Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: Rational Design of Non-Fullerene Acceptors via Side-Chain and Terminal Group Engineering: A Computational Study

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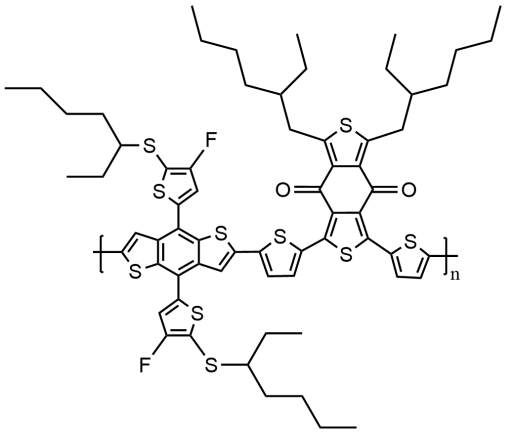
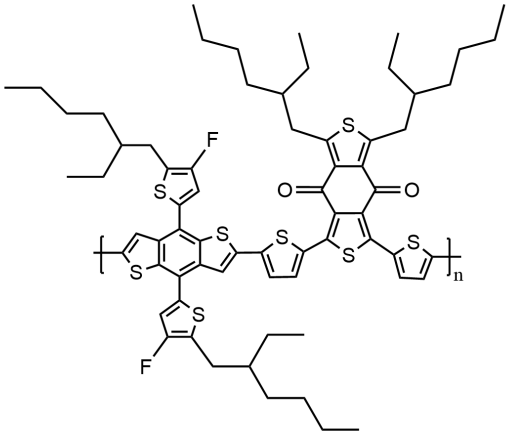
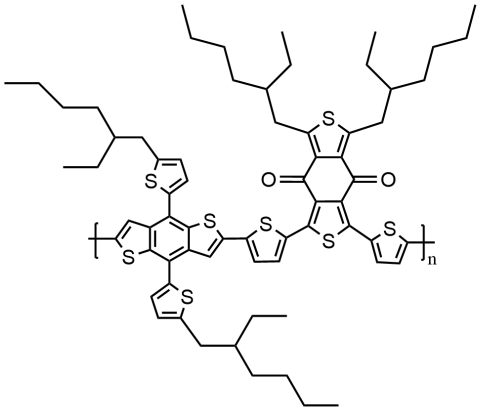


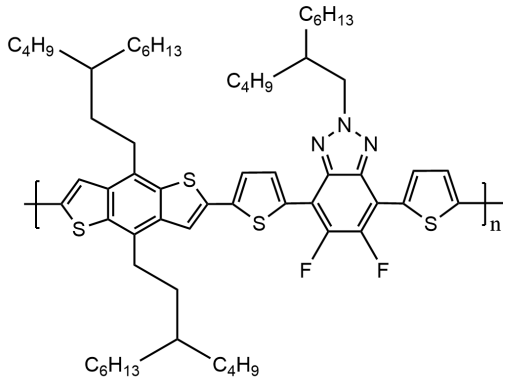
PBDB-T-SF



PM6



PBDB-T



FTAZ

Figure S1: Chemical structure of the four donors; PBDB-T-SF, PM-6, PBDB-T, and FTAZ. Optimization of the donor polymers were performed at B3LYP/6-31G(d,p) level of theory using one monomer unit.

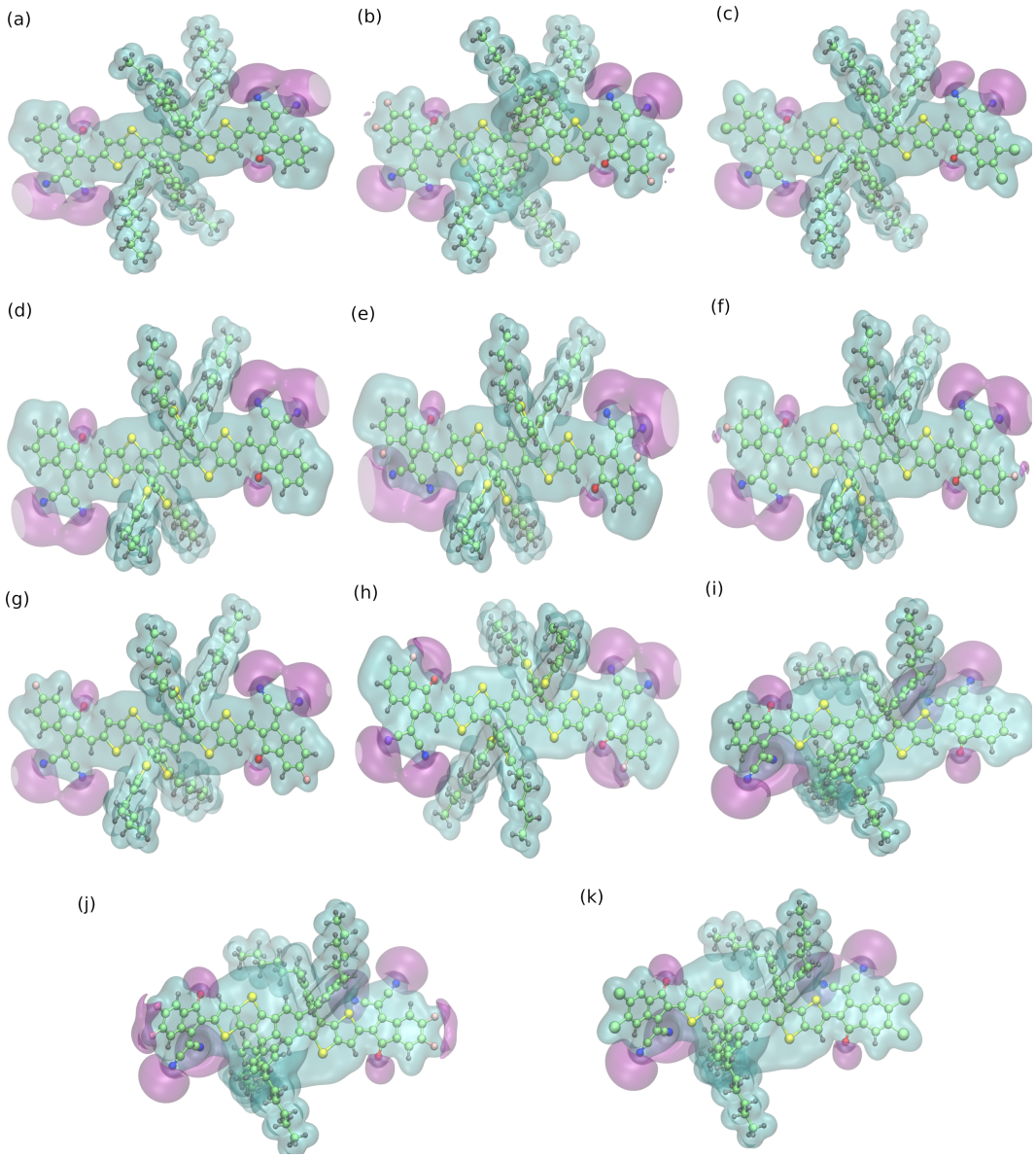


Figure S2: Iso-electrostatic potential surfaces of selected non-fullerene acceptors: (a) IT-H; (b) IT-F; (c) IT-Cl; (d) ITIC-Th; (e) ITIC-Th-1; (f) ITIC-Th-2; (g) ITIC-Th-3; (h) ITIC-Th-4; (i) SeTIC; (j) SeTIC-F; and (k) SeTIC-Cl.

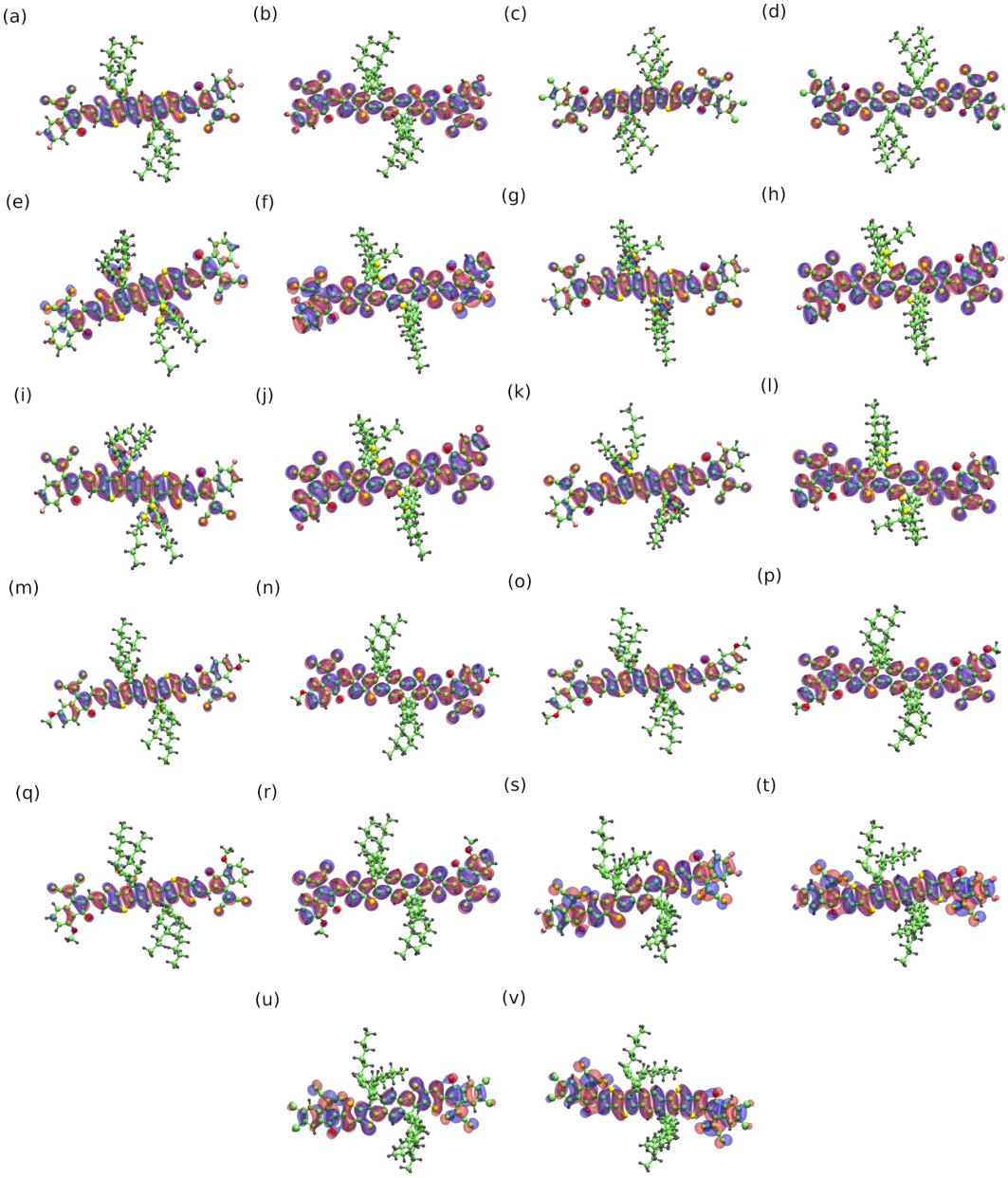


Figure S3: Frontier molecular orbitals of selected non-fullerene acceptors. **HOMO**: (a) IT-F; (c) IT-Cl; (e) ITIC-Th-1; (g) ITIC-Th-2; (i) ITIC-Th-3; (k) ITIC-Th-4; (m) IT-OMe-2; (o) IT-OMe-3; (q) IT-OMe-4; (s) SeTIC-F; (u) SeTIC-Cl. **LUMO**: (b) IT-F; (d) IT-Cl; (f) ITIC-Th-1; (h) ITIC-Th-2; (j) ITIC-Th-3; (l) ITIC-Th-4; (n) IT-OMe-2; (p) IT-OMe-3; (r) IT-OMe-4; (t) SeTIC-F; (v) SeTIC-Cl.

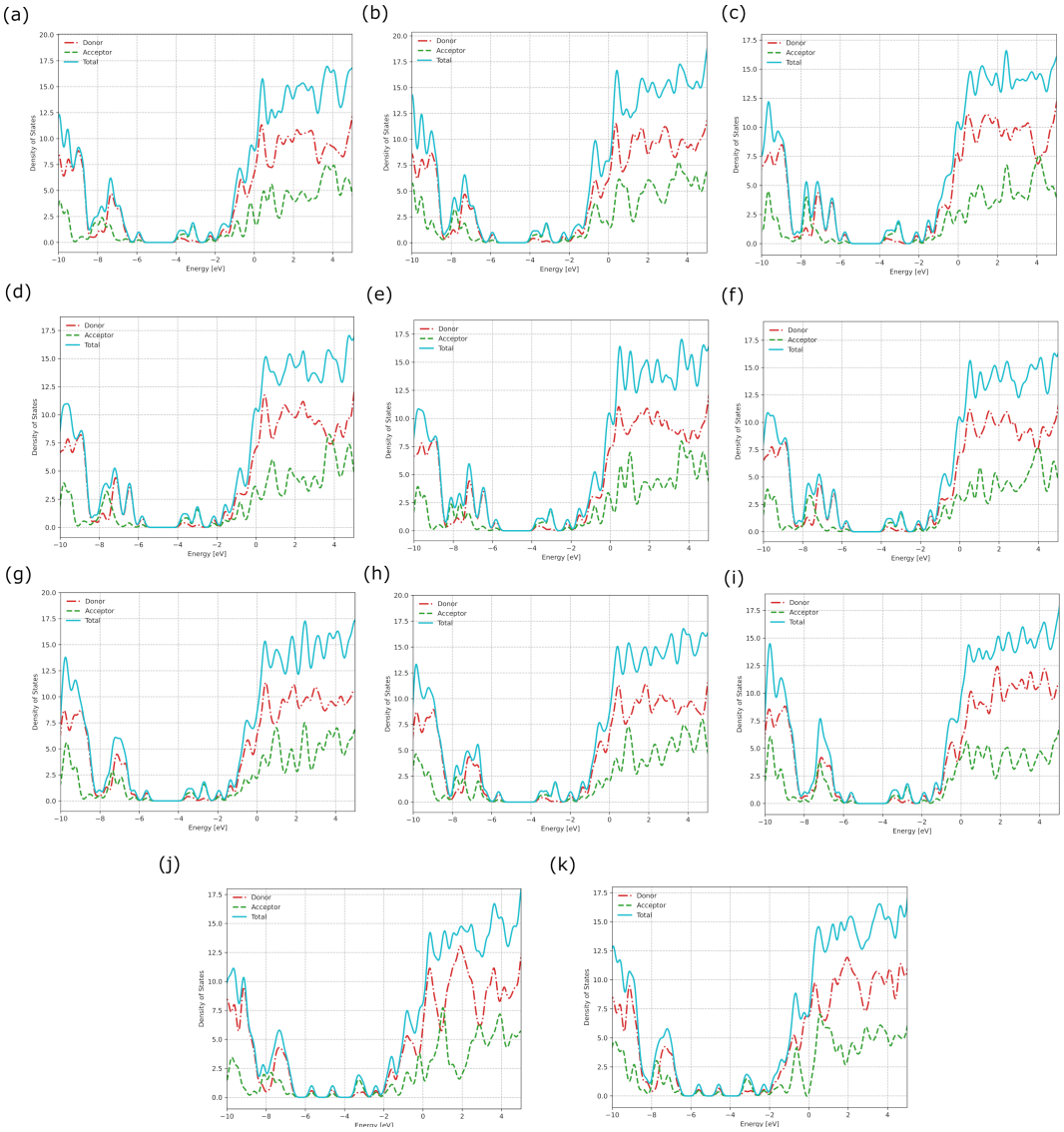


Figure S4: The total and partial density of states (PDOS) computed at the B3LYP/6-31+G(d,p) level for the selected NFA molecules – (a) IT-F; (b) IT-Cl; (c) ITIC-Th-1; (d) ITIC-Th-2; (e) ITIC-Th-3; (f) ITIC-Th-4; (g) IT-OMe-2; (h) IT-OMe-3; (i) IT-OMe-4; (j) SeTIC-F; (k) SeTIC-Cl.

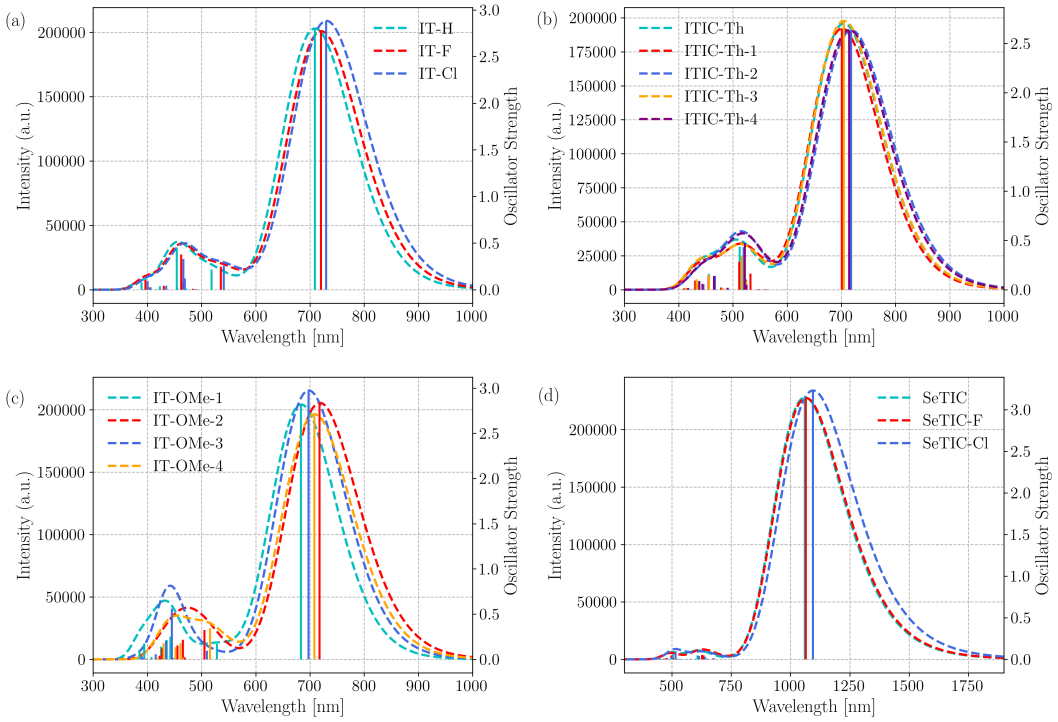


Figure S5: The absorption spectra of NFA molecules computed at TD-DFT/B3LYP/6-31+G(d,p) level in $CHCl_3$ solvent (CPCM model).

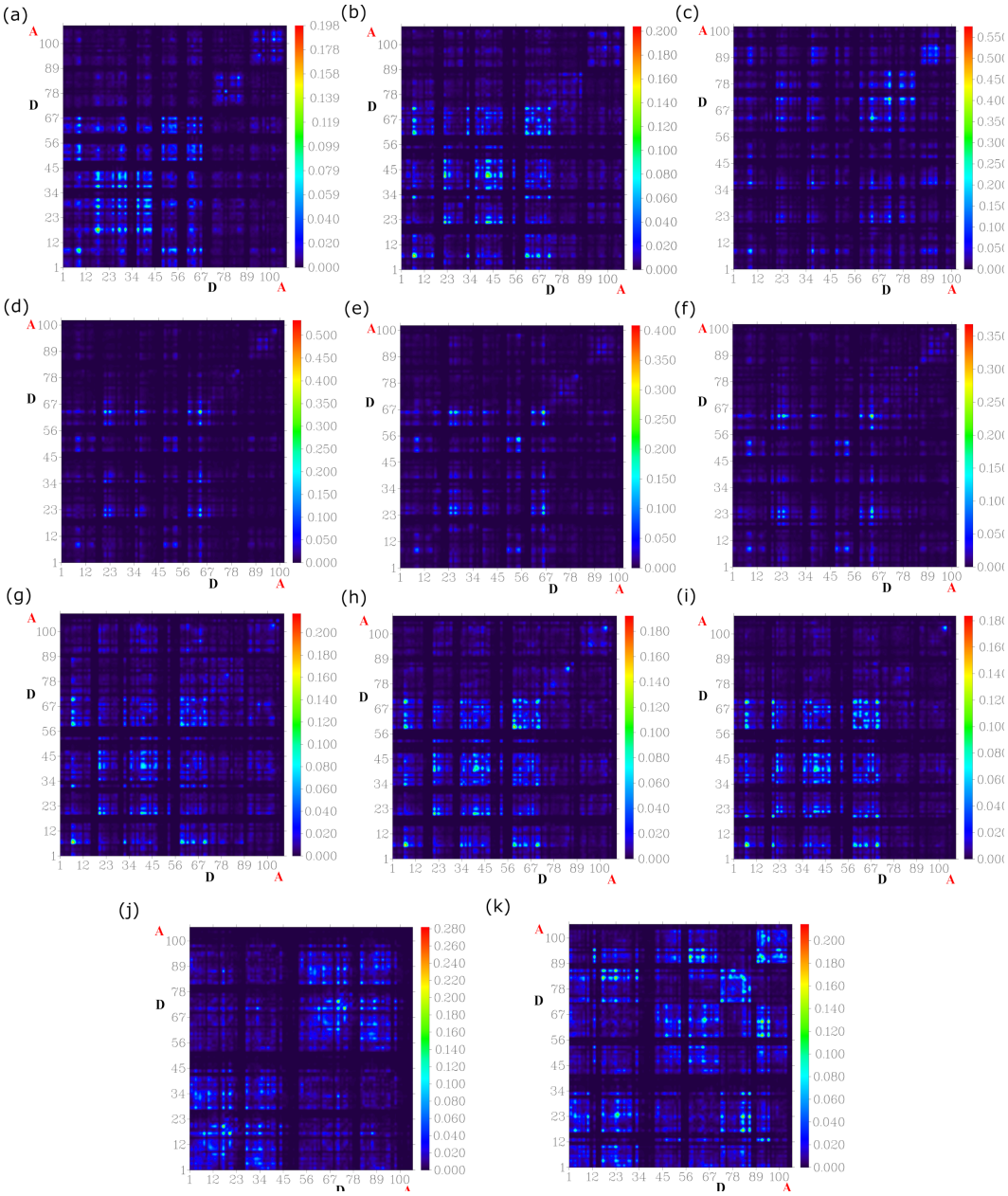


Figure S6: Transition density matrix (TDM) of selected non-fullerene acceptors: (a) IT-F; (b) IT-Cl; (c) ITIC-Th-1; (d) ITIC-Th-2; (e) ITIC-Th-3; (f) ITIC-Th-4; (g) IT-OMe-2; (h) IT-OMe-3; (i) IT-OMe-4; (j) SeTIC-F; (k) SeTIC-Cl.

Table S1: Computed ionization energy (IE), electron affinity (EA), reorganization energy of electron and hole (λ_e and λ_h), HOMO energy, LUMO energy, HOMO-LUMO (H-L) gap, dipole moment (μ), and dihedral angles ($\delta 1$ and $\delta 2$) of the neutral geometry of NFAs at B3LYP/6-31+G(d,p) level.

Compounds	IE (eV)	EA (eV)	λ_h (eV)	λ_e (eV)	HOMO (eV)	LUMO (eV)	H-L gap (eV)	μ (Debye)	$\delta 1$ (°)	$\delta 2$ (°)
IT-H	6.399	2.969	0.169	0.156	-5.730	-3.632	2.098	0.000	1.272	1.272
IT-F	6.558	3.171	0.183	0.157	-5.891	-3.824	2.067	0.033	0.134	0.322
IT-Cl	6.543	3.201	0.172	0.149	-5.896	-3.846	2.049	0.003	0.378	0.364
ITIC-Th	6.401	2.962	0.164	0.157	-5.730	-3.628	2.101	0.101	0.347	0.398
ITIC-Th-1	6.426	2.983	0.171	0.187	-5.752	-3.635	2.117	5.590	4.281	4.579
ITIC-Th-2	6.479	3.082	0.165	0.147	-5.807	-3.745	2.062	0.068	0.926	0.898
ITIC-Th-3	6.492	3.062	0.167	0.167	-5.817	-3.716	2.100	0.079	0.777	0.738
ITIC-Th-4	6.447	3.043	0.165	0.149	-5.774	-3.706	2.068	0.088	1.524	1.480
IT-OMe-1	6.228	2.757	0.183	0.212	-5.566	-3.389	2.177	0.000	5.535	5.537
IT-OMe-2	6.271	2.886	0.173	0.161	-5.618	-3.538	2.080	0.043	1.251	1.234
IT-OMe-3	6.294	2.863	0.177	0.182	-5.638	-3.501	2.136	0.064	0.470	0.614
IT-OMe-4	6.256	2.837	0.172	0.162	-5.594	-3.492	2.102	0.033	1.656	1.632
SeTIC	6.065	3.765	0.135	0.322	-5.389	-4.364	1.025	6.726	16.840	16.841
SeTIC-F	6.261	3.969	0.137	0.327	-5.581	-4.556	1.025	4.095	16.985	16.985
SeTIC-Cl	6.241	3.987	0.134	0.320	-5.593	-4.576	1.017	4.415	17.112	17.112

Table S2: The HOMO and LUMO energy levels of donor polymers, NFAs, and computed open circuit voltages (V_{OC}) for each combination of donor polymer and NFA molecule. The subscript number in V_{OC} represents the donor index against which the values are derived.

Donor	HOMO (eV)	LUMO (eV)	NFAs	LUMO (eV)	V_{OC1} (V)	V_{OC2} (V)	V_{OC3} (V)	V_{OC4} (V)
1: PBDB-T	-5.221	-2.611	IT-H	-3.632	1.289	1.526	1.434	1.302
2: PBDB-T-SF	-5.458	-2.749	IT-F	-3.824	1.097	1.334	1.242	1.110
3: PM6	-5.366	-2.712	IT-Cl	-3.846	1.075	1.312	1.220	1.088
4: FTAZ	-5.234	-2.528	ITIC-Th	-3.628	1.293	1.530	1.438	1.306
			ITIC-Th-1	-3.635	1.286	1.523	1.431	1.299
			ITIC-Th-2	-3.745	1.176	1.413	1.321	1.189
			ITIC-Th-3	-3.716	1.205	1.442	1.350	1.218
			ITIC-Th-4	-3.706	1.215	1.452	1.360	1.228
			IT-OMe-1	-3.389	1.532	1.769	1.677	1.545
			IT-OMe-2	-3.538	1.383	1.620	1.528	1.396
			IT-OMe-3	-3.501	1.420	1.657	1.565	1.433
			IT-OMe-4	-3.492	1.429	1.666	1.574	1.442
			SeTIC	-4.364	0.557	0.794	0.702	0.570
			SeTIC-F	-4.556	0.365	0.602	0.510	0.378
			SeTIC-Cl	-4.576	0.345	0.582	0.490	0.358

An useful parameter that influences the PCE in the OSC devices is the fill factor. The fill factor is determined theoretically by the following equation.

$$\mathrm{FF} = \frac{\frac{\mathrm{eV_{OC}}}{\mathrm{k_B T}} - \ln\left(\frac{\mathrm{eV_{OC}}}{\mathrm{k_B T}} + 0.72\right)}{\frac{\mathrm{eV_{OC}}}{\mathrm{k_B T}} + 1} \tag{1}$$

Here, $\frac{\mathrm{eV_{OC}}}{\mathrm{k_B T}}$ is the normalized V_{OC}, e is the elementary charge, k_{B} is the Boltzmann's constant, and T is the temperature (300 K).

Table S3: The experimental Fill-factor (FF), open circuit voltage (V_{OC}), and J_{SC} of the NFAs. The superscripts a, b, and c represent donor polymers, PBDB-T-SF, FTAZ, and PBDB-T, against which the measurements were conducted.

Acceptors	FF	J_{SC} (mAcm^{-2})	V_{OC} (V)
IT-H [S1]	0.721	17.03	0.9^a
IT-F [S1]	0.71	20.88	0.88^a
ITIC-Th [S2]	0.61	15.84	0.915^b
ITIC-Th-3 [S2]	0.73	19.33	0.849^b
IT-OMe-1 [S3]	0.51	12.31	1.01^c
IT-OMe-2 [S3]	0.73	17.53	0.93^c
IT-OMe-3 [S3]	0.68	16.38	0.97^c
IT-OMe-4 [S3]	0.56	14.69	0.96^c

References

(S1) Zhao, W.; Li, S.; Yao, H.; Zhang, S.; Zhang, Y.; Yang, B.; Hou, J. Molecular optimization enables over 13% efficiency in organic solar cells. *J. Am. Chem. Soc.* **2017**, *139*, 7148–7151.

(S2) Zhao, F.; Dai, S.; Wu, Y.; Zhang, Q.; Wang, J.; Jiang, L.; Ling, Q.; Wei, Z.; Ma, W.; You, W., et al. Single-junction binary-blend nonfullerene polymer solar cells with 12.1% efficiency. *Adv. Mater.* **2017**, *29*, 1700144.

(S3) Li, S.; Ye, L.; Zhao, W.; Zhang, S.; Ade, H.; Hou, J. Significant influence of the methoxyl substitution position on optoelectronic properties and molecular packing of small-molecule electron acceptors for photovoltaic cells. *Adv. Ener. Mater.* **2017**, *7*, 1700183.