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

Supporting Information

Understanding Charge Recombination and Light-Induced Degradation: An In-Depth Study of Tert-Butyl Modified Carbazole-Based Self-Assembled Monolayers for Enhanced Performance in Organic Solar Cells

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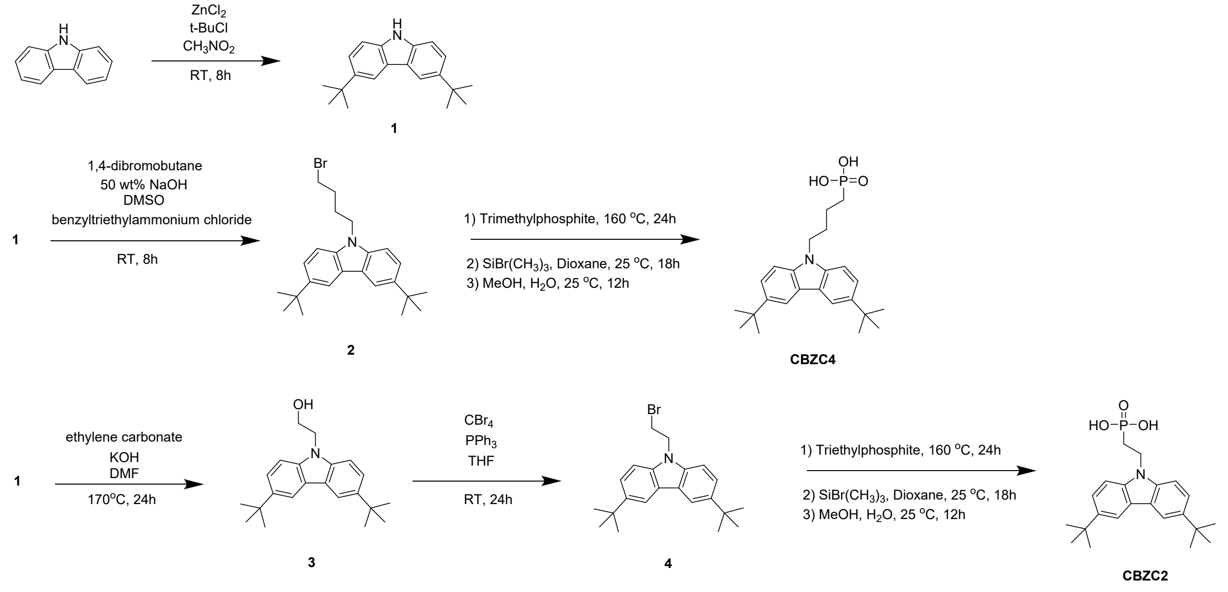
1. Materials

PBDB-T-2F (PM6), N,N'-Bis{3-[3-(Dimethylamino)propylamino]propyl}perylene-3,4,9,10-tetracarboxylic diimide (PDINN) were purchased from Derthon Optoelectronic Material S&T CO., Ltd. 2,2′- ((2Z,2′Z)-((12,13-bis(2-butyloctyl)-12,13-dihydro-[1,2,5]-thiadiazolo[3,4-] thieno[2″,3″:4′,5′]thieno[2′,3′:4,5] pyrrolo[3,2-g]-thieno[2′,3′:4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))-bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene)) dimalononitrile (Y6BO) was synthesized according to previous reports. [1] Other chemicals were purchased from Sigma-Aldrich or Fisher Scientific and were used as received unless otherwise described.



Scheme S1. Synthesis routes of anode interlayer materials.

Compound 1 and 2 were synthesized according to previous literature.[2]

2. Synthesis procedure

2.1. Synthesis of 2-(3,6-di-tert-butyl-9H-carbazol-9-yl)ethan-1-ol (3)

An oven-dried three-neck flask equipped with a condenser was vacuum backfilled three times and charged with the respective 3,6-disubstituted-9H-carbazole (1.00 eq.), ethylene carbonate (1.50 eq.) and freshly ground potassium hydroxide (0.50 eq.). Dry DMF was added and the reaction mixture was subsequently heated to 170 °C overnight. After allowing the mixture to cool to room temperature, the mixture was poured into H_2O, extracted with EtOAc three times, and washed with H_2O. The organic phase was dried over $MgSO_4$ and filtered. Purification of the crude product via column chromatography (100% DCM) afforded the desired product as a white solid in 65% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, 2H), 7.50 (dd, 2H), 7.37 (d, 2H), 4.44 (t, 2H), 4.05 (t, 2H), 1.44 (s, 18H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 142.4, 139.2, 123.6, 123.0, 116.4, 108.2, 61.5, 45.7, 34.6, 32.0. Anal. Calcd. for $C_{22}H_{29}NO$: C, 81.69; H, 9.04; N, 4.33. Found: C, 81.67; H, 9.01; N, 4.30.

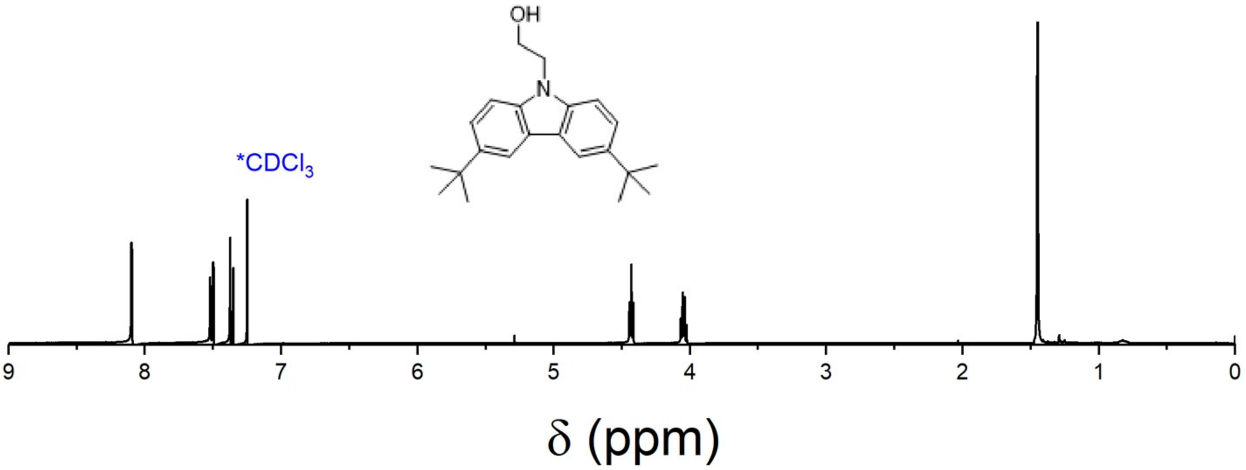


Figure S1. ^{1}H-NMR spectra of compound 3.

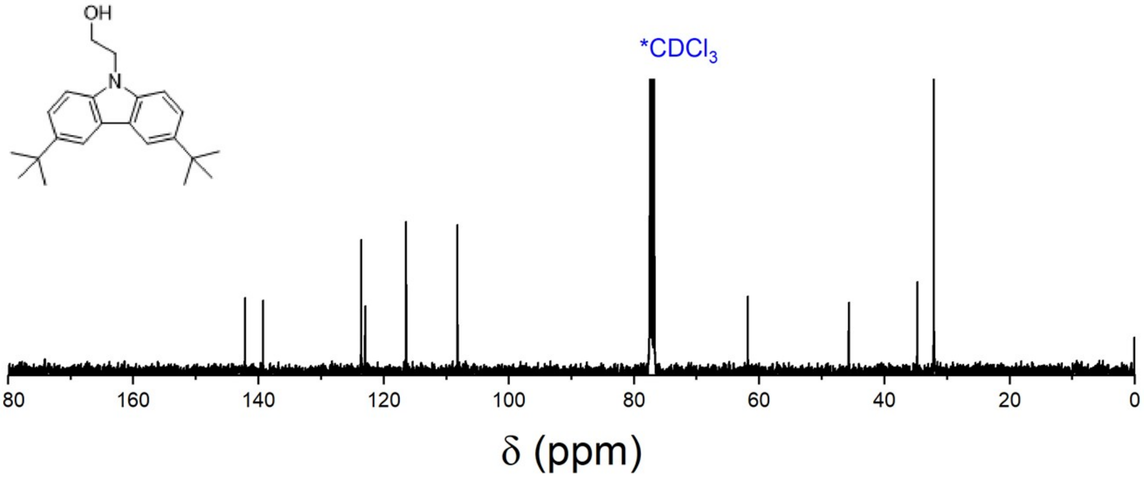


Figure S2. ^{13}C-NMR spectra of compound 3.

2.2. Synthesis of 9-(2-bromoethyl)-3,6-di-tert-butyl-9H-carbazole (4)

An oven-dried three-neck flask was vacuum backfilled three times and charged with the respective 2-(3,6-disubstituted-9H-carbazol-9-yl)ethan-1-ol (1.00 eq.) and triphenylphosphine (1.50 eq.). Dry THF was added and the resulting mixture was cooled to 0 °C. A second oven-dried three-neck flask was charged with carbon tetrabromine (1.25 eq.) and dry THF. This solution was added dropwise at 0 °C and the resulting mixture was stirred at 0 °C for another two hours before being warmed up to room temperature overnight. The reaction solvent was removed in vacuo and the crude solid was redissolved in DCM. The organic phase was washed with 10% NaOH(aq.) and twice with H_2O, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude product via column chromatography (hexane:DCM = 1:1) afforded the desired product as an off-white solid in 99% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, 2H), 7.52 (d, 2H), 7.33 (d, 2H), 4.65 (t, 2H), 3.65 (t, 2H), 1.46 (s, 18H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 142.5, 138.4, 123.7, 123.0, 116.4, 107.8, 45.0, 34.8, 32.3, 27.9. Anal. Calcd. for $C_{22}H_{28}BrN$: C, 68.39; H, 7.30; N, 3.63. Found: C, 68.21; H, 7.28; N, 3.60.

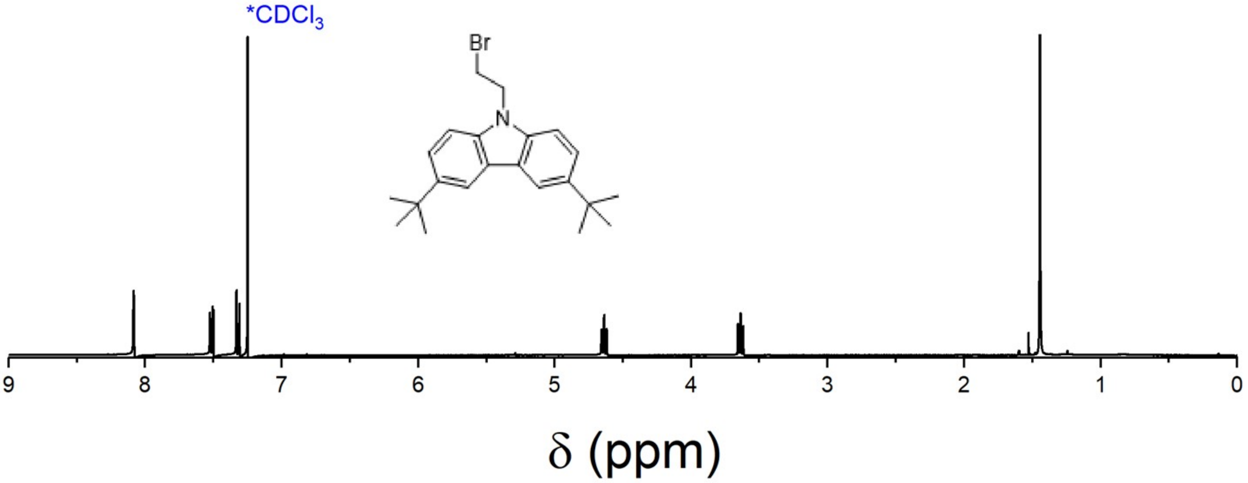


Figure S3. ^{1}H-NMR spectra of compound 4.

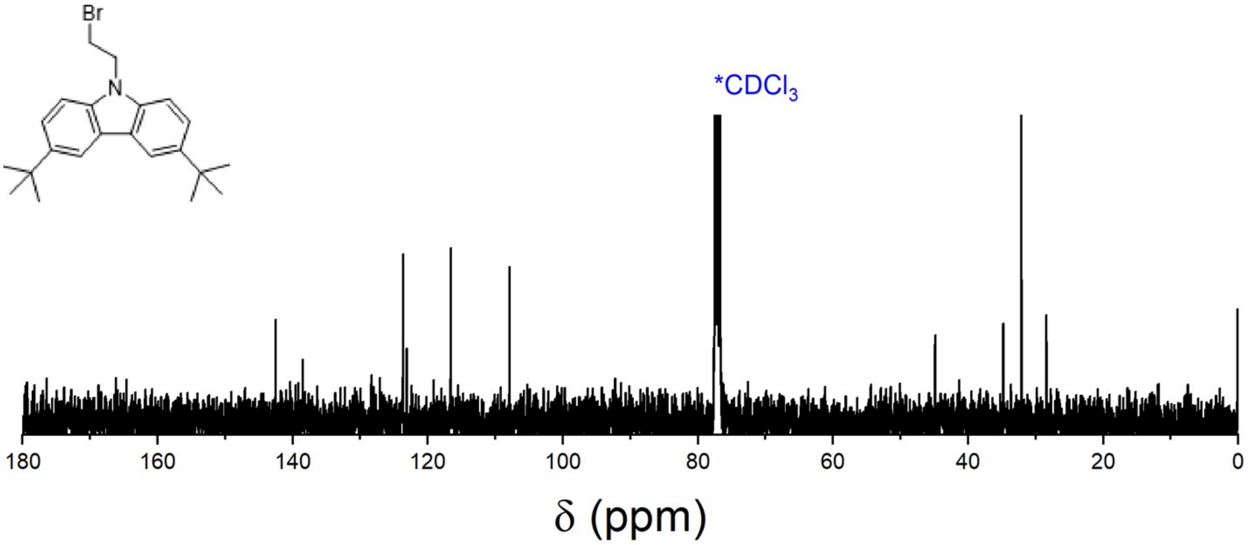


Figure S4. ^{13}C-NMR spectra of compound 4.

2.3. General procedures of phosphonic acid series (CBZC4 and CBZC2)

A 100 mL Schlenk tube was filled with alkyl bromide compound (1.5 mmol) and triethyl phosphite (10 mL), then the mixture was heated to 160 °C and stirred overnight under a nitrogen atmosphere. The extra triethyl phosphite was removed by reduced pressure distillation to give a light-yellow oil without further purification. The oil was dissolved in anhydrous 1,4-dioxane (10 mL) at room temperature and trimethylbromosilane (15 mmol) was added dropwise, then the mixture was stirred overnight. The 1,4-dioxane was removed with rotary evaporator to give a white solid. The white solid was dissolved in methanol (10 mL) at room temperature, then deionized water was added dropwise until the mixture became opaque and stirred for another 12 h. The crude product was collected by filtration and washed with deionized water. The crude product was dissolved in methanol (5 mL) and then reprecipitate in acetonitrile (10 mL) and filtrated to give the final product (yield 60~65%).

CBZC4:

^{1}H-NMR (400 MHz, DMSO-d6, ppm): δ 8.13 (m, 2H), 7.45 (m, 4H), 4.28 (t, 2H), 1.82-1.03 (m, 22H); ^{13}C-NMR (400 MHz, DMSO-d6, ppm): δ 144.3, 130.9, 129.6, 126.0, 118.2, 114.5, 46.9, 28.2, 27.5, 27.4, 26.9, 24.3, 20.7, 20.6; ^{31}P-NMR (400 MHz, DMSO-d6, ppm): δ 25.9; Q-TOF-MS (APCI) m/z: calculated for $C_{24}H_{34}NO_3P$ 415.23, found 415.23.

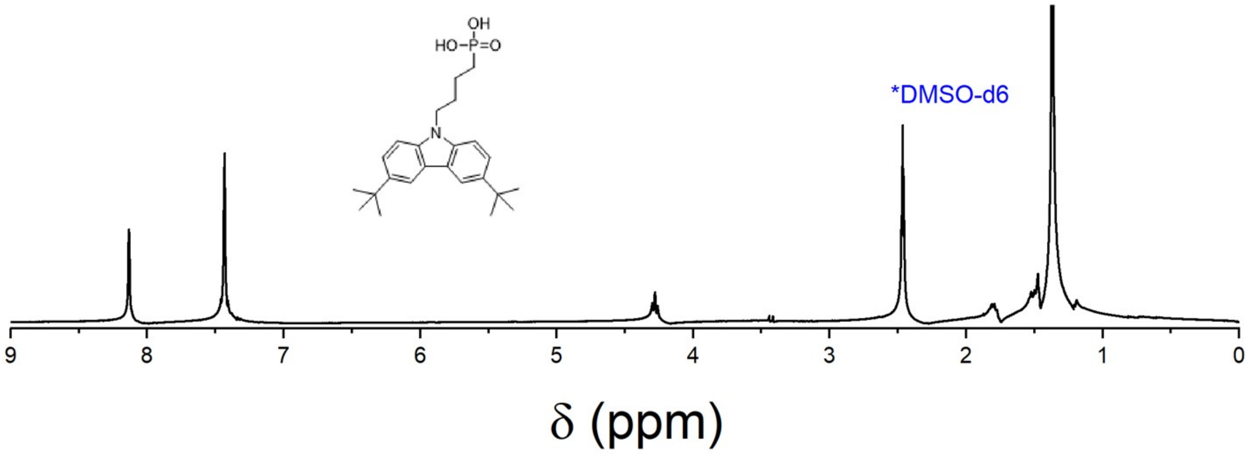


Figure S5. ^{1}H-NMR spectra of CBZC4

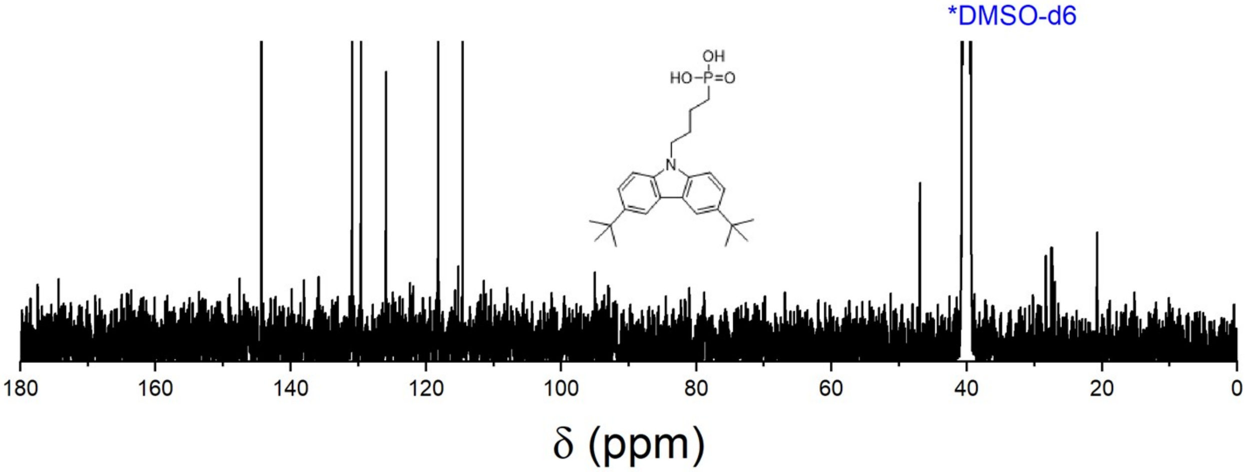


Figure S6. ^{13}C-NMR spectra of CBZC4

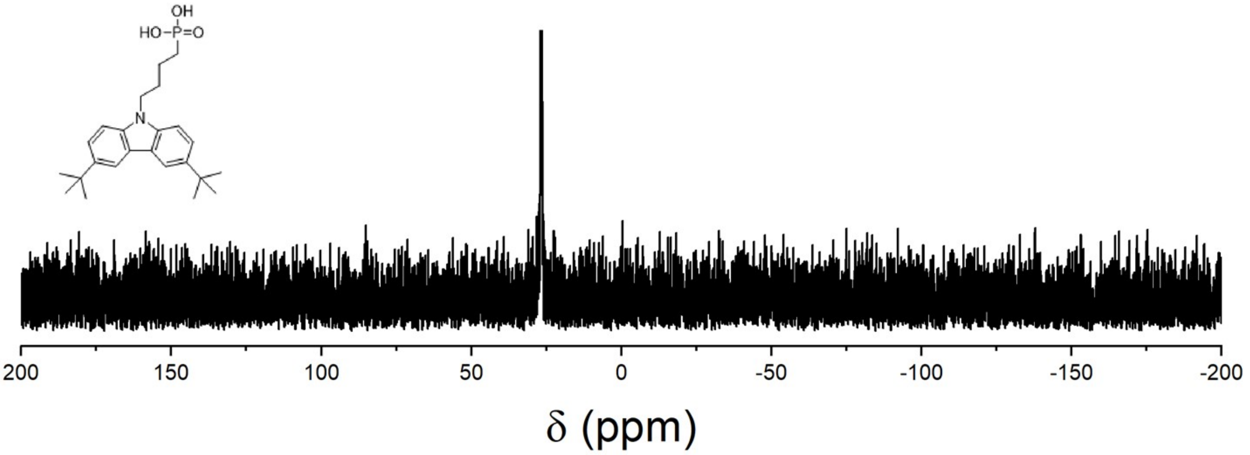


Figure S7. ^{31}P-NMR spectra of CBZC4

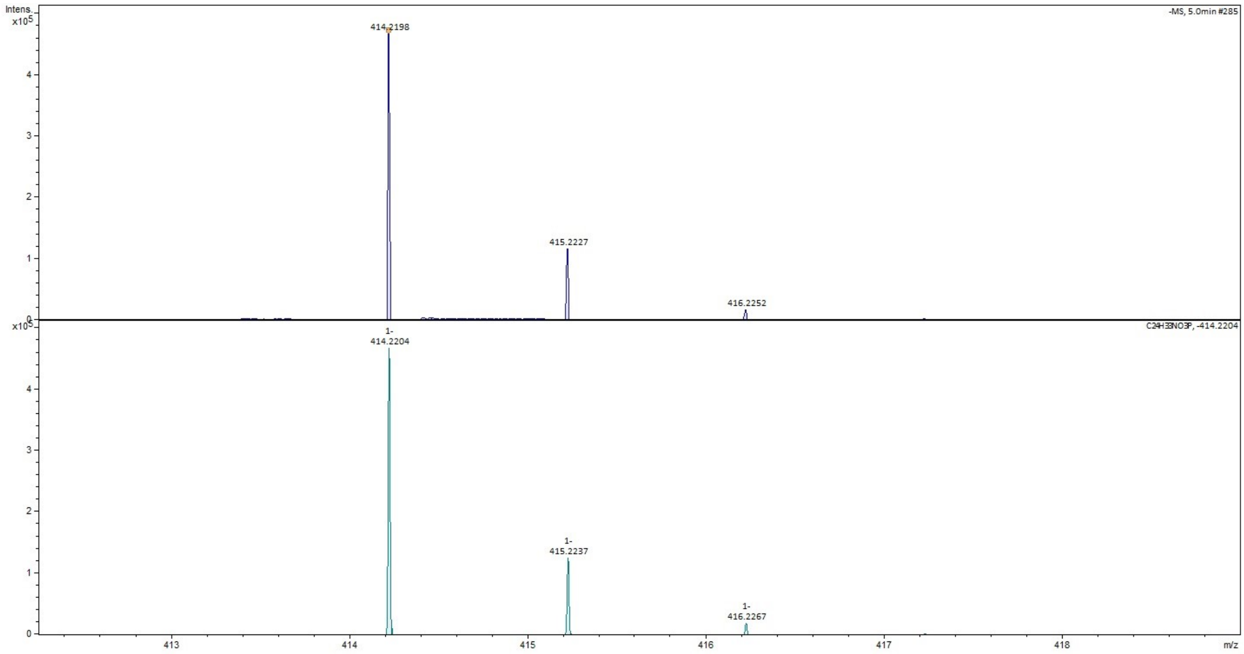


Figure S8. Mass spectra of CBZC4.

CBZC2:

^{1}H-NMR (400 MHz, DMSO-d6, ppm): δ 8.06 (m, 2H), 7.51 (m, 4H), 4.55 (m, 2H), 2.13 (m, 2H), 1.41 (m, 18H); ^{13}C-NMR (400 MHz, DMSO-d6, ppm): δ 141.7, 138.4, 123.1, 123.0, 115.5, 107.6, 40.4, 36.8, 34.5, 31.2; ^{31}P-NMR (400 MHz, DMSO-d6, ppm): δ 25.9; Q-TOF-MS (APCI) m/z: calculated for $C_{22}H_{30}NO_3P$ [+ H]$^+$ 388.2, found 388.2.

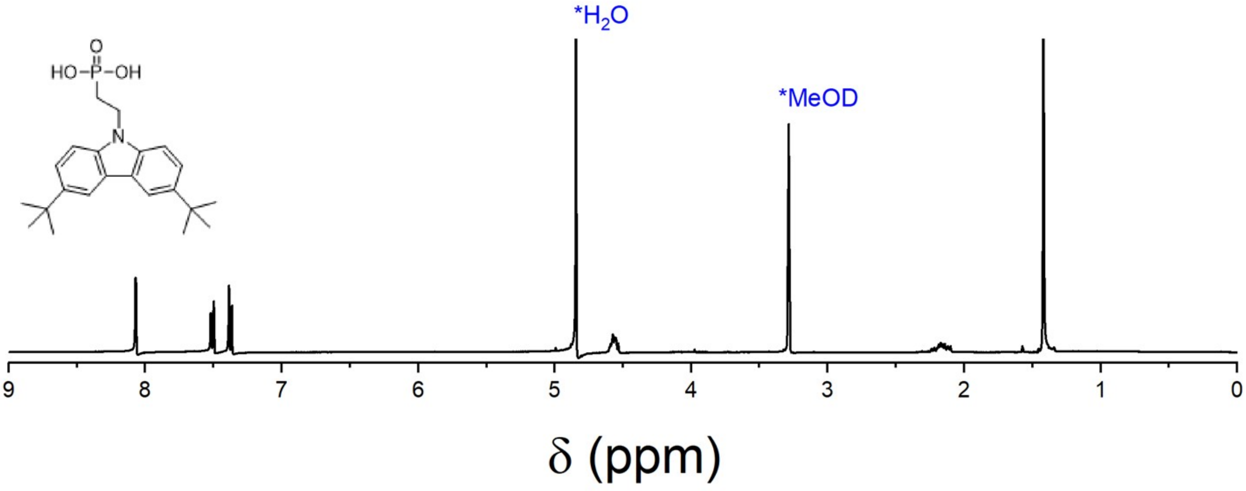


Figure S9. ^{1}H-NMR spectra of CBZC2

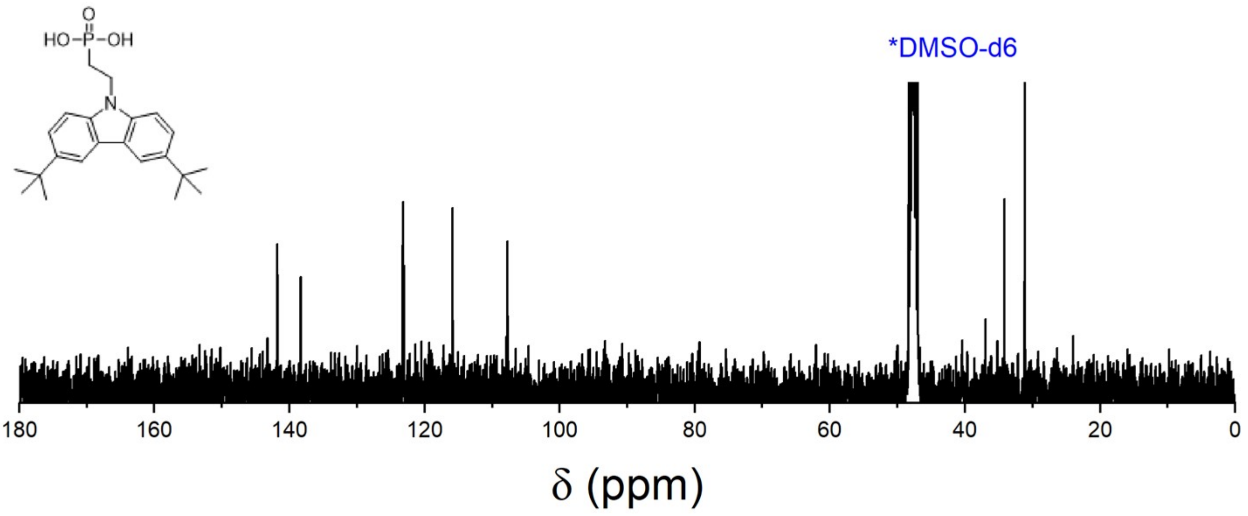


Figure S10. ^{13}C-NMR spectra of CBZC2

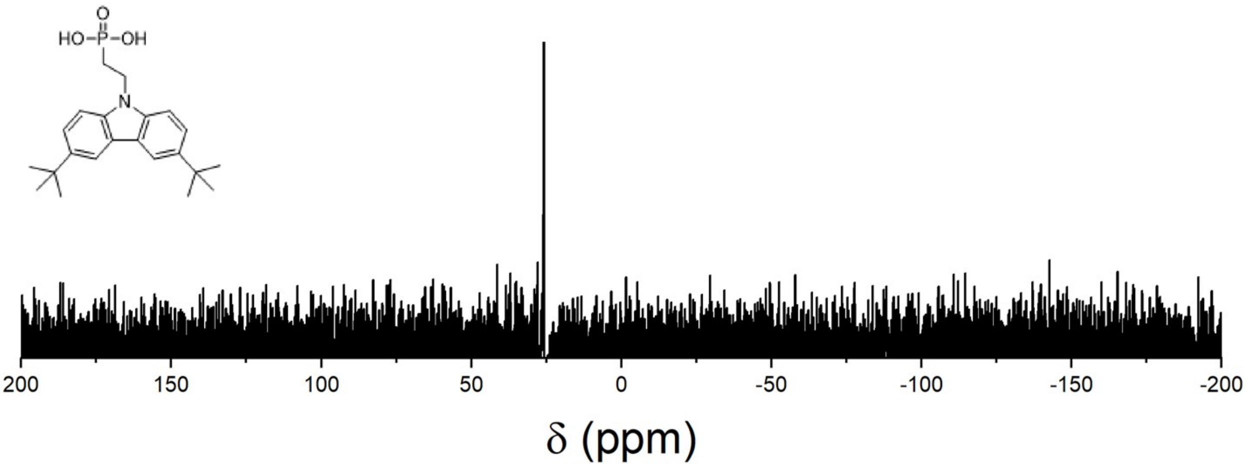


Figure S11. ^{31}P-NMR spectra of CBZC2

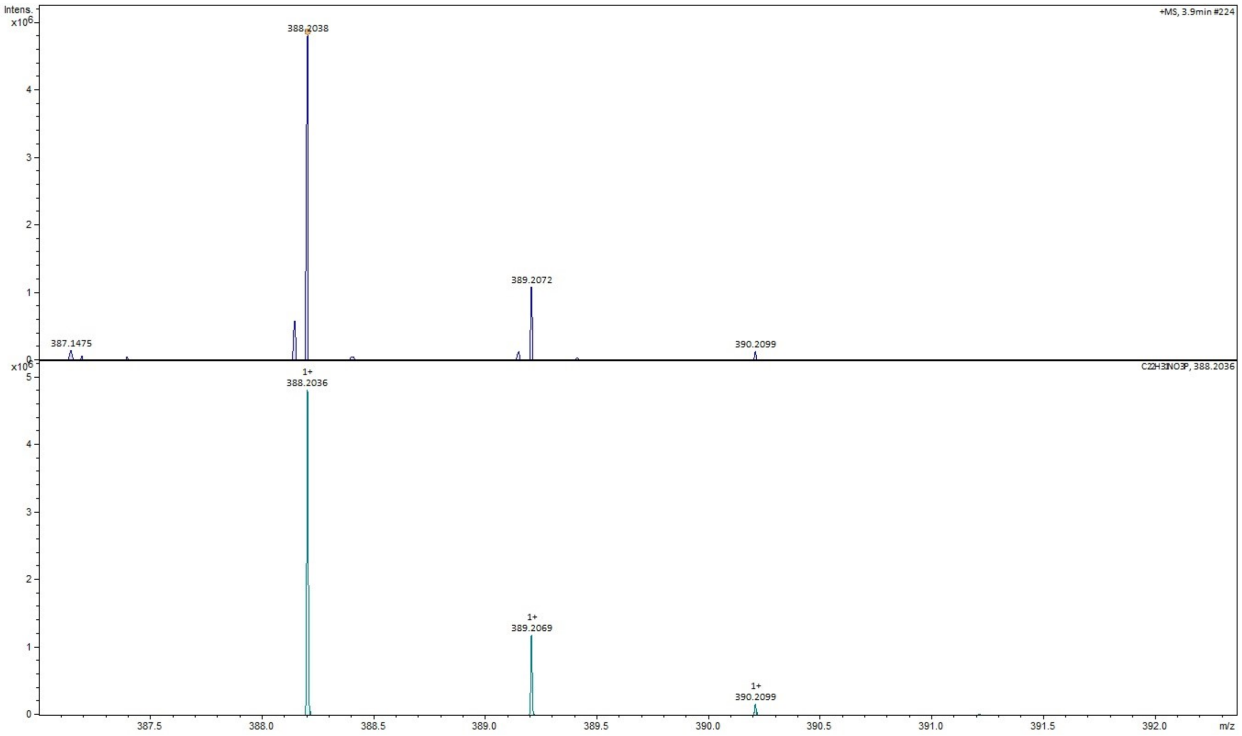


Figure S12. Mass spectra of CBZC2.

3. Fabrication of OSCs

The conventional type OSC with the structure: [ITO/HTL/PM6:Y6BO (110 ~130nm)/PDINN (9 nm)/Ag(100 nm)] was fabricated. Anode interlayer materials (CBZC4, CBZC2) were dissolved in EtOH and were filtered through a 0.45 nm mm membrane filter. The HTL solution was spin-coated by optimized conditions. The HTL films were annealed 100 °C for 15 min. The non-fullerene active layer was spin-cast from the mixture of PM6 and Y6BO (obtained by dissolving 8 mg of PM6 and 9.6 mg of Y6BO in 1 mL of chlorobenzene with 0.5 % (v/v) 1-chloronaphthalene (CN) and rotated at 1000 rpm for 60 s. The active solution was filtered through a 0.45 mm membrane filter before spin coating. PDINN was dissolved in 1 mL of MeOH and was spin-coated by optimized conditions. The PDINN solution was filtered through a 0.45 mm membrane filter before spin coating. Successive layer of Ag was thermally evaporated through a shadow mask, with a device area of 0.04 cm^2 at 2 x 10^{-6} Torr.

3. Measurements

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a JEOL JNM ECZ-400 spectrometer. UV–visible spectra of thin films were determined using a JASCO V-730. Cyclic voltammetry (CV) measurements were carried out by using a potentiostat (IVIUM Technology, COMPACTSTAT,) with tetrabutylammonium hexafluorophosphate (0.1 M, Bu_4NPF_6) as the electrolyte in dichloromethane. For CV measurements, a glassy carbon electrode coated with an interlayer and a platinum wire was used as the working and counter electrode, respectively. A silver wire was used as a pseudo-reference electrode with a ferrocene/ferrocenium external standard. The compound mass were measured with ultra-high resolution Q-TOF MS LC MS/MS system (bruker/maXis-HD Co.). The contact angles were determined with contact angle instrument (phoenix 300 touch/ SEO Co.). The morphology of films was analysed with Park NX7 (Park SYSTEMS) and JEM-F200 (JEOL Co.). The current density-voltage measurements were performed under simulated light (AM 1.5G, 1.0 sun condition/100 mW/cm^{2}) from a 150 W Xe lamp, using a KEITHLEY Model 2400 source-measure unit. A calibrated Si reference cell with a KG5 filter certified by the National Institute of Advanced Industrial Science and Technology was used to confirm the 1.0 sun condition. The compound chemical bonding and work function were measured with Electron spectrometer (AXIS SUPRA/KRATOS Analytical Ltd), The Fluorescence luminescence spectrometer system were measure with HORIBA/Fluorolog-QM), An impedance analyzer (WonATech, ZconTM Impedance Monitor) was used to perform non-modulated impedance spectroscopy at zero bias, The Grazing-incidence wide-angle X-ray scattering (GIWAXS) spectra were obtained on the 3C beamline with 13 keV ($\lambda = 0.123$ nm) X-ray irradiation source and the beam size of 300 μm (height) 23 μm (width) in the Pohang Accelerator Laboratory (PAL). A two-dimensional charge-coupled device detector (Mar165 CCD) was used, and the distance from the sample to the detector was 0.2 m. The X-ray beam angle of the incidence was chosen such that the beam would penetrate the entire active layer while minimizing scattering from the substrate: ~ 0.12°.

The samples were partially completed devices so that the entire exposed surface is composed of active layer on the Si wafer and were examined under ambient. Preparation of film for GIWAXS was followed same as the preparation of the active layer.

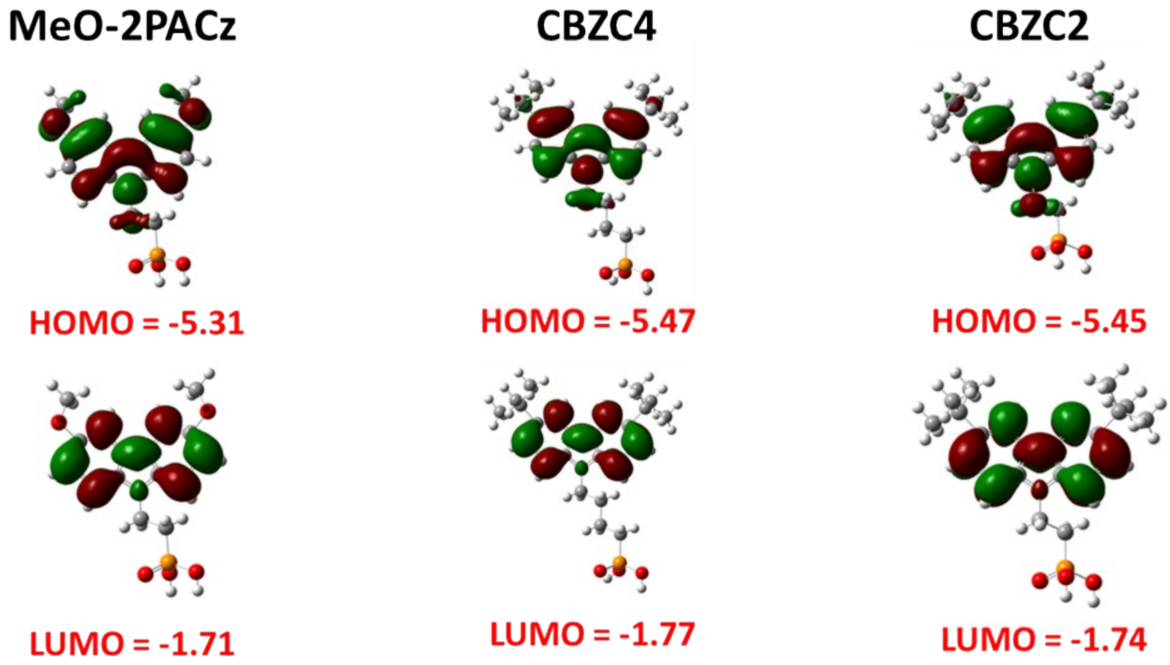


Figure S13. DFT calculation of SAMs

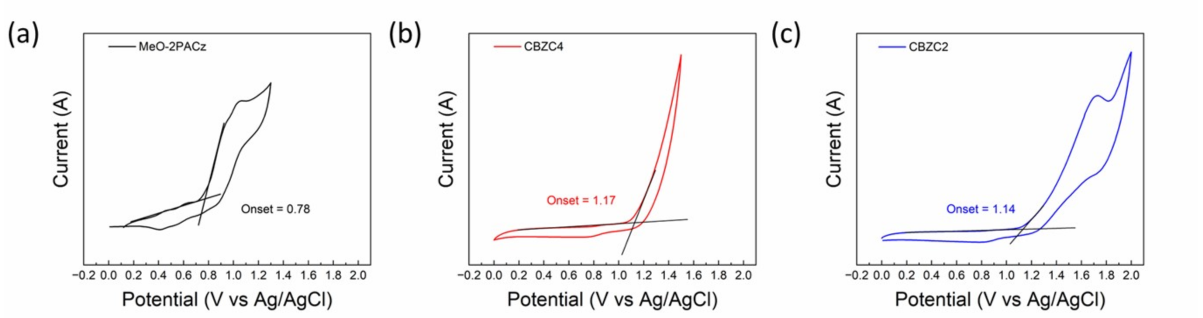


Figure S14. Cyclic voltammograms of SAMs

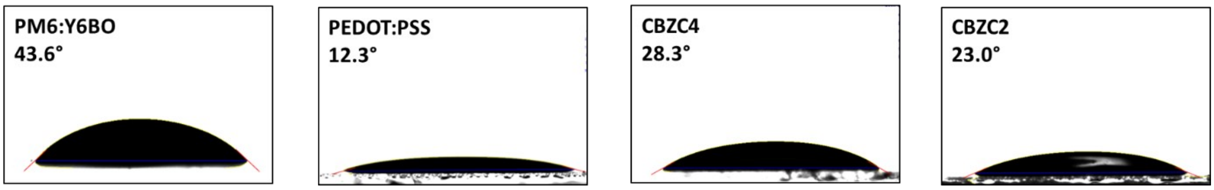


Figure S15. Diiodomethane contact angles of pristine active layer or HTLs.

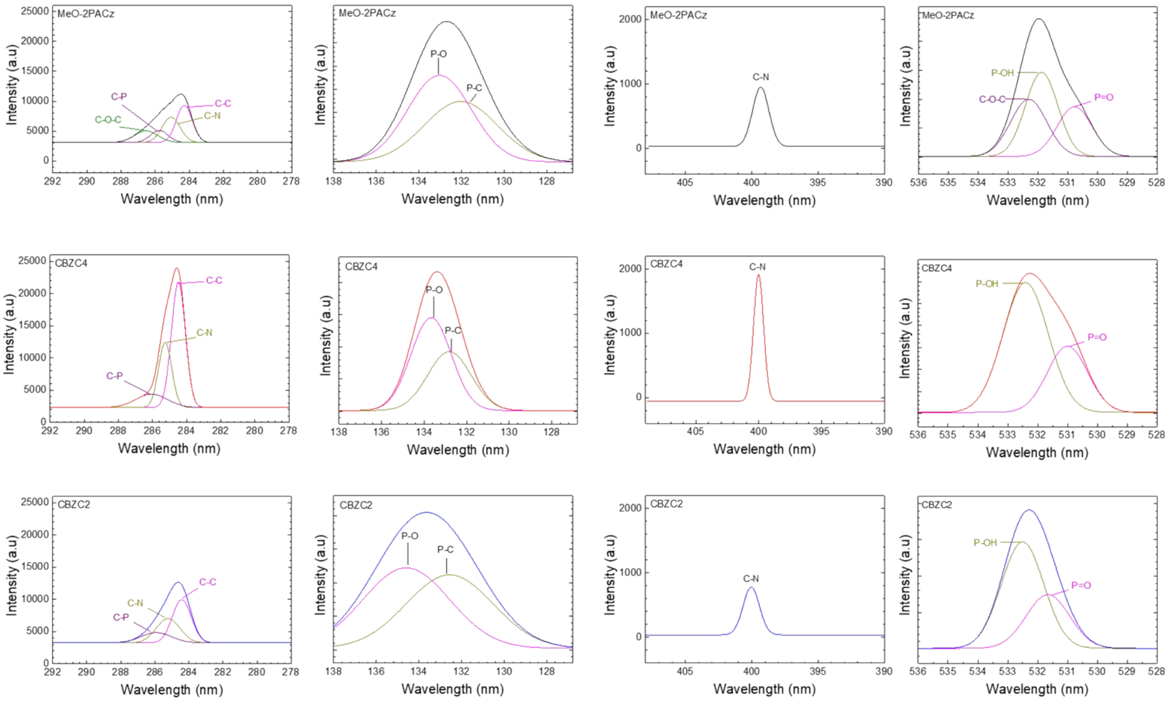


Figure S16. XPS spectra of each component.

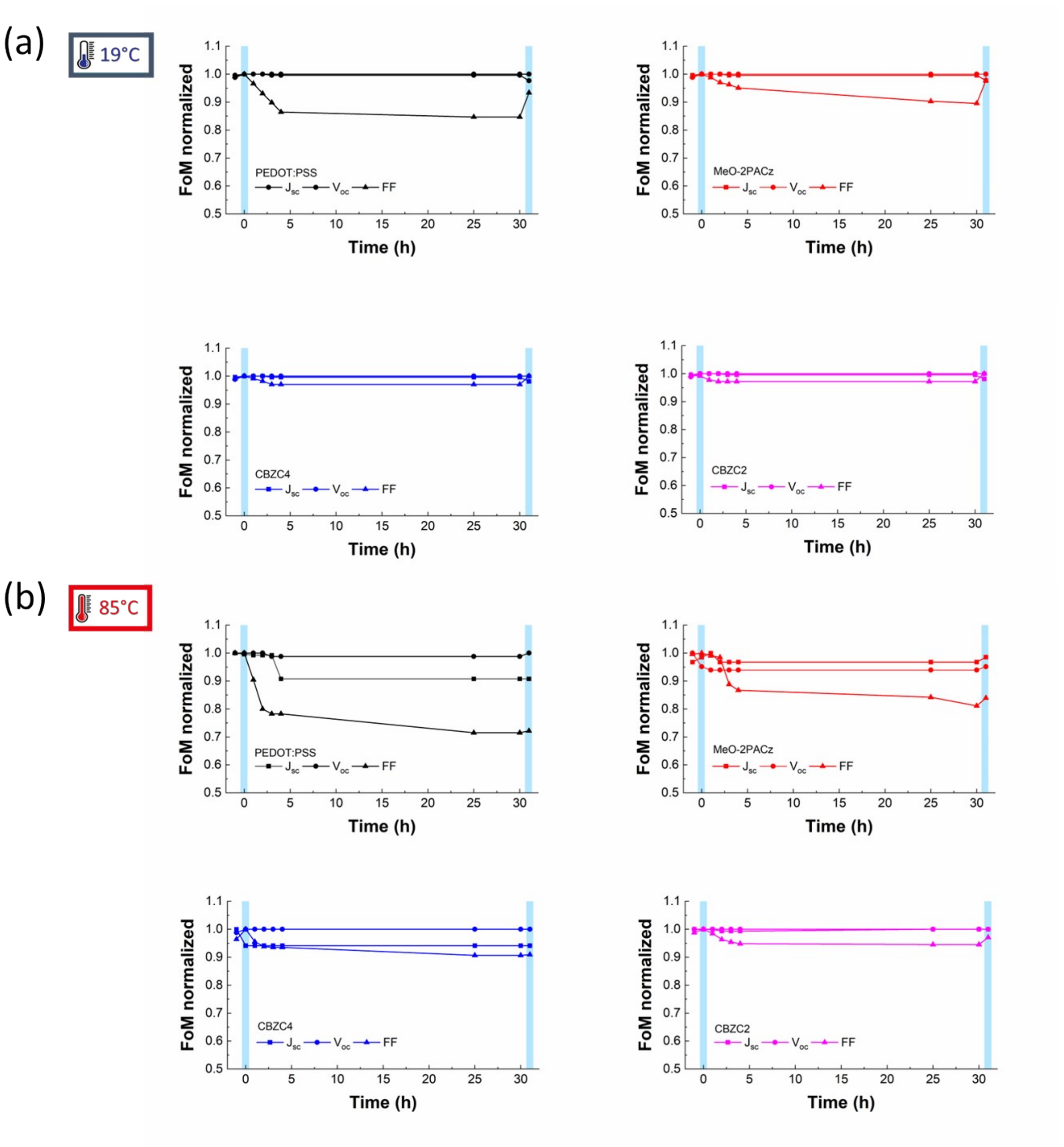


Figure S17. Normalized different figures of merit (FoM) of the device as a function of time under room temperature (a) and under heat treatment at 85°C (b). The blue mark indicates UV illumination time.

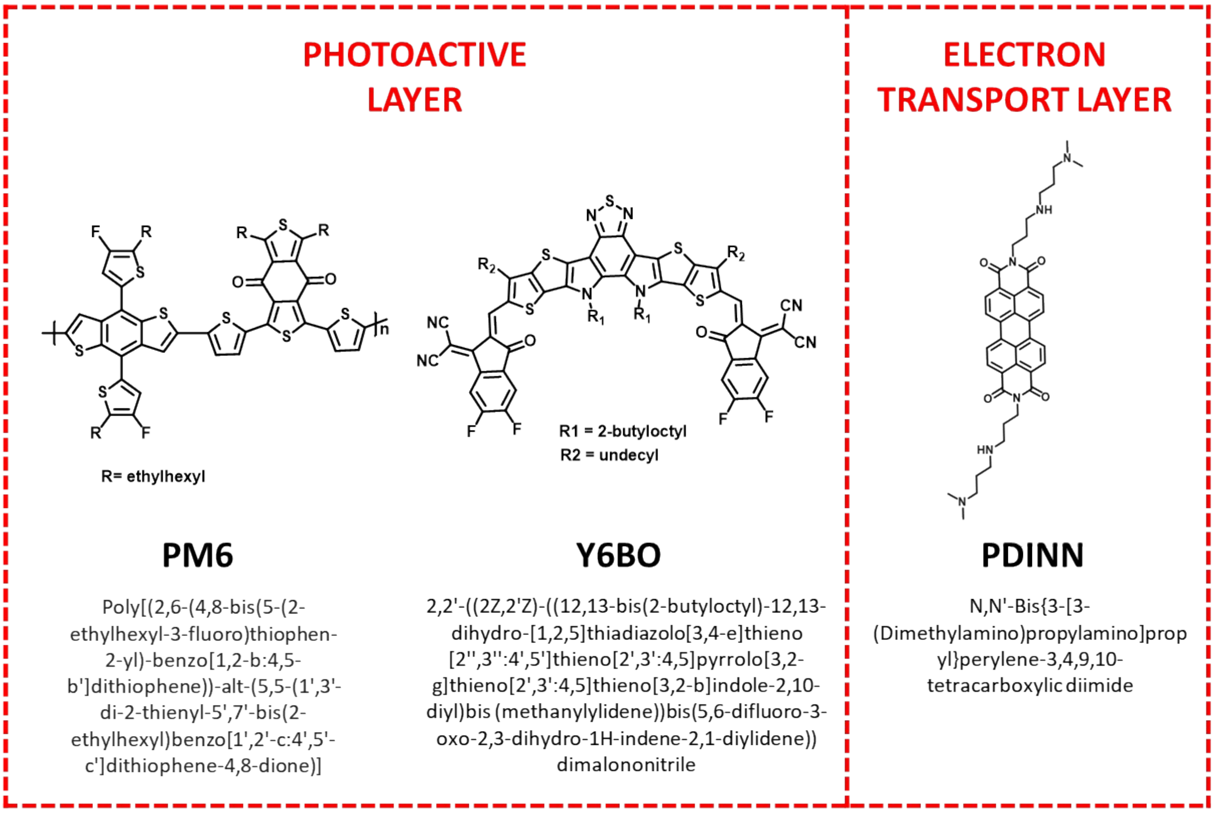


Figure S18. Chemical structure and full name of photoactive layer and ETL.

Table S1. The best photovoltaic parameters of the interlayer material. The average values for the photovoltaic parameters of each device are also provided in parentheses.

Interlayer	**Spinrate (rpm/s)**	***J_{sc}*** **(mA/cm^2)**	***V_{oc}*** **(*V*)**	***FF*** **(%)**	***PCE*** **(%)**
PEDOT:PSS	2000/60	25.4 (24.9±0.64)	0.83 (0.83±0.01)	74.0 (73.7±0.42)	15.6 (15.3±0.36)
	3000/60	25.2 (24.7±0.71)	0.83 (0.83±0.01)	73.8 (73.5±0.42)	15.4 (15.2±0.35)
	4000/60	**25.8** **(25.7±0.18)**	**0.85** **(0.85±0.00)**	**72.4** **(72.2±0.21)**	**15.9** **(15.8±0.13)**
	5000/60	24.5 (24.3±0.22)	0.83 (0.83±0.00)	73.2 (73.2±0.10)	14.9 (14.8±0.13)
MeO-2PACz	2000/60	26.0 (25.9±0.40)	0.83 (0.83±0.00)	71.3 (71.0±0.30)	15.4 (15.2±0.14)
	3000/60	26.5 (26.3±0.36)	0.83 (0.83±0.00)	71.0 (70.3±0.17)	15.6 (15.3±0.22)
	4000/60	**26.3** **(25.6±0.83)**	**0.84** **(0.84±0.01)**	**71.7** **(71.6±0.54)**	**15.8** **(15.5±0.41)**
	5000/60	26.7 (26.4±0.49)	0.83 (0.83±0.00)	68.7 (68.7±0.92)	15.2 (15.2±0.08)
CBZC4	2000/60	26.6 (26.0±0.73)	0.83 (0.83±0.01)	70.9 (70.6±0.29)	15.7 (15.3±0.36)
	3000/60	26.7 (26.0±0.73)	0.84 (0.84±0.01)	71.6 (70.9±0.58)	16.1 (15.4±0.51)
	4000/60	**26.8** **(26.0±0.63)**	**0.85** **(0.85±0.01)**	**71.2** **(71.5±0.28)**	**16.2** **(15.7±0.38)**
	5000/60	26.4 (25.9±0.71)	0.84 (0.84±0.00)	70.2 (69.8±0.02)	15.6 (15.3±0.42)
CBZC2	2000/60	26.8 (26.9±0.53)	0.83 (0.83±0.01)	71.3 (70.9±0.35)	15.9 (15.9±0.15)
	3000/60	26.8 (26.8±0.23)	0.84 (0.84±0.01)	71.5 (71.2±0.30)	16.1 (15.9±0.15)
	4000/60	**26.5** **(25.9±0.97)**	**0.85** **(0.85±0.01)**	**73.0** **(73.3±0.31)**	**16.4** **(15.9±0.57)**
	5000/60	25.9 (25.7±0.45)	0.84 (0.83±0.01)	70.9 (71.2±0.55)	15.4 (15.2±0.20)

Table S2. Fitted results of the TRPL spectra of BHJ film deposited on ITO/HTL substrates

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	τave (ns)
PEDOT: PSS	33.171	0.383	9.746	3.02	3.94	22.15	2.76
MeO-2PACz	44.198	0.561	10.855	6.03	1.93	37.61	2.88
CBZC4	89.537	0.751	19.881	8.69	3.19	83.85	4.50
CBZC2	94.154	0.764	18.699	10.66	3.14	122.72	5.66

The TRPL decay spectra were fitted by a biexponential function:

$$y = y_0 + A_1 e^{-x/\tau 1} + A_2 e^{-x/\tau 2} + A_3 e^{-x/\tau 3}$$

and the average decay lifetime was calculated with function:

$$\tau\text{ave} = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3}$$

(1) L. Hong, H. Yao, Z. Wu, Y. Cui, T. Zhang, Y. Xu, R. Yu, Q. Liao, B. Gao, K. Xian, H.Y. Woo, Z. Ge, and J. Hou, *Adv. Mater.*, **31**, 1 (2019).

(2) H. Jia, C. Feng, W. Han, Y. Xue, Y. Jin, and D. Li, *J. Fluoresc.*, **32**, 267 (2022).