Supporting Information

Novel amphiphilic corannulene additive for moisture-resistant perovskite solar cells

Bening Tirta Muhammad,[abc] Viktor Barát,[d] Koh Teck Ming,[a] Xihu Wu,[c] Abhijith Surendran,[c] Natalia Yantara,[a] Annalisa Bruno,[a] Andrew C. Grimsdale,[e] Mihaiela C. Stuparu*[de] and Wei Lin Leong*[ac]

[a] *Energy Research Institute@NTU (ERI@N), Research Techno Plaza, X-Frontier Block, Level 5, 50 Nanyang Drive, 637553, Singapore*

[b] *Interdisciplinary Graduate Programme, Nanyang Technological University, 639798, Singapore*

[c] *School of Electrical and Electronic Engineering, Nanyang Technological University, 639798, Singapore*

[d] *Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore*

[e] *School of Materials Science and Engineering, Nanyang Technological University, 639798, Singapore*

Experimental Section

Cor-TEG Synthesis

All chemicals and solvents were obtained commercially and used as received. *m*-CPBA was used as 77% technical grade. Column chromatography was carried out on silica gel 40−63 mesh. Reactions were monitored by thin-layer chromatography (TLC) on silica gel-coated aluminium plates (60 F254, Merck) and visualized with UV light (λ = 254 and 365 nm). Purity of the reported compounds was established by comparing the integrals of the peaks of the desired compounds to the ones arising from impurities. ^{1}H NMR spectra were recorded at 400 MHz JEOL ECA instruments (and the corresponding frequencies for ^{13}C) in $CDCl_3$ unless otherwise noted. Chemical shifts are given in ppm and coupling constants in Hz ($CDCl_3$ ^{1}H: 7.26 ppm, ^{13}C: 77.23 ppm). High-resolution mass spectra (HRMS) were recorded by using Waters Q-Tof Premier spectrometer in ESI+ mode with TOF mass analyser.

Corannulene-pentakis-(triethyleneglycol-monomethyl ether)sulfide[1] (11 mg, 0.01 mmol) and *m*-CPBA (67 mg, 0.3 mmol) was dissolved in DCM (3 mL) and stirred at room temperature for 65 hours. The reaction was quenched with aqueous $NaHSO_3$ and washed twice with aqueous Na_2CO_3. The organic layer was dried on anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by silica gel chromatography using $CHCl_3$:MeOH 98:2 as the eluent. An orange oil was obtained: 10.4 mg (0.008 mmol), 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 5H), 4.05 – 3.98 (m, 10H), 3.75 – 3.68 (m, 10H), 3.51 – 3.44 (m, 10H), 3.37 – 3.25 (m, 30H), 3.24 (s, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.40, 137.14, 133.99, 126.44, 71.84, 70.75, 70.49, 70.30, 64.65, 59.10, 58.07. HRMS calcd. for $C_{55}H_{81}O_{25}S_5$ (MH^+) 1301.3671, found 1301.3593 (ESI+). HRMS calcd. for $C_{55}H_{80}O_{25}S_5Na$ (MNa^+) 1323.3490, found 1323.3500Synthetic scheme, ^{1}H and ^{13}C NMR spectra can be seen in Fig. S7, S8, and S9, respectively.

Device Fabrication

Fluorine-doped tin oxide (FTO)-coated glass substrates were cleaned by ultrasonication in 2% (v/v) Hellmanex III aqueous solution, deionised water, and isopropanol for 15 minutes for each step. FTO substrates were UV-Ozone treated for at least 25 minutes before spin-coating 0.05 M $SnCl_2.2H_2O$ solution in 95:5 ethanol:water solvent mixture at 5000 rpm, followed by annealing at 180 ^oC for 1 hour to form SnO_2 electron transport layer (ETL). The triple cation perovskite was prepared by mixing 18 mg CsI, 25.4 methylammonium bromide (MABr), 84.7 mg $PbBr_2$, 198.5 mg formamidinium iodide (FAI), and 585 mg PbI_2 in a mixture of 0.8 mL *N,N*-dimethyl formamide (DMF) and 0.2 mL dimethyl sulfoxide. For Cor-TEG additive, respective volume of 1 mg/mL TEG-branched corannulene derivative (M_w = 1310 g/mol) solution in DMF was added into perovskite solution to obtain 4, 10, and 30 µg/mL solutions. The precursor mixtures were stirred for at least 1 hour to homogenize. SnO_2 ETL was UV-Ozone treated for 20 min before spin-coating perovskite layer in Ar-filled glovebox. The perovskite precursor was deposited by two-step spinning, 1000 rpm for 10 s and 5000 rpm for 20 s. In the second step, 0.1 mL anhydrous chlorobenzene (Sigma-Aldrich) was dispensed as anti-solvent treatment. The forming film was then annealed at 100 ^oC for 1 hour. Hole transport layer was made by spin-coating spiro-OMeTAD solution (72 mg/mL chlorobenzene) doped with 28.5 µL *tert*-butylpyridine and 17.5 µL lithium bistrifluoromethanesulfonimidate (520 mg/mL acetonitrile). Lastly, 80 nm Au was deposited by thermal evaporation as top electrode. All chemicals were purchased from Sigma-Aldrich without further purification, except MABr and FAI were obtained from Dyesol and lead halide salts from TCI.

Device Characterization

X-ray diffraction measurement was carried out by a D8 ADVANCE Bruker X-ray diffractometer with Cu Kα radiation of λ = 1.54 Å. *J*-V characteristics were measured under one-sun AM 1.5G (100 mW/cm^2) with metal mask to define active area of 0.09 cm^2 using Keithley 2612 as source meter, measured in the reverse scanning direction (from V_{oc} to J_{sc}). Shimadzu UV-3600 and HORIBA FluoroMax-4 were used to acquire absorbance and photoluminescence spectra, respectively. TRPL measurement was conducted using a Picoquant PicoHarp 300 time-correlated single photon counting (TCSPC) setup. The samples were excited at 405 nm with pulsed laser emitting diode at 40 MHz repetition rate. The full width half maximum of the setup's respond function is about 50 ps. Top-view of perovskite layer and cross-sectional image of the devices were analyzed by field emission scanning electron microscope (FESEM) JEOL JSM-7600F. Attenuated total reflection (ATR) FTIR spectroscopy was carried out by JASCO FT/IR-6700 with resolution 4 cm^{-1}, scanning from 400 to 4000 cm^{-1}. Photocurrent decay profiles were extracted using Nova Chrono method with Autolab PGSTAT302N in which an exponential decay fitting was applied to the obtained photocurrent signals. Lastly, maximum power points were recorded using Autolab PGSTAT302N under one-sun equivalent light intensity from MAX-303 Asahi Spectra Xenon light source.

Supplementary Figures

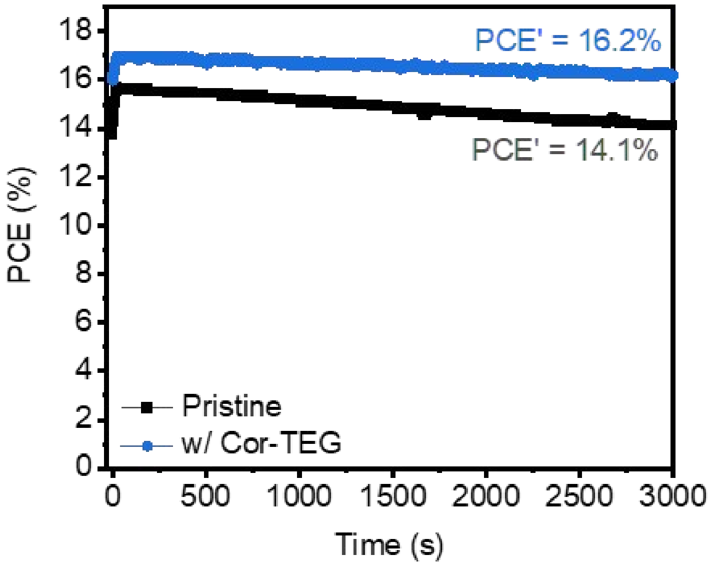


Fig. S1 Maximum power point tracking done in argon atmosphere for pristine and Cor-TEG modified devices. PCE' notation refers to final PCE after 3000 s tracking at fixed bias voltage.

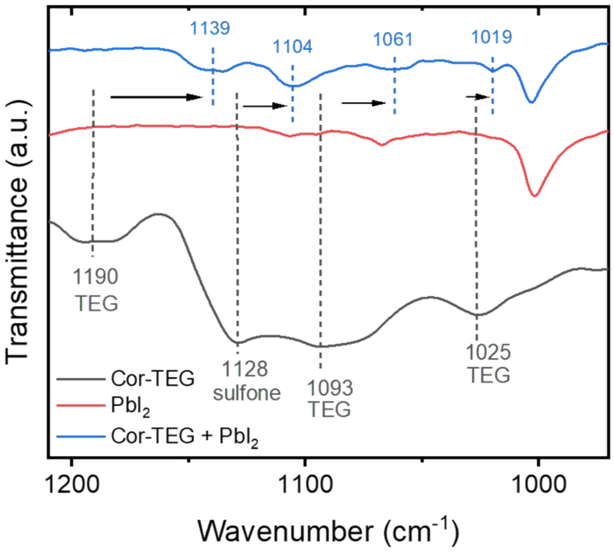


Fig. S2 FTIR spectrum in the region of interest comparing Cor-TEG molecule, PbI_2 powder, and PbI_2/Cor-TEG mixture powder. The peaks referred to sulfone and triethyleneglycol functional groups of Cor-TEG are red-shifted after mixing with PbI_2. For instances, the S=O and C-O bond stretching peaks shift from 1128 to 1104 cm^{-1} and 1025 to 1019 cm^{-1}, respectively.

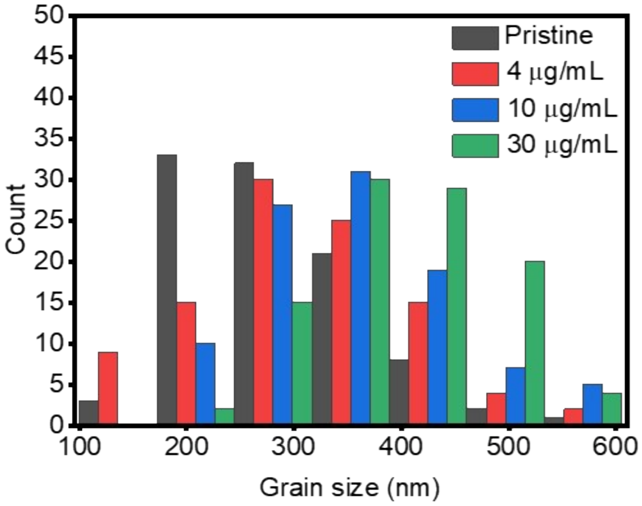


Fig. S3 Grain size distribution (taken from 100 random measurements) with average grain sizes of 281 nm, 316 nm, 358 nm, and 399 nm for perovskite films with Cor-TEG contents of 0 (pristine), 4, 10, and 30 μg/mL perovskite precursor.

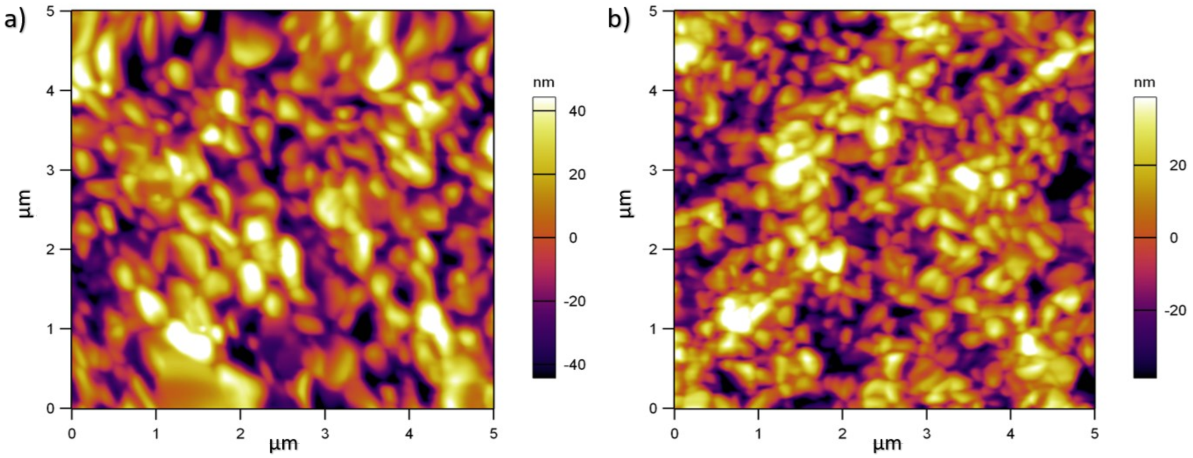


Fig. S4 Atomic-force microscopy images for a) pristine and b) Cor-TEG treated perovskite films with root-mean square roughness of 22.0 and 18.7 nm, respectively.

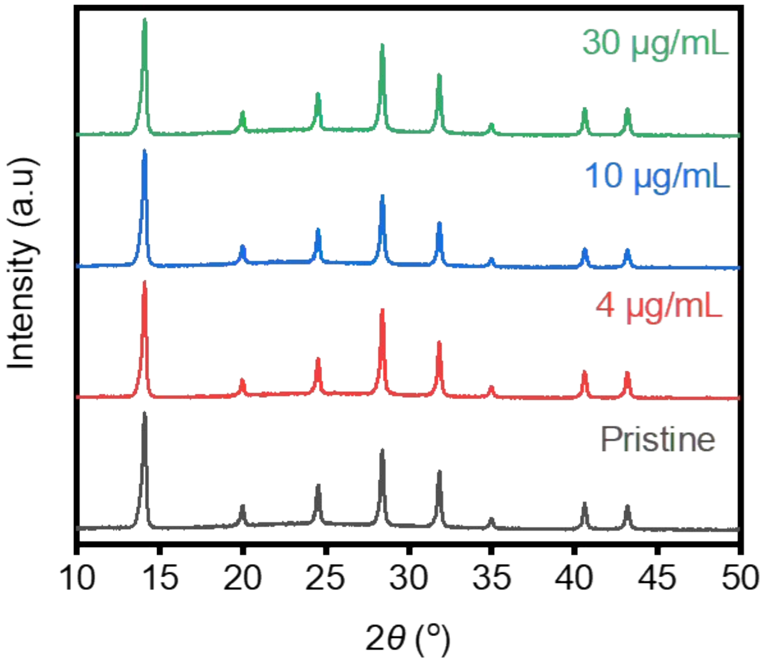


Fig. S5 X-ray diffraction spectra of pristine and treated perovskite films with 4, 10, and 30 μg/mL Cor-TEG additive.

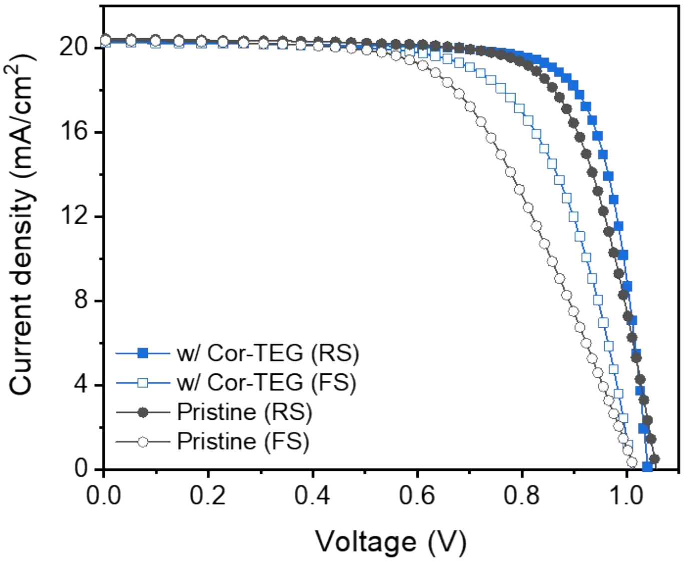


Fig. S6 *J*-V curve comparison between pristine and modified devices in the reverse scan (RS) and forward scan (FS) directions.

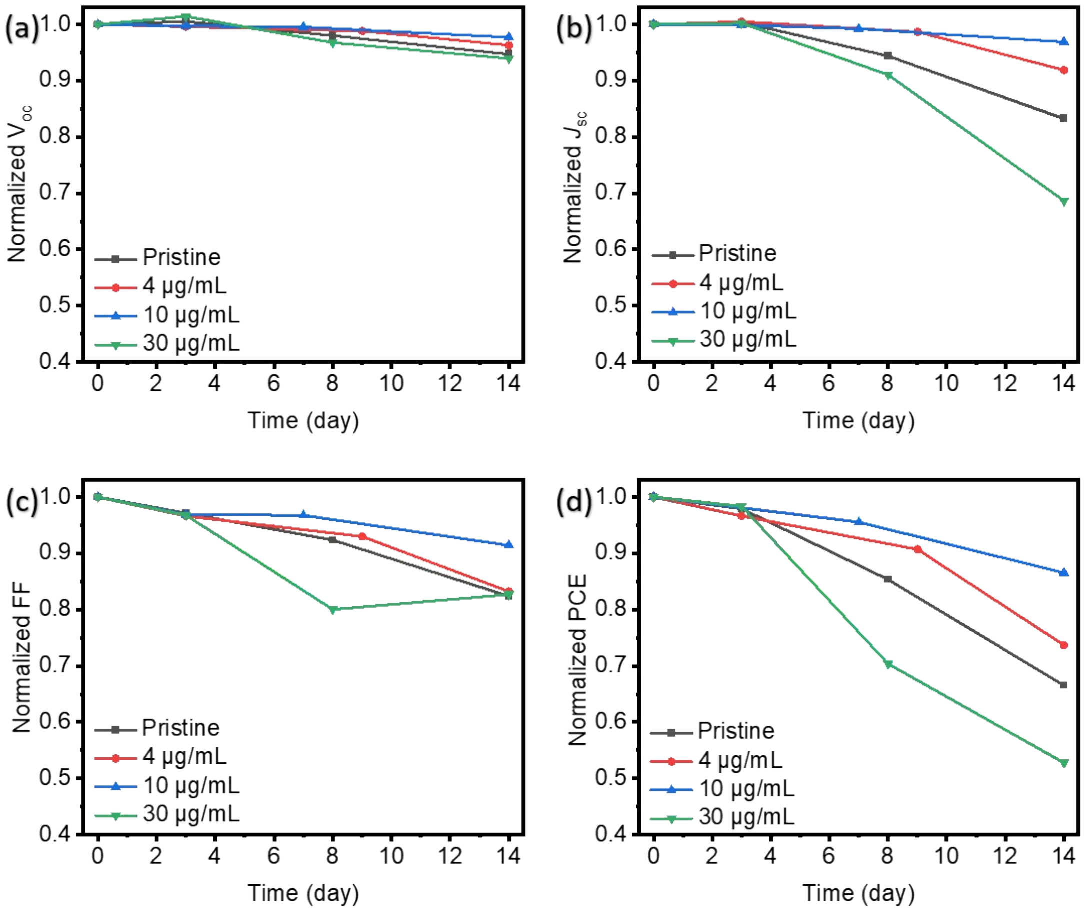


Fig. S7 Photovoltaic parameters for pristine and Cor-TEG treated devices over 2-week course of high humidity exposure (RH=70%).

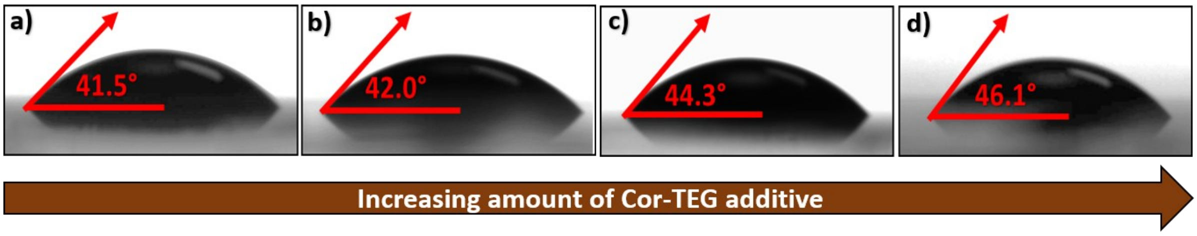


Fig. S8 Water droplet contact angle measurements for a) pristine and b-d) treated perovskite films with 4, 10, and 30 μg/mL Cor-TEG additive, respectively.

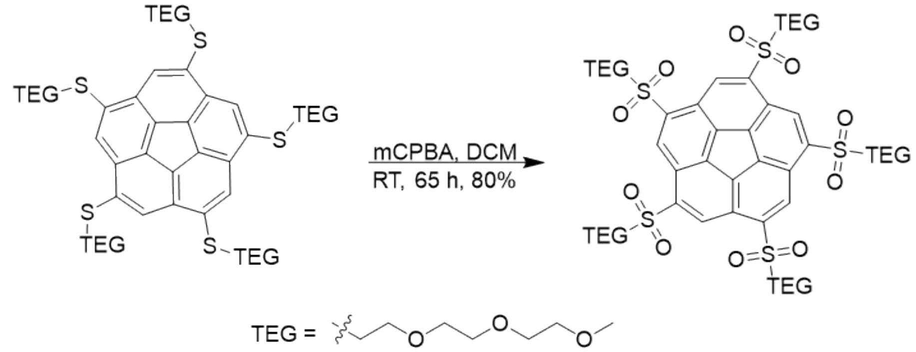
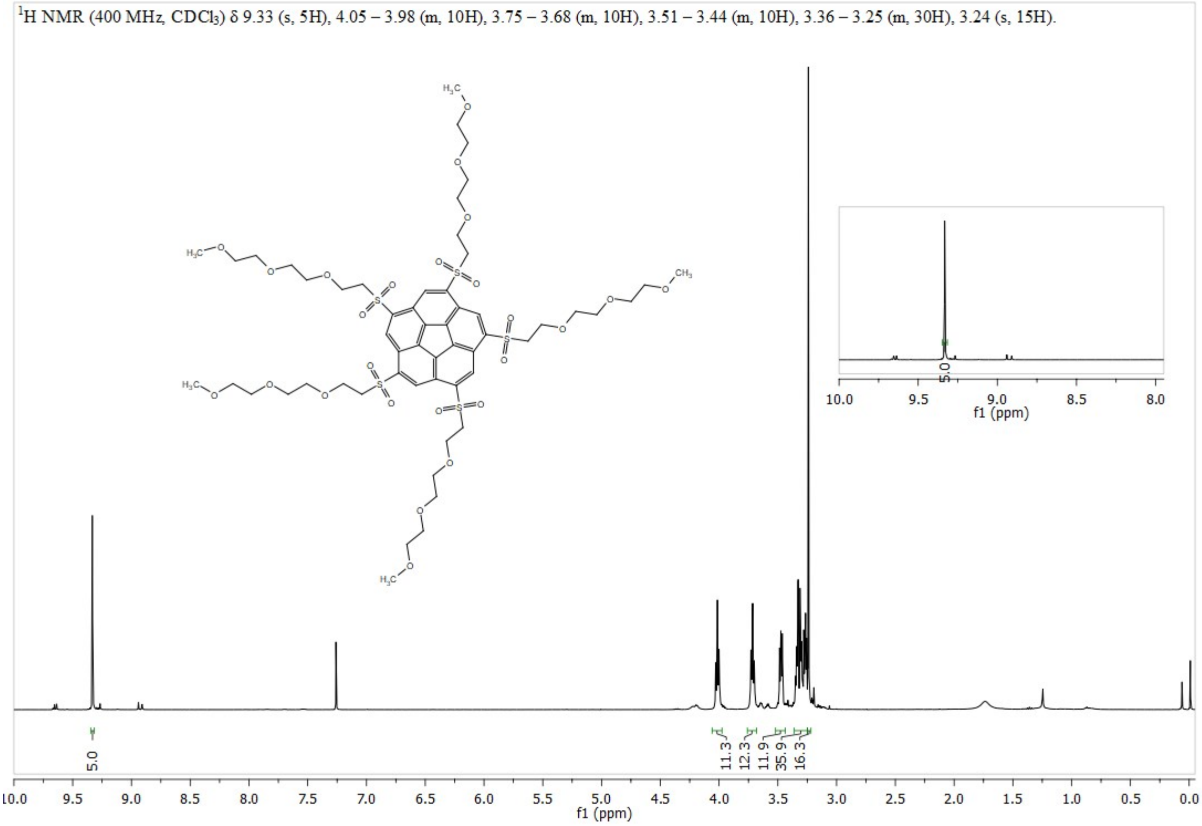
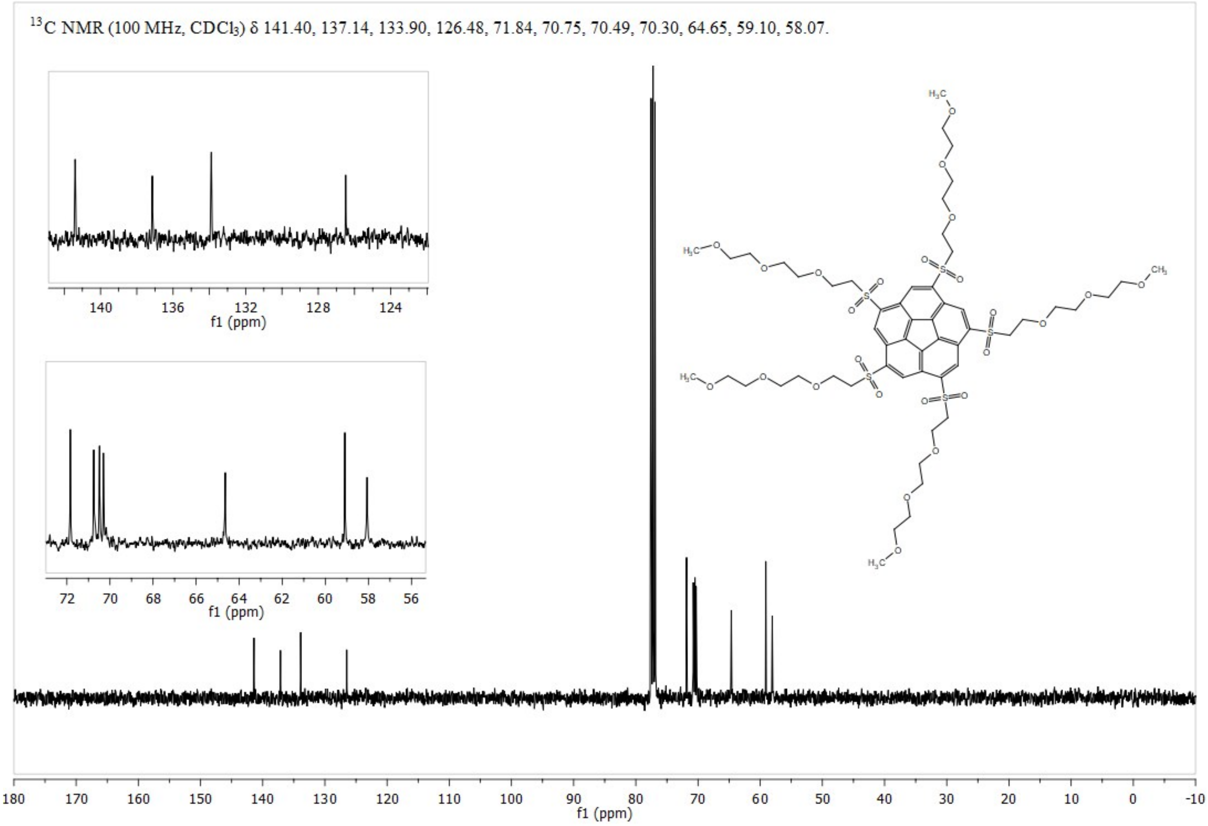


Fig. S9 Synthesis of Cor-TEG.



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 5H), 4.05 – 3.98 (m, 10H), 3.75 – 3.68 (m, 10H), 3.51 – 3.44 (m, 10H), 3.36 – 3.25 (m, 30H), 3.24 (s, 15H).

Fig. S10 ^{1}H-NMR of Cor-TEG in deuterated chloroform.



^{13}C NMR (100 MHz, $CDCl_3$) δ 141.40, 137.14, 133.90, 126.48, 71.84, 70.75, 70.49, 70.30, 64.65, 59.10, 58.07.

Fig. S11 ^{13}C-NMR of Cor-TEG in deuterated chloroform.

Table S1 Photovoltaic parameters of PSCs with different Cor-TEG concentrations.

Cor-TEG concentrations	**V_{oc} (V)**	**Jsc (mA.cm^{-2})**	**FF (%)**	**PCE (%)**
0 μg/mL (pristine)	1.04±0.01	20.3±0.2	75.2±2.1	15.9±0.5
4 μg/mL	1.03±0.01	20.2±0.3	77.6±0.9	16.2±0.1
10 μg/mL	1.04±0.01	20.4±0.1	79.0±1.0	16.8±0.2
30 μg/mL	1.03±0.00	20.3±0.2	77.8±1.1	16.3±0.4

Table S2 Time-resolved photoluminescence decay fitting parameters.

Condition	**A_1**	**τ_1 (ns)**	**A_2**	**τ_2 (ns)**	**τ_{ave} (ns)**
Pristine	0.32	21.2	0.68	221	157
Cor-TEG treated	0.14	29.3	0.86	523	454

Reference

(1) Mahadevegowda, S. H.; Stuparu, M. C. Thermoresponsive Corannulene. *European J. Org. Chem.* **2017**, 570–576.