

α -PC₇₁BM: ¹H NMR (500MHz, CDCl₃) δ : 7.902 (s, 2H), 7.522 (t, ³J = 7.5Hz, 2H), 7.448-7.414 (m, 1H), 3.674 (s, 3H), 2.499-2.427 (m, 4H), 2.219-2.046 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ : 173.36, 156.01, 155.31, 152.20, 151.97, 151.53, 151.25, 151.18, 150.93, 150.88, 150.63, 150.57, 149.48, 149.44, 149.25, 149.23, 149.18, 149.16, 148.63, 148.61, 148.57, 148.47, 148.36, 148.07, 147.95, 147.61, 147.57, 147.48, 147.41, 147.08, 146.36, 145.97, 145.87, 145.85, 145.70, 144.94, 144.55, 144.13, 143.97, 143.92, 143.79, 143.68, 143.38, 143.29, 142.69, 142.55, 141.76, 141.64, 141.46, 140.99, 140.19, 139.34, 138.95, 137.97, 137.34, 134.05, 133.89, 132.86, 131.61, 130.95, 130.81, 130.79, 130.70, 130.47, 128.57, 128.24, 71.98, 69.90, 51.68, 35.94, 34.16, 33.84, 21.75; APCI-MS: M⁺ = 1030.2 m/z (calcd. 1030.1).

β ₁-PC₇₁BM: ¹H NMR (500MHz, CDCl₃/CS₂) δ : 7.772 (d, ³J = 7.0Hz, 2H), 7.562 (t, ³J = 7.5Hz, 2H), 7.501 (t, ³J = 7.5Hz, 1H), 3.512 (s, 3H), 2.180 (t, ³J = 7.0Hz, 2H), 2.118-2.085 (m, 2H), 1.825-1.764 (m, 2H). ¹³C NMR (125 MHz, CDCl₃/CS₂) δ : 171.98, 152.97, 151.19, 149.70, 149.54, 149.41, 149.19, 149.01, 148.91, 148.29, 148.28, 147.97, 147.89, 147.00, 146.97, 146.88, 146.69, 146.62, 146.04, 145.71, 145.64, 145.32, 145.13, 144.61, 144.31, 143.96, 142.91, 142.59, 142.49, 142.26, 141.60, 139.46, 137.81, 132.30, 131.97, 131.62, 131.44, 131.02, 128.47, 128.15, 127.65, 65.13, 51.03, 37.27, 33.34, 33.28, 21.67 ; APCI-MS: M⁺ = 1030.1 m/z (calcd. 1030.1).

β ₂-PC₇₁BM: ¹H NMR (500MHz, CDCl₃) δ : 7.417-7.398 (m, 2H), 7.236-7.180 (m, 3H), 3.745 (s, 3H), 2.520-2.442 (m, 4H), 2.048-1.985 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ : 173.44, 153.23, 151.23, 150.01, 149.70, 149.58, 149.51, 149.37, 148.88, 148.67, 148.33, 148.27, 147.96, 147.20, 147.12, 147.03, 146.83, 146.59, 145.86, 145.50, 144.90, 144.59, 144.57, 144.52, 144.16, 143.55, 143.13, 142.69, 141.79, 141.53, 141.51, 141.35, 136.74, 132.25, 132.24, 131.88, 131.52, 131.23, 128.23, 127.92, 127.04, 65.65, 51.75, 37.87, 35.27, 33.87, 22.11; APCI-MS: M⁺ = 1030.1 m/z (calcd. 1030.1).

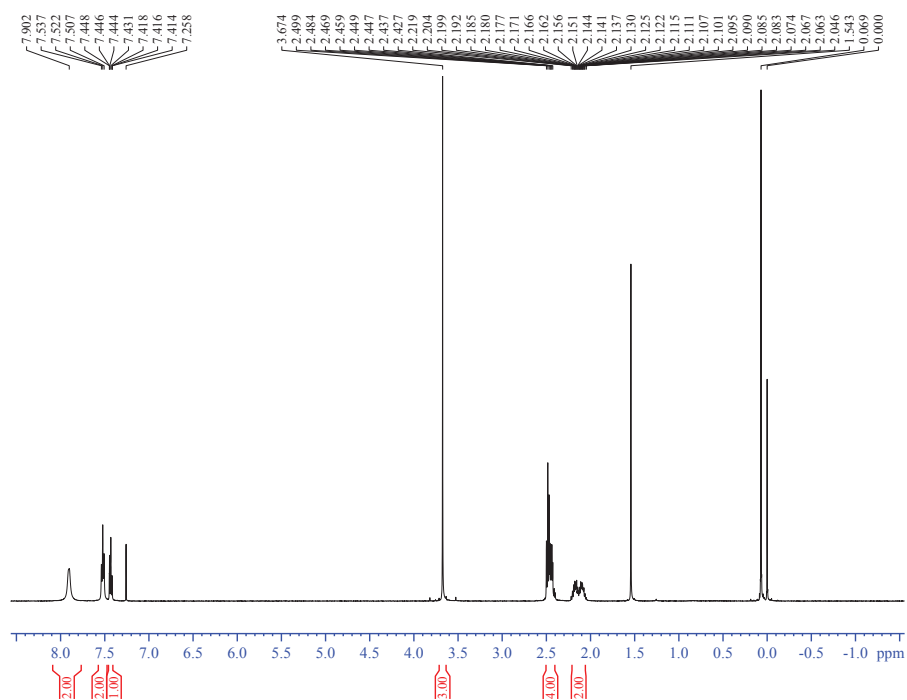


Fig. S1. ^1H NMR spectrum of $\alpha\text{-PC}_{71}\text{BM}$ in chloroform-d.

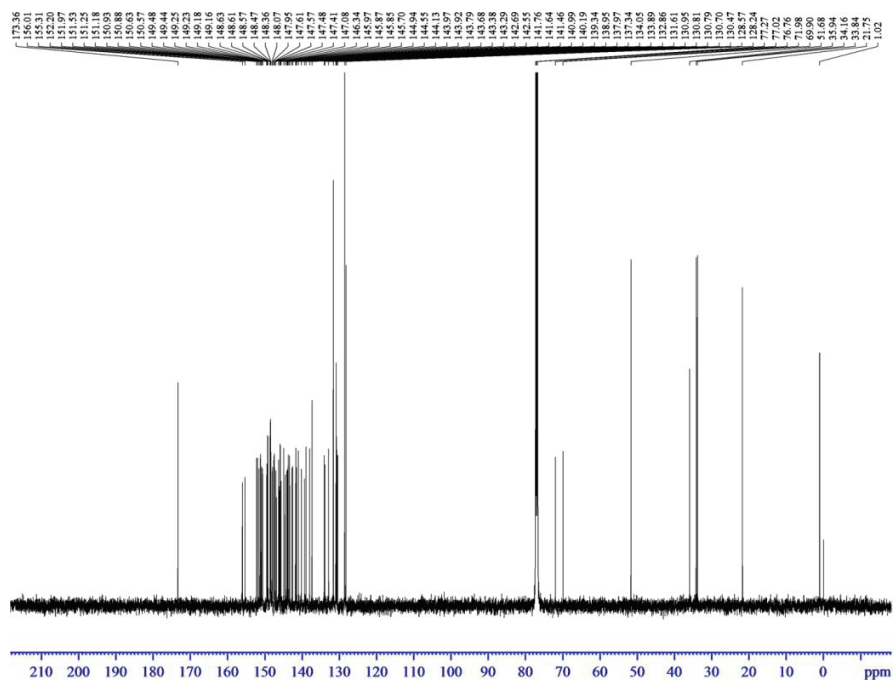


Fig. S2. ^{13}C NMR spectrum of $\alpha\text{-PC}_{71}\text{BM}$ in chloroform-d.

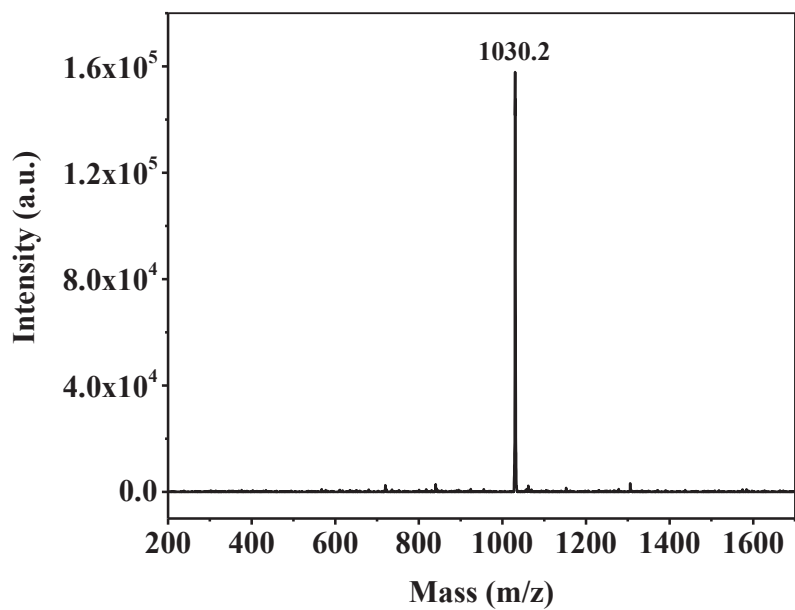


Fig. S3. APCI-MS spectrum of α -PC₇₁BM.

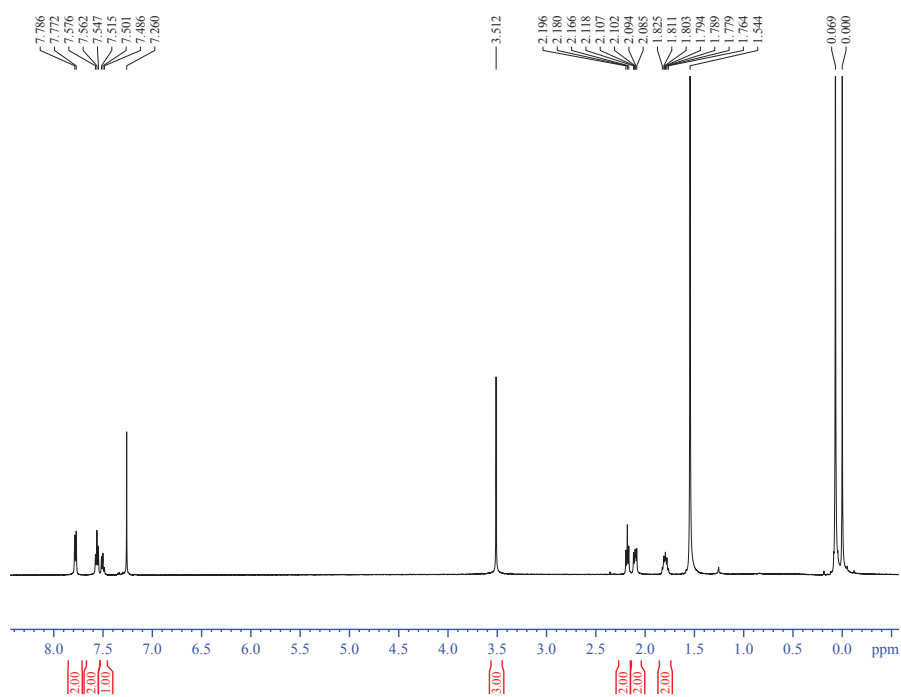


Fig. S4. ¹H NMR spectrum of β_1 -PC₇₁BM in chloroform-d and CS₂.

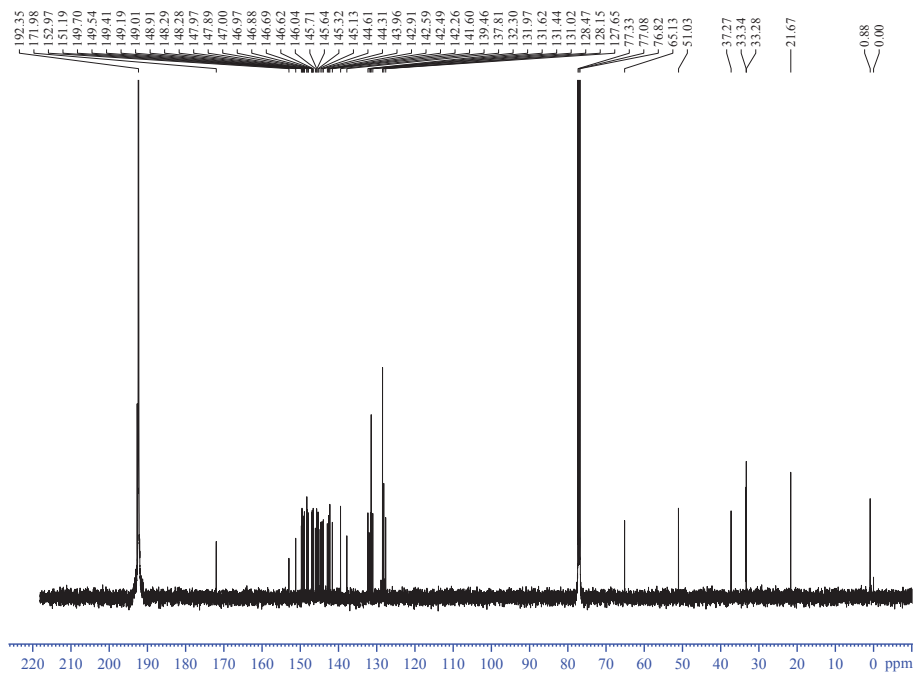


Fig. S5. ^{13}C NMR spectrum of $\beta_1\text{-PC}_{71}\text{BM}$ chloroform- d and CS_2 .

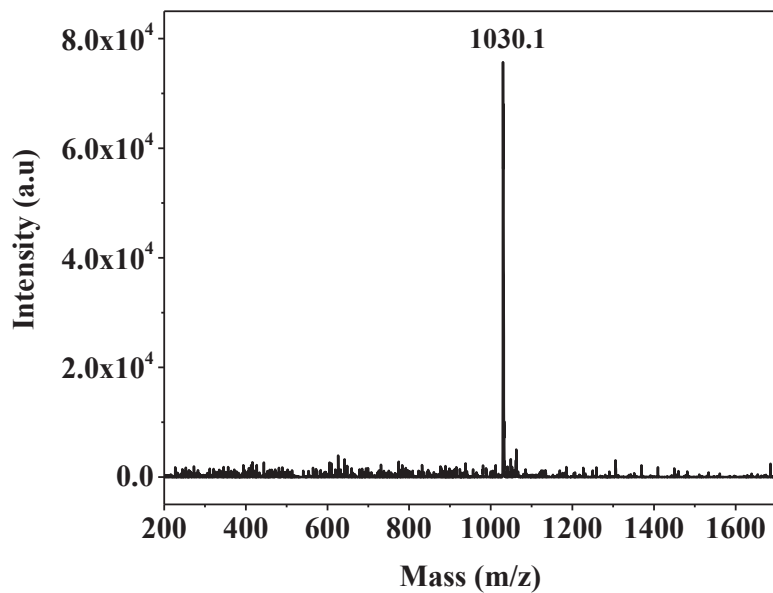


Fig. S6. APCI-MS spectrum of $\beta_1\text{-PC}_{71}\text{BM}$.

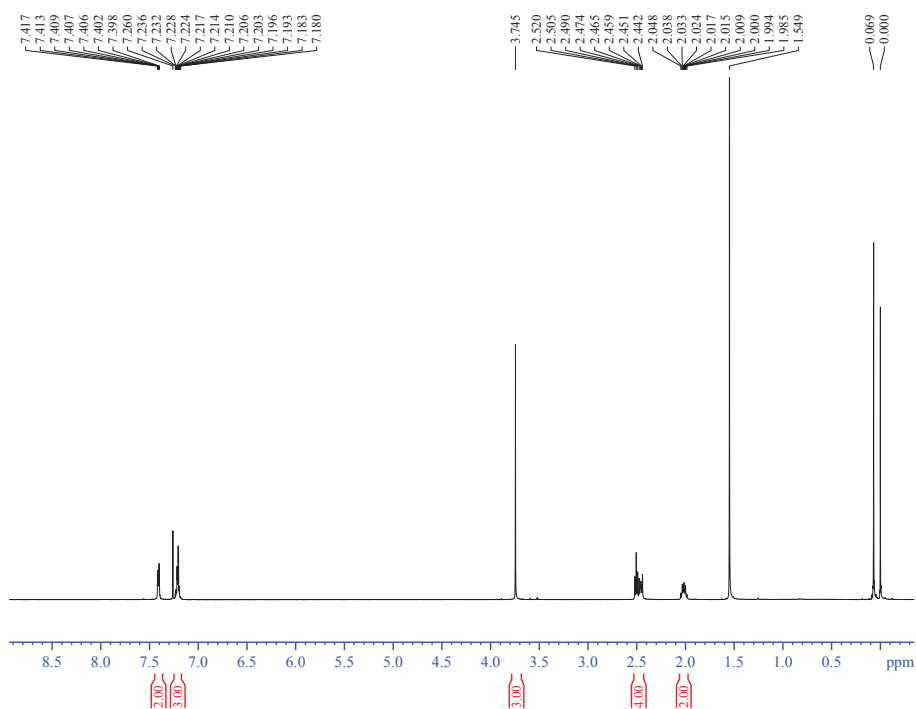


Fig. S7. ^1H NMR spectrum of $\beta_2\text{-PC}_{71}\text{BM}$ in chloroform-d.

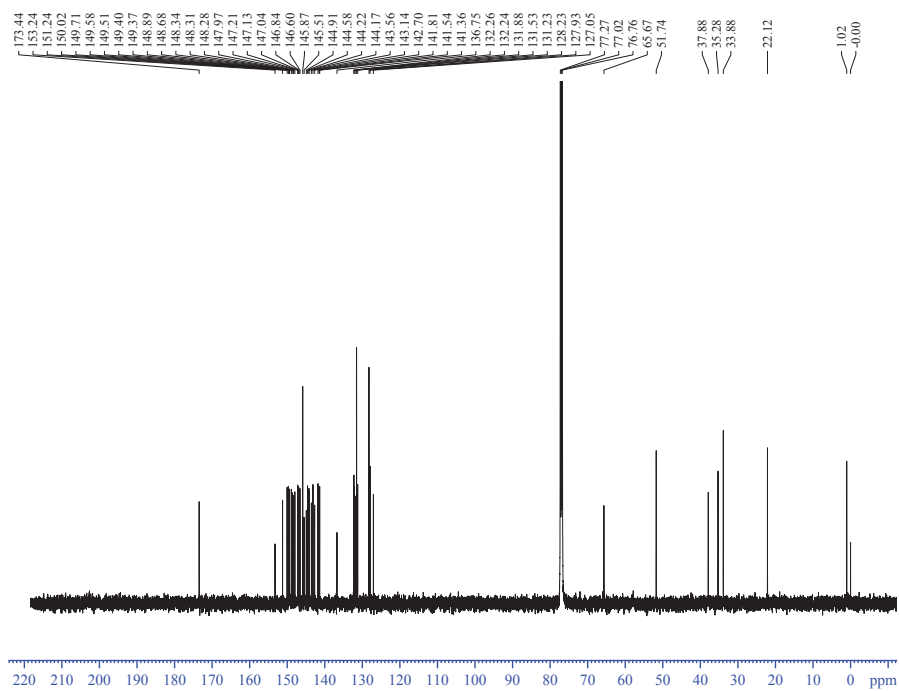


Fig. S8. ^{13}C NMR spectrum of $\beta_2\text{-PC}_{71}\text{BM}$ chloroform-d.

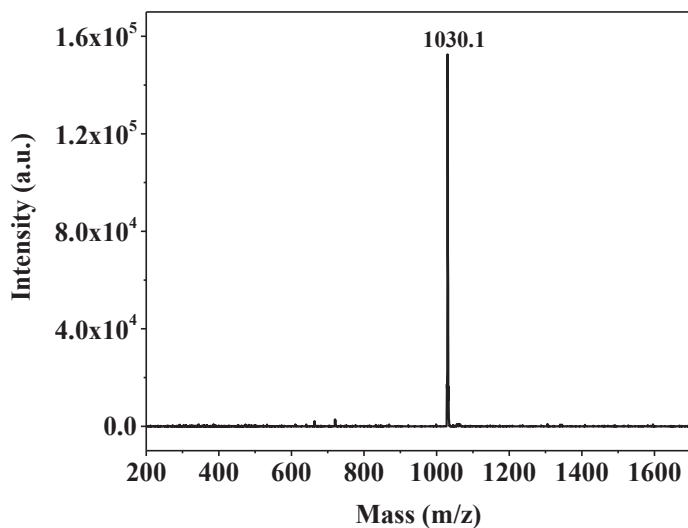


Fig. S9. APCI-MS spectrum of $\beta_2\text{-PC}_{71}\text{BM}$.

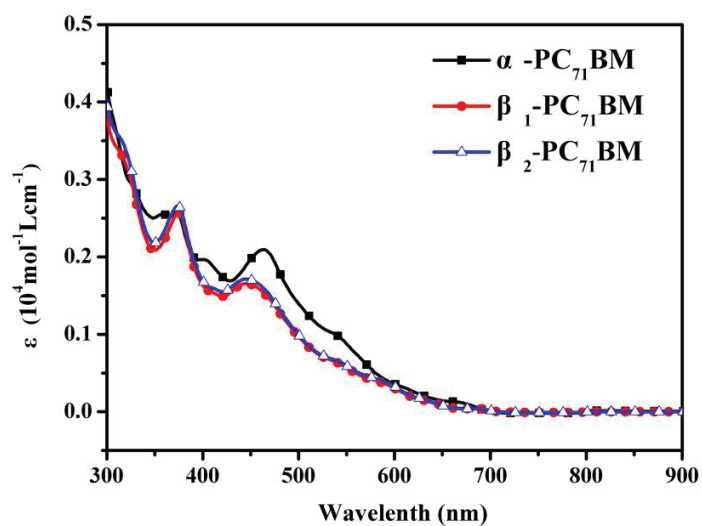


Fig. S10. UV-vis spectra of $\alpha\text{-PC}_{71}\text{BM}$, $\beta_1\text{-PC}_{71}\text{BM}$ and $\beta_2\text{-PC}_{71}\text{BM}$ in toluene solutions (10^{-5} mol/L).

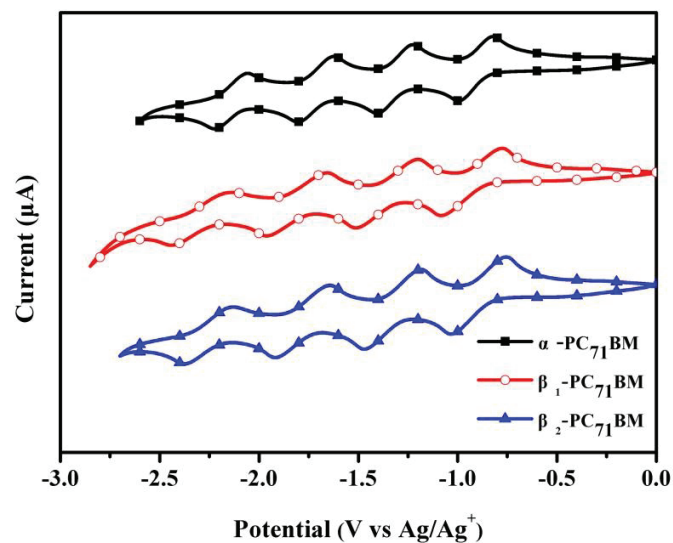


Fig. S11. Cyclic voltammograms of α -PC₇₁BM, β_1 -PC₇₁BM and β_2 -PC₇₁BM in a mixed solution of *o*-dichlorobenzene/acetonitrile (5:1) with 0.1 M Bu₄NPF₆ at a scan rate of 100 mV/s.

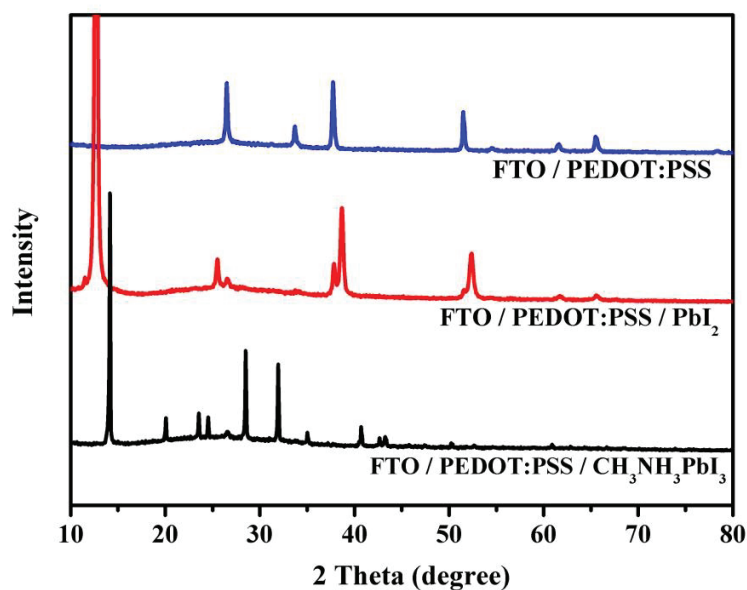


Fig. S12. X-ray diffraction spectra of the FTO/PEDOT: PSS, FTO/PEDOT: PSS/PbI₂, and FTO/PEDOT: PSS/CH₃NH₃PbI₃ on glass substrates.

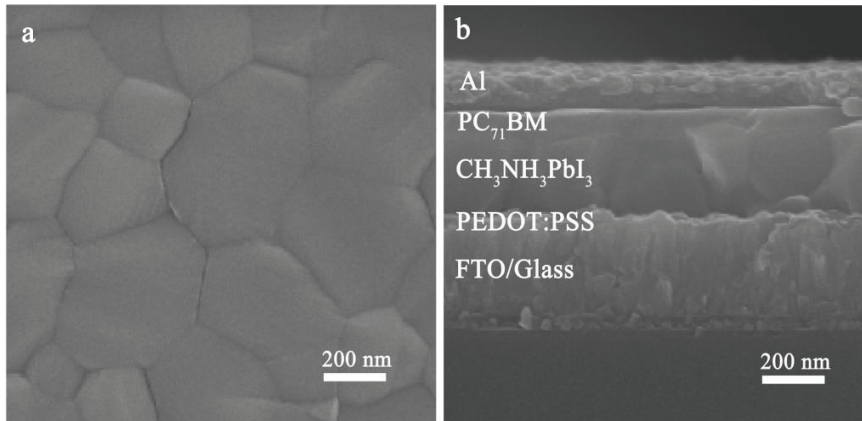


Fig. S13. SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film and device configuration. **a**, SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film on FTO/PEDOT:PSS substrate. **b**, Cross-sectional SEM images of the device configuration with PC_{71}BM isomers ($\alpha:\beta_1:\beta_2=17:1:2$) as electron conductors.

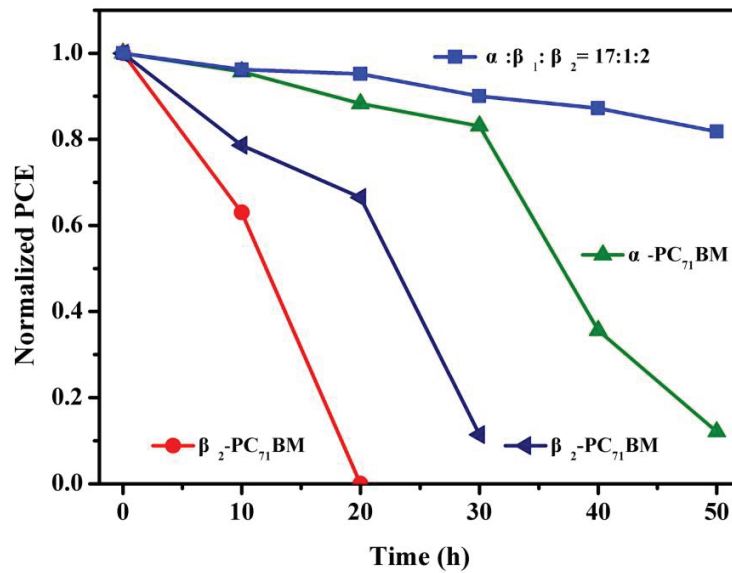


Fig. S14. Stability of the perovskite solar cells at the typical PC_{71}BM isomers formulations.

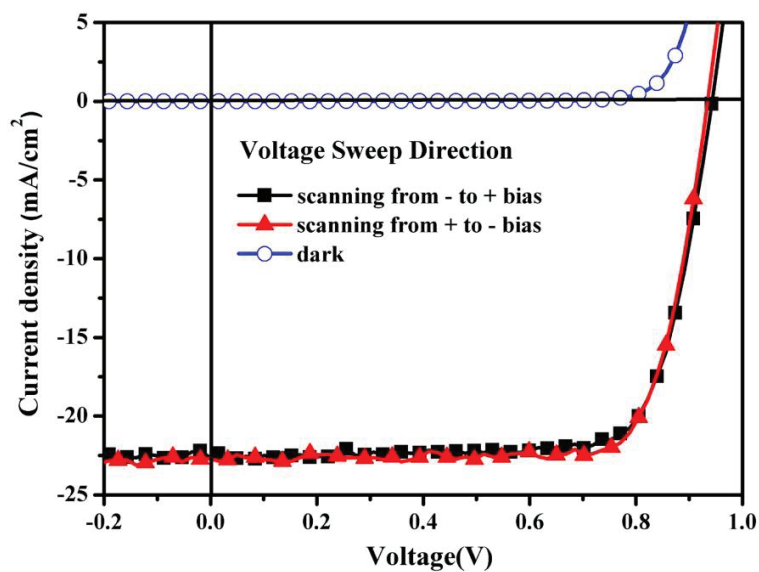


Fig. S15. J - V curves of devices using PC₇₁BM isomers (α : β_1 : β_2 =17:1:2) as electron acceptor measured at different sweep directions under AM 1.5 simulated illumination with a scan rate of 0.1 Vs⁻¹.

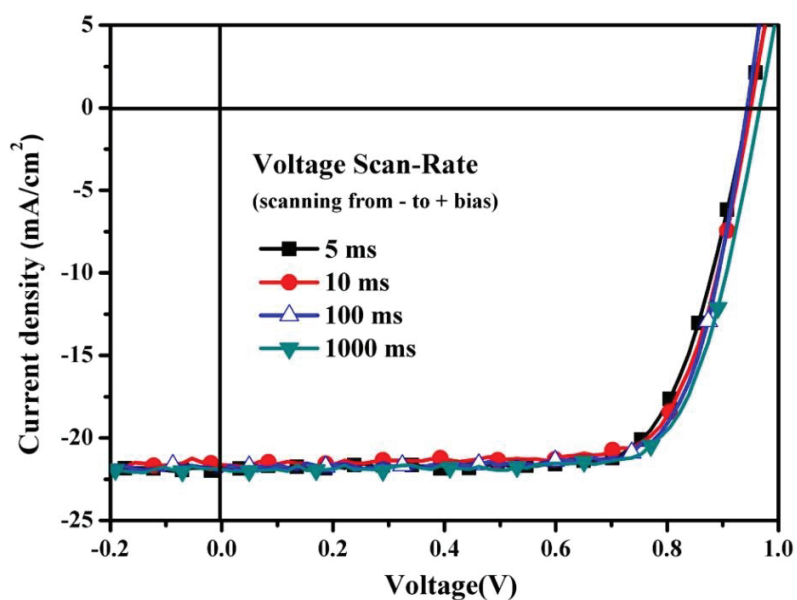


Fig. S16. J - V curves of devices using PC₇₁BM isomers (α : β_1 : β_2 =17:1:2) as electron acceptor measured at selected voltage scan rates in delay time (ms).

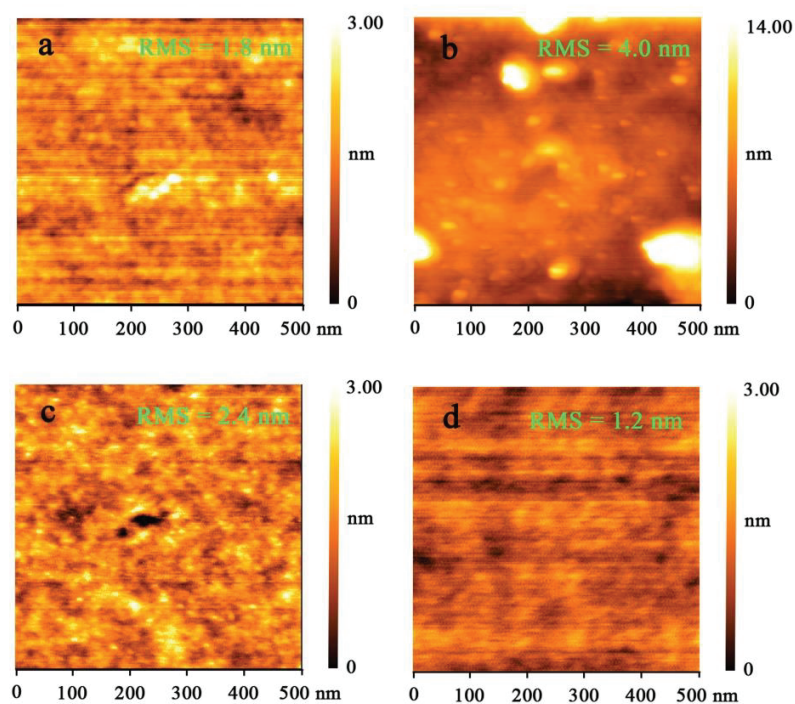


Fig. S17. AFM images of the films of α -PC₇₁BM-only film (a), β_1 -PC₇₁BM-only film (b), β_2 -PC₇₁BM-only film (c), and α : β_1 : β_2 =17:1:2 film (d). The films were prepared by spin-coating the chlorobenzene solutions of samples onto fresh cleaved mica substrates.

Table S1. Half-wave potentials of the reduction process, onset reduction potentials and LUMO energy levels of α -PC₇₁BM, β_1 -PC₇₁BM, and β_2 -PC₇₁BM.

Compound	E₁ (V)	E₂ (V)	E_{red}^{on} (V)	LUMO (eV)
α -PC ₇₁ BM	-0.992	-1.404	-0.835	-3.87
β_1 -PC ₇₁ BM	-1.074	-1.506	-0.842	-3.87
β_2 -PC ₇₁ BM	-1.027	-1.473	-0.827	-3.88

Table S2. The best photovoltaic performances of devices with different compositions of PC₇₁BM isomers as the electron acceptors.

$\alpha:\beta_1:\beta_2$	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
80:11:9 (commercial)	0.958	22.98	69.20	15.23
1:0:0	0.870	19.70	54.72	9.37
0:1:0	0.797	1.676	28.70	0.38
0:0:1	0.785	11.57	40.70	3.70
1:1:1	0.765	18.70	54.75	7.83
1:1:0	0.904	13.84	38.11	4.76
0:1:1	0.918	9.493	48.12	4.19
1:0:1	0.944	20.82	49.82	9.79
4:1:1	0.945	20.64	53.89	10.52
1:4:1	0.936	6.770	54.16	3.43
1:1:4	0.923	8.180	42.65	3.22
5:5:2	0.915	16.47	47.30	7.12
2:5:5	0.891	8.492	54.74	4.14
5:2:5	0.944	19.29	46.65	8.50
7:1:1	0.956	22.56	69.89	15.07
16:1:1	0.929	24.00	71.67	15.98
17:2:1	0.928	24.07	73.27	16.37
17:1:2	0.952	23.37	78.96	17.56