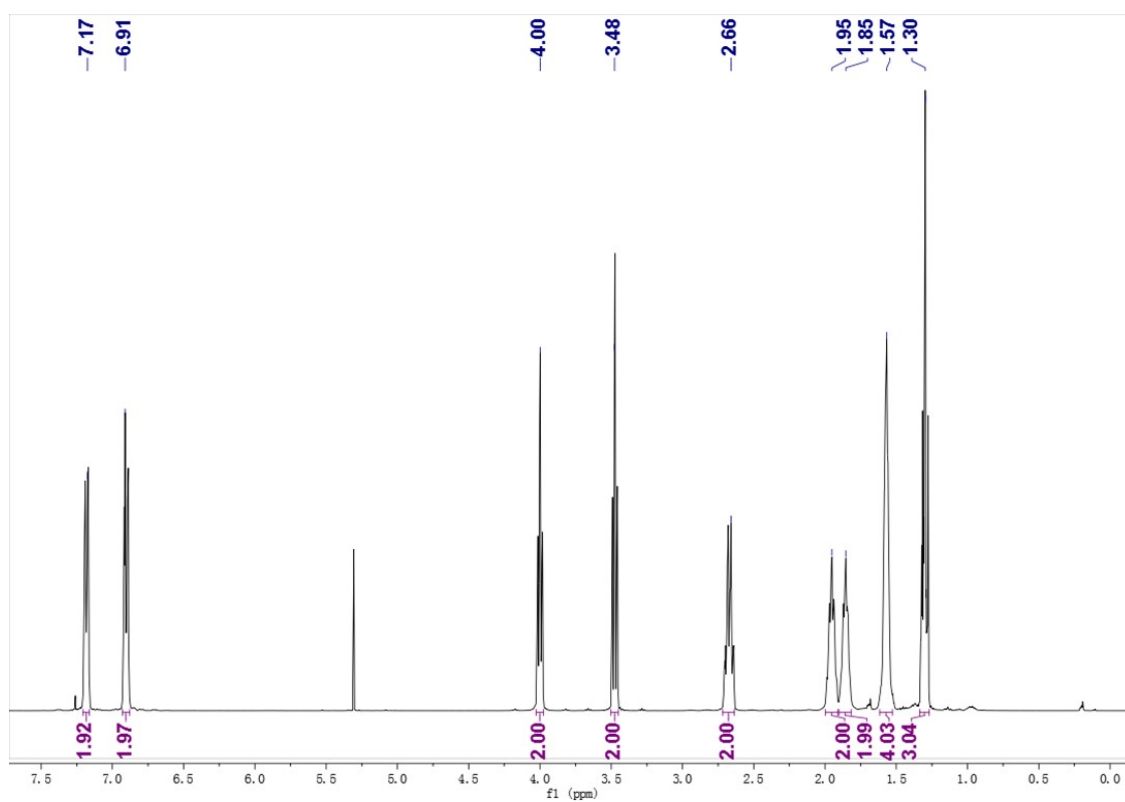


Figure S1. ¹H NMR spectra and ¹³C NMR spectra of CmC6Br.



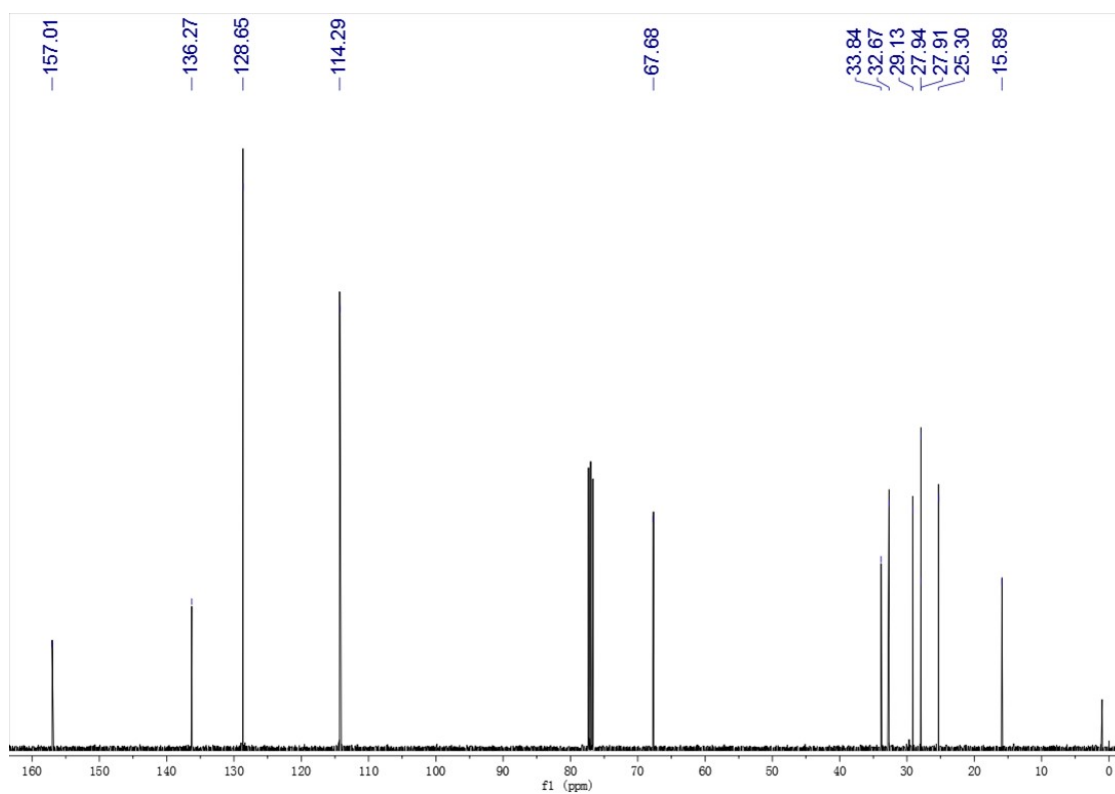
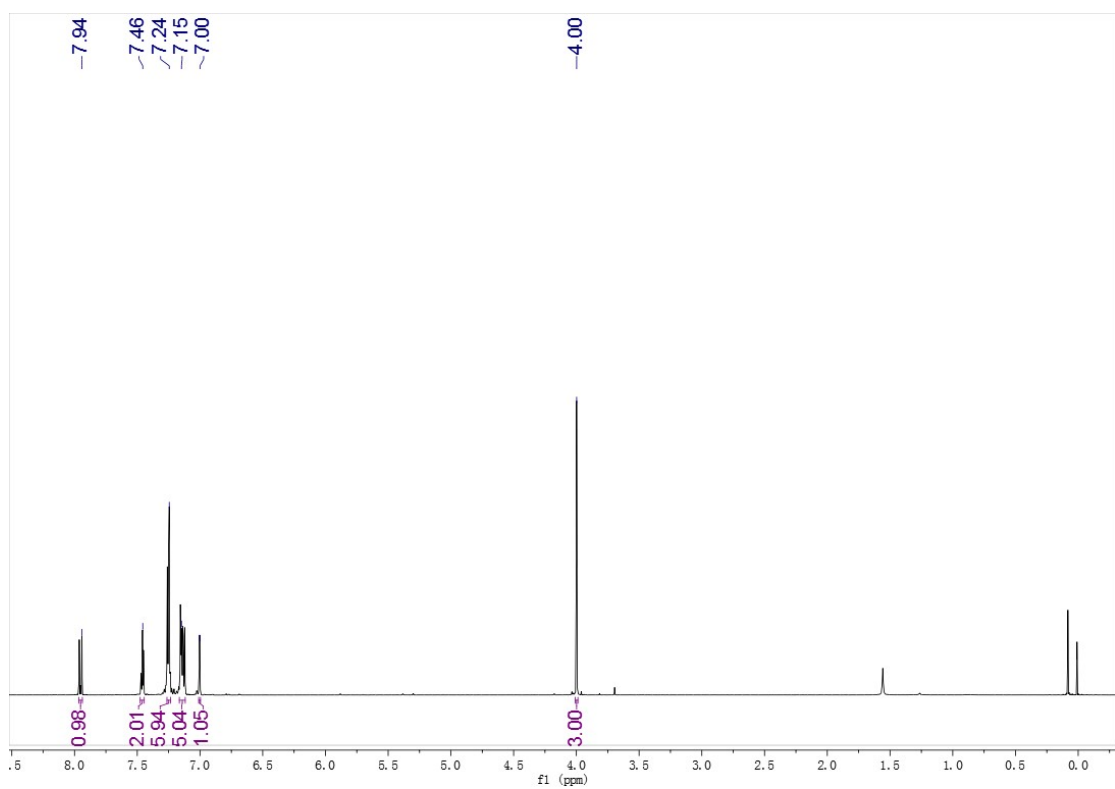


Figure S2. ¹H NMR spectra and ¹³C NMR spectra of EtC6Br.



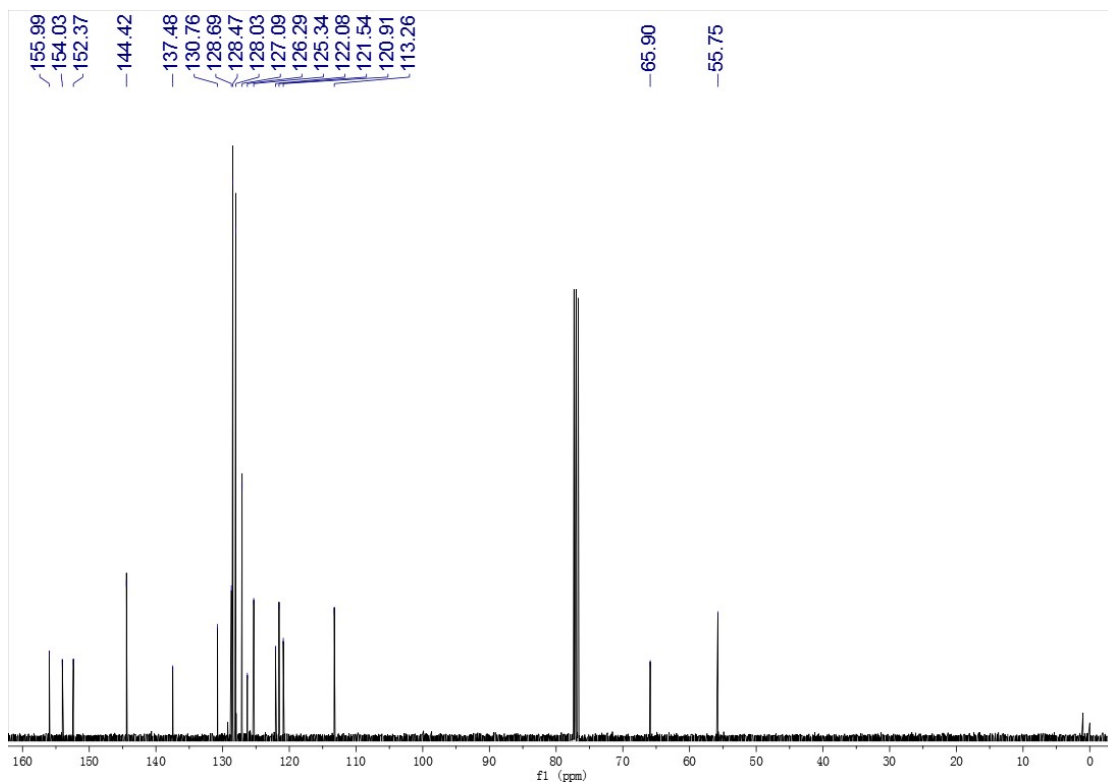
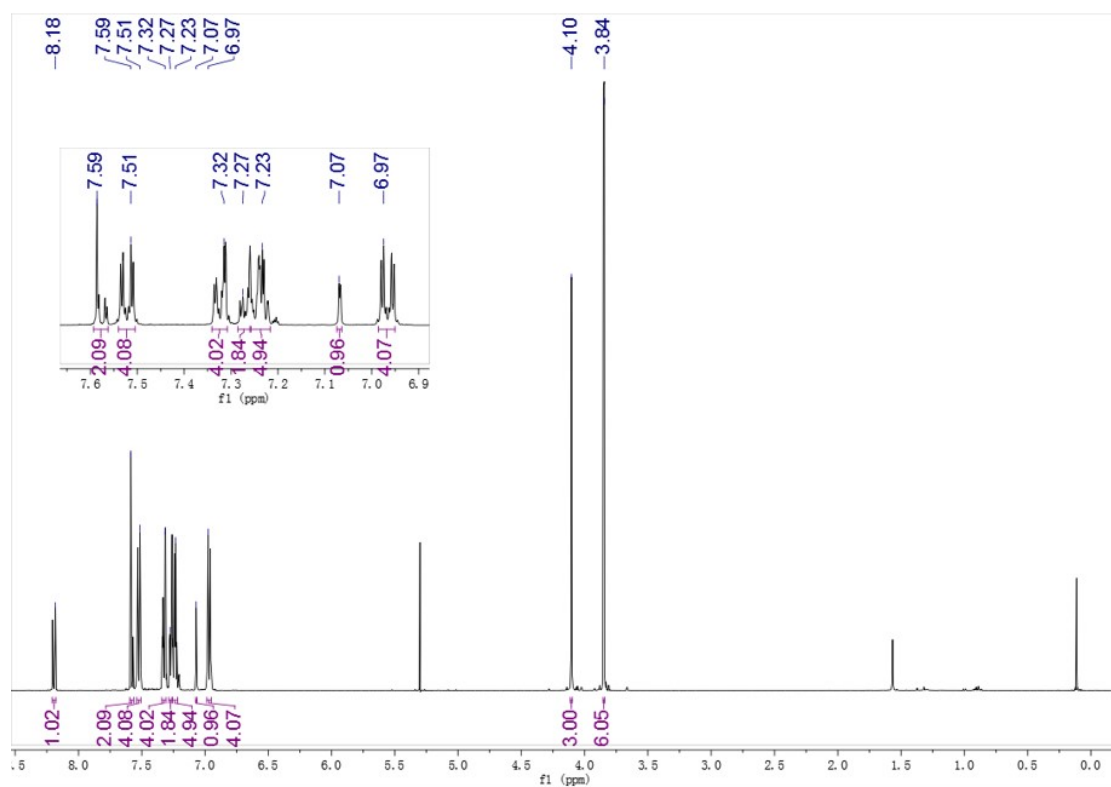


Figure S3. ¹H NMR spectra and ¹³C NMR spectra of MOCH₃.



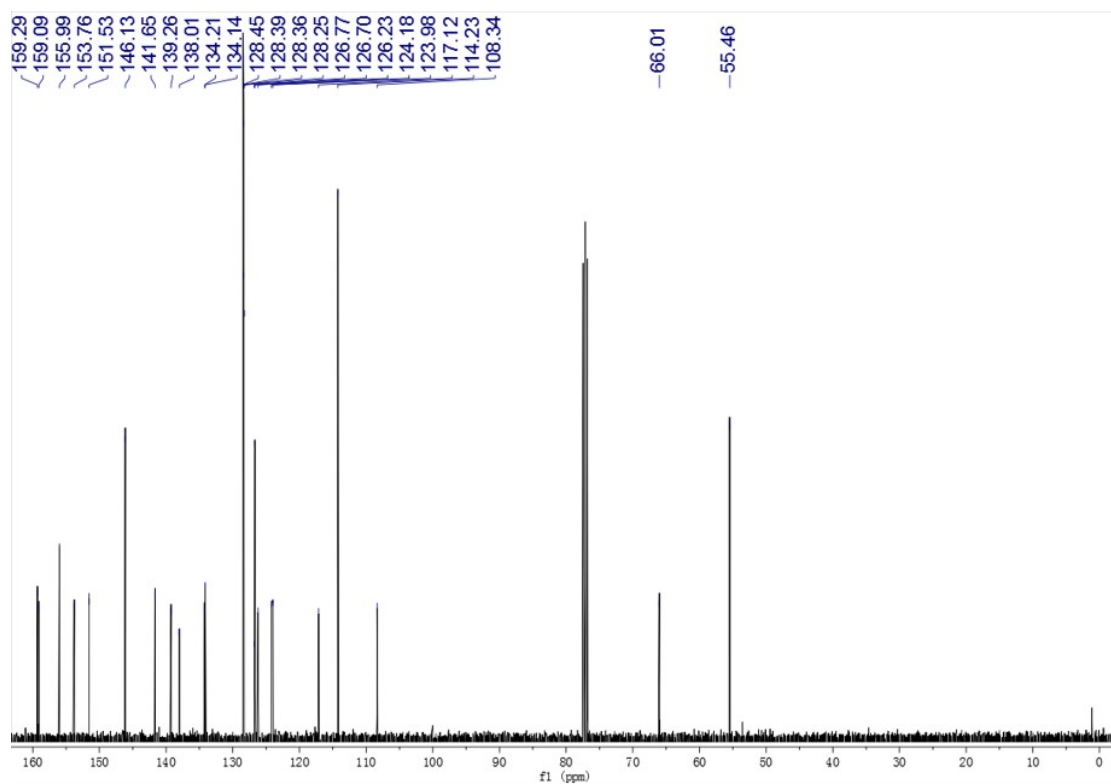
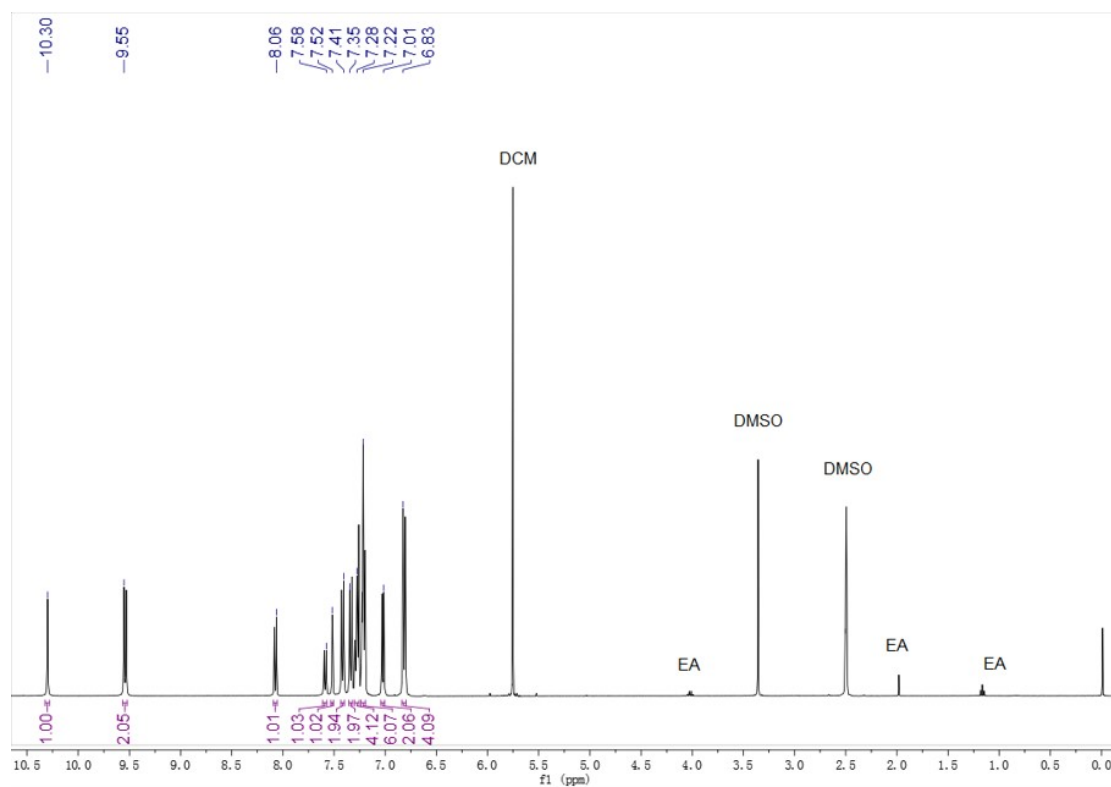


Figure S4. ¹H NMR spectra and ¹³C NMR spectra of F-3OCH₃.



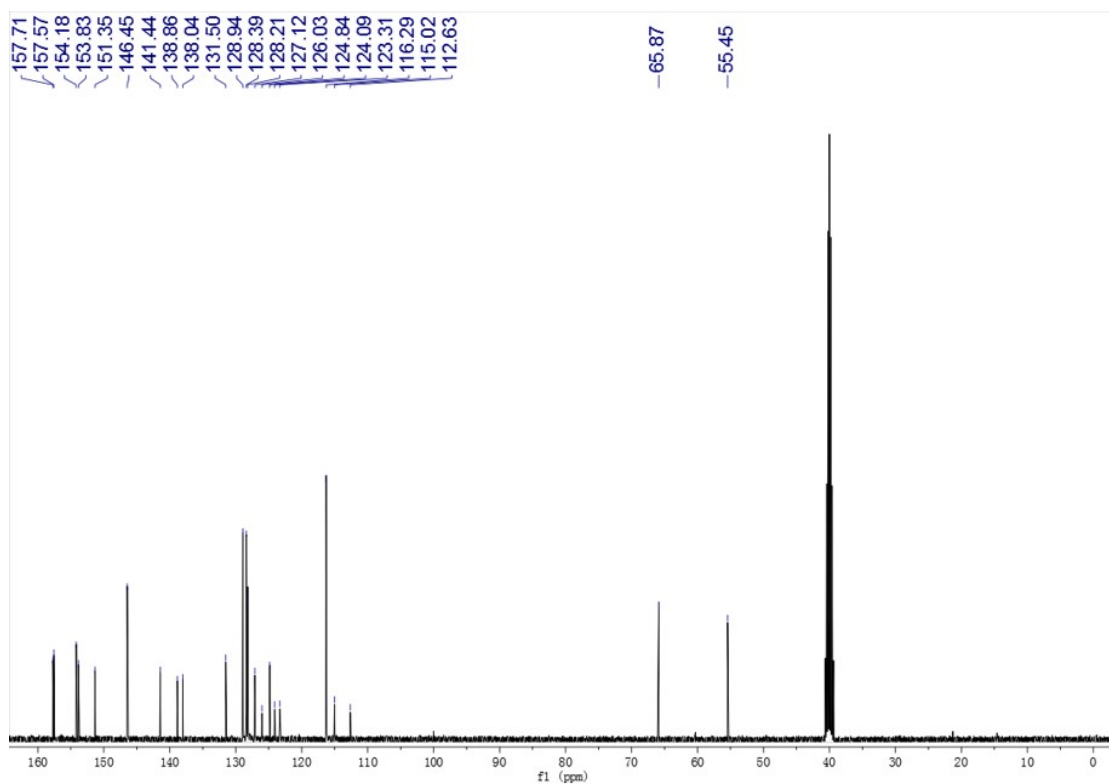
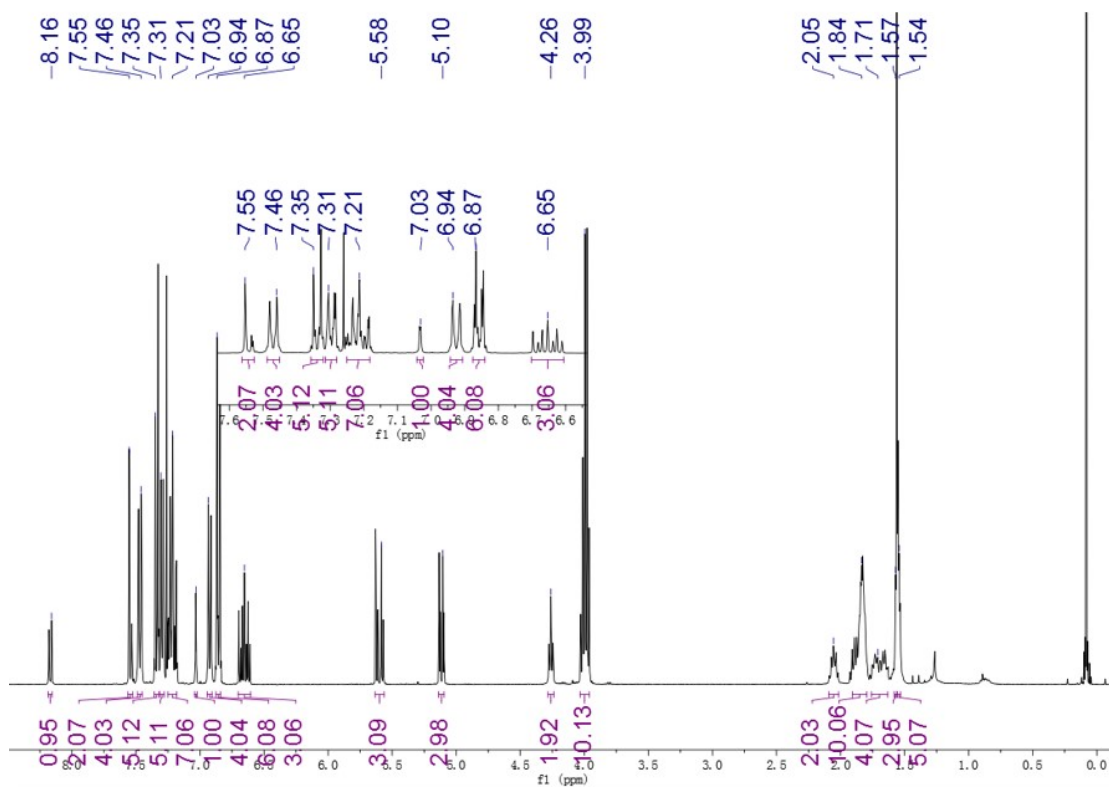


Figure S5. ¹H NMR spectra and ¹³C NMR spectra of F-3OH.



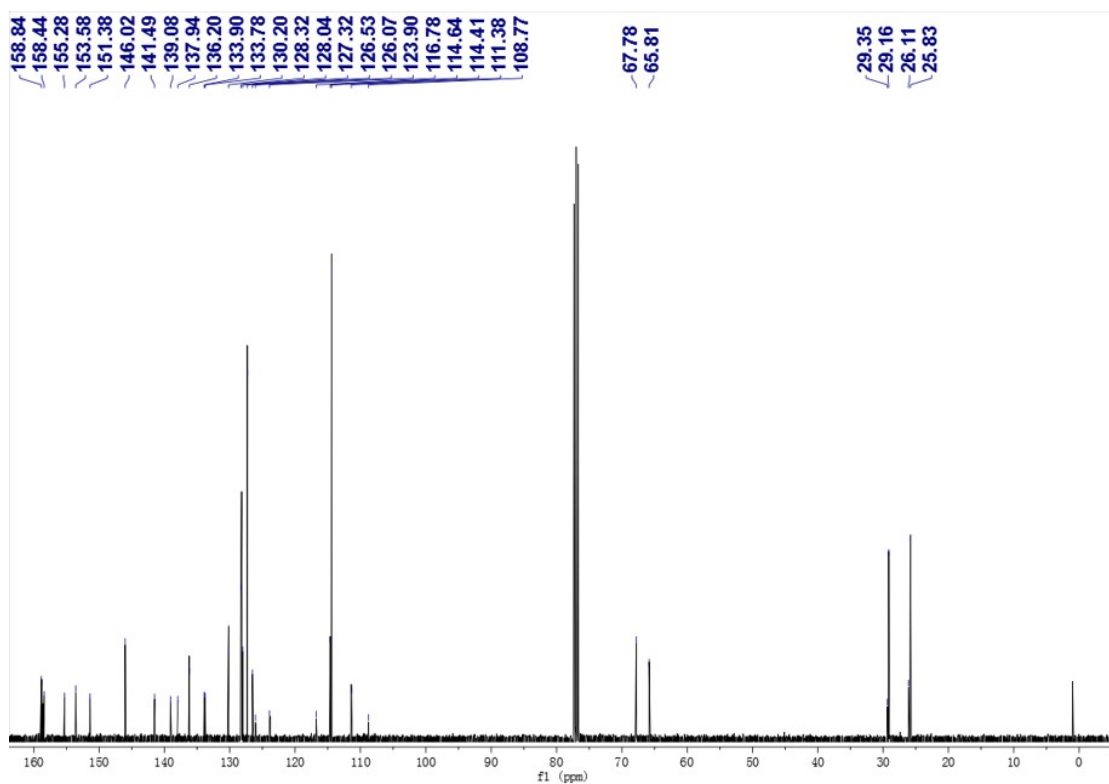
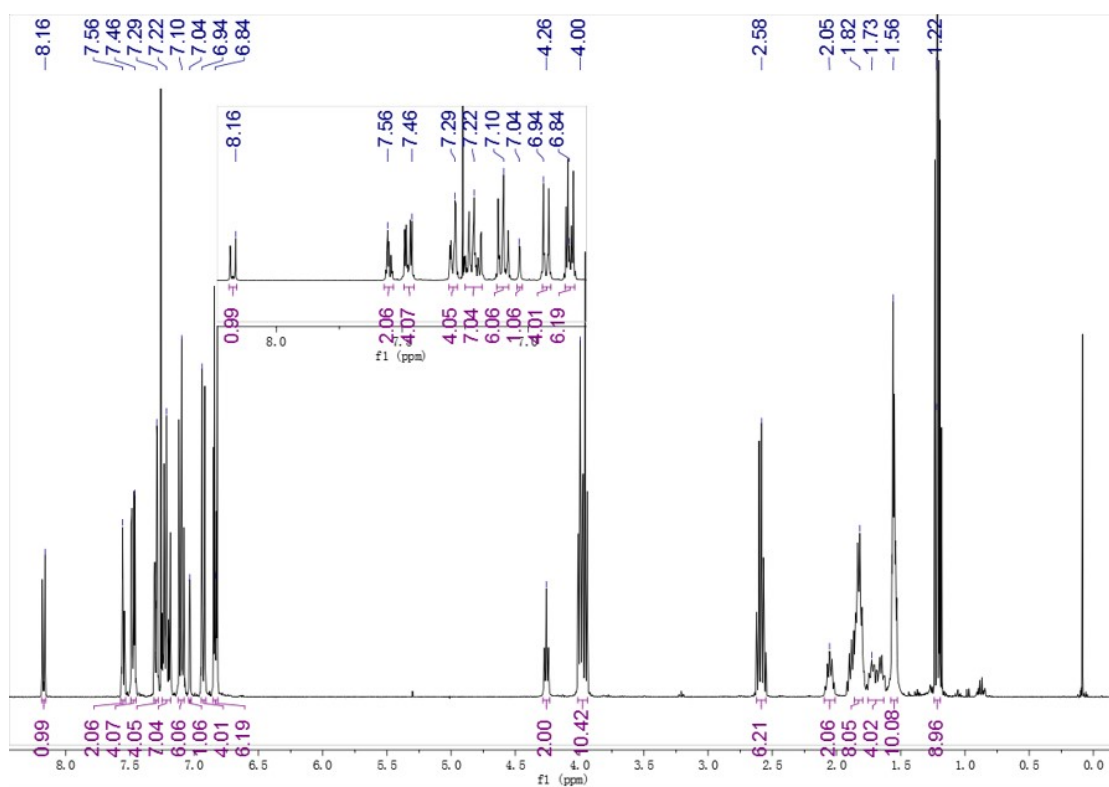


Figure S6. ^1H NMR spectra and ^{13}C NMR spectra of F-3OCm.



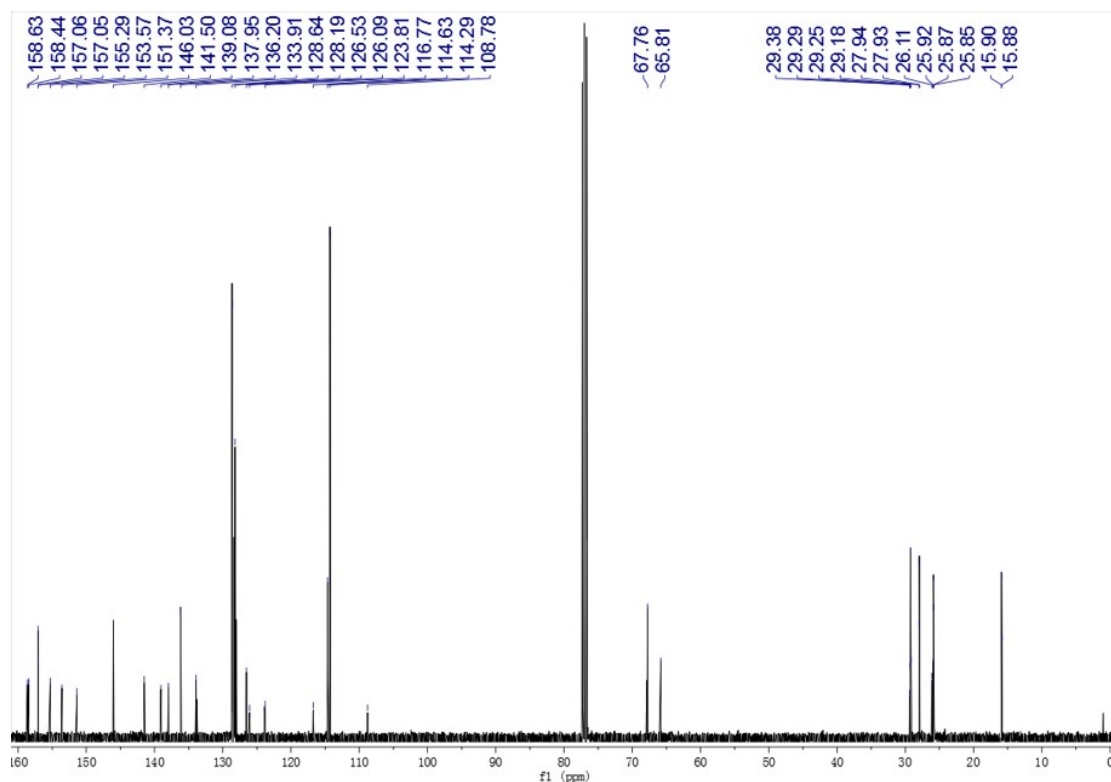


Figure S7. ^1H NMR spectra and ^{13}C NMR spectra of F-3OEt.

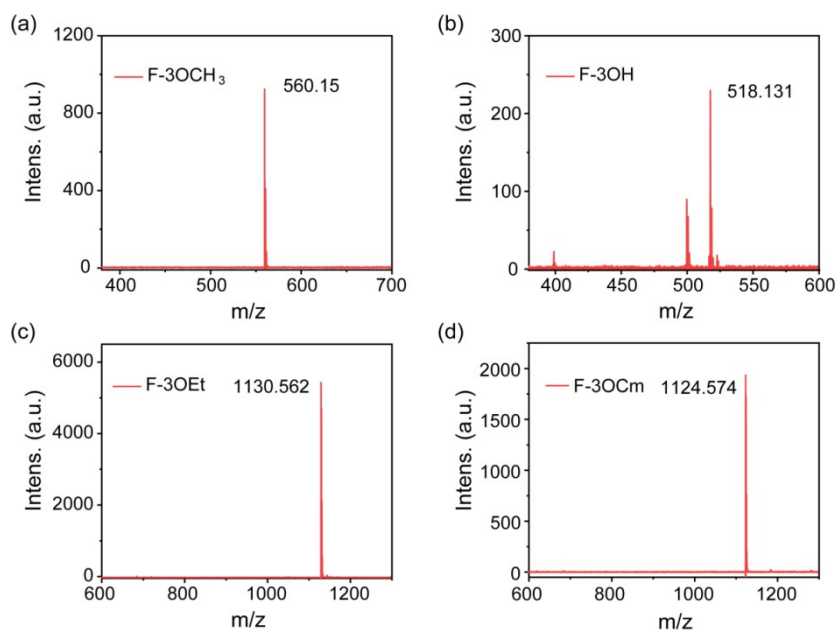


Figure S8. Modi-ToF of intermediate for F-3OCH₃ and F-3OH, and target products for F-3OEt and F-3OCm.

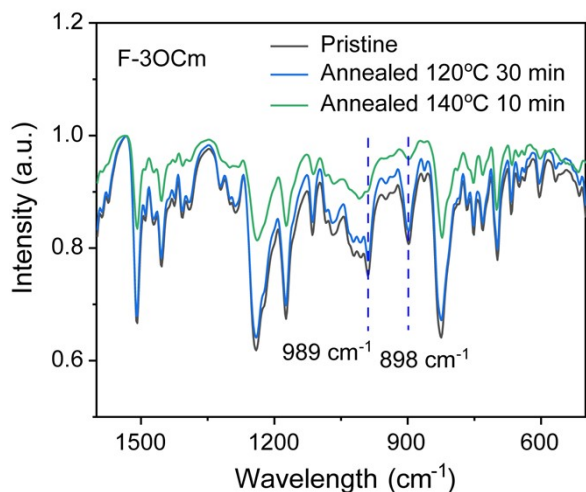


Figure S9. IR curves of F-3OCm pristine powder and drop films that annealed at 120°C for 30 min or 140°C for 10 min.

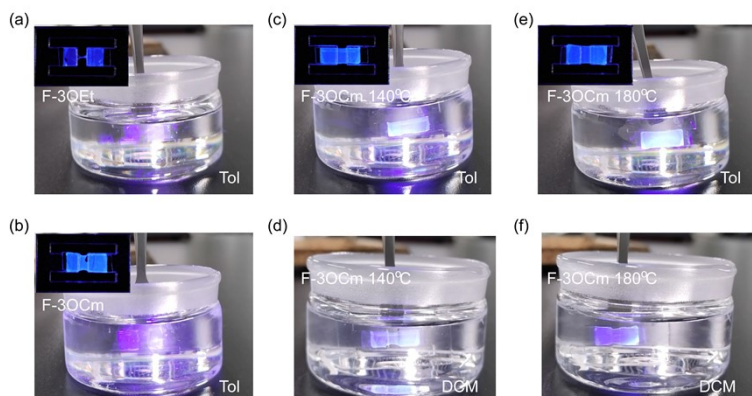


Figure S10. Experiments on solvent-resistance of prepared baseless films treated under different conditions. Experiments on solvent resistance in toluene solvents: (a) F-3OEt pristine film. (b) F-3OCm pristine film. (c) F-3OCm annealed film at 140°C for 10 min. (e) F-3OCm annealed film at 180°C for 10 min. (d, f) The samples for the antisolventability test in dichloromethane solvent were 140°C and 180°C annealed films of F-3OCm which remained intact after soaking in toluene solvent.

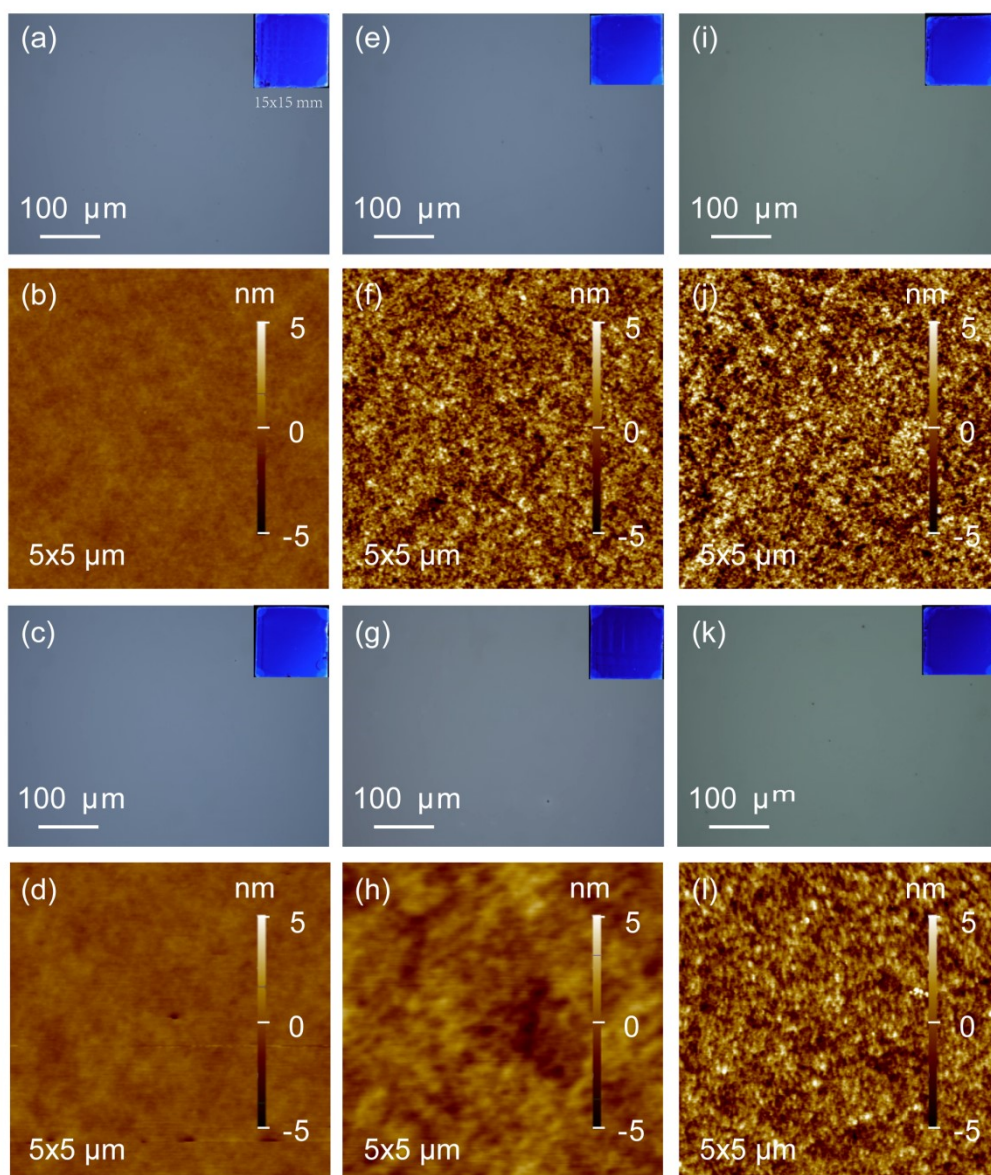


Figure S11. The prepared films were characterized by Nikon microscope and atomic force microscope (AFM). Nikon microscopic images (a) and AFM (b) of the F-3OEt pristine film. Nikon microscopic images (c) and AFM (d) of the F-3OCm pristine film. Nikon microscopic images (e) and AFM (f) of a 140°C annealed film of F-3OCm. Nikon micrograph (g) and AFM (h) of 140°C annealed film of F-3OCm after rinsing with toluene solvent. Nikon microscopic images (i) and AFM (j) of F-3OCm annealed film at 180°C. Nikon microscopic images (k) and AFM (l) of F-3OCm annealed film at 180°C after rinsing with toluene solvent. Annealing time was 10 min. Inset show fluorescent image of the films under 365 nm ultraviolet lamp.

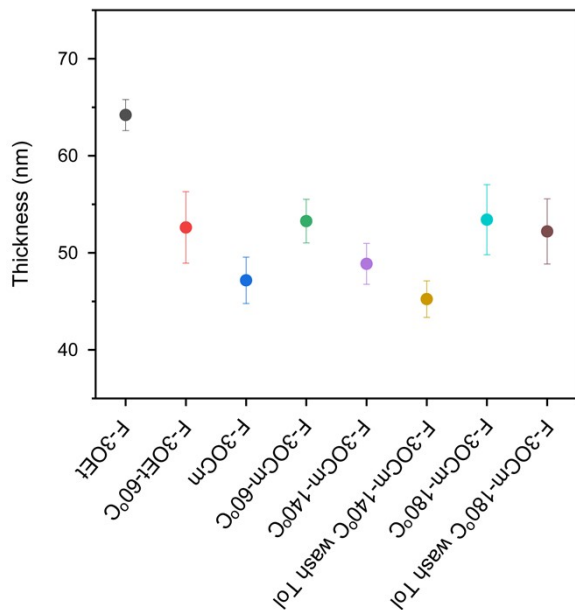


Figure S12. Film thickness of F-3OEt and F-3OCm pristine film, annealed film and toluene solvent rinsed film at different annealing temperatures.

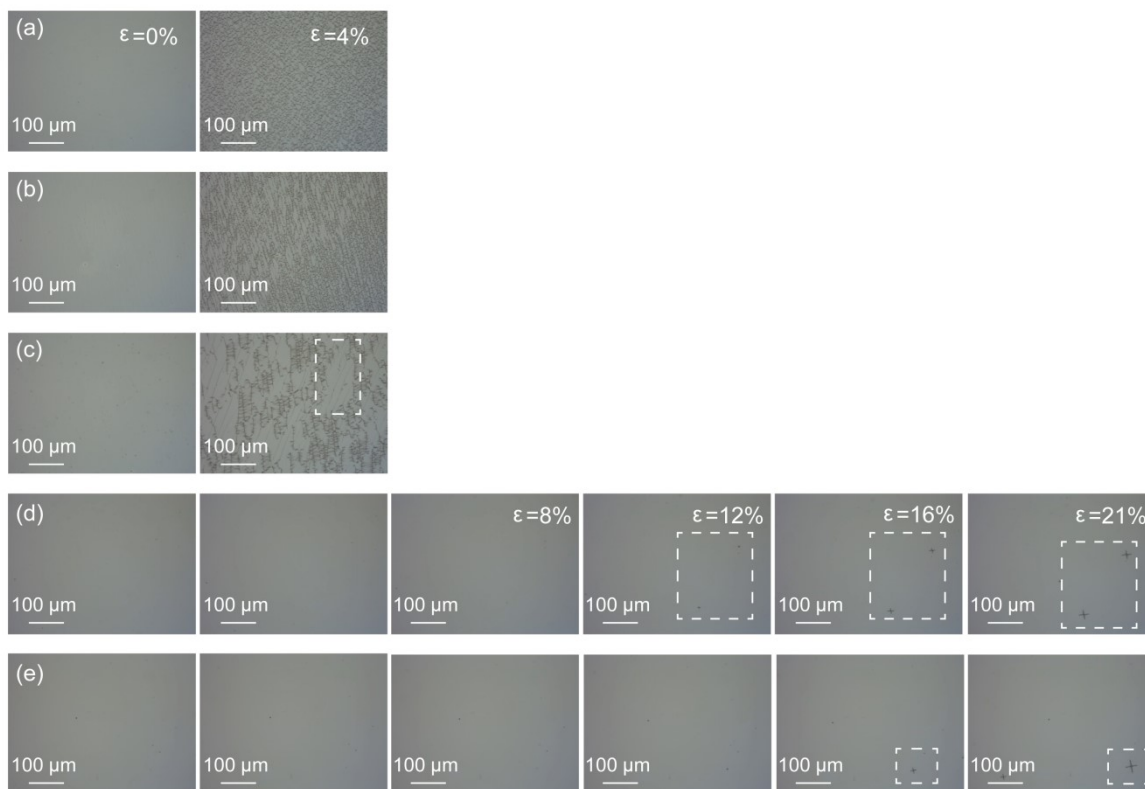


Figure S13. Optical microscope images of F-3OEt annealed 60°C film (a), F-3OCm pristine film (b), F-3OCm annealed 60°C film (c), F-3OCm annealed 140°C film (d) and F-3OCm annealed 180°C film (e) upon applied stress with a stretch rate of 0%, 4%, 8%, 12%, 16% and 21%, respectively.

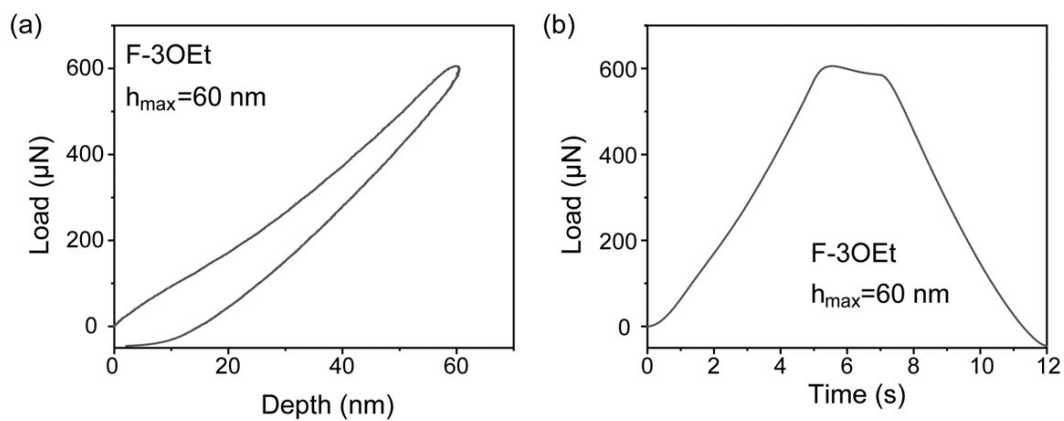


Figure S14. (a) Load-depth curves ($h_{\max} = 60$ nm). (b) Load-time curves (60 nm) of F-3OEt obtained at the constant displacement rate mode.

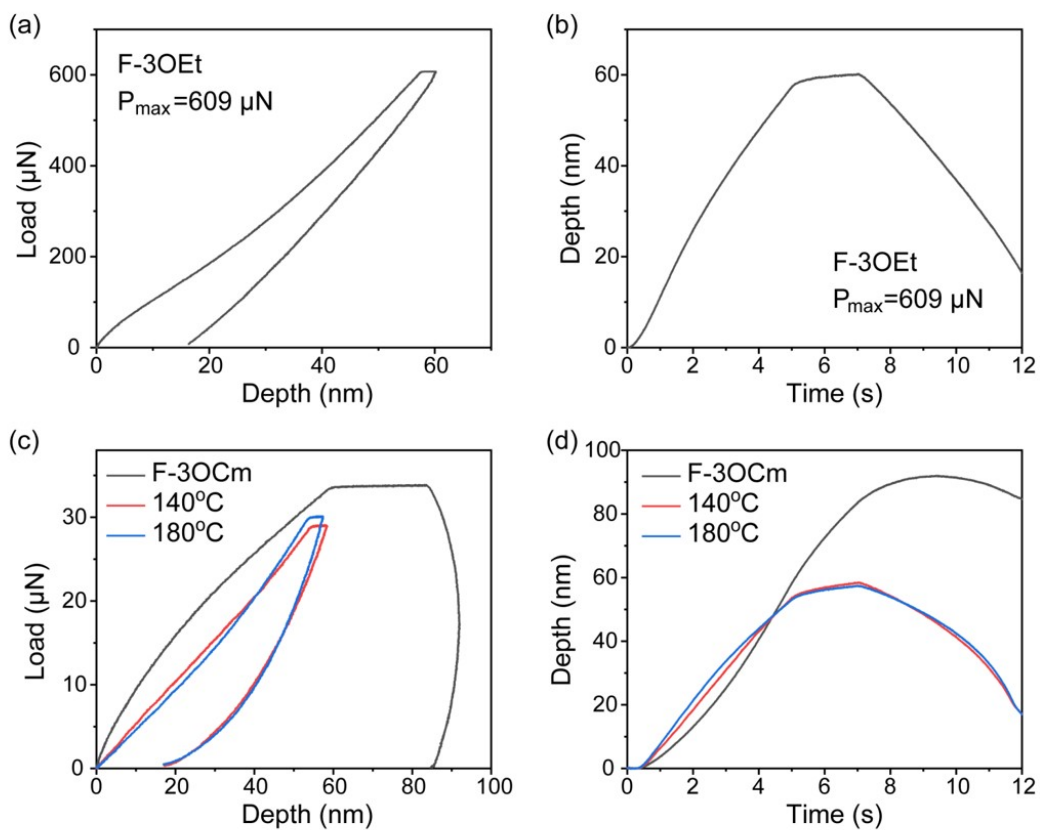
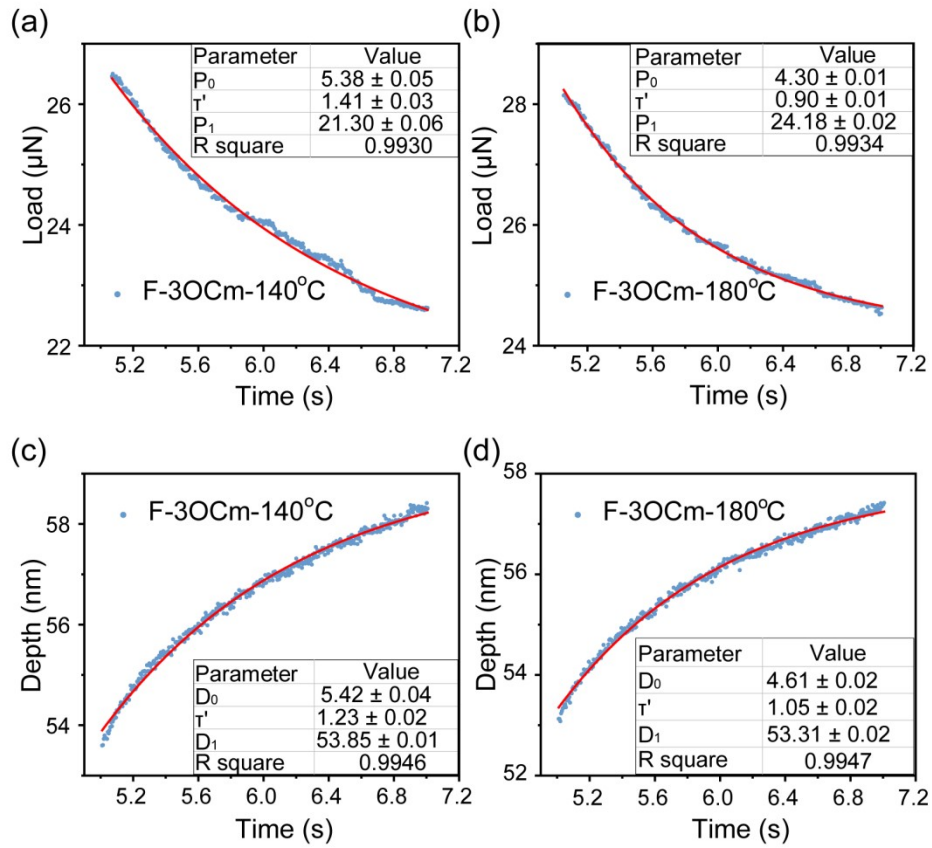


Figure S15. Depth-load curve under constant pressure mode.



Fitting formula of slack under three-parameter model: $P = P_0 e^{-\frac{t-5}{\tau}} + P_1$

Fitting formula of creep under three-parameter model: $D = D_0 \left(1 - e^{-\frac{t-5}{\tau}}\right) + D_1$

Figure S16. Three-parameter model fitting curve of F-3OCm annealed 140°C film (a) and F-3OCm annealed 180°C film (b) measured at constant displacement rate. Three-parameter model fitting curve of F-3OCm annealed 140°C film (c) and F-3OCm annealed 180°C film (d) measured at constant load rate.

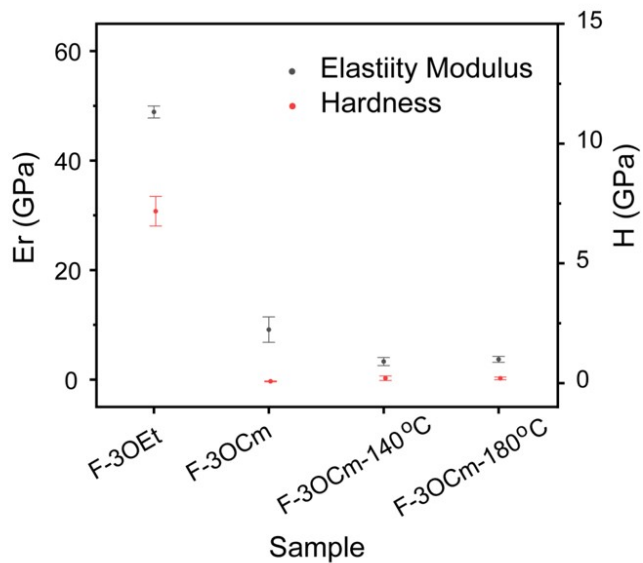


Figure S17. Young's modulus and hardness curves of the F-3OEt pristine, F-3OCm, F-3OCm annealed 140°C film and F-3OCm annealed 180°C film measured at the constant displacement rate mode.

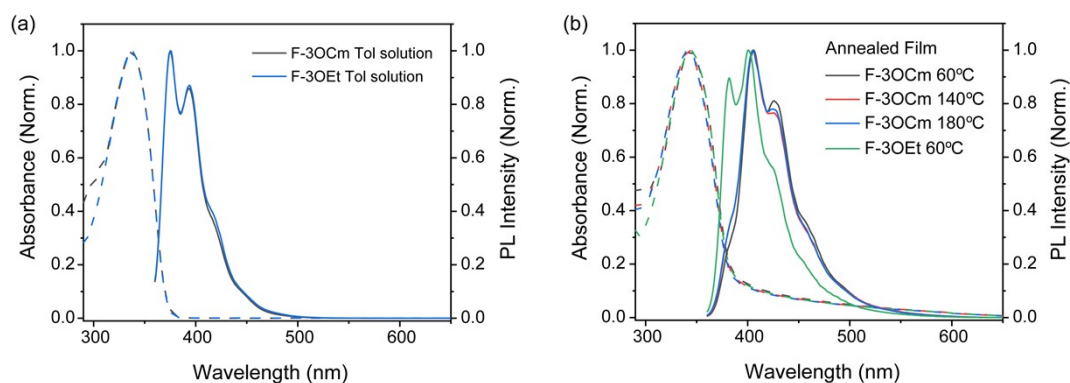


Figure S18. (a) UV-*vis* absorption and PL spectra of F-3OCm and F-3OEt for toluene solution. (b) UV-*vis* absorption and PL spectra of annealed films.

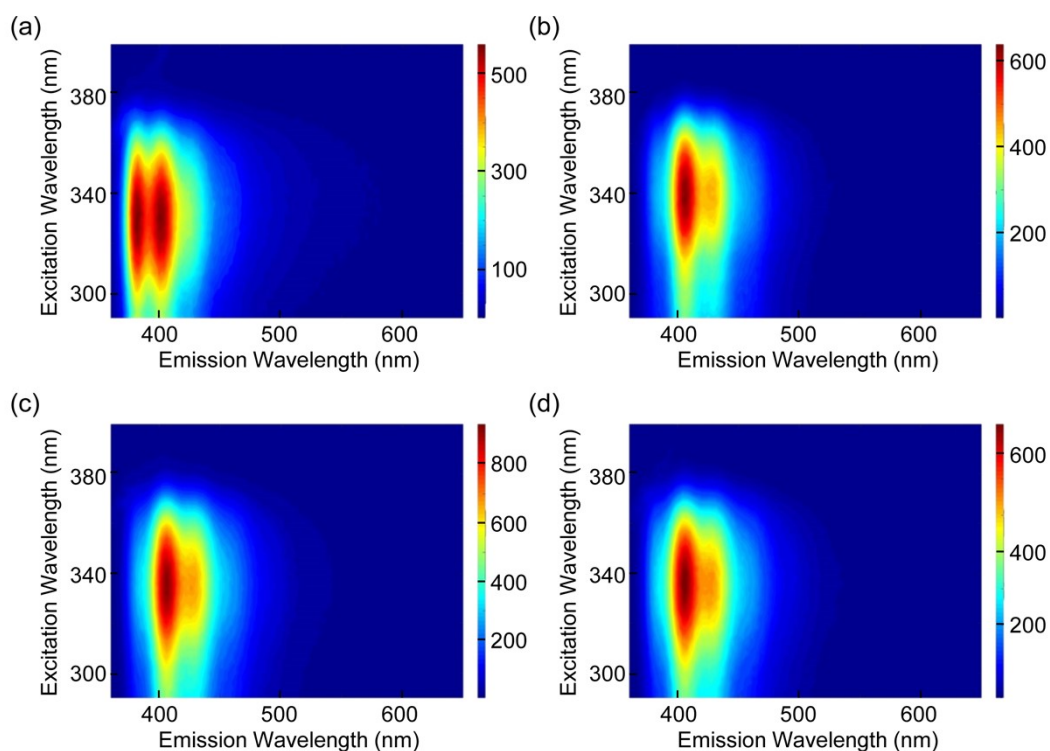


Figure S19. 3D PL mapping of F-3OEt annealed 60°C film (a), F-3OCm annealed 60°C film (b), F-3OCm annealed 140°C film (c) and F-3OCm annealed 180°C film (d).

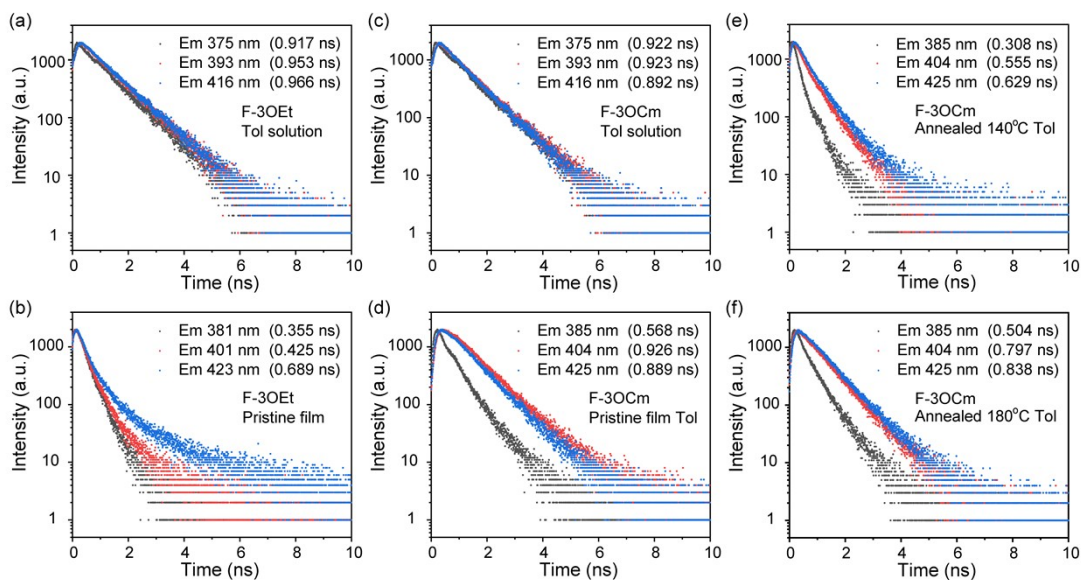


Figure S20. Decay time spectra of F-3OEt in toluene solution (a), F-3OEt pristine film (b), F-3OCm in toluene solution (c), F-3OCm pristine film (d), F-3OCm annealed 140°C film (e) F-3OCm annealed 180°C film. The emission wavelength measured corresponds to the position of fluorescence emission peak under different states.

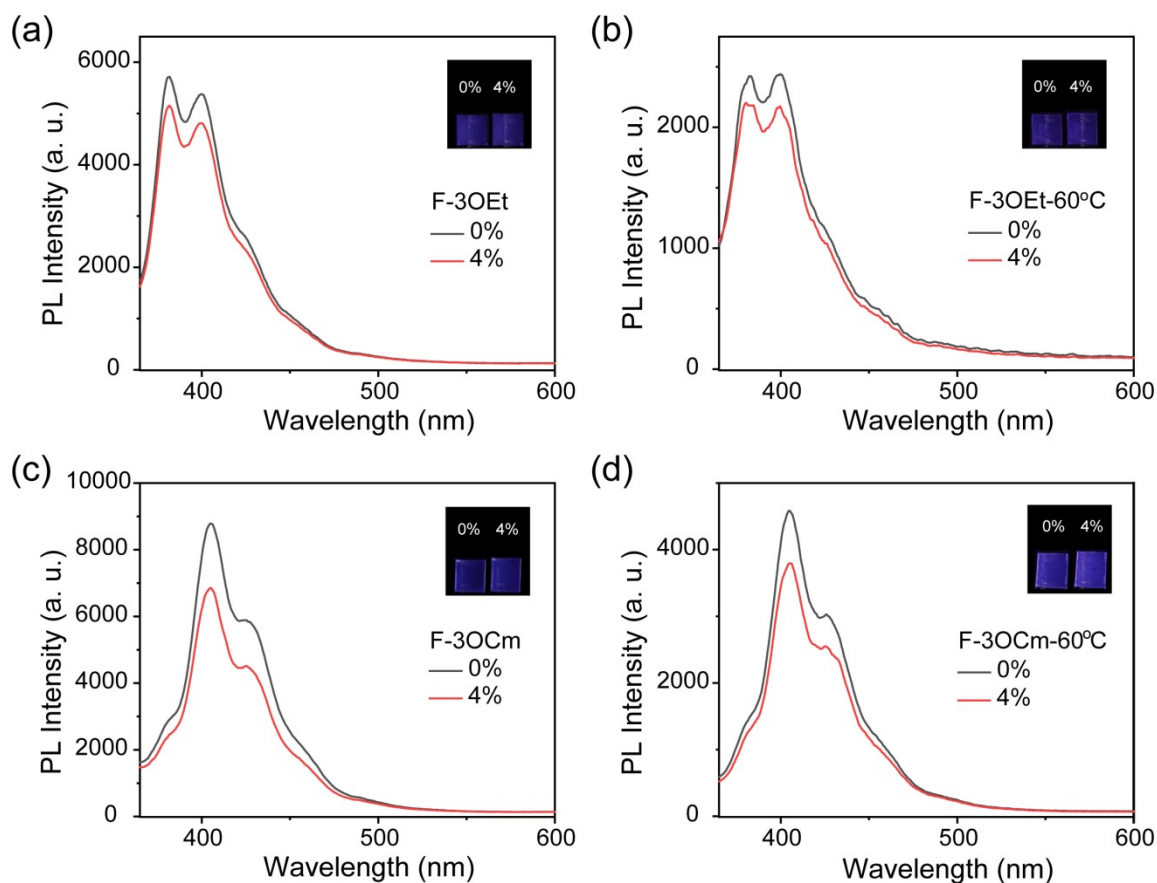


Figure S21. Tensile spectrum and state of F-3OEt and F-3OCm for pristine films and 60°C annealed films.

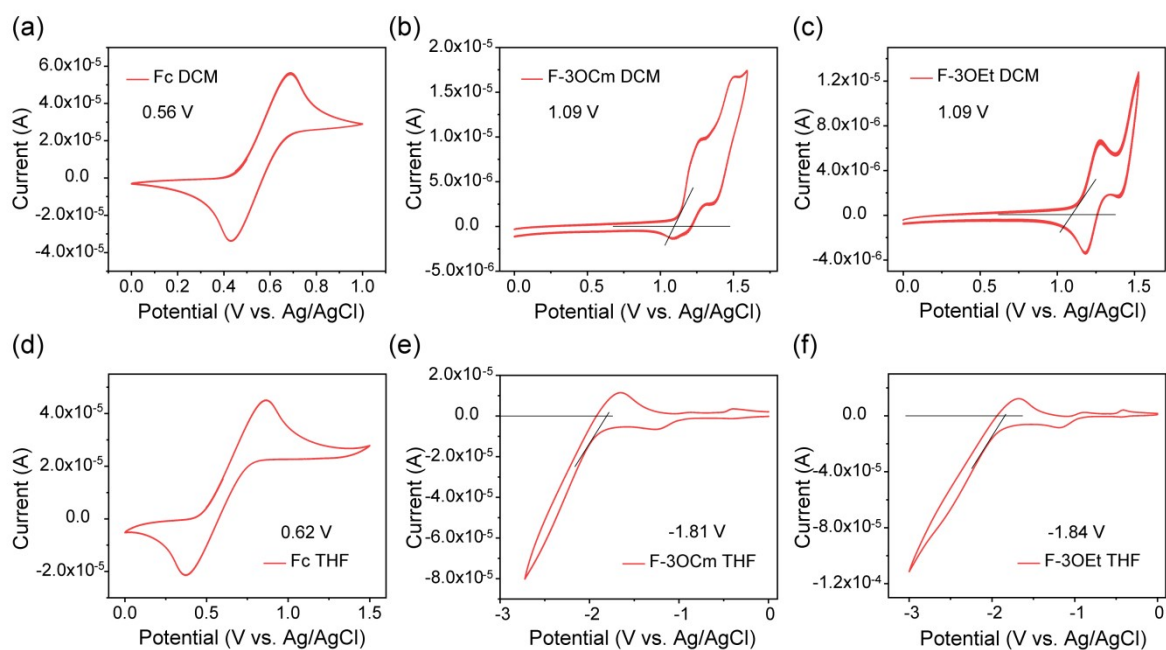


Figure S22. CV curves of F-3OEt and F-3OCm pristine films.

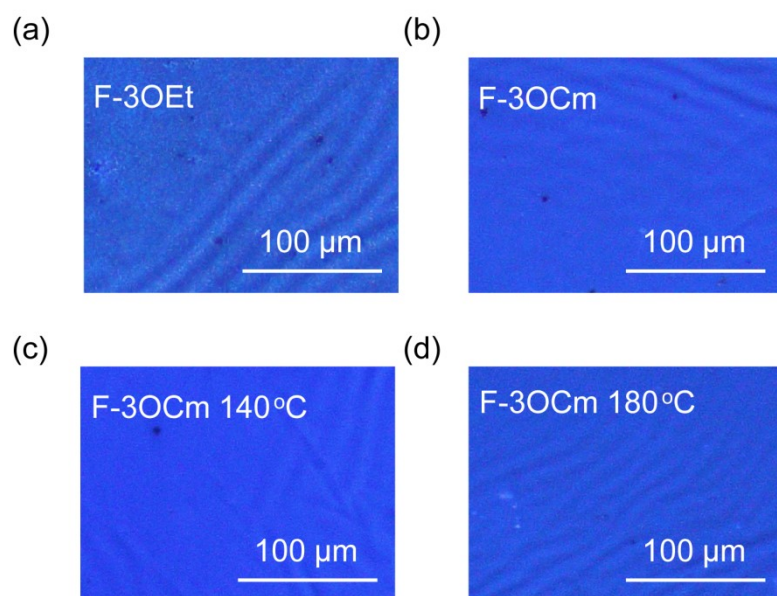


Figure S23. Fluorescence microscopic images of the interior to PLEDs devices before fatigue.

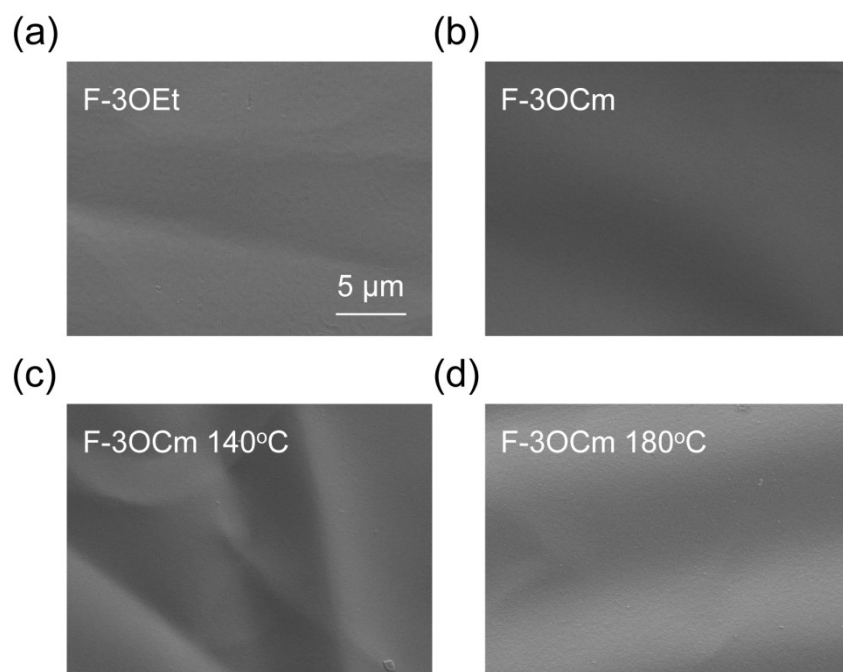


Figure S24. SEM images of the interior to PLEDs devices before fatigue.

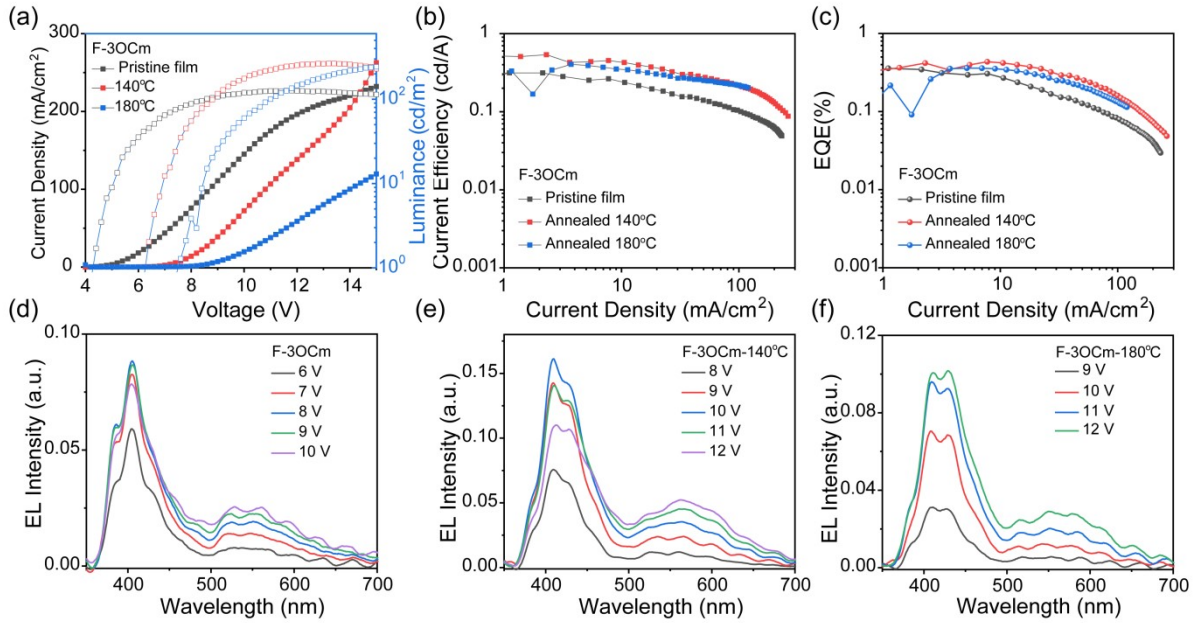


Figure S25. Performance of F-3OCm-based OLEDs. (a) Current density–luminance–voltage characteristics of the devices. (b) Current efficiency and (c) external quantum efficiencies (EQE) versus current density curves of the devices. EL spectra of F-3OCm pristine film (d), F-3OCm annealed 140°C film (e) and F-3OCm annealed 180°C film-based devices with increasing applied voltage from 8 to 12 V.

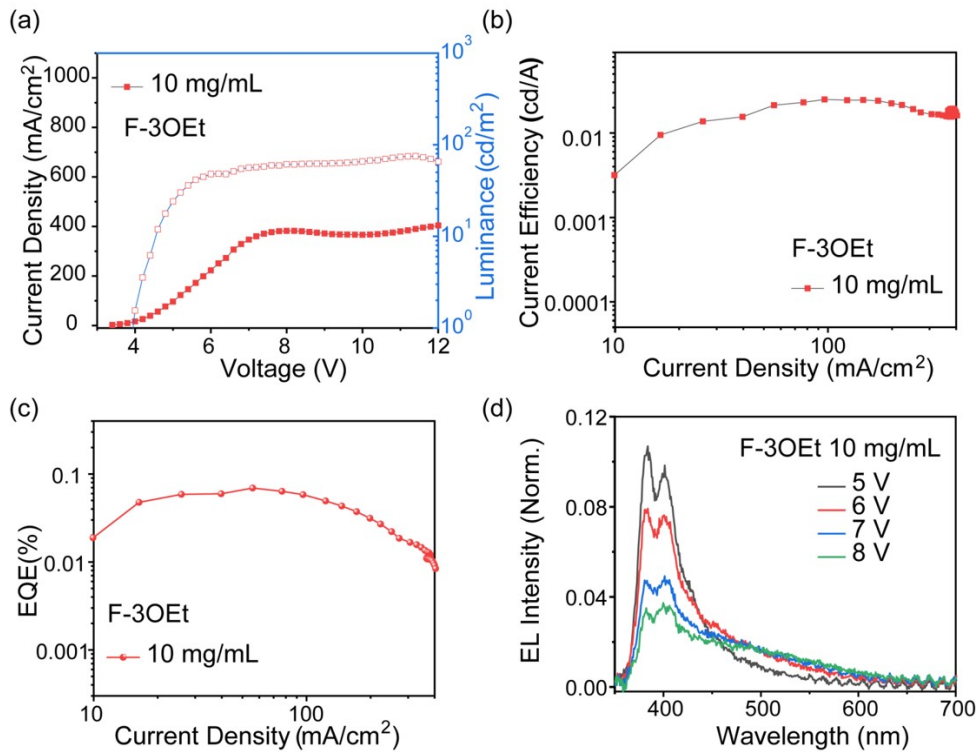


Figure S26. Performance of F-3OEt-based OLEDs. (a) Current density–luminance–voltage characteristics of the devices. (b) Current efficiency and (c) external quantum efficiencies (EQE) versus current density curves of the devices. (d) EL spectra of F-3OEt-based devices with increasing applied voltage from 5 to 8 V.

with increasing applied voltage from 5 to 8 V.

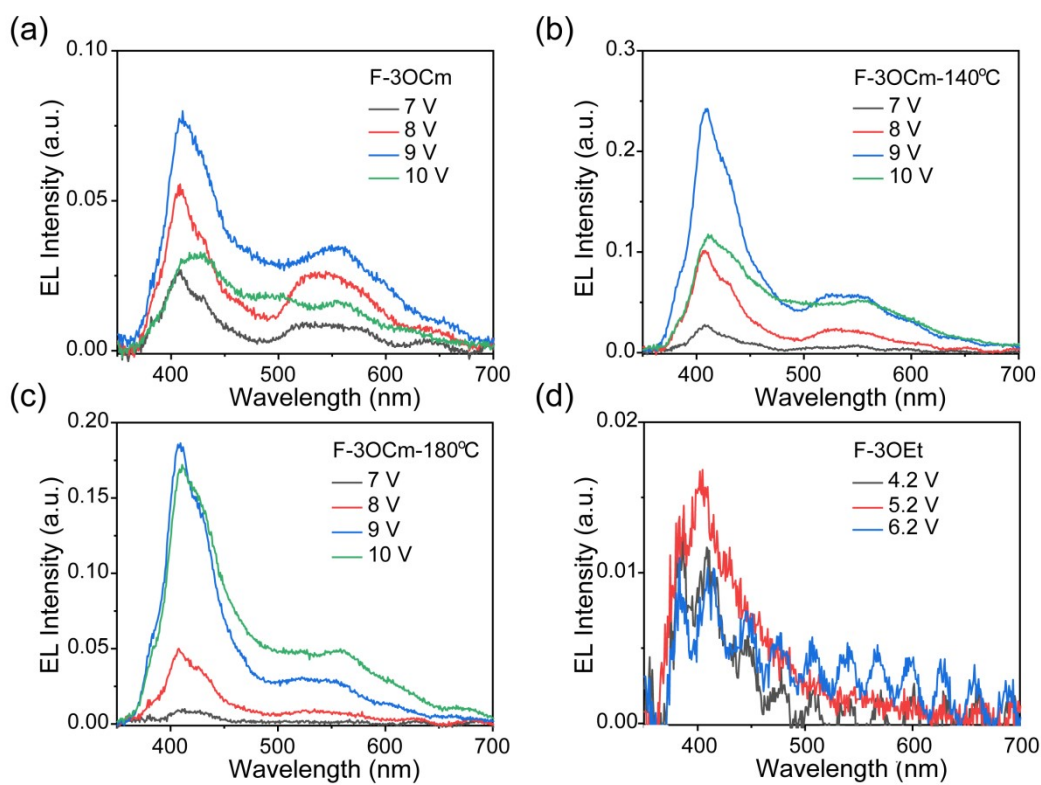


Figure S27. EL spectra of F-3OCm pristine film, F-3OCm annealed 140°C film, F-3OCm annealed 180°C film and F-3OEt pristine film based flexible devices.

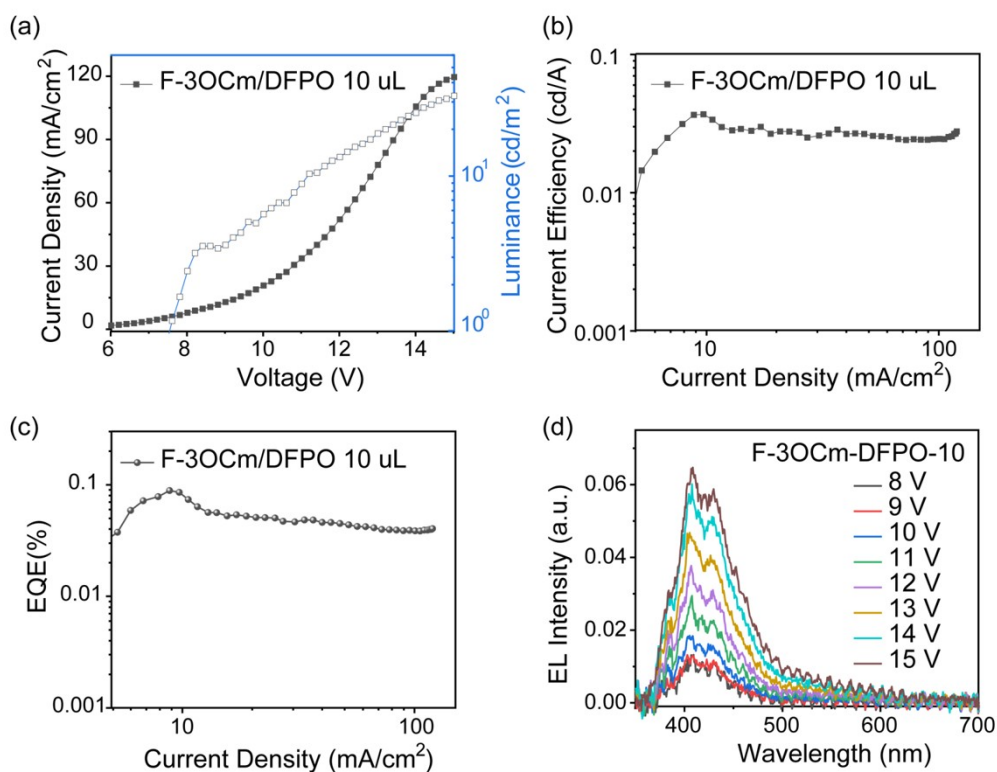


Figure S28. Performance of F-3OCm-based OLEDs with free radical catcher DFPO. (a) Current density–luminance–voltage characteristics of the devices. (b) Current efficiency and (c) external quantum efficiencies (EQE) versus current density curves of the devices. (d) EL spectra of the devices with increasing applied voltage from 8 to 15 V.

Movie S1. Solvent resistance experiment of F-3OEt (solvent: toluene).

Movie S2. Solvent resistance experiment of F-3OCm (solvent: toluene).

Movie S3. Solvent resistance experiment of F-3OCm annealed 140°C film (solvent: toluene).

Movie S4. Solvent resistance experiment of F-3OCm annealed 180°C film (solvent: toluene).

Movie S5. Flexible device based on F-3OEt.

Movie S6. Flexible device based on F-3OCm.

Movie S7. Flexible device based on F-3OCm annealed 140°C film.

Movie S8. Flexible device based on F-3OCm annealed 180°C film.

Table S1. The Young's modulus and hardness of samples.

Sample	Constant Displacement Rate ^a		Constant Load Rate ^b	
	E _r (GPa)	H (GPa)	E _r (GPa)	H (GPa)

F-3OEt	48.65	6.95	50.12	7.36
F-3OCm	8.49	0.08	-8.46	0.10
F-3OCm 140°C	3.00	0.16	3.41	0.24
F-3OCm 180°C	3.46	0.17	4.13	0.24

Table S2. The mechanical parameters of samples obtained from three-parameter models.

Sample	P_0 (μN)	P_1 (μN)	τ (s)	D_0 (nm)	D_1' (nm)	τ' (s)	$P_1:P_0$	$D_1':D_0$
F-3OCm 140°C	5.38±0.06	21.30±0.07	1.41±0.04	5.43±0.04	36.71±0.02	1.23±0.02	3.96	6.76
F-3OCm 180°C	4.30±0.01	24.19±0.01	0.90±0.01	4.62±0.03	36.28±0.02	1.05±0.02	5.63	7.85

Table S3. Summary of the data of F-3OCm and F-3OEt.

	PLQY (%)	K_r (ns^{-1})	K_{nr} (ns^{-1})	HOMO (eV)	LUMO (eV)	E_g (eV)
F-3OCm	57.6	0.62	0.46	-5.33	-2.37	3.31
F-3OCm 140°C	46.9	0.84	0.96	/	/	/
F-3OCm-180°C	39.9	0.50	0.75	/	/	/
F-3OEt	29.5	0.69	1.66	-5.33	-2.34	3.31

Table S4. Devices performance summary.

Sample	Glass substrate				PET substrate			
	V_{on} (V)	Luminance (cd/m^2)	C.E. (cd/A)	EQE (%)	V_{on} (V)	Luminance (cd/m^2)	C.E. (cd/A)	EQE (%)
F-3OCm	4.4	126.5	0.315	0.358	5.2	162.0	0.091	0.052
F-3OCm-140°C	6.4	264.9	0.537	0.434	5.6	296.2	0.262	0.211
F-3OCm-180°C	7.6	242.8	0.405	0.359	6.2	242.4	0.175	0.175
F-3OEt	4.0	75.2	0.025	0.069	4.2	17.8	0.007	0.012