Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information

Asymmetric alkoxy side chain engineering on A-DA'D-A non-fullerene acceptors：An effective strategy to enhance crystallinity and electron mobility

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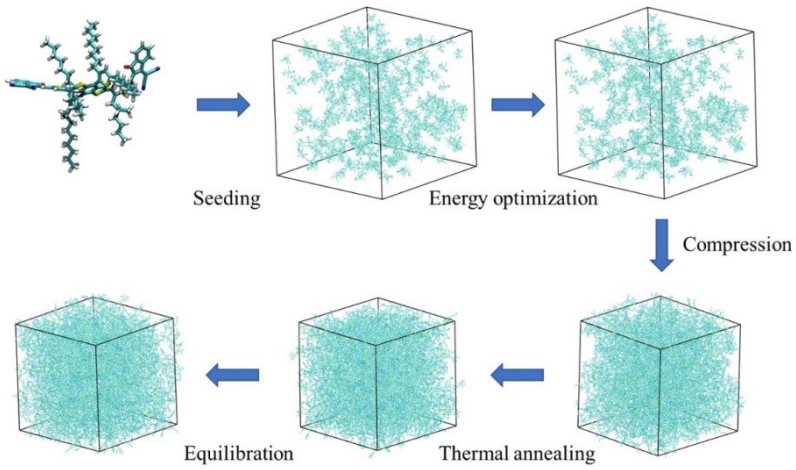


Figure S1. Classical molecular dynamics simulation process.

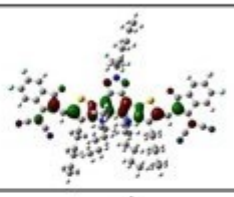
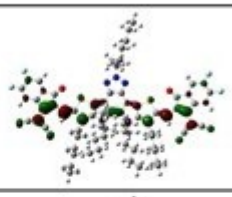
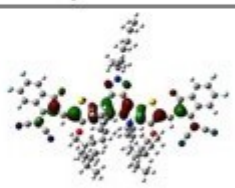
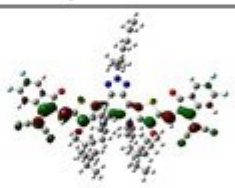
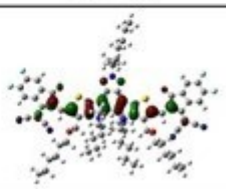
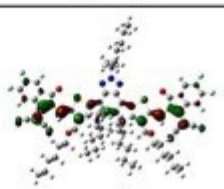
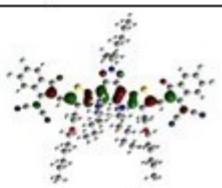
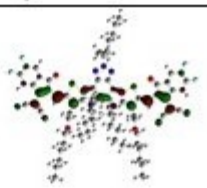
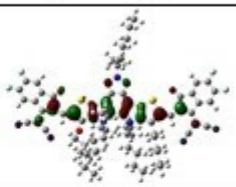
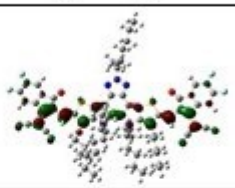
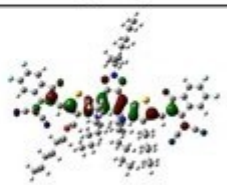
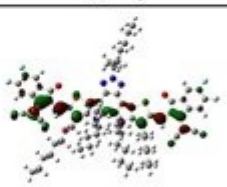
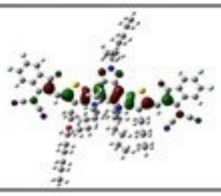
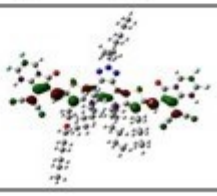
	HOMO	LUMO
BZ4F		
BZ4F-O-1		
BZ4F-O-2		
BZ4F-O-3		
BZ4F-O-1-asy		
BZ4F-O-2-asy		
BZ4F-O-3-asy		

Figure S2. FMO maps of BZ4F series, obtained with B3LYP/6-31G*/PCM.

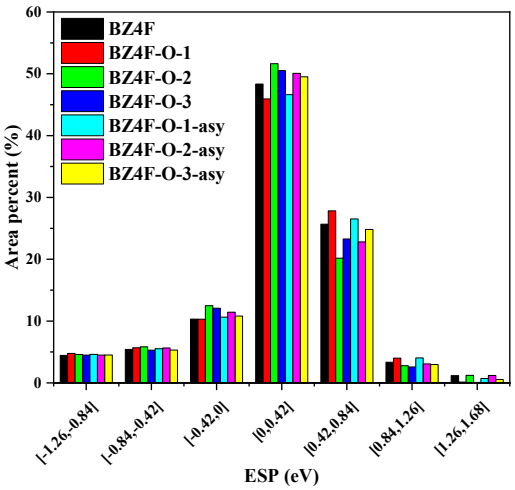


Figure S3. The percent of area with ESP in a specific region.

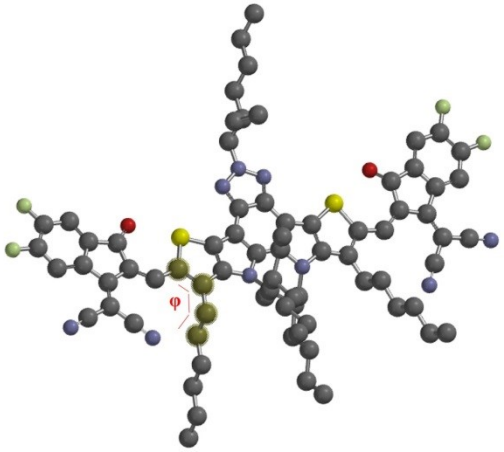


Figure S4. Selected dihedral angle of side chains in BZ4F series.

Table S1. The relative energy of side chain conformations, obtained with MMFF method via Spartan 18 software package.[1] The symmetric molecules BZ4F-O-1/2/3 have similar angles and relative energy as their asymmetric counterparts. For simplicity, we only list the data of BZ4F and asymmetric molecules.

BZ4F	Dihedral angle φ (degree)	Energy (kJ/mol)
	100	1331.6725
	90	1327.4367
	86.9 (DFT optimized)	1326.4993
	80	1325.5790
	70	1329.1753
	60	1345.7146
BZ4F-O-1-asy	90	1358.1849
	80	1344.6257
	77.08 (DFT optimized)	1346.1129
	70	1352.9117
	60	1376.1634
	50	1440.6452
BZ4F-O-2-asy	80	1340.6218
	70	1335.4040
	60.15 (DFT optimized)	1333.6924
	50	1338.2629
	40	1356.6187
	30	1416.1576
BZ4F-O-3-asy	110	1386.7009
	100	1380.6207
	93.34 (DFT optimized)	1378.5846
	90	1378.2675
	80	1382.1523
	70	1402.3971

Table S2. The dipole moments and their components of BZ4F series.

	Dipole moment (Debye)	θ (°)	In the plane (Debye)	Out of the plane (Debye)
BZ4F	1.14	16	1.09	0.33
BZ4F-O-1	0.9	22	0.90	0.01
BZ4F-O-2	0.68	42	0.27	0.62
BZ4F-O-3	2.15	15	1.63	1.40
BZ4F-O-1-asy	2.37	63	2.34	0.40
BZ4F-O-2-asy	0.46	0	0.46	0
BZ4F-O-3-asy	1.77	18	1.17	1.33

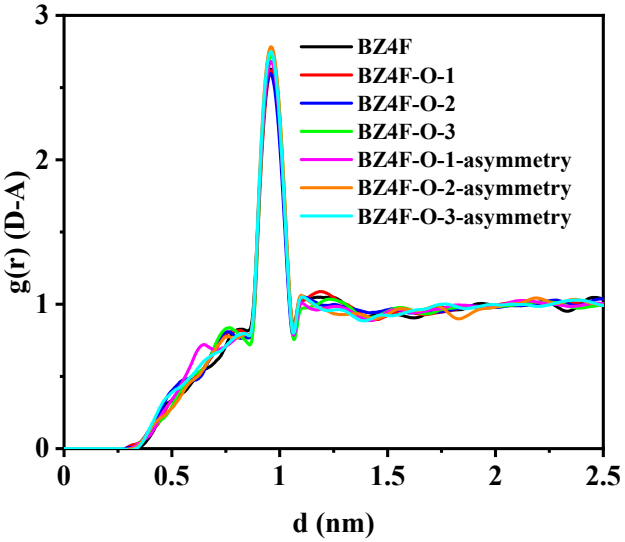


Figure S5. RDF of electron-absorbing end groups and electron-giving core units (D-A).

Table S3. Detailed value of the configuration ratio for A-A and D-D stacking.

	A-A face-on	A-A edge-on	D-D face-on	D-D edge-on
BZ4F	42.60%	57.40%	30.49%	69.51%
BZ4F-O-1	43.17%	56.83%	33.14%	66.86%
BZ4F-O-2	39.82%	60.18%	32.24%	67.76%
BZ4F-O-3	39.47%	60.53%	20.59%	79.41%
BZ4F-O-1-asy	43.06%	56.94%	31.82%	68.18%
BZ4F-O-2-asy	42.90%	57.10%	24.86%	75.14%
BZ4F-O-3-asy	41.72%	58.28%	30.51%	69.49%

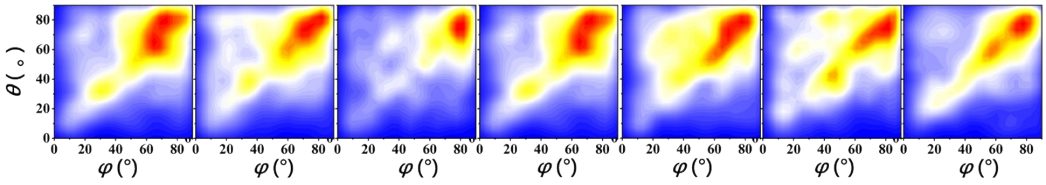


Figure S6. The density contour plots of A-A stacking *d* -*θ* in the final CMD simulation box.

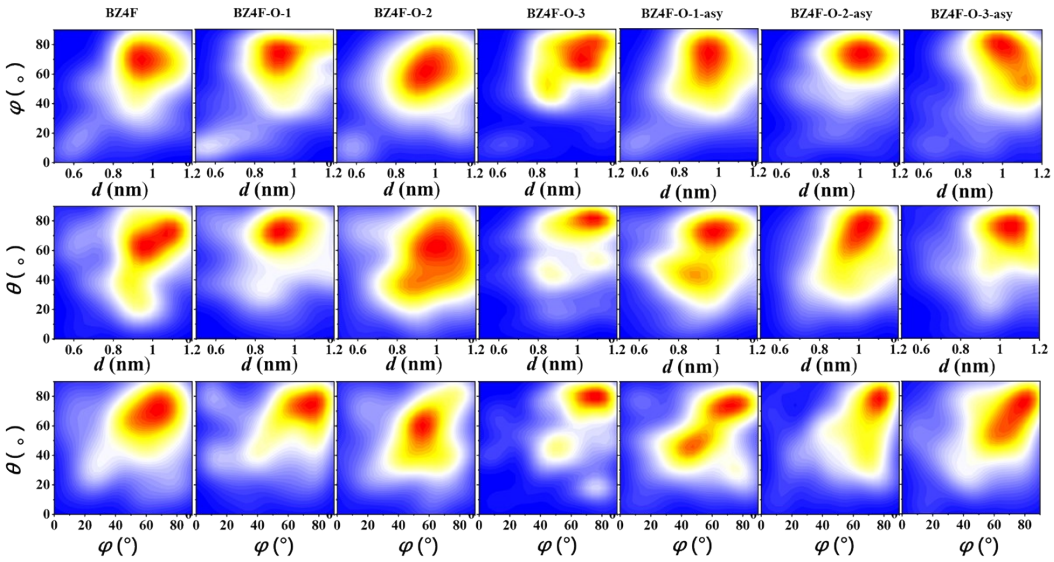


Figure S7. The density contour plots of D-D stacking *d*-*φ*, *d*-*θ* and *φ*-*θ* in the final CMD simulation box.

Table S4. Detailed values of hole (λ_h) reorganization energy of BZ4F series. Unit: eV.

	λ_h
BZ4F	0.165
BZ4F-O-1	0.165
BZ4F-O-2	0.176
BZ4F-O-3	0.165
BZ4F-O-1-asy	0.166
BZ4F-O-2-asy	0.169
BZ4F-O-3-asy	0.165

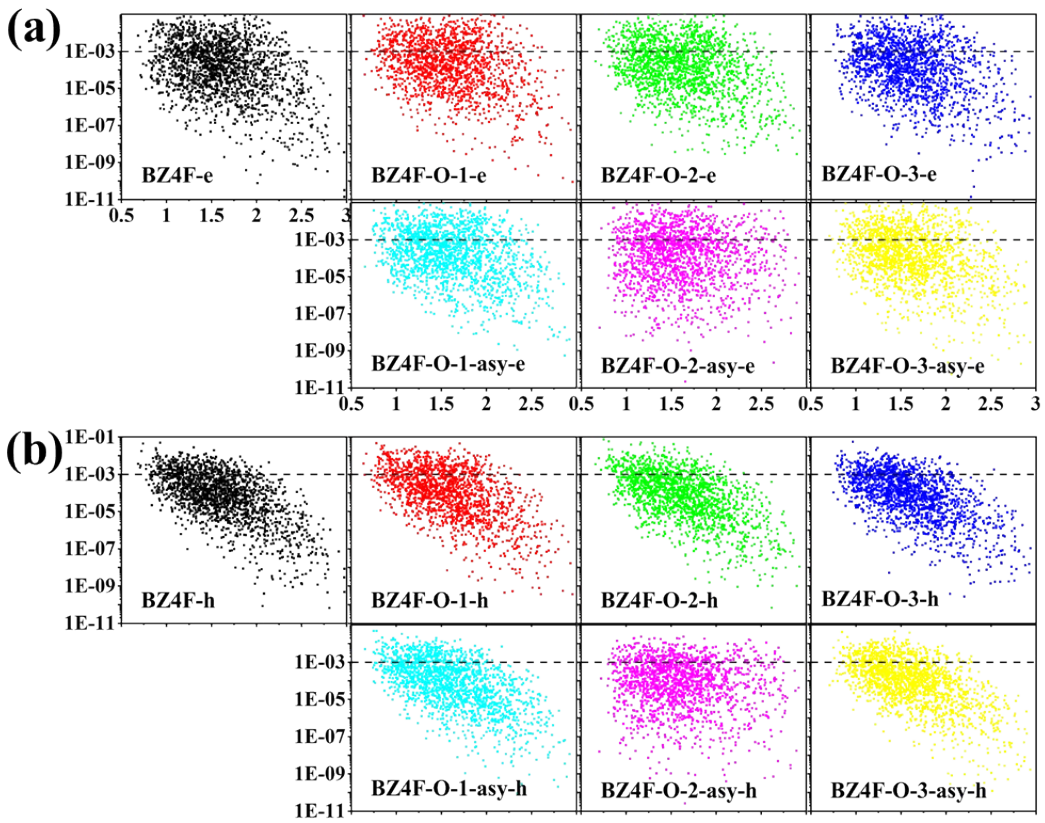


Figure S8. (a) Electron transfer and (b) hole transfer integral as a function of backbone-backbone COM distance of molecular pairs inside the final boxes of CMD simulations.

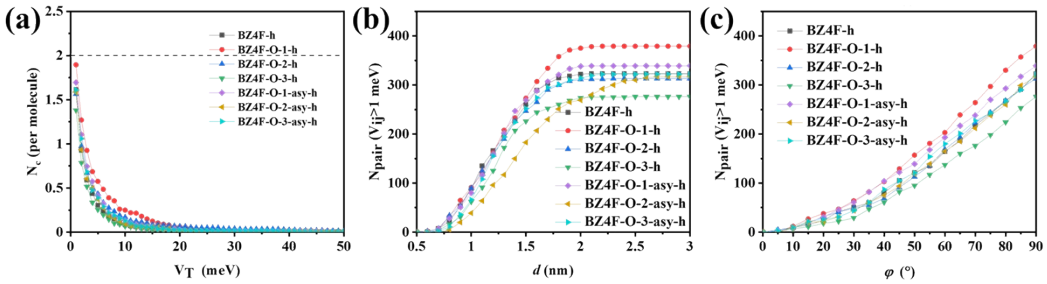


Figure S9. (a) Hole connectivity (N_c) as a function of V_T. (b) and (c) The number of pairs with V_{ij} > 1 meV as the function of center-of-mass distance (d) and dihedral angle (φ).

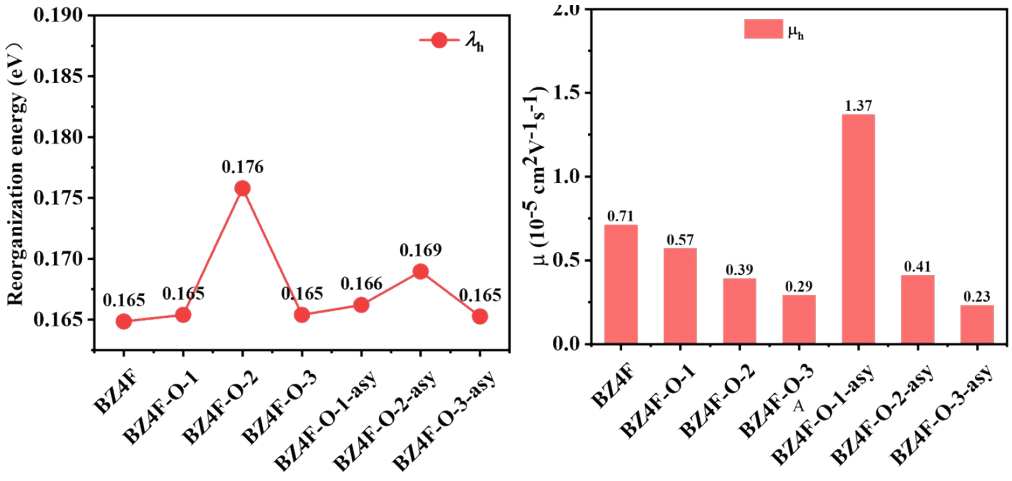


Figure S10. (a) Hole reorganization energy (λ_h) of BZ4Fs. (b) Hole mobility μ_h of BZ4Fs obtained by classical molecular dynamics simulation and KMC.

References

1. Spartan'18 (2018) Wavefunction Inc., Irvine.