## Supporting information

# Bulk heterojunction organic photovoltaic cells based on D-A type BODIPY small molecules as nonfullerene acceptor

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**General**

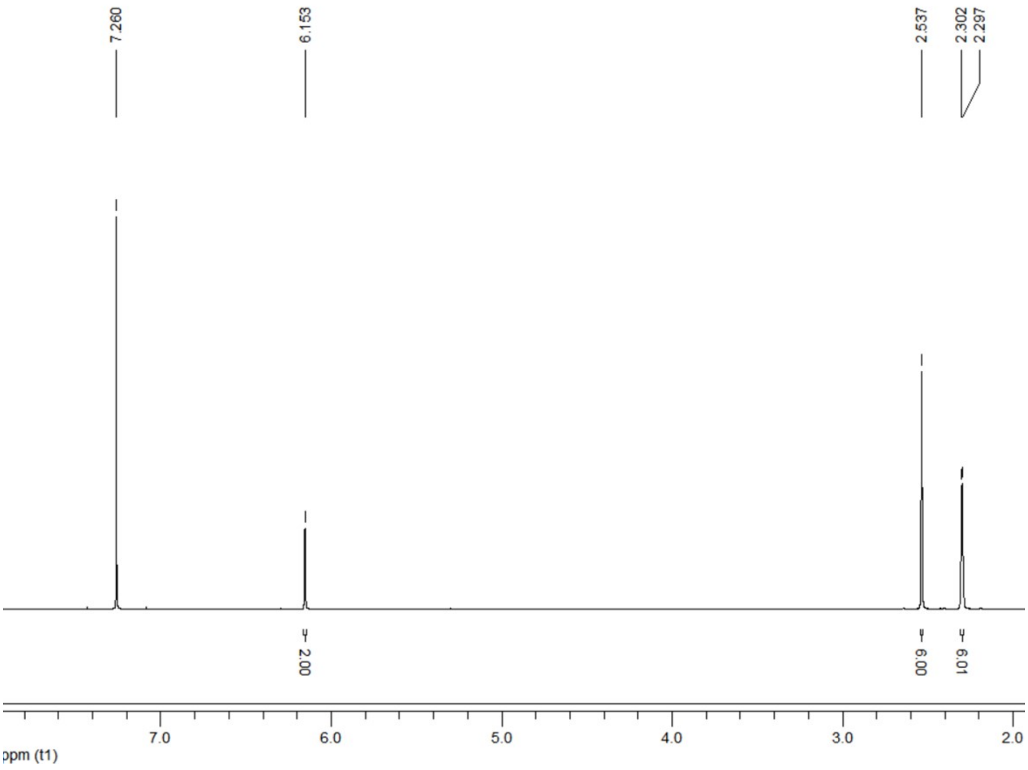
All chemicals and solvents were of analytical reagent grade and used directly as received unless otherwise noted. $^1$H-NMR /$^{13}$C-NMR spectra were recorded on a Bruker AVANCE III 400M/600 MHz spectrometer. Chemical shifts for $^1$H NMR spectra were expressed in parts per million (ppm) relative to $CDCl_3$ ($\delta$ = 7.26 ppm) or DMSO-$d_6$ ($\delta$ = 2.50 ppm) as the internal standard. UV-Vis spectra were recorded on Shimadzu UV-2600 spectrophotometer at ambient temperature with a 1 cm quarts cell. The high-resolution mass spectra (HRMS) data was performed on a LTQ Orbitrap XL spectrometer equipped with an electrospray ionization (ESI) source. Cyclic voltammetry was performed with a three-electrode-compartment cell in $CH_2Cl_2$ solutions with 0.1 M [n-$Bu_4N$]($ClO_4$) as supporting electrolyte using CHI-730D electrochemistry workstation. A glassy carbon electrode of diameter 3 mm was used as the working electrode while platinum wire and Fc/$Fc^+$ electrodes were used as the counter and reference electrodes respectively.

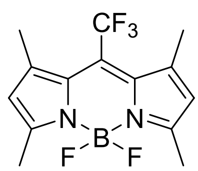
**Synthesis of $CF_3$-BDP.** In a 100 mL three-necked flask, 2, 4-dimethylpyrrole(1.5 mL, 14.6 mmol) was dissolved in $CH_2Cl_2$ (30 mL) under an argon atmosphere. $PhSiCl_3$(1.2 mL, 7.0 mmol) was added into the reaction system and stirred at room temperature for 10 min, then adding triethylamine and boron trifluoride ether in an ice bath and stir for 3 h. The mixture was extractedwith $CH_2Cl_2$ and washed water, and the organic layer was dried over anhydrous $Na_2SO_4$. The organic solvent was evaporated on a rotary evaporator under reduced pressure. The resulting residue was purified by silica gel column chromatography using $CH_2Cl_2$- petroleum ether ($V_1$:$V_2$= 1:1) as the eluent to afford the desired compound **$CF_3$-BDP** (168 mg, 8%). $^1$H-NMR (600 MHz, $CDCl_3$, ppm): $\delta$ 2.54 (s, 6H), 2.31-2.29 (m, 6H), 6.15 (s, 2H).

**Synthesis of 9-butyl-9H-carbazole-3-carbaldehyde.** Carbazole (1.67 g, 10 mmol), bromobutane (1.09 g, 12.5 mmol) and NaOH (5 g, 125 mmol) were dissolved in DMSO (30 mL) at room temperature for 6 h. Then the mixture was poured into ice water, extracted with ether, and the organic layer was dried over anhydrous $Na_2SO_4$. The organic solvent was evaporated on a rotary evaporator under reduced pressure to afford **9-butyl-9H-carbazole**(1.93 g, 86%). After that, in a single 50 mL flask, $POCl_3$ (3.2 mL) was added drop by drop into DMF (1.5 mL) in ice bath and the reaction mixture stirred at room temperature for 2 hours. **9-butyl-9H-carbazole** (1.5 g, 6.7 mmol) was added into the reaction system. The reaction was carried out at 60℃ for 12 hours. The reaction was quenched by saturated $NaHCO_3$ solution and stirred at room temperature for 1 hour. The mixture was extracted with $CH_2Cl_2$ and was washed water, and the organic layer was dried over $Na_2SO_4$. The organic solvent was evaporated on a rotary evaporator under reduced pressure. The resulting residue was purified by silica gel column chromatography using $CH_2Cl_2$ as the eluent to afford **9-butyl-9H-carbazole-3-carbaldehyde** (1.5 g, 89%). $^1$H-NMR (600 MHz, $CDCl_3$, ppm): δ 10.10 (d, J = 11.4 Hz, 1H), 8.15 (d, J = 7.8 Hz, 1H), 8.01 (dd, J = 8.4, 1.2 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.49-7.43 (m, 2H), 7.33 (t, J = 7.2 Hz, 1H), 0.96 (t, J = 7.2Hz, 3H), 1.48-1.36 (m, 2H), 1.94-1.83 (m, 2H), 4.34 (dd, J = 14.4, 7.2 Hz, 2H), 8.68-8.45 (m, 1H).

**Synthesis of $CF_3$-BDP-TPA.** Compound **$CF_3$-BDP** (50 mg, 0.16 mmol), 4-(diphenylamino)benzaldehyde (109 mg, 0.4 mmol), *p*-toluenesulfonic acid (28 mg, 0.16 mmol) were dissolved in the mixture of toluene (25 mL) and piperidine (0.5 mL) were added in a 100 mL double neck round bottom flask with a dean-stark apparatus. After heating to reflux, the progress of the reaction was monitored by TLC, and the reaction stopped until compound **$CF_3$-BDP** disappeared completely. Cooled to room temperature, the mixture was dissolved with dichloromethane, washed with brine (50 mL) and dried over anhydrous $Na_2SO_4$. The organic solvent evaporated on a rotary evaporator under reduced pressure. The resulting residue was purified by silica gel column chromatography using $CH_2Cl_2$- petroleum ether ($V_1$:$V_2$= 2:3) as the eluent to afford the desired compound **$CF_3$-BDP-TPA** (56 mg, 40%). $^1$H NMR (600 MHz, DMSO-$d_6$, ppm) δ 7.65 (d, J = 16.2 Hz, 2H), 7.52 (d, J = 9.0 Hz, 4H), 7.39 (dd, J = 18.0, 10.8 Hz, 10H), 7.25 (s, 2H), 6.95 (d, J = 8.4 Hz, 4H), 7.17 (t, J = 7.2 Hz, 4H), 7.13 (d, J = 7.8 Hz, 8H), 2.32 (d, J = 2.4 Hz, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 154.2, 149.2, 146.9, 140.5, 137.7, 133.8, 129.8, 129.4, 129.1, 129.0, 125.3, 123.9, 121.9, 120.5, 116.9, 15.9, 15.8.

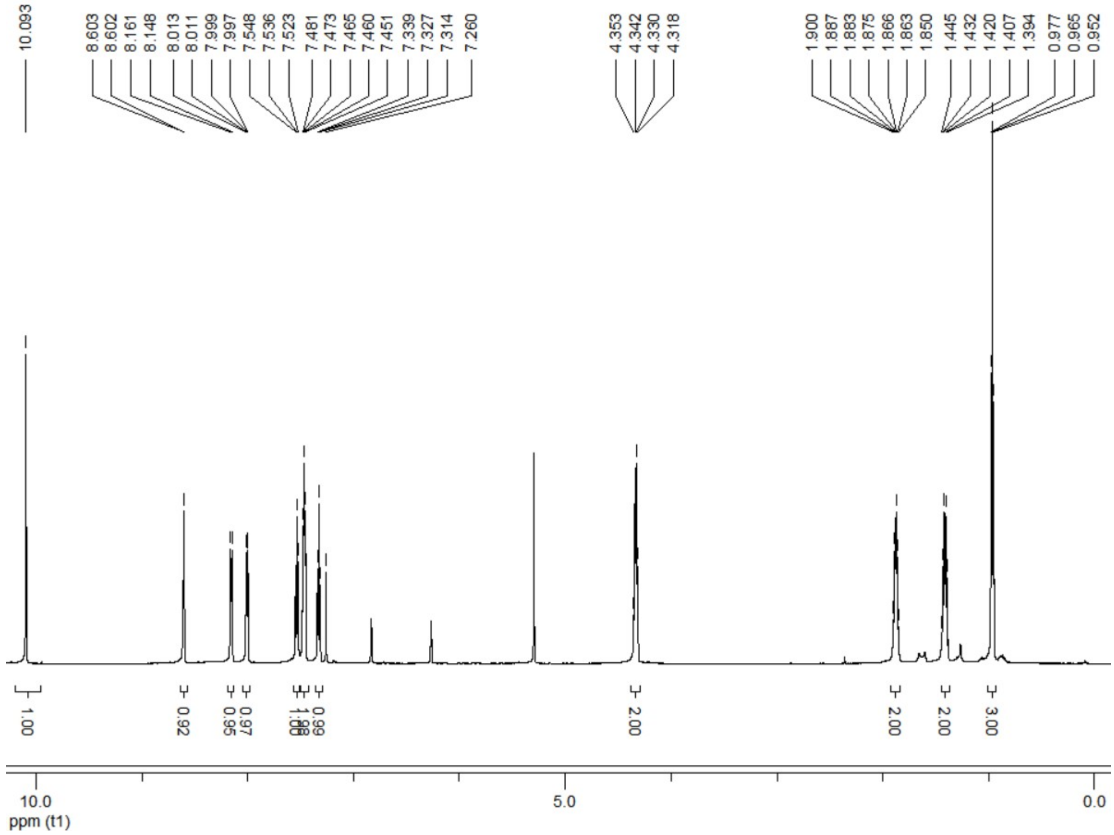
**Synthesis of $CF_3$-BDP-Cz.** Compound **$CF_3$-BDP** (50 mg, 0.16 mmol), **9-butyl-9H-carbazole-3-carbaldehyde** (100 mg, 0.4 mmol), *p*-toluenesulfonic acid (28 mg, 0.16 mmol) were dissolved in the mixture of toluene (25 mL) and piperidine (0.5 mL) were added in a 100 mL double neck round bottom flask with a dean-stark apparatus. After heating to reflux, the progress of the reaction was monitored by TLC, and the reaction stopped until compound **$CF_3$-BDP** disappeared completely. Cooled to room temperature, the mixture was dissolved with dichloromethane, washed with brine (50 mL) and dried over anhydrous $Na_2SO_4$. The organic solvent evaporated on a rotary evaporator under reduced pressure. The resulting residue was purified by silica gel column chromatography using $CH_2Cl_2$- petroleum ether ($V_1$:$V_2$= 3:7) as the eluent to afford the desired compound **$CF_3$-BDP-Cz** (69 mg, 56%). $^1$H NMR (600 MHz, $CDCl_3$, ppm) δ 8.35 (s, 2H), 8.21 (d, J = 7.8 Hz, 2H), 7.86-7.82 (m, 4H), 7.57 (d, J = 16.2 Hz, 2H), 7.51 (t, J = 7.8 Hz, 2H), 7.43 (d, J = 7.2 Hz, 4H), 7.30 (t, J = 7.2 Hz, 2H), 6.88 (s, 2H), 4.33 (t, J = 7.2 Hz, 4H), 0.98 (t, J = 7.2 Hz, 6H), 1.46-1.41 (m, 4H), 1.55 (s, 6H), 1.91-1.86 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 154.5, 141.5, 141.0, 140.4, 139.8, 133.7, 127.8, 126.1, 125.9, 124.4, 123.4, 123.0, 121.6, 120.9, 120.8, 120.6, 119.6, 116.2, 109.2, 109.1, 43.0, 31.1, 20.6, 15.9, 13.9.

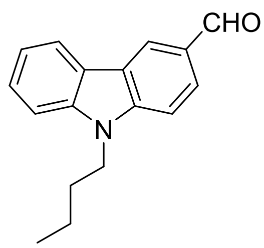



Chemical Formula: $C_{14}H_{14}BF_5N_2$
Exact Mass: 316.12
Molecular Weight: 316.08

Figure S**1**. $^{1}$H NMR spectrum of compound **$CF_3$-BDP** ($CDCl_3$, 600 MHz)



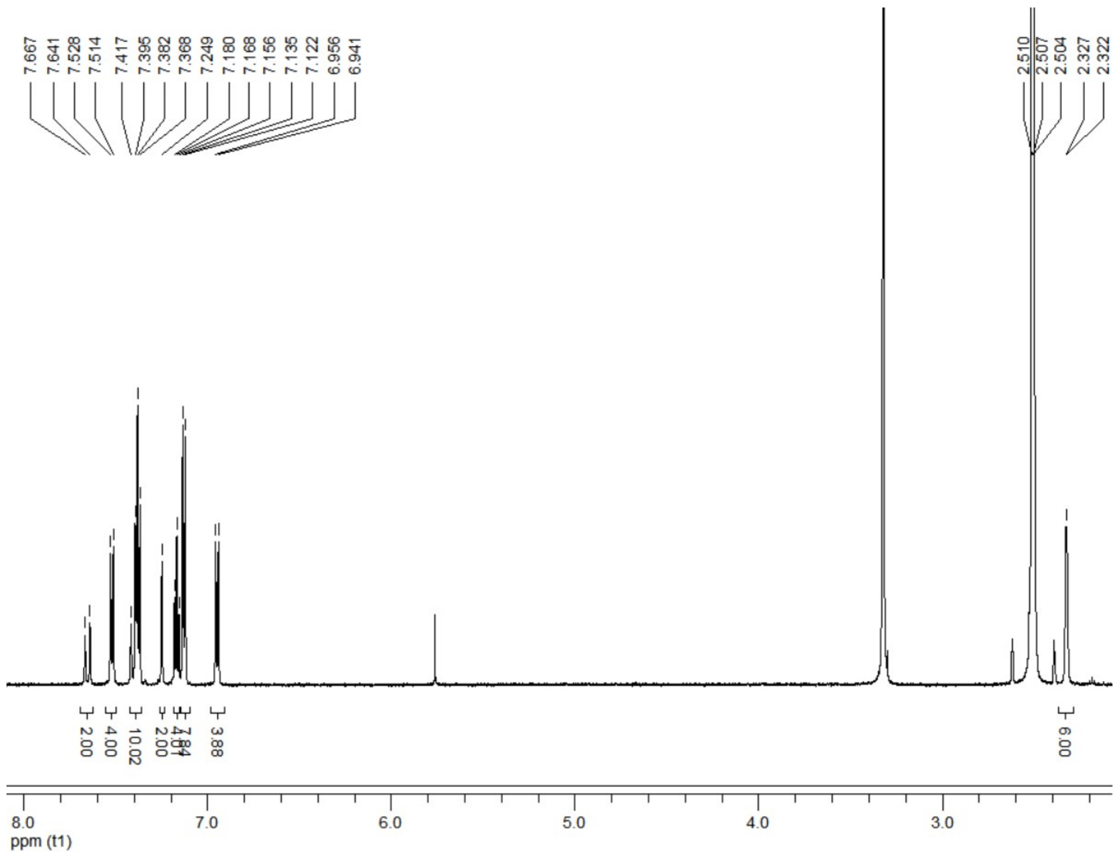



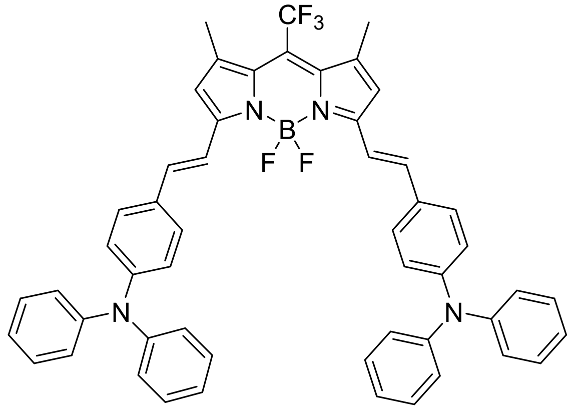

Chemical Formula: $C_{17}H_{17}NO$

Exact Mass: 251.1310

Molecular Weight: 251.3290

Figure S**2**. $^{1}H$ NMR spectrum of compound **9-butyl-9H-carbazole-3-carbaldehyde** ($CDCl_3$, 600 MHz)





Chemical Formula: $C_{52}H_{40}BF_5N_4$
Exact Mass: 826.3266
Molecular Weight: 826.7220

Figure S3. $^{1}$H NMR spectrum of compound **$CF_3$-BDP-TPA** (DMSO-$d_6$, 600 MHz)

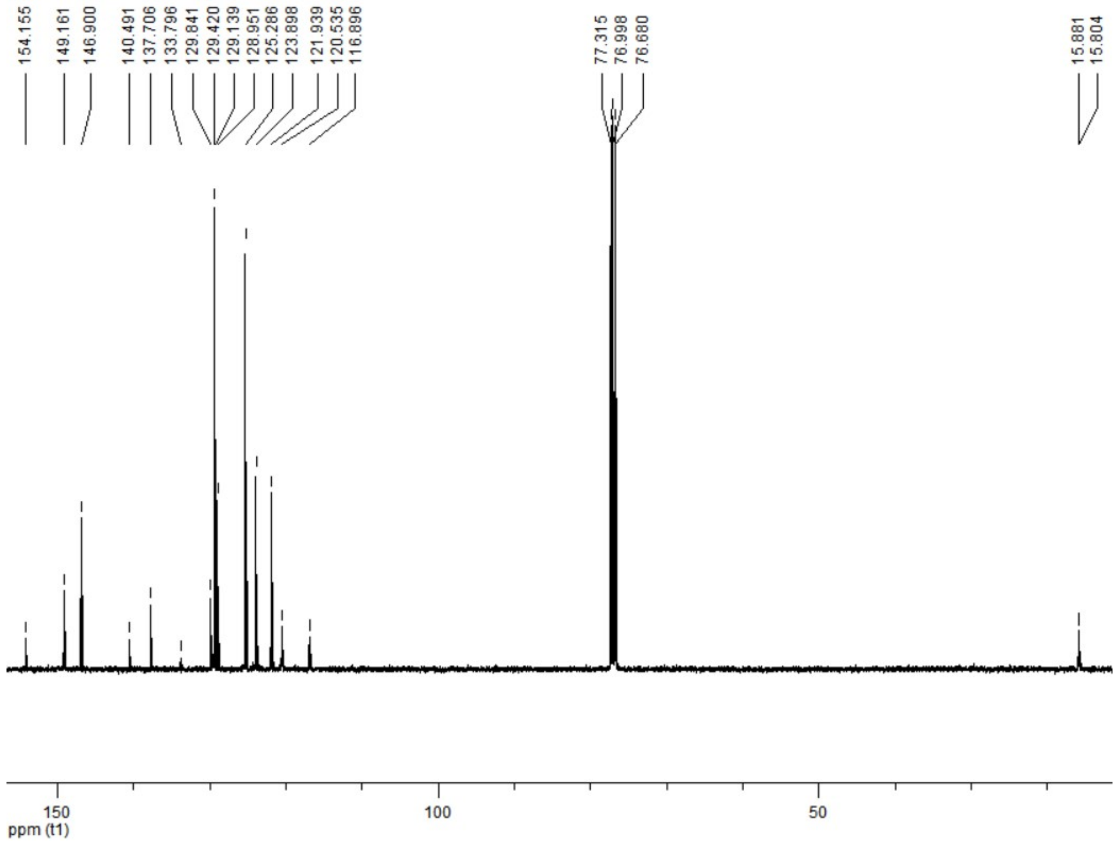
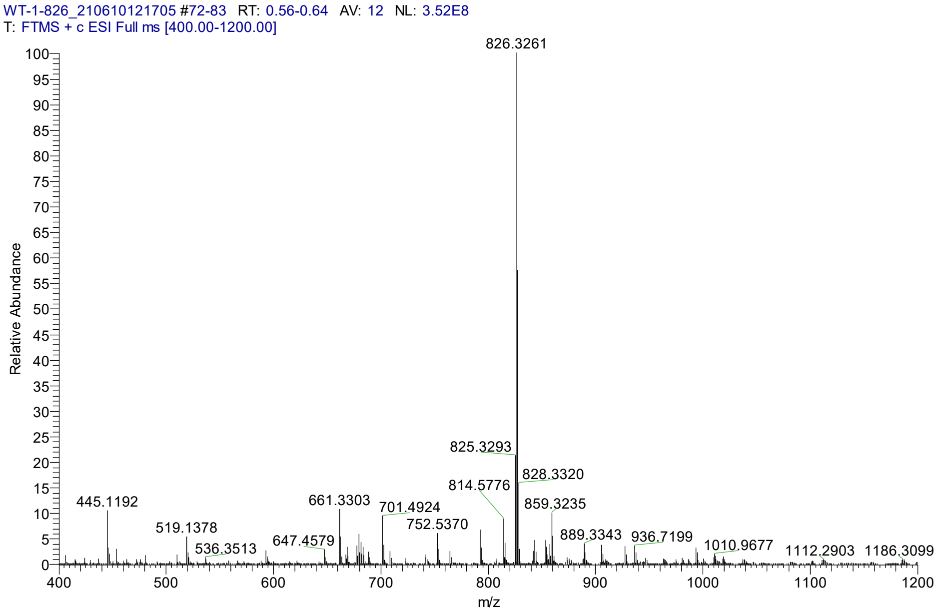
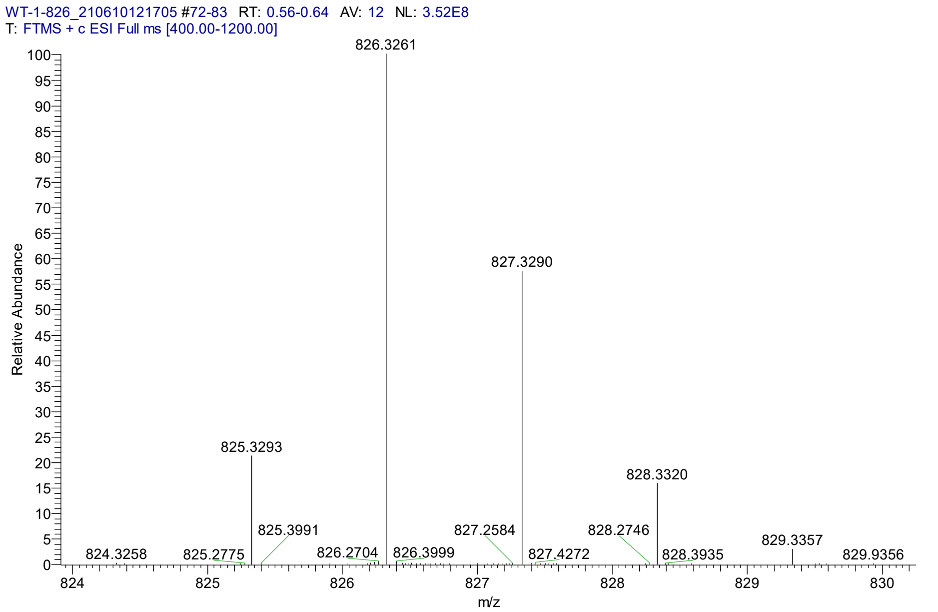
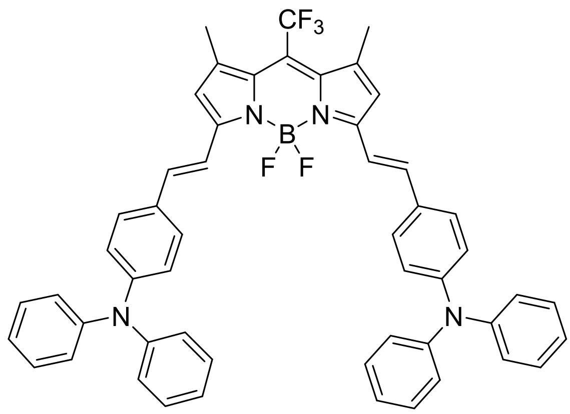



Figure S**4**. $^{13}$C NMR spectrum of compound **$CF_3$-BDP-TPA** ($CDCl_3$, 400 MHz)

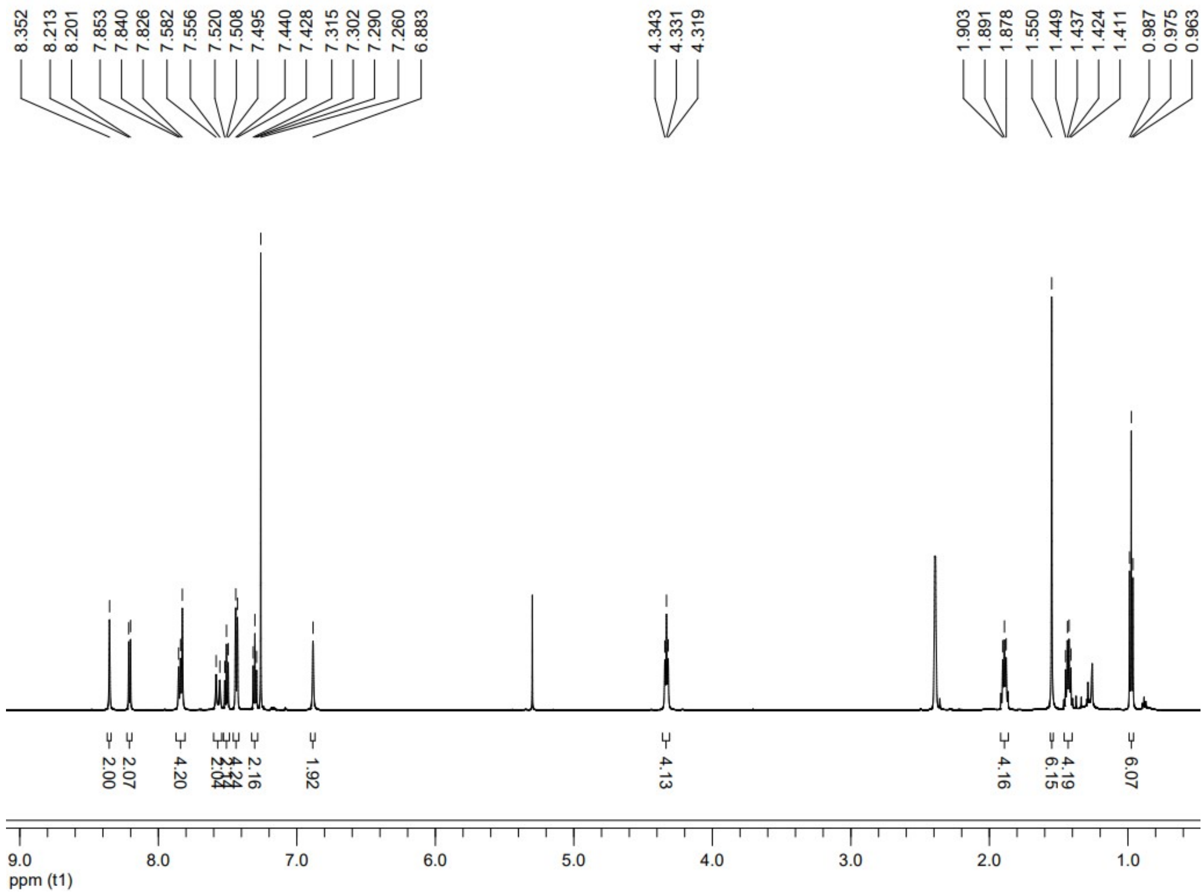


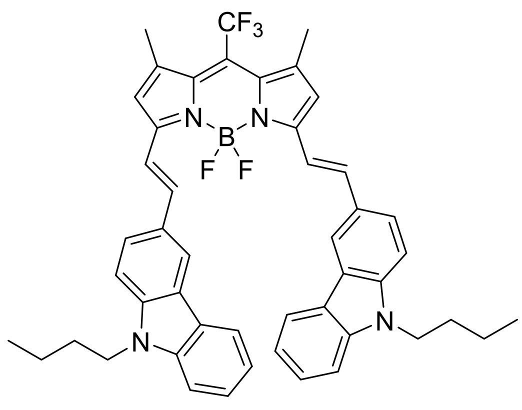




Chemical Formula: $C_{52}H_{40}BF_5N_4$
Exact Mass: 826.3266
Molecular Weight: 826.7220

Figure S**5**. ESI HRMS of compound **$CF_3$-BDP-TPA**




Chemical Formula: $C_{48}H_{44}BF_5N_4$

Exact Mass: 782.3579

Molecular Weight: 782.7100

Figure S**6**. $^1$H NMR spectrum of compound **CF$_3$-BDP-Cz** ($CDCl_3$, 600 MHz)

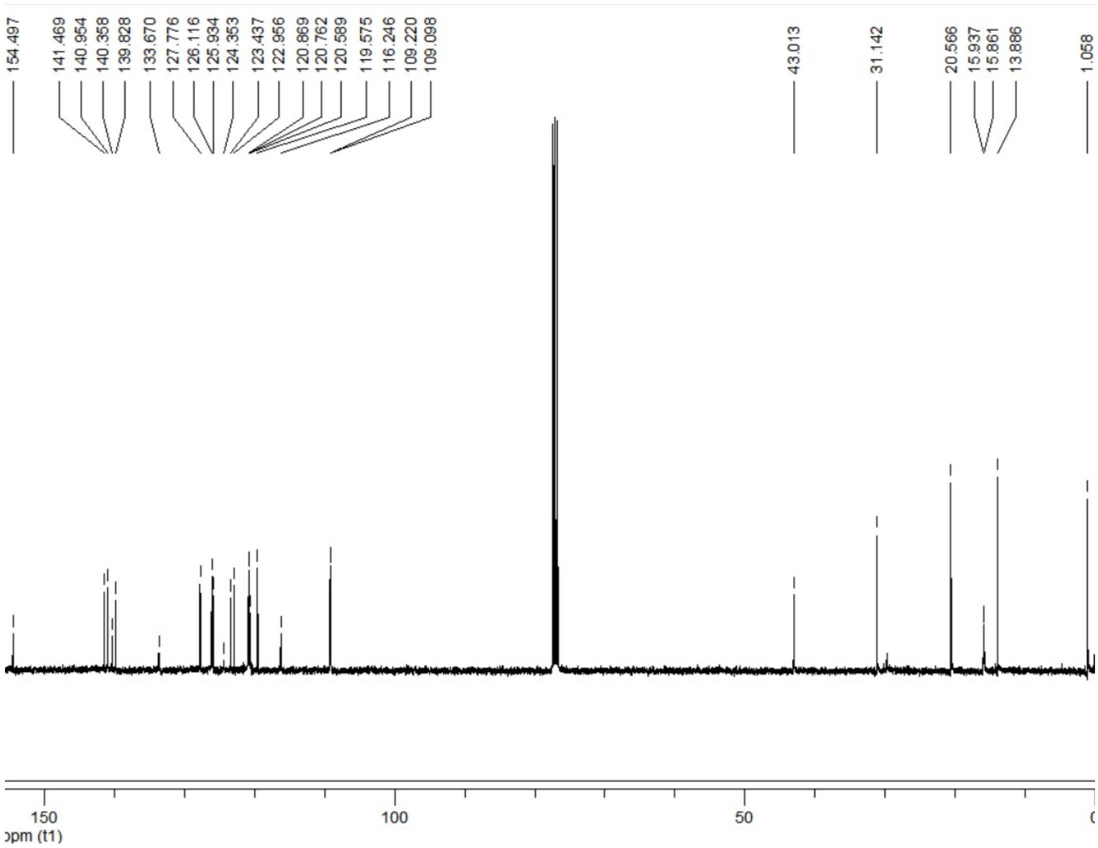
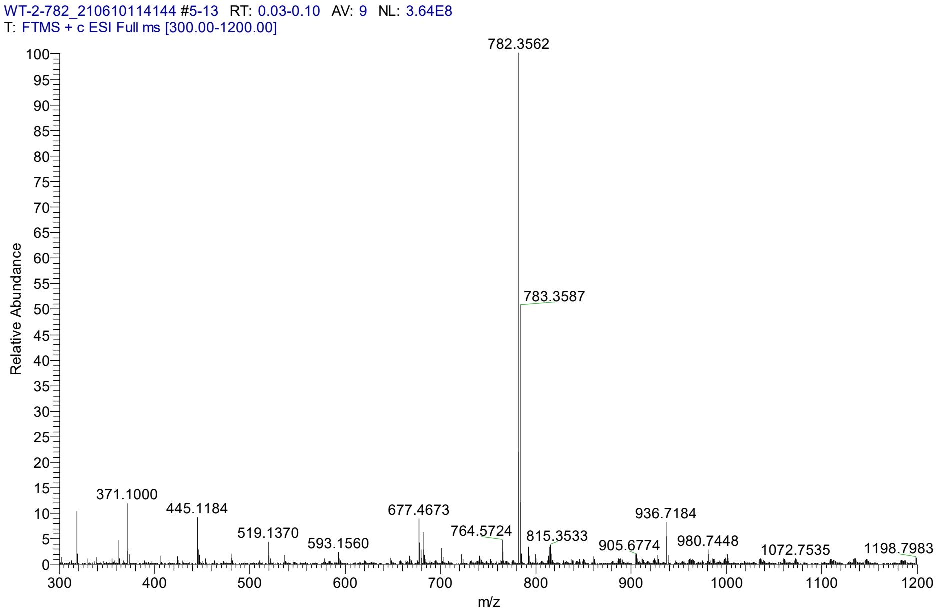
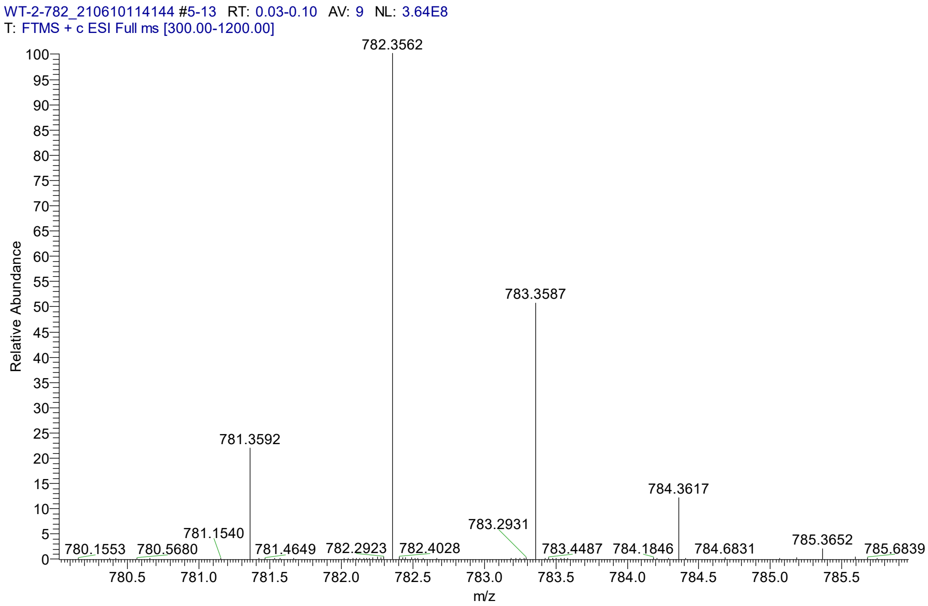
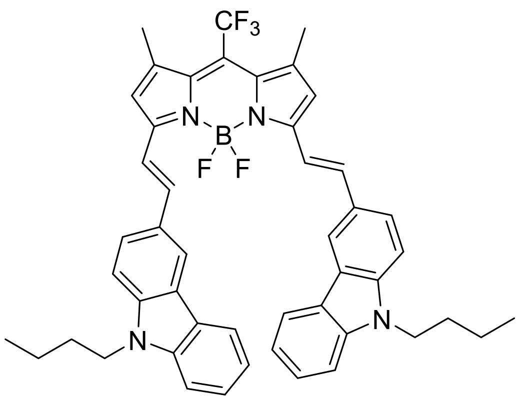



Figure S7. $^{13}C$ NMR spectrum of compound **$CF_3$-BDP-Cz** ($CDCl_3$, 400 MHz)




Chemical Formula: $C_{48}H_{44}BF_5N_4$
Exact Mass: 782.3579
Molecular Weight: 782.7100

Figure S**8**. ESI HRMS of compound **$CF_3$-BDP-Cz**

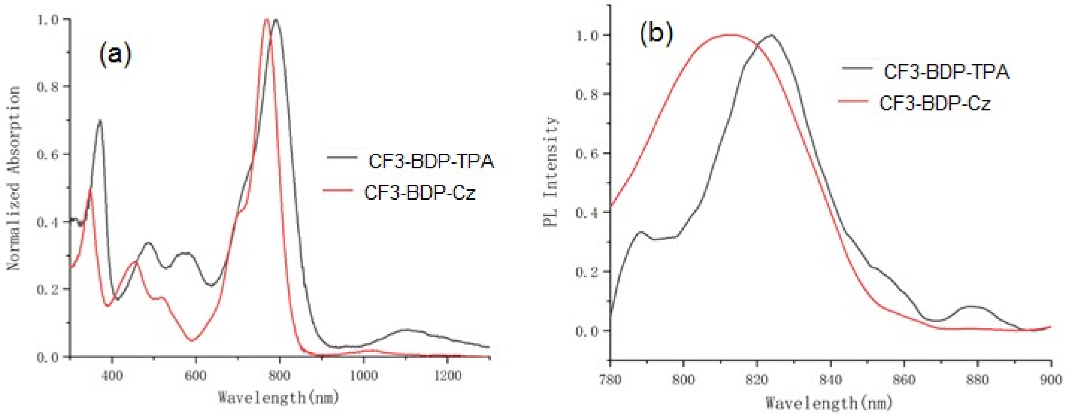



Figure S**9.** (a) Normalized electronic absorption spectra and (b) PL spectra of **$CF_3$-BDP-TPA** and **$CF_3$-BDP-Cz** in $CH_2Cl_2$

**Bonding Feature Analysis Using QTAIM and NCI-Plot Tools**

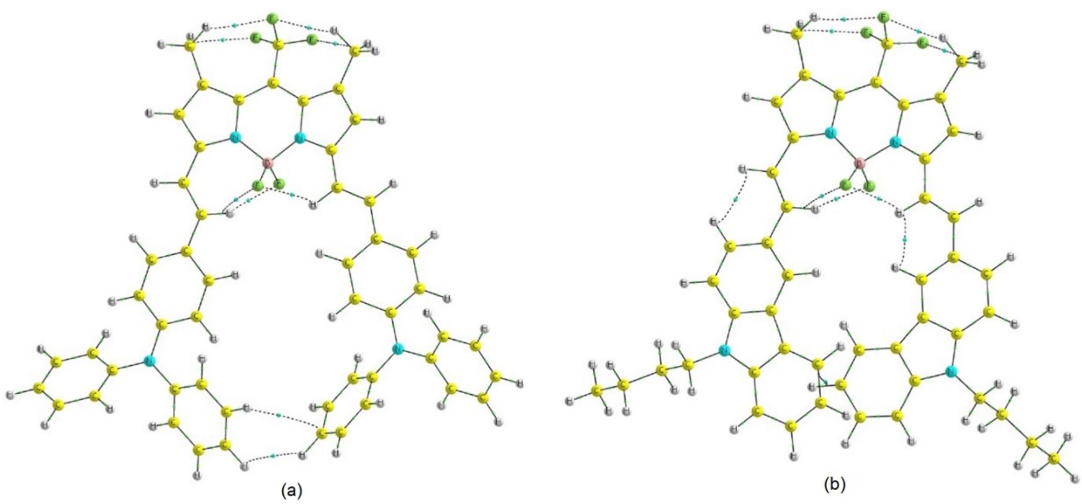



Figure **S10**. QTAIM Based Molecular Graph (a) **$CF_3$-BDP-TPA** and (b) **$CF_3$-BDP-Cz**

Table **S1**. Some useful and chosen extra QTAIM based topological parameters (excluding the common interactions involved therein)

| Species | **$CF_3$-BDP-TPA** | | **$CF_3$-BDP-Cz** | | |
|---|---|---|---|---|---|
| NCI→ Parameters↓ | C···H | H···H | C-H···π | H···H | H···H |
| BL (Å) | 2.928 | 2.631 | 3.085 | 2.171 | 2.023 |
| BPL (Å) | 3.042 | 2.726 | 3.893 | 2.443 | 2.248 |
| ρ (au) | 0.0052 | 0.003 | 0.0068 | 0.0094 | 0.0122 |
| $\nabla^2\rho$(au) | +0.015 | +0.0102 | +0.0218 | +0.0372 | +0.0466 |
| V (kcal/mol) | -1.6 | -1.0 | -2.1 | -3.6 | -4.6 |

Using the NCI-reduced density gradient (NCI-RDG) approach, in getting deep insights into the recognition and graphical representation of the NCIs (kind and nature) can be fabricated which can provide an inclusive illustration of the H-bonding, van der Waals (vdW) interactions, and steric repulsion in both model dyes. Usually, the localized blue lentils describe the strong attractive NCIs (i.e., H-bonding), and thin as well as delocalized green regions exemplify the vdW (extremely weak) interactions. The red isosurface interprets the steric clashes engaged within the species (e.g., see Figure **S10**a).

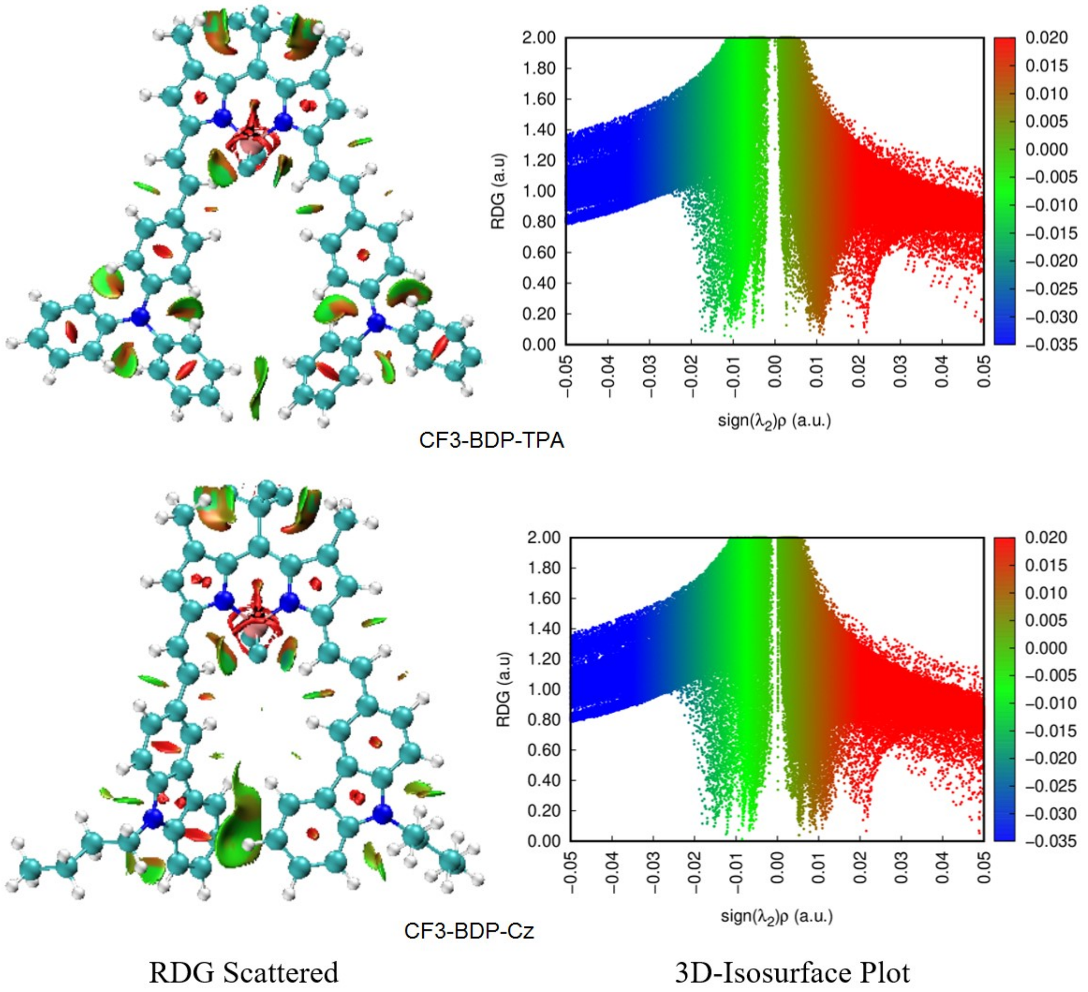



Figure **S11**. RDG Scattered 2D Plot and 3D iso-surface Maps

Complete information in understanding the NCI-plots is given by three color codes, red, green, and blue. The RDG iso-surface shown on the horizontal axis is 0.05 (ranging from −0.05 to +0.05). The Ω(r) values ranging from −0.035 atomic unit (au) to +0.02 au on the vertical axis (Figure **S11**, right) show the coloured surfaces of the species on a blue−green−red scale. The detailed description of the NCI tool clarifies that the higher density values (Ω(r) < 0) show stronger attractive interactions, while the very low-density values (Ω(r) > 0) indicate the repulsive interactions. The light blue colour spikes (values ranging from 0.015 au to 0.02 au) in the 2D-scattered plot illustrate the weak H-bonding interactions like C-H···F interactions. The green color spikes (values ranging from−0.002 au to −0.013 au) in the 2D scatter plot and green color disc-shaped NCI 3D-isosurface demonstrate a variety of vdW interactions like

C···H and H···H, and C-H···π interactions involved therein both species. The presence of the steric effect is evidently shown by the low-gradient spikes appearing at the positive side (+0.005 to +0.025) (see Figure **S11**, right). This effect, as shown by the red ellipsoid, depicts the ED depletion, which is because of the electrostatic repulsion.

**Experimental details for fabrication of polymer solar cells**

We have fabricated the polymer solar cells (PSCs) with the conventional configuration ITO/PEDOT:PSS/PBDB-T:CF3-BDP-TPA or CF3-BDP-Cz/ PFN/Al. The ITO coated glass substrates were cleaned in detergent, and subsequently ultra-sonicated in deionized water, acetone and isopropyl alcohol and dried *in vacuum* oven to remove all the traces of residues. For each molecule, the photovoltaic performance optimization process was started with identifying the donor to acceptor ratio (weight percentage, varying from 1:05 to 1:4) and after that solvent vapor annealing was applied to maximize the performance of the PSCs. The $PC_{71}BM$ was used as acceptor and the total concentration of D:A blend mixture was 16 mg/mL in chloroform. The devices were fabricated by depositing PEDOT:PSS as hole transport layer having thickness of 35-40 nm. The active layer was deposited by spin coating (2500 rpm, 60 s) on the top of PEDOT:PSS layer under ambient conditions. For the solvent vapor annealing (SVA), the optimized (as cast 1:1.2 D/A wt ratio) was exposed to the THF vapors for 40s. A thin layer of PFN was spin coated on the top of the active layer from the methanol solution. The aluminum (Al) electrode was deposited onto the top of PFN layer *via* thermal evaporation at the pressure less than $10^{-5}$ Torr. The current-voltage characteristics of the OSCs were measured under illumination intensity of 100 mW/cm$^2$ (AM1.5 G) using a solar simulator and a Keithley 2400 source meter unit. The incident photon to current conversion efficiency (IPCE) measurements were performed using Bentham IPCE system.

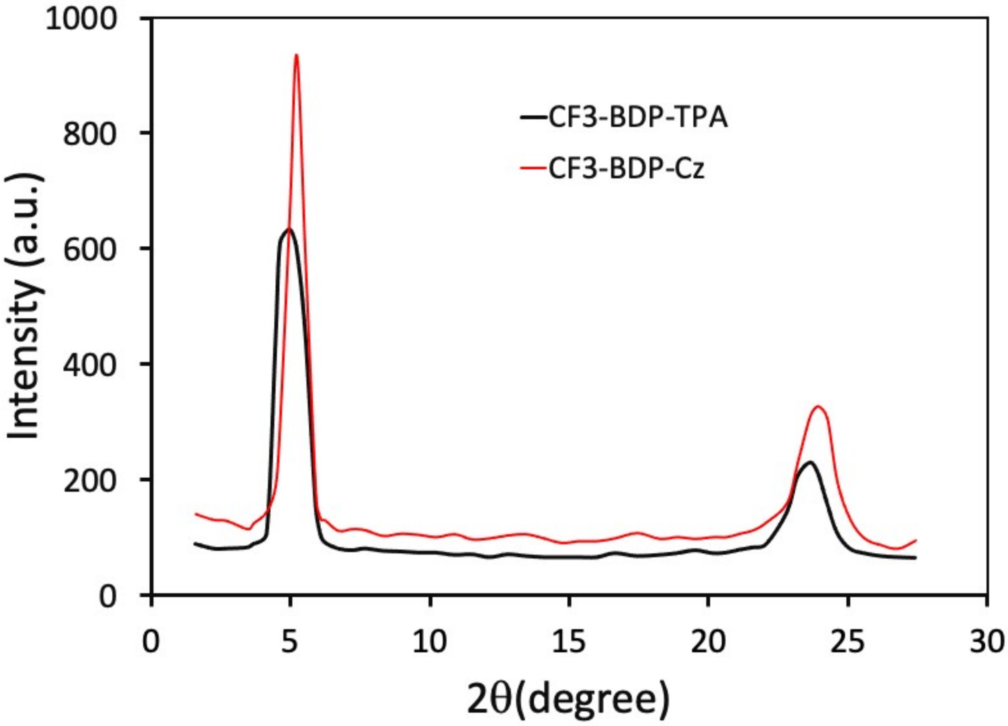



Figure S**12**. XRD patterns of pristine films

Table **S2**. Some important and chosen optimized parameters of the Compounds **$CF_3$-BDP-TPA** and **$CF_3$-BDP-Cz** Using the M06-2X/6-311G (d, p) Method where bond lengths are given in Å and bond angle as well as torsional angles are in degree, °)

| Species | **$CF_3$-BDP-TPA** | **$CF_3$-BDP-Cz** |
|---|---|---|
| C-F | 1.345(b), 1.336(f) | 1.345(b), 1.336(f) |
| B-F | 1.393(b), 1.39(f) | 1.396 (b), 1.39 (f) |
| C-N(1) | 1.406(r), 1.408(l) | 1.377(r), 1.379(l) |
| C-N(2) | 1.418(r), 1.417(l) | 1.389(r), 1.385(l) |
| C-N(3) | 1.421(r), 1.419(l) | 1.447(r), 1.448(l) |
| C-C-N | 122.4(r), 127.7(l) | 121.4(r), 127.5(l) |
| C-N-C(12) | 121.1(r), 120.5(l) | 108.8(r), 108.7(l) |
| C-N-C(23) | 118.7(r), 119.5(l) | 125.4(r), 125.7(l) |
| C-N-C(13) | 120.1(r), 120(l) | 125.5(r), 125.3(l) |
| C-C=C-C | 179(r), 178.7(l) | 180(r), 175.6(l) |