Supporting Information

The Finale of a Trilogy: Comparing Terpolymer and Ternary Blend with Structurally Similar Backbones for Organic Bulk Heterojunction Solar Cells

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Synthesis of polymers

BnDT monomer, TAZ monomers, $Pd_2(dba)_3 \cdot CHCl_3$ and $P(o\text{-tol})_3$ (monomer ratio for each polymer was summarized below) were charged into a 10 mL vial designed for microwave reactor. The mixture was evacuated and refilled with argon for three cycles before addition of 0.7 mL anhydrous *o*-xylene under argon stream. The reaction was heated up to 200 °C and held for 10 min in a CEM microwave reactor. When polymerization is done, the crude polymer was dissolved in hot chlorobenzene and precipitated into stirring methanol. The collected polymer was extracted via a Soxhlet extractor with Ethyl acetate, hexanes and chloroform (monoCNTAZ were extracted with chlorobenzene). The polymer solution in chloroform was concentrated via rotavap. The collected polymer was re-dissolved into hot chlorobenzene and precipitated into methanol. The polymer was then collected via filtration and dried under vacuum.

Monomer ratio for polymerization:

***mC:F = 1:9*:** *m*-BnDT/*m*-FTAZ/*m*-monoCNTAZ/$Pd_2(dba)_3 \cdot CHCl_3$/$P(o\text{-tol})_3$ = 1.020/0.900/0.100/0.020/0.160. M_n = 50.4 kg/mol, M_w = 104.4 kg/mol, PDI = 2.1

mC:F = 3:7: *m*-BnDT/*m*-FTAZ/*m*-monoCNTAZ/$Pd_2(dba)_3 \cdot CHCl_3$/$P(o\text{-tol})_3$ = 1.020/0.700/0.300/0.020/0.160. M_n = 46.6 kg/mol, M_w = 94.0 kg/mol, PDI = 2.0

mC:F = 1:1: *m*-BnDT/*m*-FTAZ/*m*-monoCNTAZ/$Pd_2(dba)_3 \cdot CHCl_3$/$P(o\text{-tol})_3$ = 1.020/0.500/0.500/0.020/0.160. M_n = 37.9 kg/mol, M_w = 83.4 kg/mol, PDI = 2.2

mC:F = 7:3: *m*-BnDT/*m*-FTAZ/*m*-monoCNTAZ/$Pd_2(dba)_3 \cdot CHCl_3$/$P(o\text{-tol})_3$ = 1.020/0.300/0.700/0.020/0.160. M_n = 40.8 kg/mol, M_w = 96.6 kg/mol, PDI = 2.4

***mC:F = 9:1*:** *m*-BnDT/*m*-FTAZ/*m*-monoCNTAZ/$Pd_2(dba)_3 \cdot CHCl_3$/$P(o\text{-tol})_3$ = 1.020/0.100/0.900/0.020/0.160. M_n = 55.0 kg/mol, M_w = 167.3 kg/mol, PDI = 3.0

monoCNTAZ: *m*-BnDT/*m*-monoCNTAZ/$Pd_2(dba)_3 \cdot CHCl_3$/$P(o\text{-tol})_3$ = 1.020/1.000/0.020/0.160. M_n = 70.0 kg/mol, M_w = 221.1 kg/mol, PDI = 3.2

GPC of the terpolymers

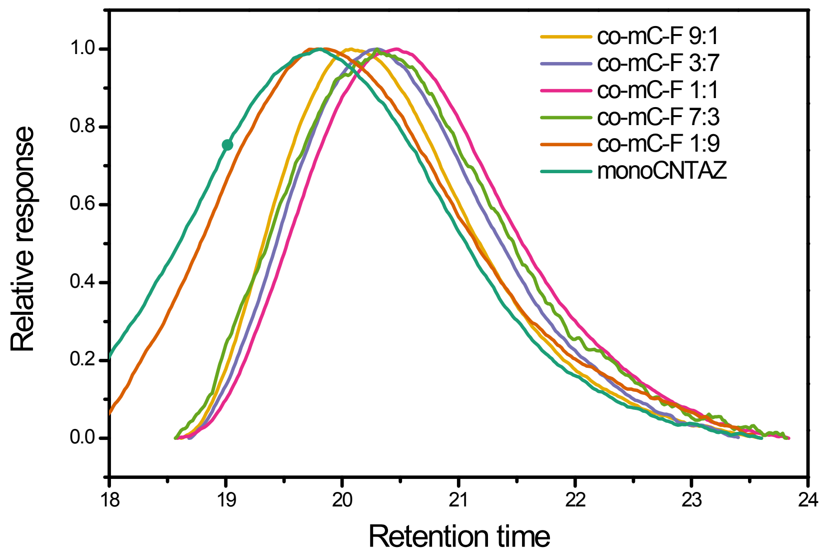


Figure S1*. GPC curves of the FTAZ: monoCNTAZ terpolymers and monoCNTAZ polymer.*

Table S1. GPC results of polymers.

Sample details	Mn (kg/mol)	Mw (kg/mol)	PDI
co-mC-F 1:9	50.4	104.4	2.1
co-mC-F 3:7	46.6	94.0	2.0
co-mC-F 1:1	37.9	83.4	2.2
co-mC-F 7:3	40.8	96.6	2.4
co-mC-F 9:1	55.0	167.3	3.0
monoCNTAZ	70.0	221.1	3.2

Elemental Analysis

Table S2. Elemental analysis of polymers.

Polymer	**C**		**H**		**N**		**S**		**F**	
	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp
FTAZ	71.70	71.89	8.25	8.22	4.05	4.03	12.35	12.10	3.66	3.56
co-mC-F 1:9	71.89	72.14	8.27	8.41	4.19	4.03	12.36	12.34	3.30	3.20
co-mC-F 3:7	72.23	72.10	8.30	8.24	4.46	4.36	12.39	12.23	2.57	2.56
co-mC-F 1:1	72.66	72.88	8.34	8.38	4.74	4.51	12.41	12.14	1.84	1.59
co-mC-F 7:3	73.05	73.17	8.38	8.24	5.03	4.92	12.44	12.38	1.11	1.07
co-mC-F 9:1	73.44	73.92	8.42	8.80	5.31	4.92	12.49	11.69	0.37	0.57
monoCNTAZ	73.63	73.51	8.43	8.43	5.45	5.31	12.48	12.29		

Cyclic Voltammetry Measurements

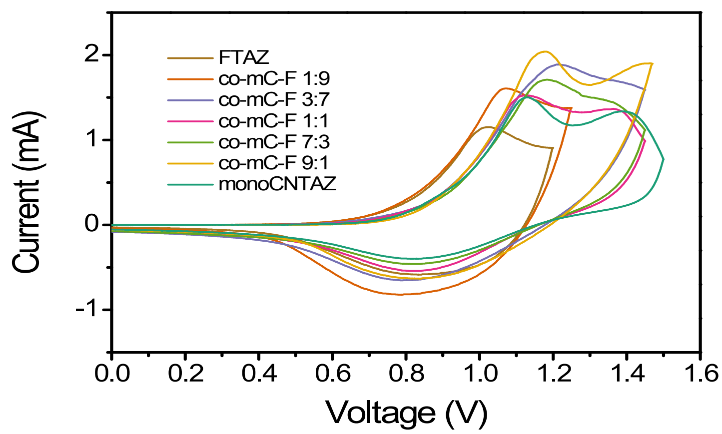


***Figure S2**. CV curves of the polymers*

Table S3. HOMO level of the polymers.

Polymers	HOMO (eV)
FTAZ	-5.51
co-mC-F 1:9	-5.52
co-mC-F 3:7	-5.57
co-mC-F 1:1	-5.57
co-mC-F 7:3	-5.59
co-mC-F 9:1	-5.61
monoCNTAZ	-5.61

Note for CV: Clearly, when CN amount is increased to 30%, the HOMO level of polymer is pinned to that of monoCNTAZ based on the CV curves. The difference between HOMO of F:CN = 7:3 and that of monoCNTAZ is very small.

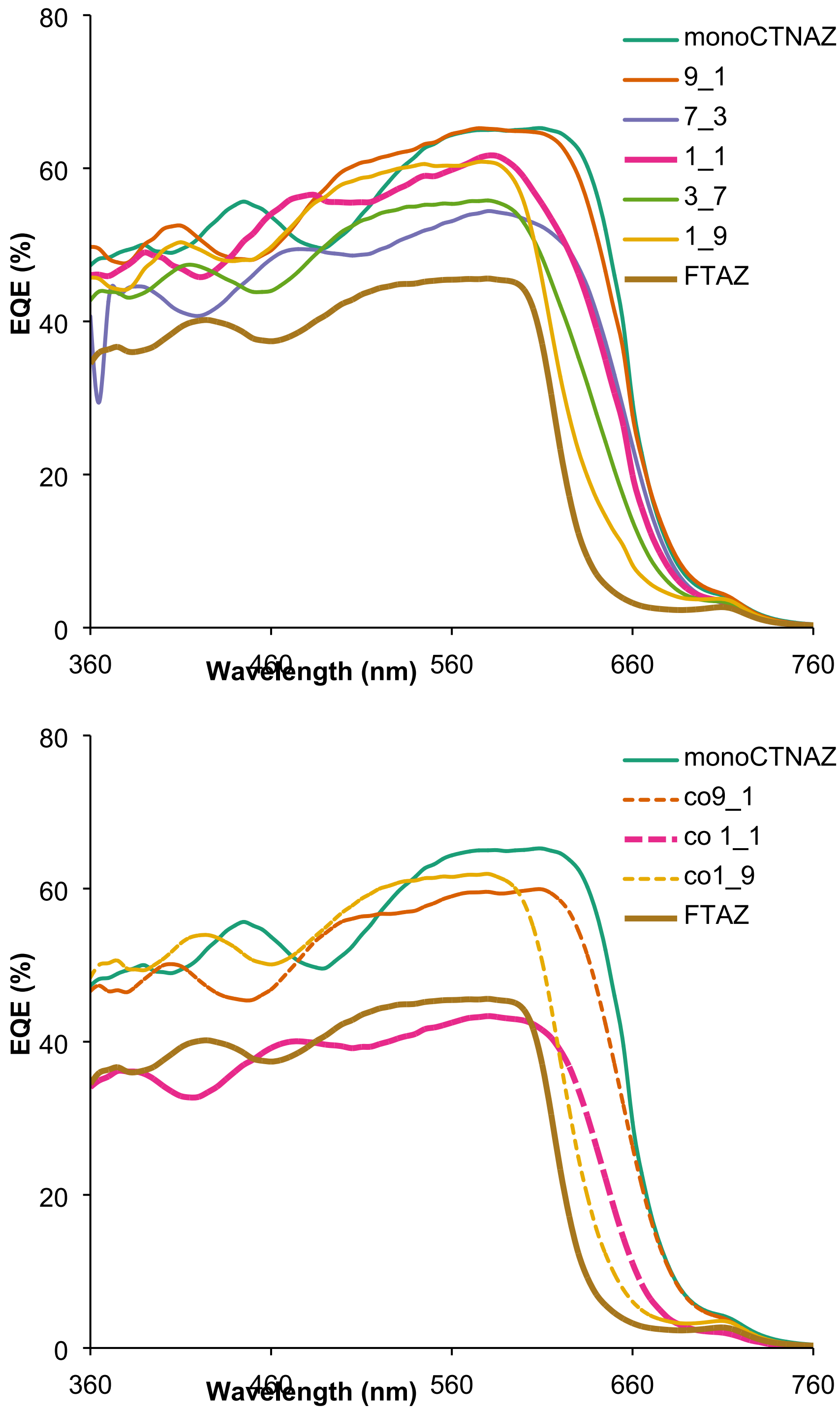
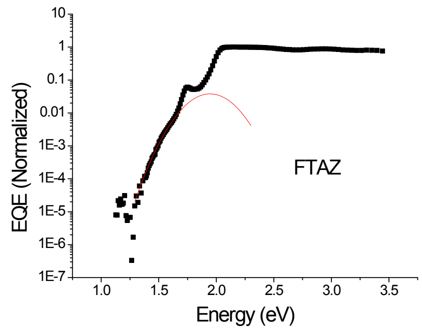
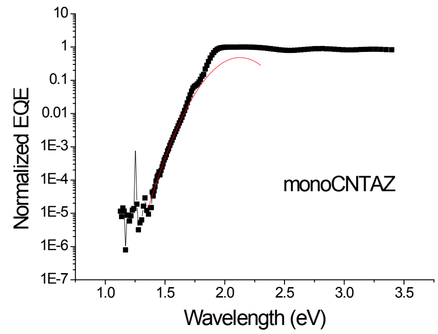
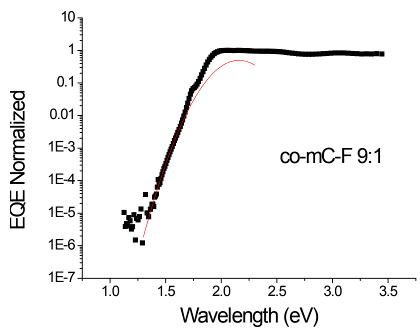


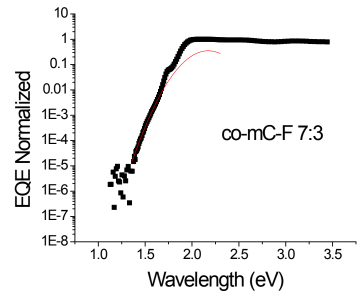
Figure S3 *EQE of all of FTAZ, monoCNTAZ, the PBHJs and the copolymers.*

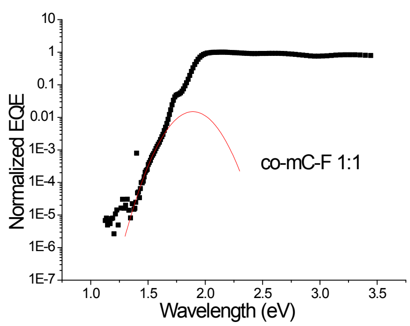
<u>Sensitive-EQE Measurements and Fittings</u>

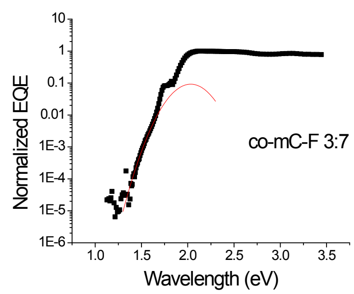

EQE (Normalized)
10
1
0.1
0.01
1E-3
1E-4
1E-5
1E-6
1E-7
1.0 1.5 2.0 2.5 3.0 3.5
Energy (eV)
FTAZ

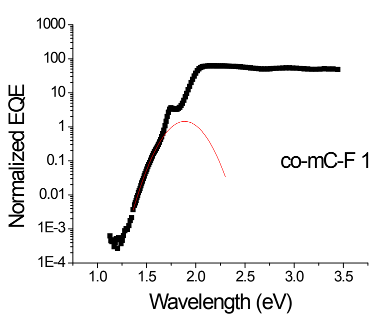

Normalized EQE
10
1
0.1
0.01
1E-3
1E-4
1E-5
1E-6
1E-7
1.0 1.5 2.0 2.5 3.0 3.5
Wavelength (eV)
monoCNTAZ

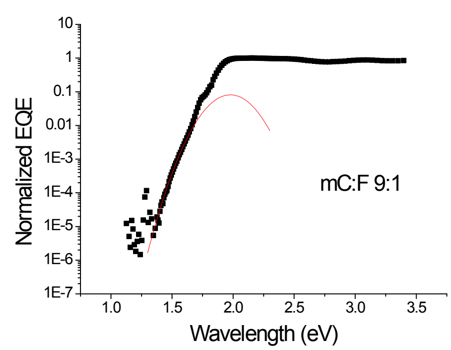

EQE Normalized
10
1
0.1
0.01
1E-3
1E-4
1E-5
1E-6
1E-7
1.0 1.5 2.0 2.5 3.0 3.5
Wavelength (eV)
co-mC-F 9:1


EQE Normalized
10
1
0.1
0.01
1E-3
1E-4
1E-5
1E-6
1E-7
1E-8
1.0 1.5 2.0 2.5 3.0 3.5
Wavelength (eV)
co-mC-F 7:3


Normalized EQE
10
1
0.1
0.01
1E-3
1E-4
1E-5
1E-6
1E-7
1.0 1.5 2.0 2.5 3.0 3.5
Wavelength (eV)
co-mC-F 1:1


Normalized EQE
10
1
0.1
0.01
1E-3
1E-4
1E-5
1E-6
1.0 1.5 2.0 2.5 3.0 3.5
Wavelength (eV)
co-mC-F 3:7


Normalized EQE
1000
100
10
1
0.1
0.01
1E-3
1E-4
1.0 1.5 2.0 2.5 3.0 3.5
Wavelength (eV)
co-mC-F 1:9


Normalized EQE
10
1
0.1
0.01
1E-3
1E-4
1E-5
1E-6
1E-7
1.0 1.5 2.0 2.5 3.0 3.5
Wavelength (eV)
mC:F 9:1

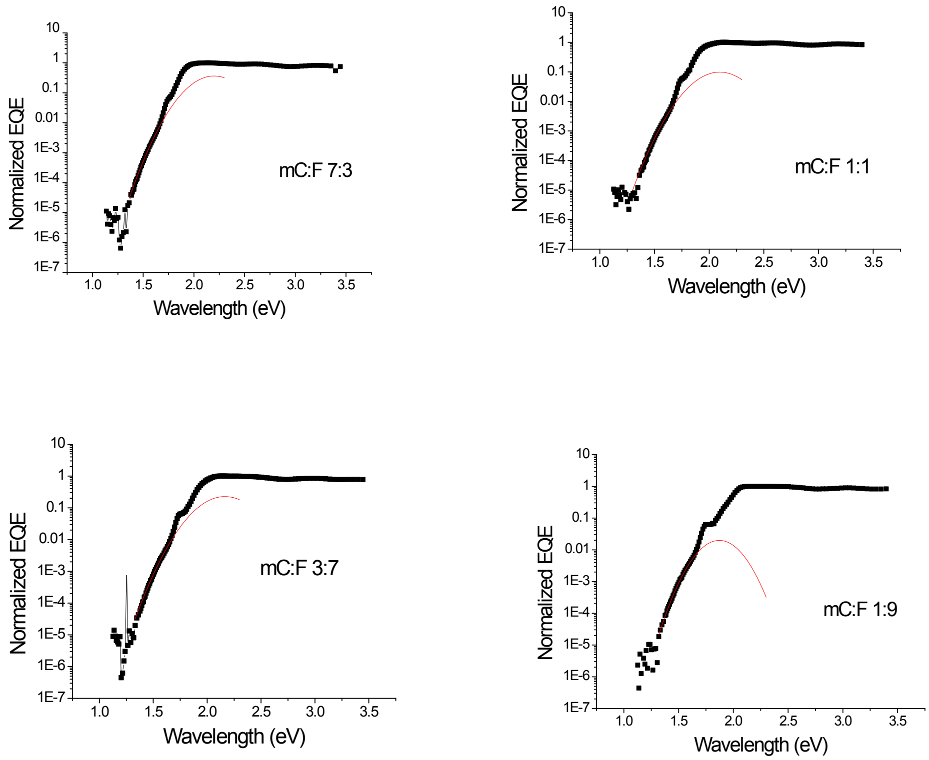


***Figure S4**. Low-wavelength EQE and fits for modelling the CT state.*

Table S4. Calculated values for the energy of the CT state, the difference between the lowest optical bandgap (PCBM) and the CT state, and the CT state and the $V_{OC.}$

Polymer	**E_{CT} (eV)**	**E_{opt}-E_{CT} (eV)**	**E_{CT} -eV_{OC} (eV)**
monoCNTAZ	1.596 $_{\pm 0.005}$	0.064	0.661
mC:F 9:1	1.578 $_{\pm 0.005}$	0.082	0.658
mC:F 7:3	1.499 $_{\pm 0.01}$	0.161	0.616
mC:F 1:1	1.448 $_{\pm 0.02}$	0.212	0.581
mC:F 3:7	1.432 $_{\pm 0.02}$	0.228	0.582
mC:F 1:9	1.453 $_{\pm 0.01}$	0.207	0.625
FTAZ	1.412 $_{\pm 0.015}$	0.248	0.601
***co*-mC-F 9:1**	1.603 $_{\pm 0.005}$	0.057	0.681
***co*-mC-F 7:3**	1.557 $_{\pm 0.005}$	0.103	0.694
***co*-mC-F 1:1**	1.510 $_{\pm 0.009}$	0.15	0.611
***co*-mC-F 3:7**	1.483 $_{\pm 0.017}$	0.177	0.579
***co*-mC-F 1:9**	1.458 $_{\pm 0.005}$	0.202	0.624