

Supplementary Information

Polyacetylene derivatives in Perovskite Solar Cells: From Defect Passivation to Moisture Endurance

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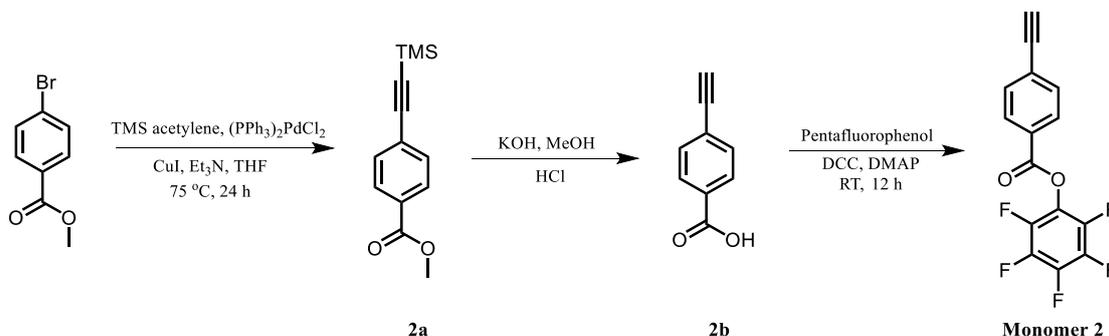
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Chemicals

Materials. Methyl 4-bromobenzoate, Trimethylsilylacetylene (TMS acetylene), (PPh₃)₂PdCl₂, Cuprous iodide (CuI), Potassium hydroxide (KOH), Pentafluorophenol, Dicyclohexylcarbodiimide (DCC), 4-Dimethylaminopyridine (DMAP), [Rh(nbd)Cl]₂ were purchased from Energy Chemical. Ethynylbenzene (Monomer 1, M1), 1-ethynyl-4-(trifluoromethyl)benzene (Monomer 3, M3), and 4-ethynyl-N,N-diphenylaniline (Monomer 4, M4) were commercially available and used without further purification. Perfluorophenyl 4-Ethynylbenzoate (Monomer 2) were synthesized according to reference 1.

Monomer Preparation. Perfluorophenyl 4-Ethynylbenzoate (Monomer 2) were prepared by the synthetic route as shown in Scheme S1. Detailed experimental procedures are given below.¹



Scheme S1

Methyl 4-((trimethylsilyl)ethynyl)benzoate (2a). Methyl 4-bromobenzoate (2 g, 9.3 mmol), $(\text{PPh}_3)_2\text{PdCl}_2$ (0.2 g, 0.279 mmol), CuI (0.1 g, 0.558 mmol) were dissolved in 80 ml of Et_3N . Trimethylsilylacetylene (1.4 g, 14 mmol) was then injected to this solution. The reaction mixture was heated to 85 °C and stirred for 24 h under N_2 atmosphere. The solvent was removed by evaporation and the product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1/10, v/v) to yield 1.52 g of brown powder. Yield: 70%. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 0.26 (s, 9H), 3.91 (s, 3H), 7.52 (d, 2H), 7.97 (d, 2H); ^{13}C NMR (101 MHz, CDCl_3), δ (ppm): 166.62, 131.97, 129.76, 129.47, 127.85, 104.14, 97.79, 52.33, 1.12.

4-Ethynylbenzoic acid (2b). Compound 2a (1.5 g, 6.5 mmol), KOH (1.1 g, 19.5 mmol) and methanol (80 mL) were added into 200 mL round-bottom flask. After refluxing the reaction system for 5 h, the solvent was removed by evaporation. The crude product was dissolved in aqueous solution and then the solution was acidified to pH 3 by dropwise addition of 1 M HCl aqueous solution. Brown precipitate was collected by filtration and the compound 2b was obtained by drying as brown powder (0.86 g). Yield: 90%. ^1H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 4.42 (s, 1H); 7.58 (d, 2H); 7.92 (d, 2H); 13.1 (s, 1H). ^{13}C NMR (101 MHz, DMSO-D_6), δ (ppm): 167.18, 132.44, 131.41, 130.02, 126.56, 84.11, 83.28.

Perfluorophenyl 4-Ethynylbenzoate (Monomer 2). Compound 2a (0.86 g, 5.8 mmol), Pentafluorophenol (1.07 g, 5.8 mmol), DMAP (0.71 g, 5.8 mmol), and 40 mL of dry THF were added into a 100 mL round-bottom flask. The temperature was maintained at 0 °C in an ice bath, 10 mL of DCM solution of DCC (1.44 g, 7 mmol) was added dropwise to the above cooled solution through a 25 mL dropping funnel within 30 min. The solution was stirring at room temperature for 12 h, and then the white precipitate was removed by filtration. After evaporating the solvent, the product was obtained by column chromatography (silica gel, petroleum ether as eluent) to yield 1.52 g of white solid. Yield: 85%. ^1H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 8.14 (d, 2H), 7.71 (d, 2H), 4.59 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3), δ (ppm): 162.07, 142.75, 140.99, 140.24, 139.32, 138.43, 136.62, 132.60, 130.66, 128.83, 126.87, 82.42, 81.53.

Polymer synthesis. All polymers were prepared by using Schlenk technique under N_2 atmosphere. Typical polymerization procedures are as follows.

Polymer 1. In a 25 mL polymerization tube, $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (4.9 mg, 0.01 mmol) and one drop TEA were added to 1 mL of THF under nitrogen. After stirring for 15 min, 1 mL THF solution of monomer 1 (51 mg, 0.5 mmol) was injected to the above tube. And then the mixture was stirred for 24 h at room temperature. The polymer 1 was yielded as a light-yellow solid (84%) by adding dropwise to 250 mL methanol. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.31-6.50 (m, Ar-H, 5H), 5.85 (s, C=CH, 1H).² ^{13}C NMR (101 MHz, CDCl_3), δ (ppm): 142.4, 138.4, 128.9, 128.6, 127.9, 114.6.

Polymer 2. In a 25 mL polymerization tube, $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (4.9 mg, 0.01 mmol) and one

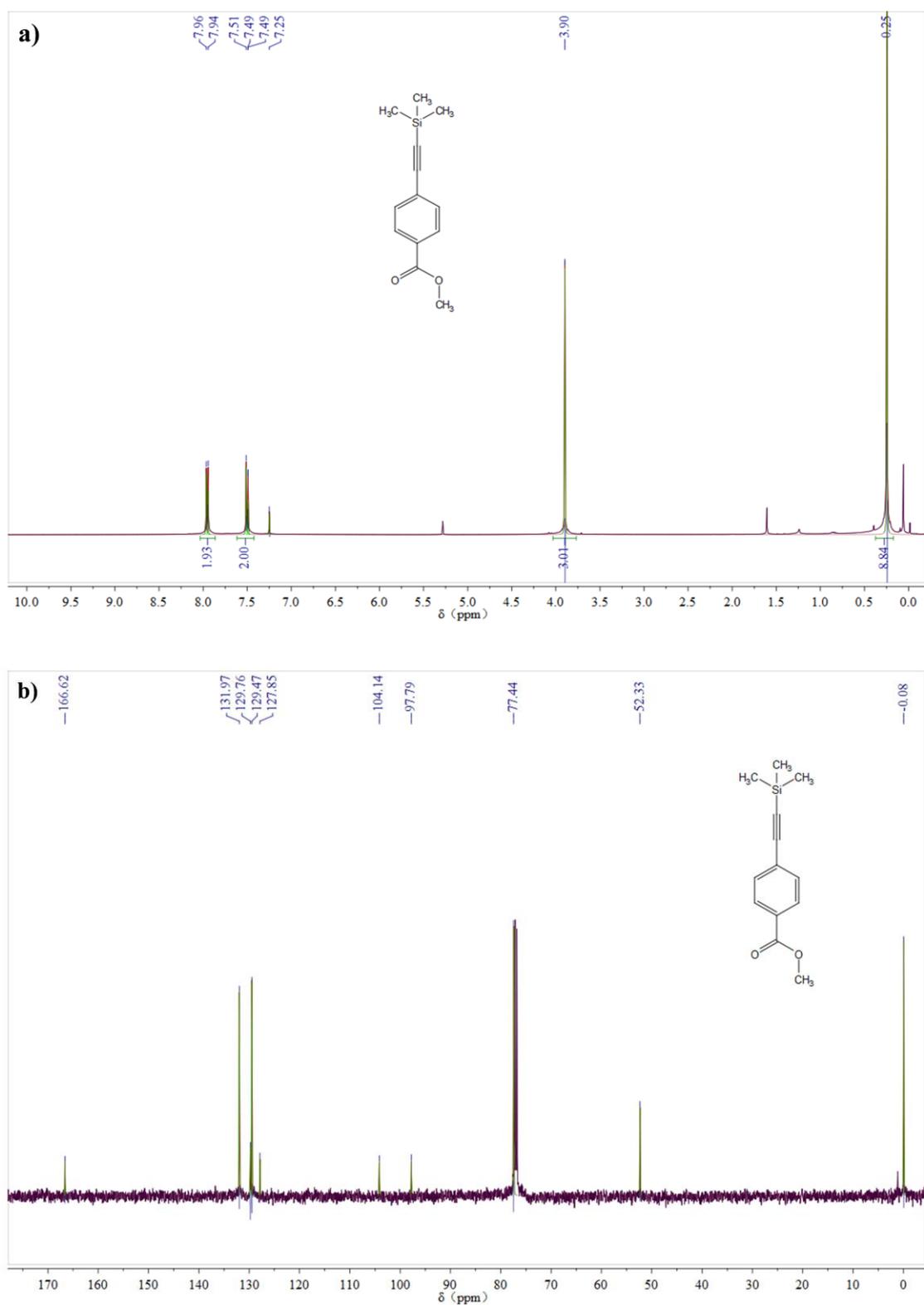
drop TEA were added to 1 mL of THF under nitrogen. After stirring for 15 min, 1 mL THF solution of monomer 2 (150 mg, 0.5 mmol) was injected to the above tube. And then the mixture was stirred for 24 h at room temperature. The polymer 2 was yielded as a yellow solid (84%) by adding dropwise to 250 mL methanol. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.80, 6.79, 5.97. ^{13}C NMR (101 MHz, CDCl_3), δ (ppm): 161.60, 147.30, 142.47, 141.04, 140.06, 139.14, 138.47, 136.76, 132.85, 130.82, 127.67, 126.74, 124.94. ^{19}F NMR (125 MHz, CDCl_3), δ (TMS, ppm): -153.0, -157.1, -162.1.

Polymer 3. In a 25 mL polymerization tube, $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (4.9 mg, 0.01 mmol) and one drop TEA were added to 1 mL of THF under nitrogen. After stirring for 15 min, 1 mL THF solution of monomer 3 (85 mg, 0.5 mmol) was injected to the above tube. And then the mixture was stirred for 24 h at room temperature. The polymer 3 could be yielded as a yellow solid (30%) by adding dropwise to 250 mL methanol. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.44, 7.36, 5.85. ^{19}F NMR (100 MHz, DMSO-D_6), -62.85. ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 142.4, 141.7, 134.9, 130.2, 125.0, 124.1, 118.9.

Polymer 4. In a 25 mL polymerization tube, $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (4.9 mg, 0.01 mmol) and one drop TEA were added to 1 mL of THF under nitrogen. After stirring for 15 min, 1 mL THF solution of monomer 4 (135 mg, 0.5 mmol) was injected to the above tube. And then the mixture was stirred 24 h at room temperature. The polymer 4 could be yielded as a brownish yellow solid (81%) by adding dropwise to 250 mL methanol. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.9-5.8 (broad, m). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 148.0, 146.8, 136.2, 132.6, 129.1, 124.6, 123.2, 121.8, 116.1, 114.1.³

References

- 1 X. A. Zhang, M. R. Chen, H. Zhao, Y. Gao, Q. Wei, S. Zhang, A. Qin, J. Z. Sun and B. Z. Tang, *Macromolecules*, 2011, **44**, 6724-6737.
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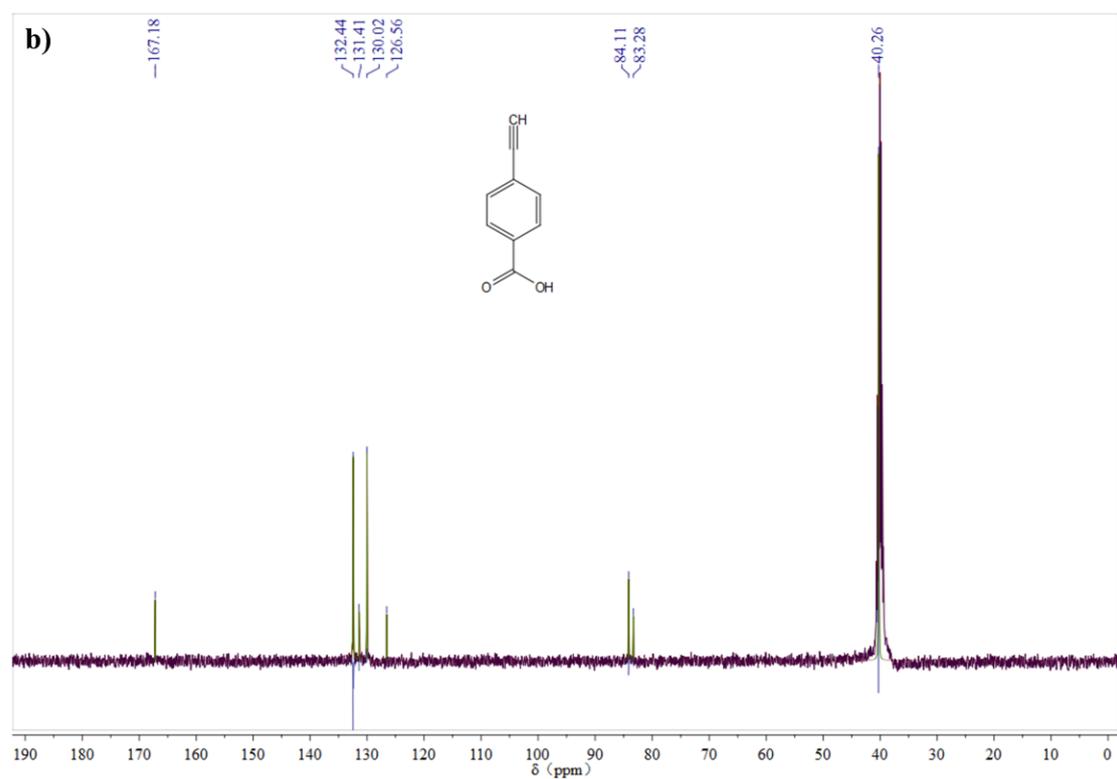
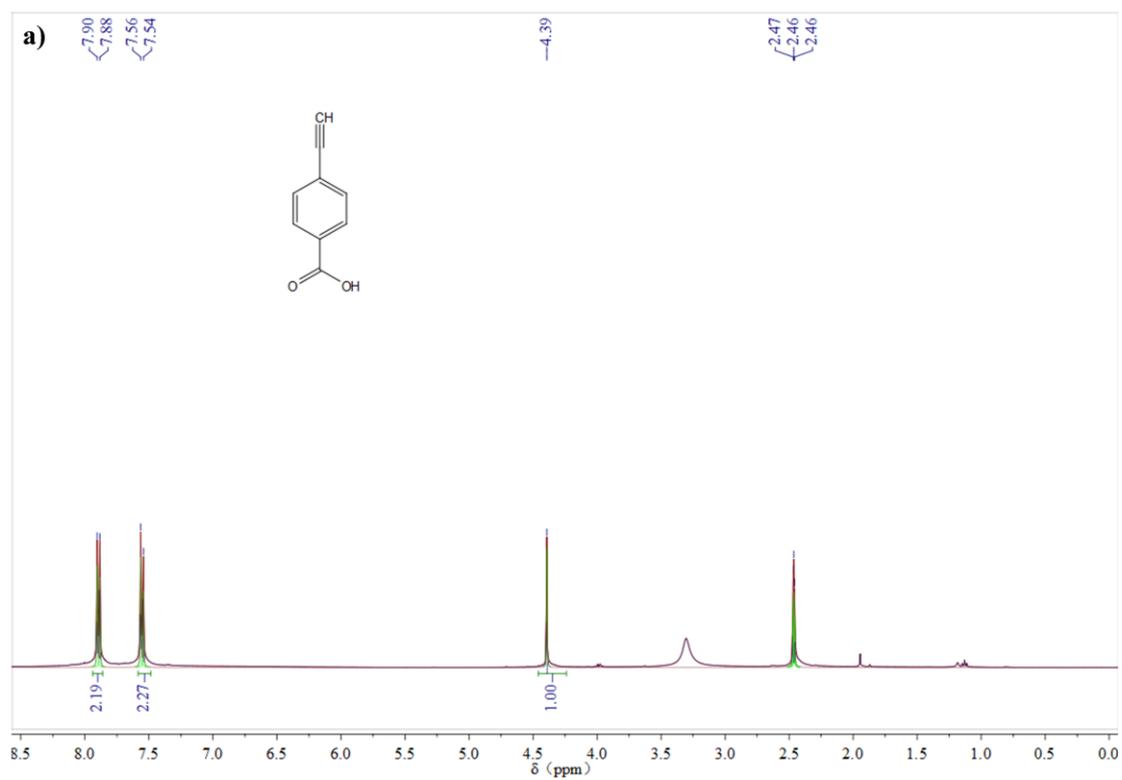


Figure S2. a-b) ^1H NMR spectra (400 MHz, $\text{DMSO-}D_6$) and ^{13}C NMR spectra (100 MHz, $\text{DMSO-}D_6$) of the 4-Ethynylbenzoic acid in Scheme S1 (2b).

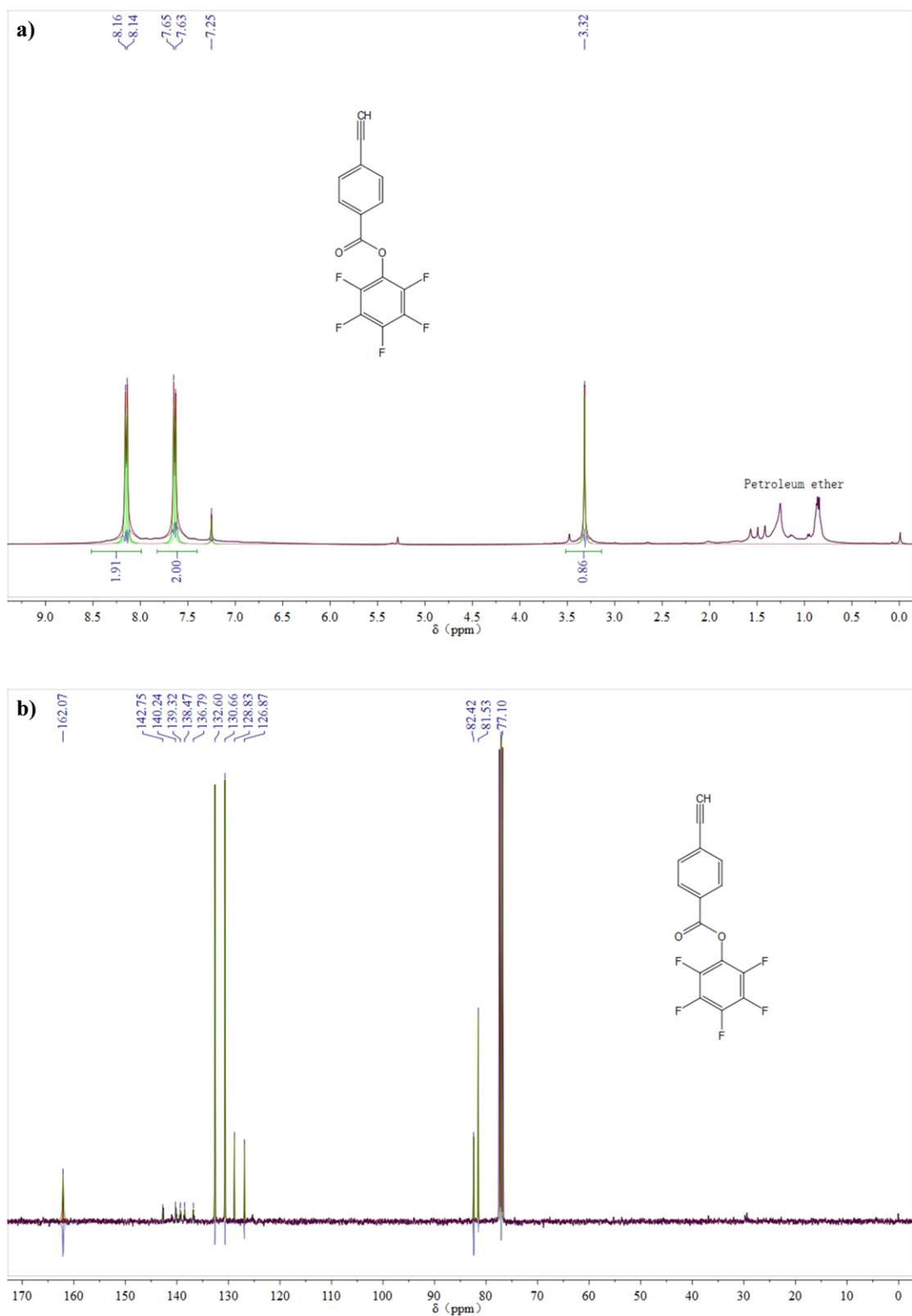


Figure S3. a-b) ^1H NMR spectra (400 MHz, CDCl_3) and ^{13}C NMR spectra (100 MHz, CDCl_3) of the Perfluorophenyl 4-Ethynylbenzoate in Scheme S1 (Monomer 2).

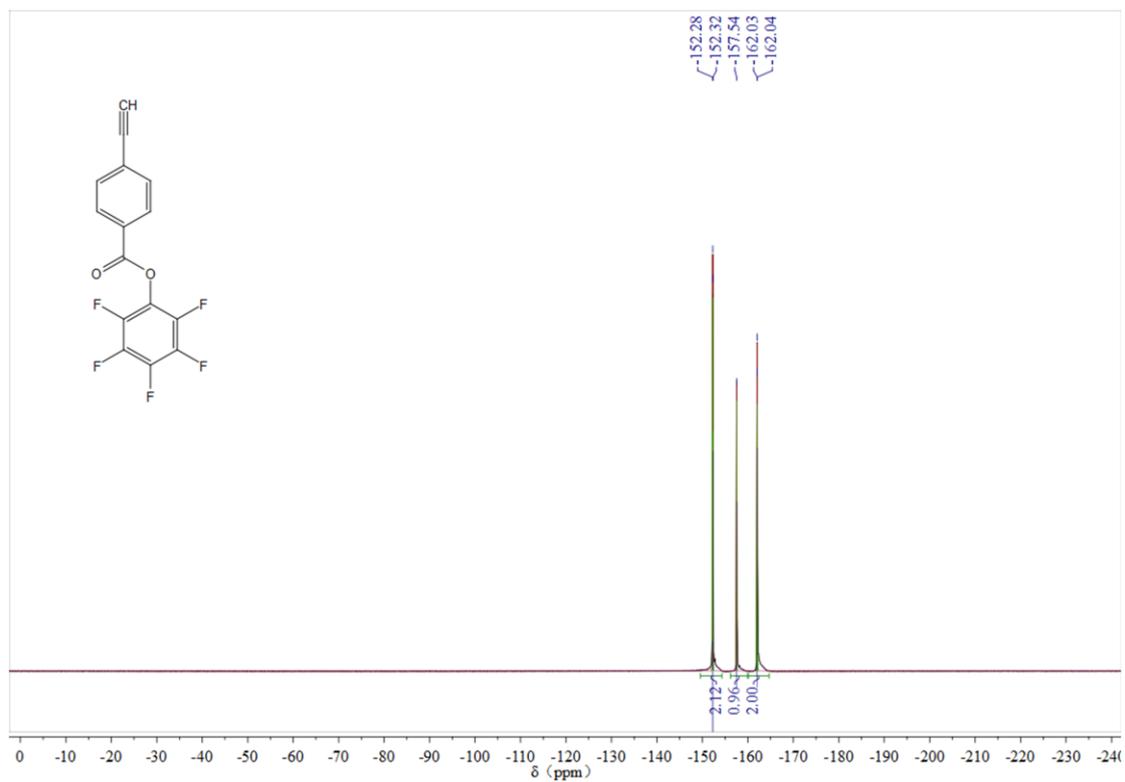


Figure S4. ^{19}F NMR spectra (100 MHz, CDCl_3) of the Perfluorophenyl 4-Ethynylbenzoate in Scheme S1 (Monomer 2).

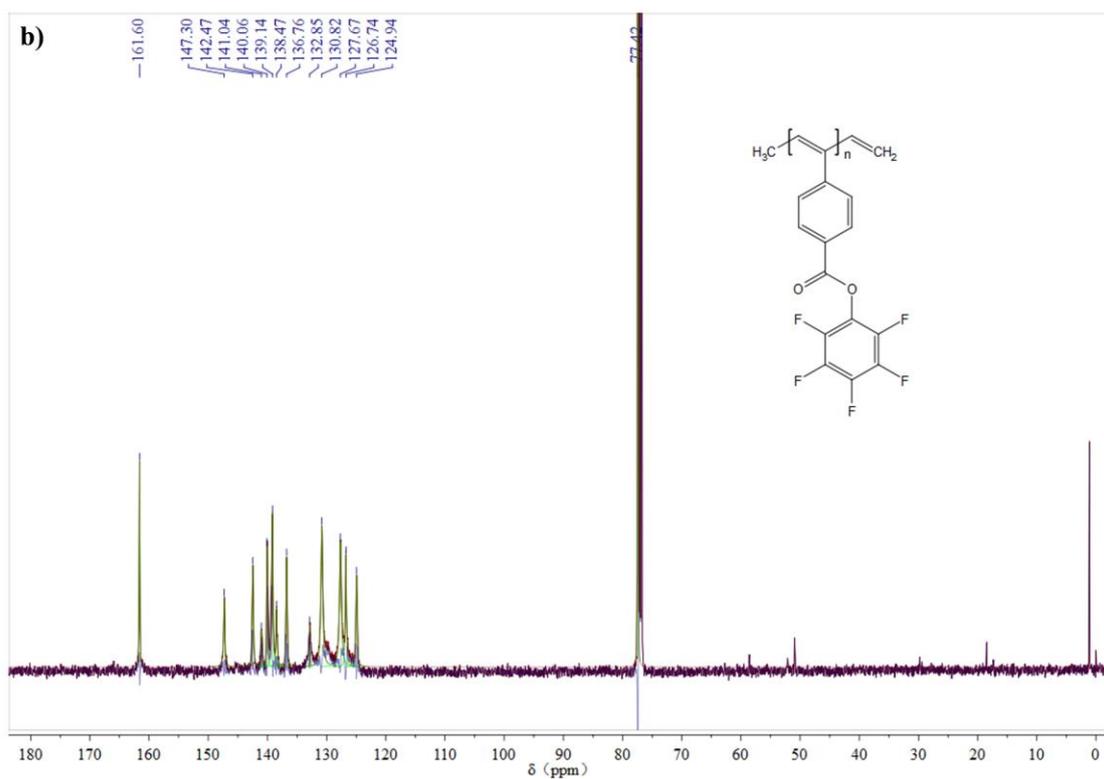
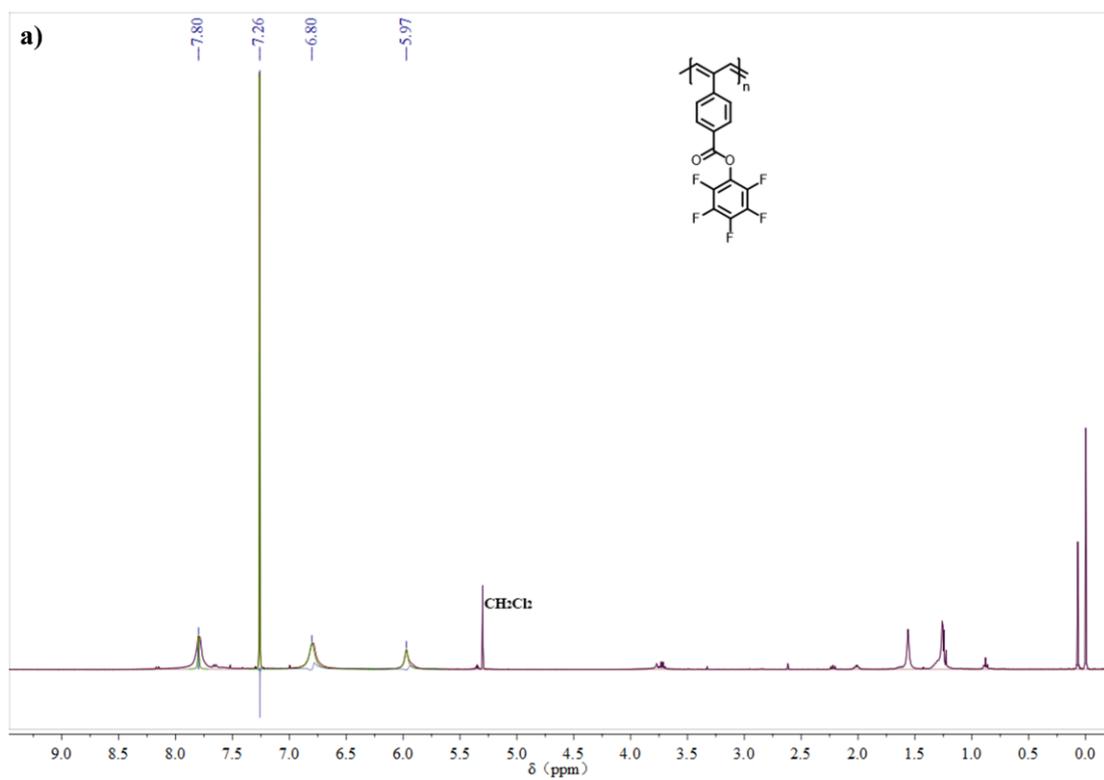


Figure S5. a-b) ¹H NMR spectra (400 MHz, CDCl₃) and ¹³C NMR spectra (100 MHz, CDCl₃) of the P2 polymer.

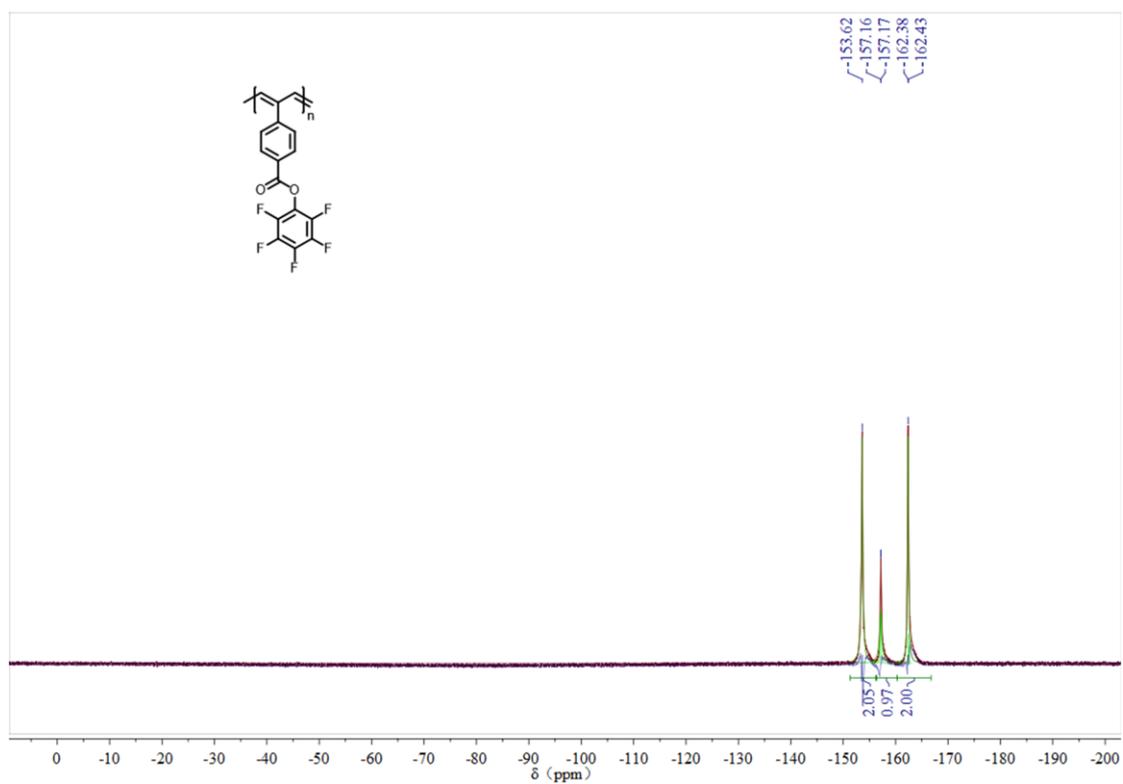


Figure S6. ^{19}F NMR spectra (100 MHz, CDCl_3) of the P2 polymer.

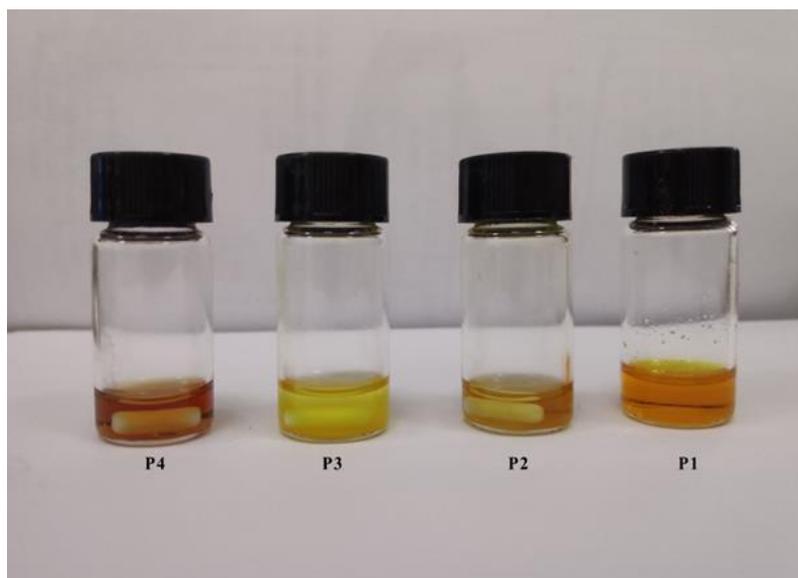


Figure S7. Photograph of the polymers dissolved in DMF.

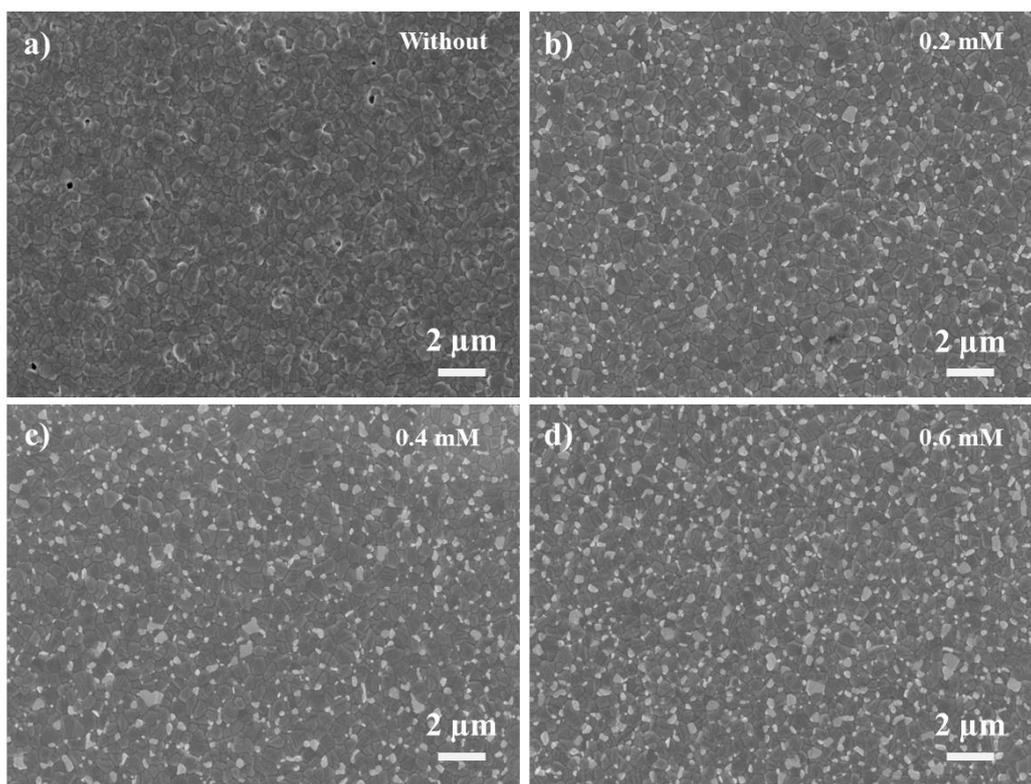


Figure S8. a-d) SEM images of perovskite ($\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_{2.55}\text{Br}_{0.45}$) thin films formed using different amounts of P2 (0, 0.2, 0.4 and 0.6 mM, respectively).

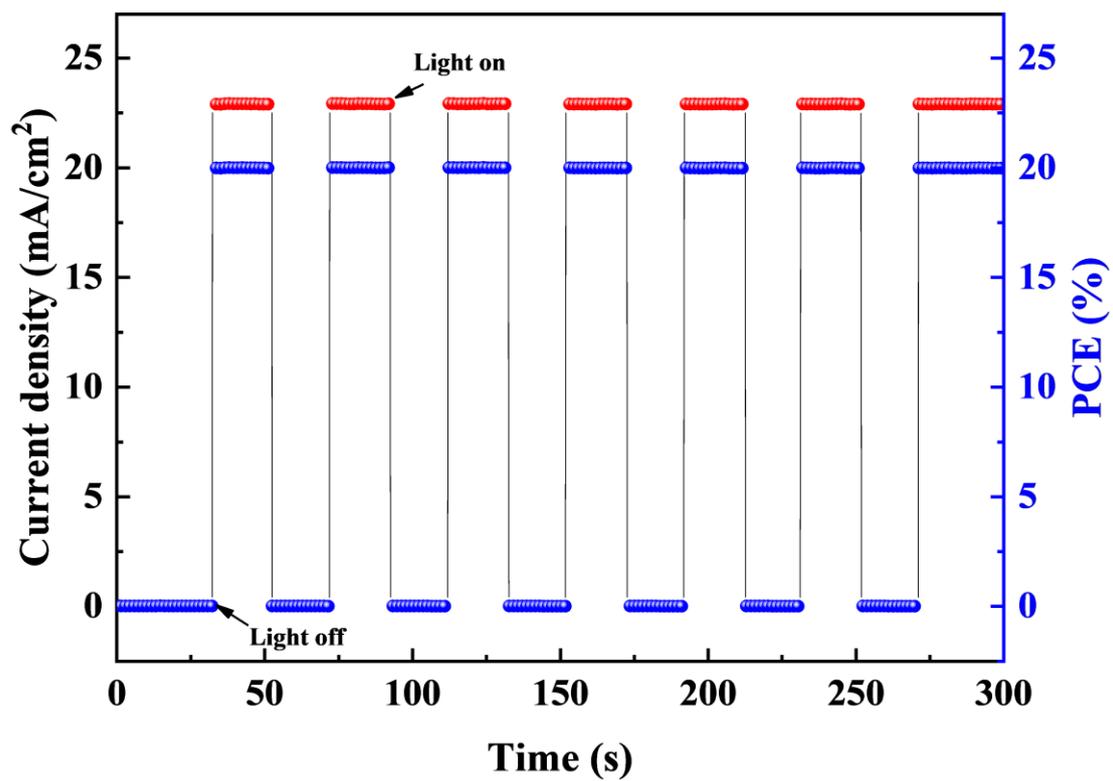


Figure S9. Steady-state photocurrent and power output with 20 s light on/off cycles for P2-optimized PSC.

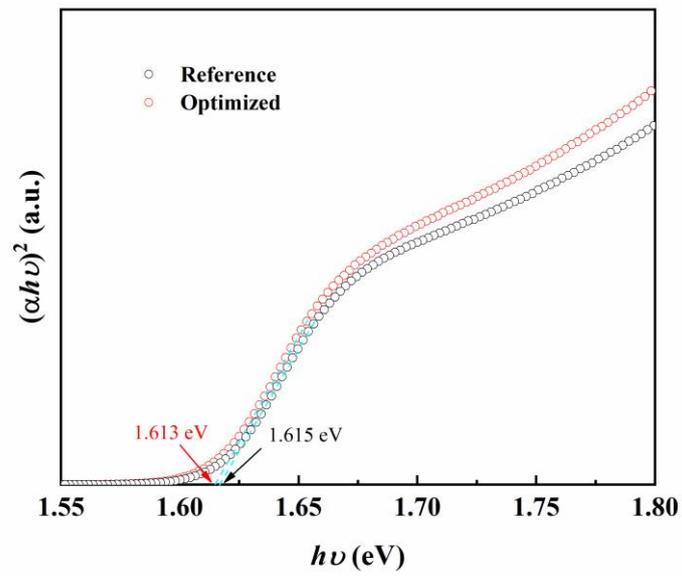


Figure S10. Tauc plots of the absorption spectra of the reference and P2-optimized perovskite films.

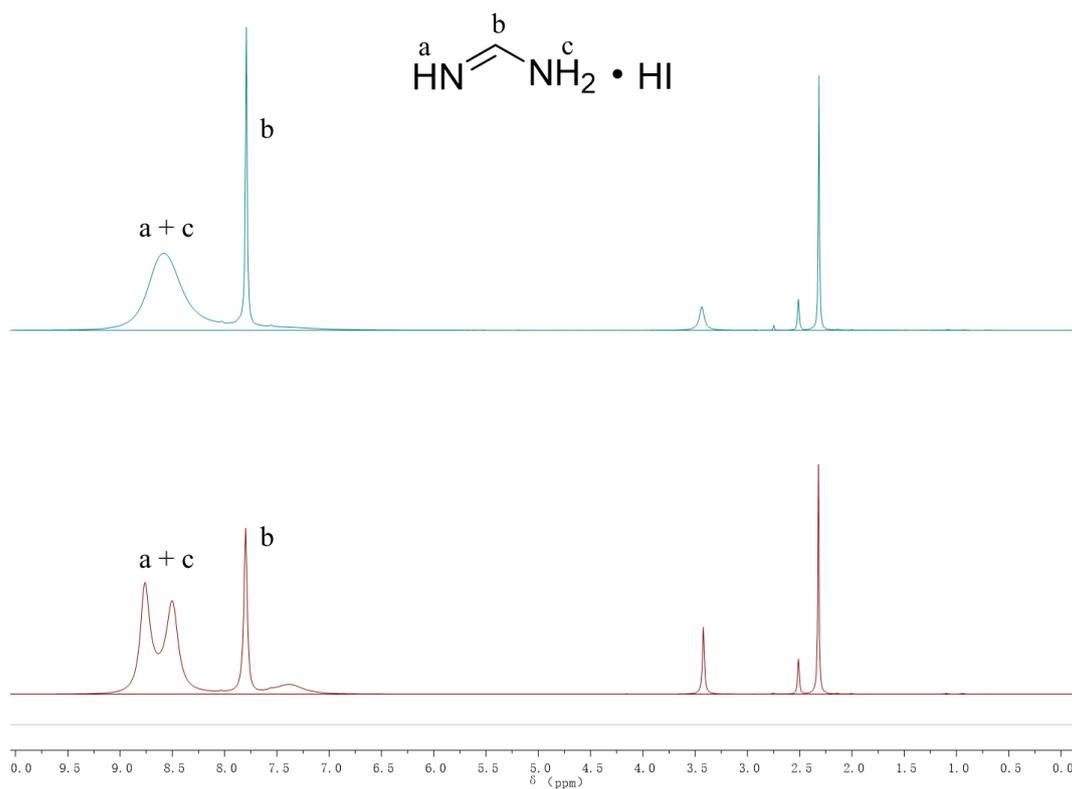


Figure S11. ^1H NMR wide spectra of the perovskite solutions with (bottom) and without (top) P2 addition in DMSO- d_6 .

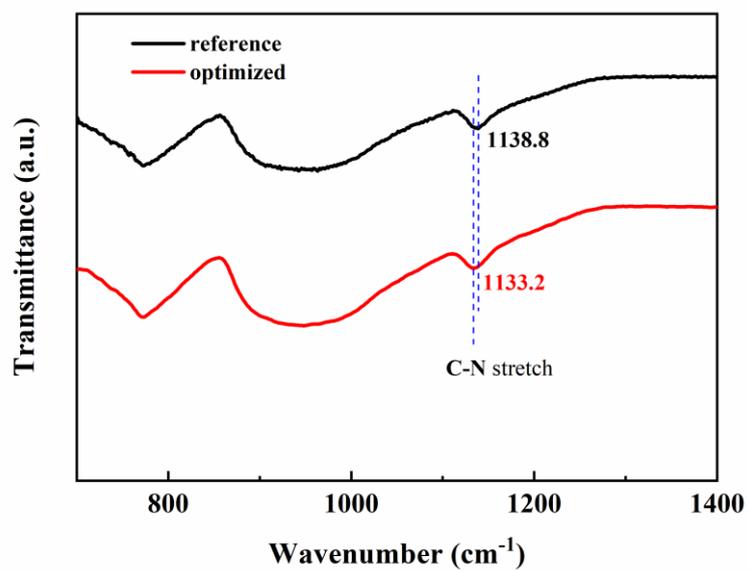


Figure S12. FTIR spectra of the pristine and P2-modified perovskite films prepared on quartz substrates.

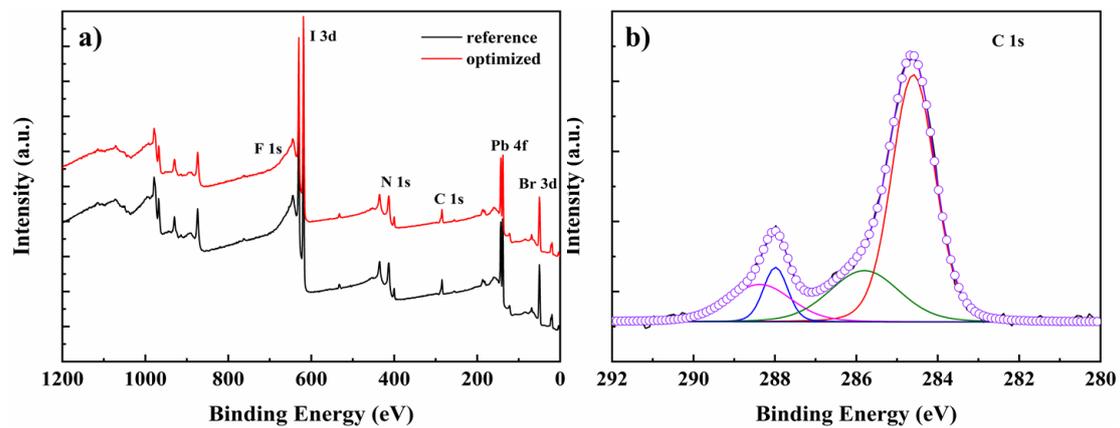


Figure S13. a) Wide-scan XPS spectra of the pristine and P2-modified perovskite films. b) C 1s core-level spectrum of the P2-modified perovskite film.

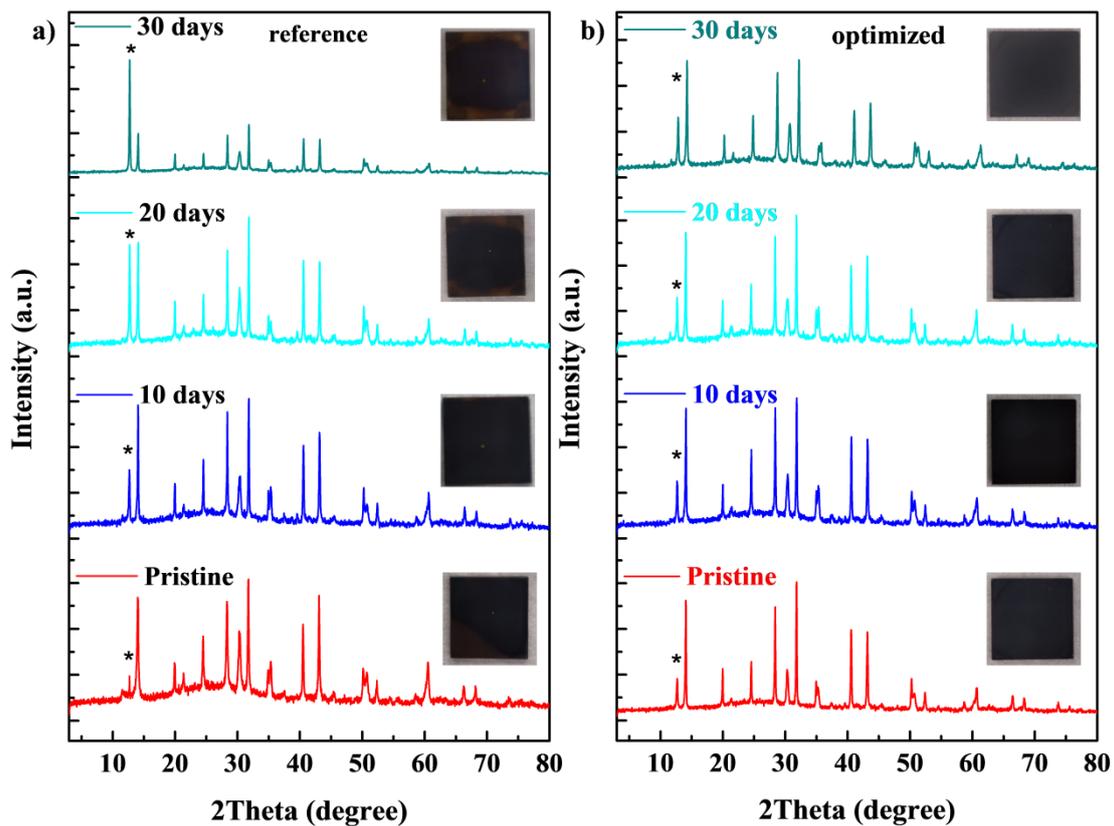


Figure S14. a-b) XRD pattern and photograph of the pristine and P2-modified perovskite films stored in air with $55 \pm 10\%$ RH for 30 days at room temperature.

Table S1. Fitted parameters of the TRPL spectra of perovskite films on different substrates.

Different substrate	τ_{ave} (μs)	τ_1 (μs)	% of τ_1	τ_2 (μs)	% of τ_2
Glass/reference PVK	1.489	1.525	96.97	0.033	3.03
Glass/optimized PVK	1.815	1.828	99.25	0.012	0.75
NiO/reference PVK	0.344	0.394	84.81	0.066	15.19
NiO/optimized PVK	0.212	0.247	81.66	0.056	18.34

Table S2. Fitted EIS parameters for the PSCs prepared with reference and P2-optimized perovskite.

Device	R_s (Ω)	R_{rec} (Ω)	C_{tr} (F)	τ_n (μs)
reference	9.85	150.2	1.14×10^{-8}	3.99
optimized	5.36	358.3	1.36×10^{-8}	6.34