Supplementary Information

Regulating through space charge transfer in thermally activated delayed fluorescence molecules via donor architectures: Theoretical perspective and molecular design

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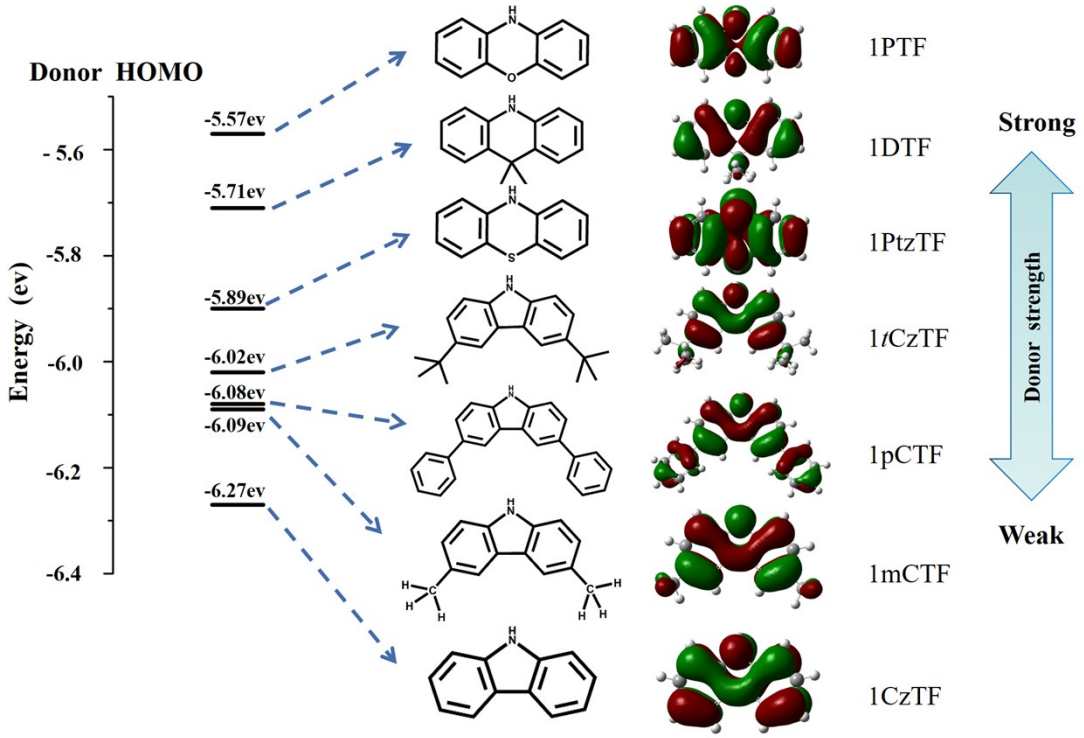

Figure S1. The energy of highest occupied molecular orbital for donor units.

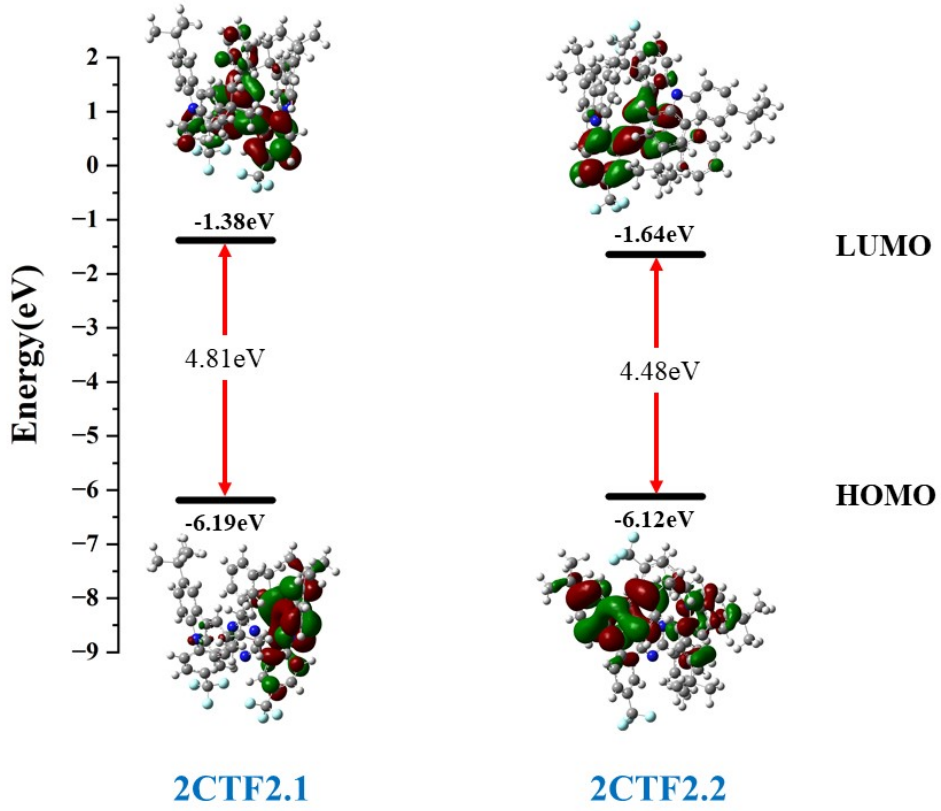

Figure S2. Calculated distributions and energies of HOMO and LUMO for 2CTF2.1 and 2CTF2.2.

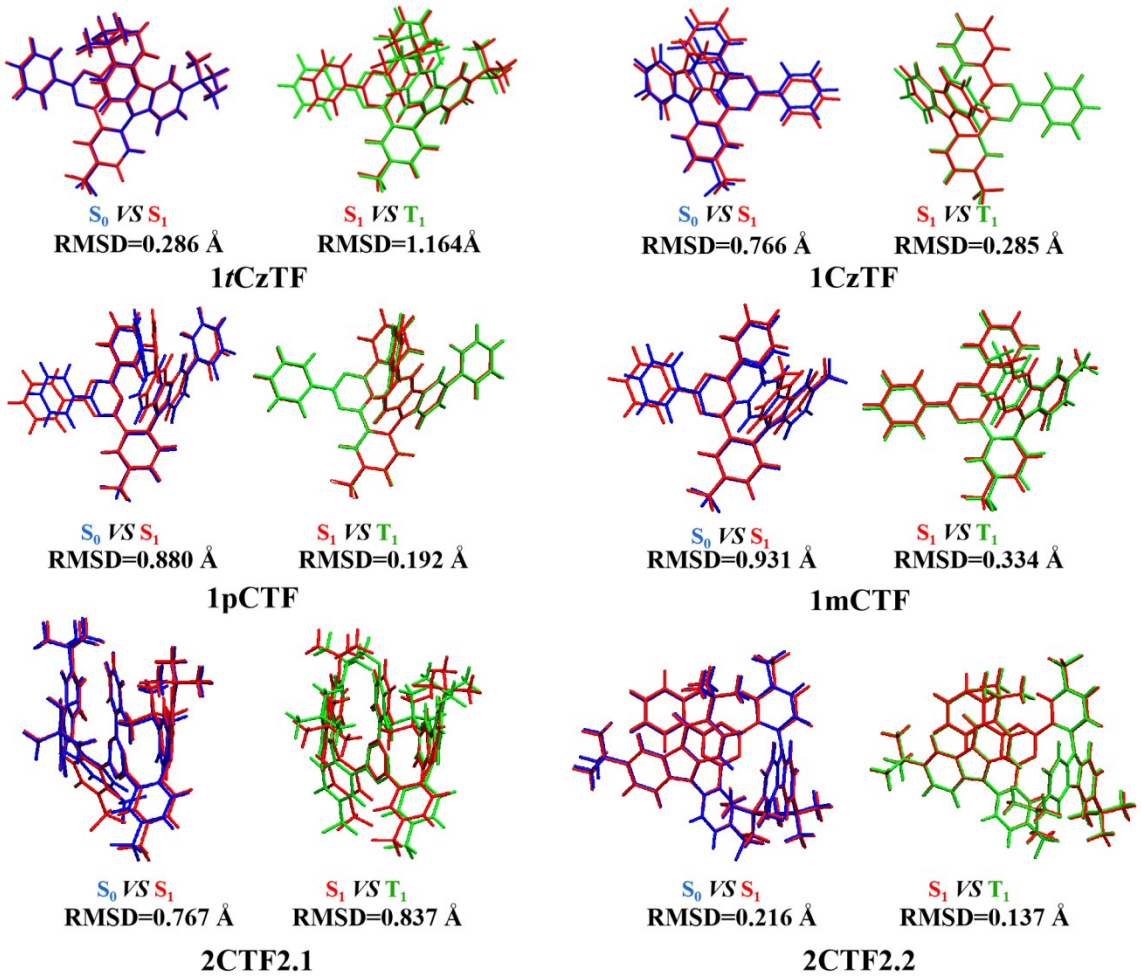

Figure S3. Geometry comparisons and RMSD values of molecules with carbazole rings in different states in toluene.

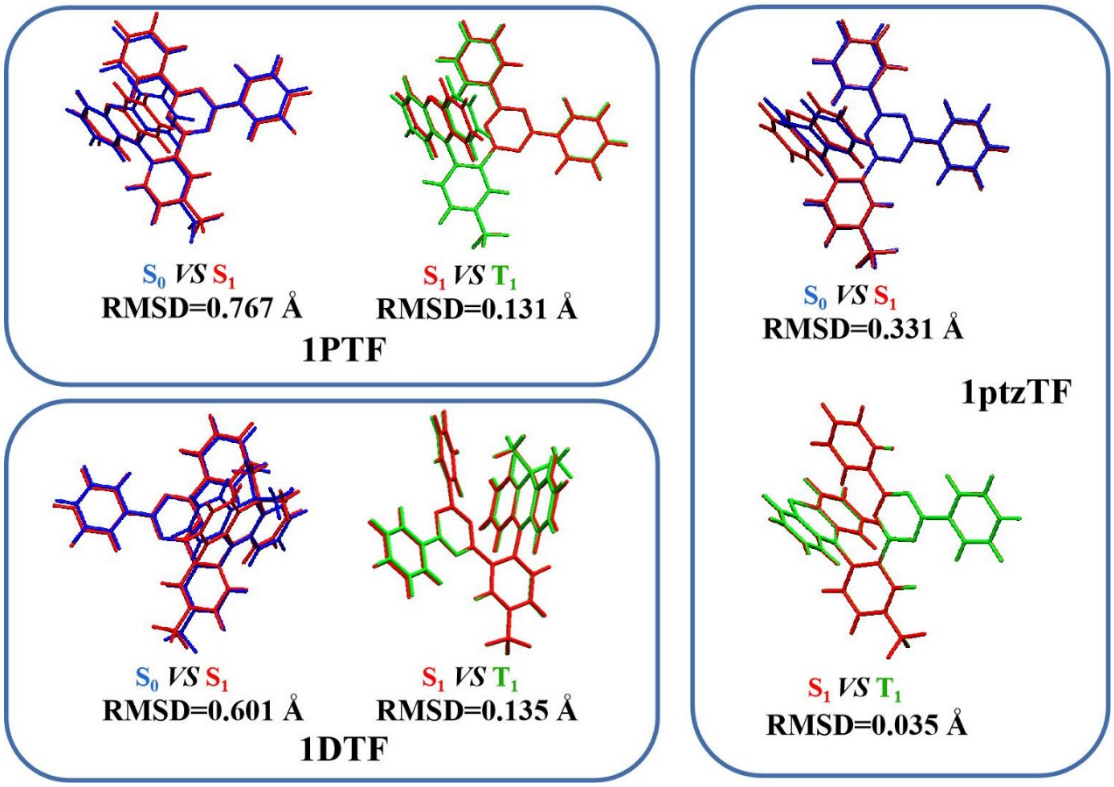

Figure S4. Geometry comparisons and RMSD values of molecules with phenazine rings in different states in toluene.

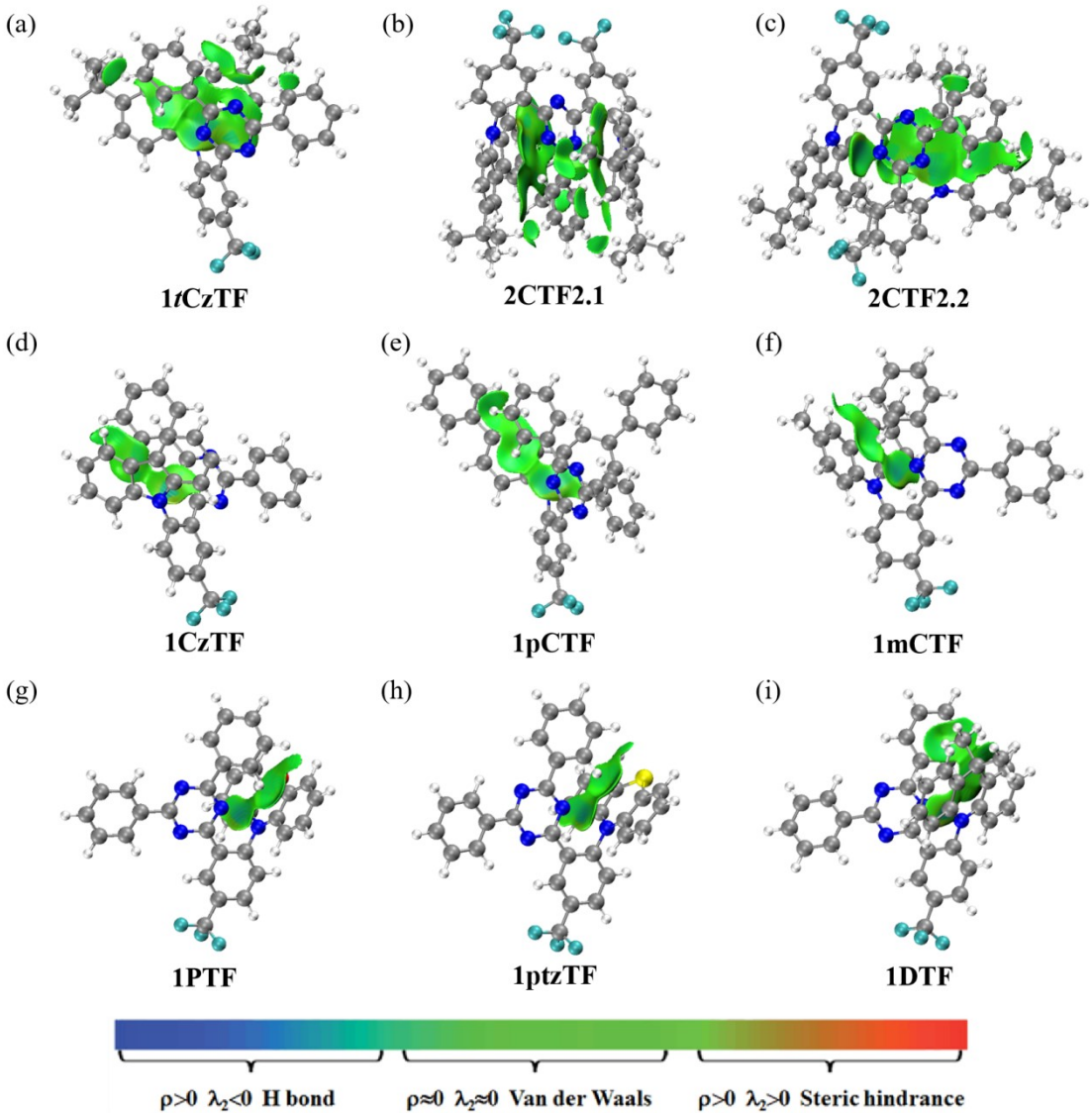

Figure S5. Inter-fragment intramolecular interactions for studied molecules measured by IGMH method. (Iso-surface values are all 0.005).

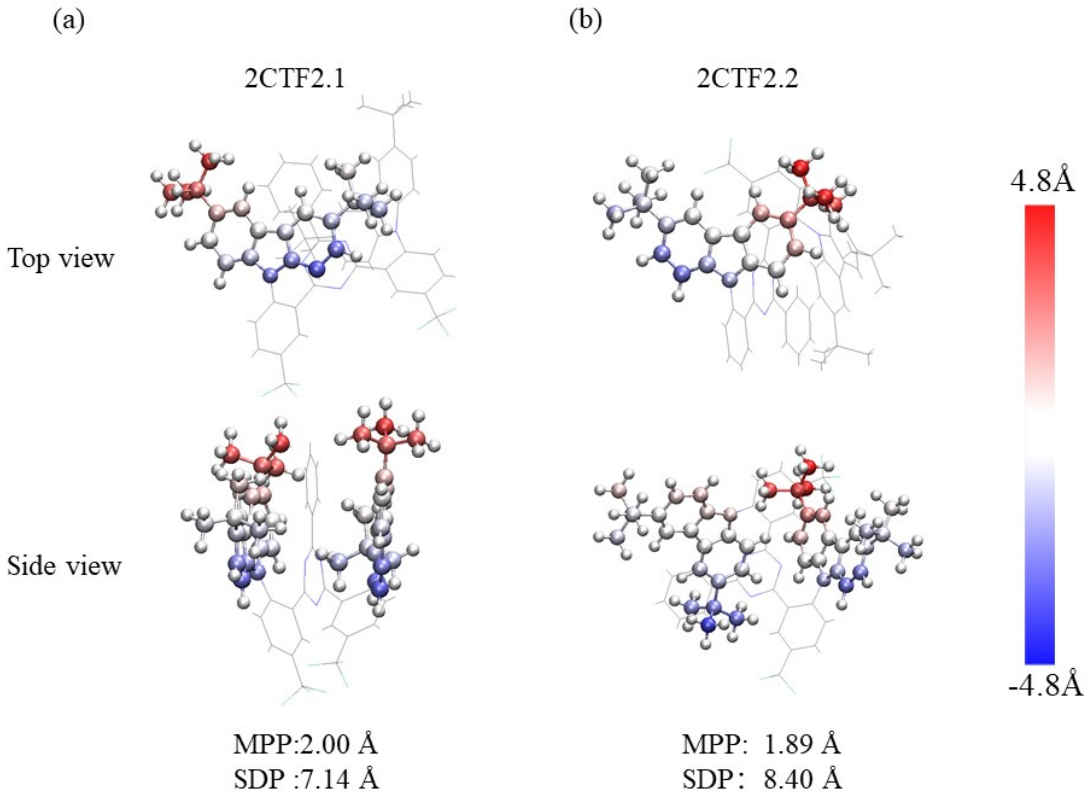

Figure S6. Molecular planarity parameters of donors for 2CTF2.1 (a) and 2CTF2.2 (b).

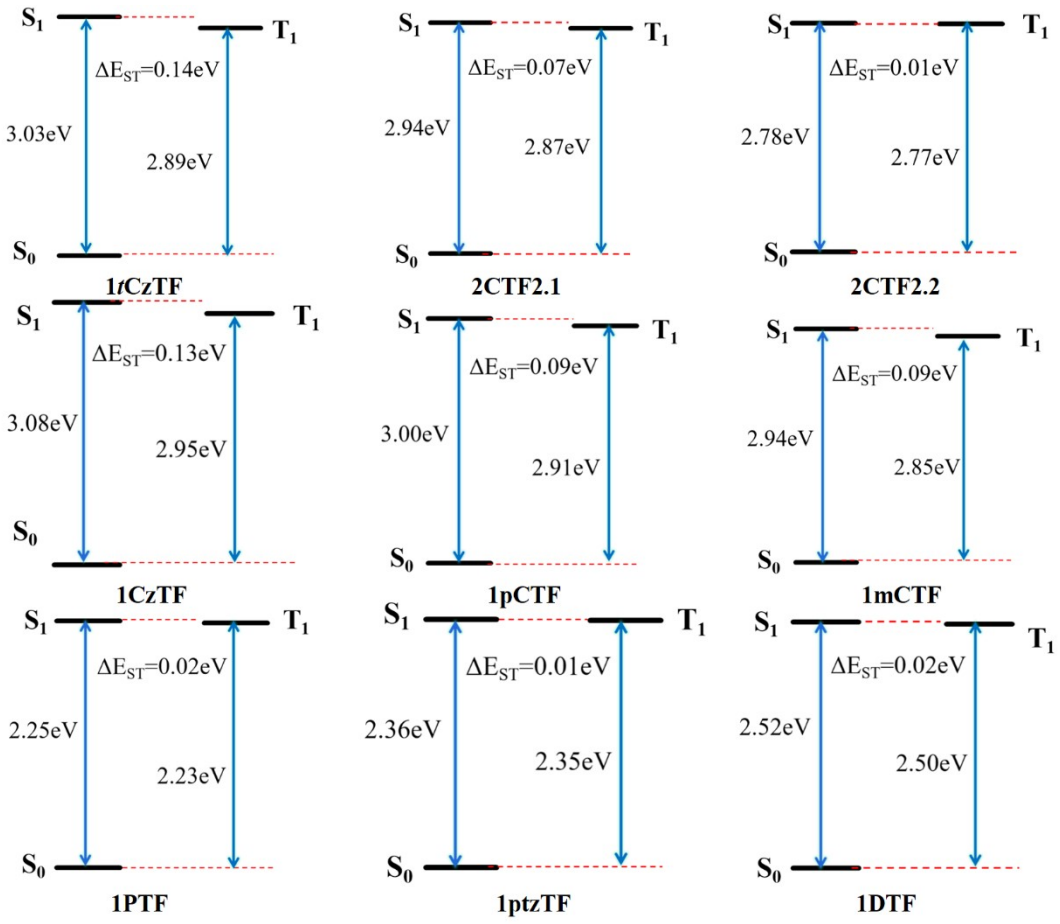

Figure S7. Adiabatic excitation energies for S_1 states and T_1 states as well as their energy gaps for all studied molecules.

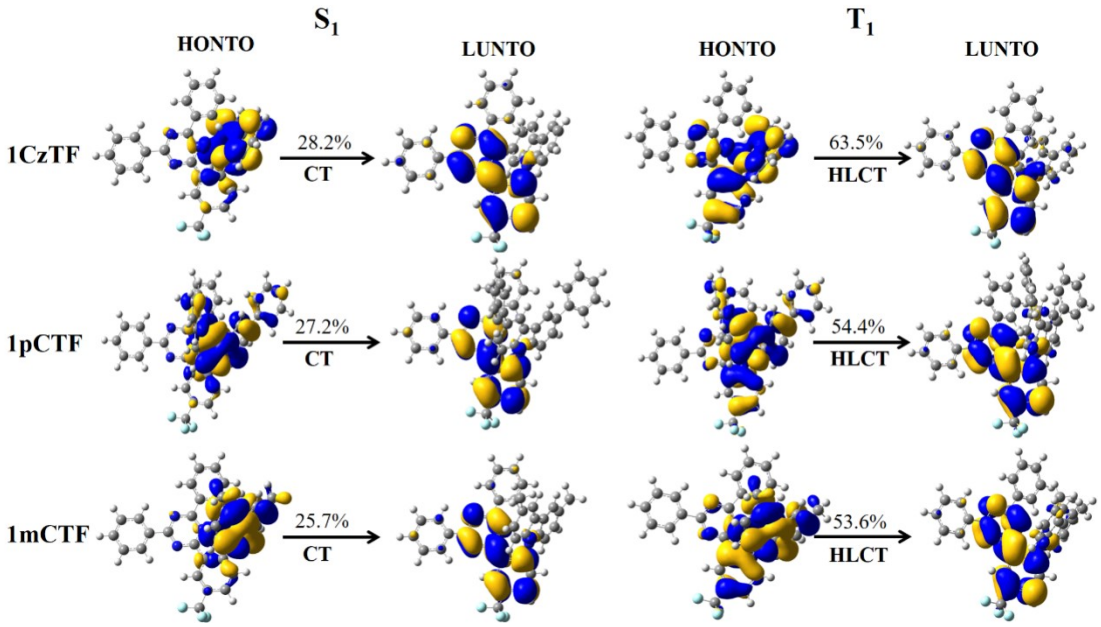

Figure S8. Natural transition orbitals (NTOs) of the S_1 and T_1 states for 1CzTF, 1pCzTF and 1mCTF in toluene. The values above the arrows are the LE proportions in excitation. (Iso-value=0.02)

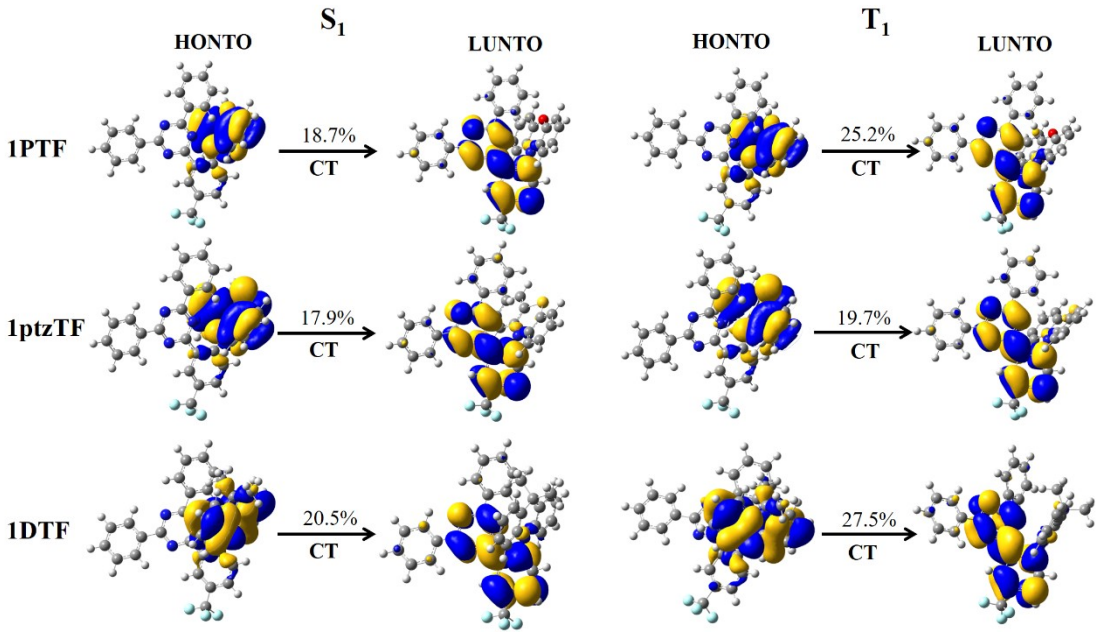

Figure S9. Natural transition orbitals (NTOs) of the S_1 and T_1 states for 1PTF, 1ptzTF and 1DTF in toluene. The values above the arrows are the LE proportions in excitation. (Iso-value=0.02)

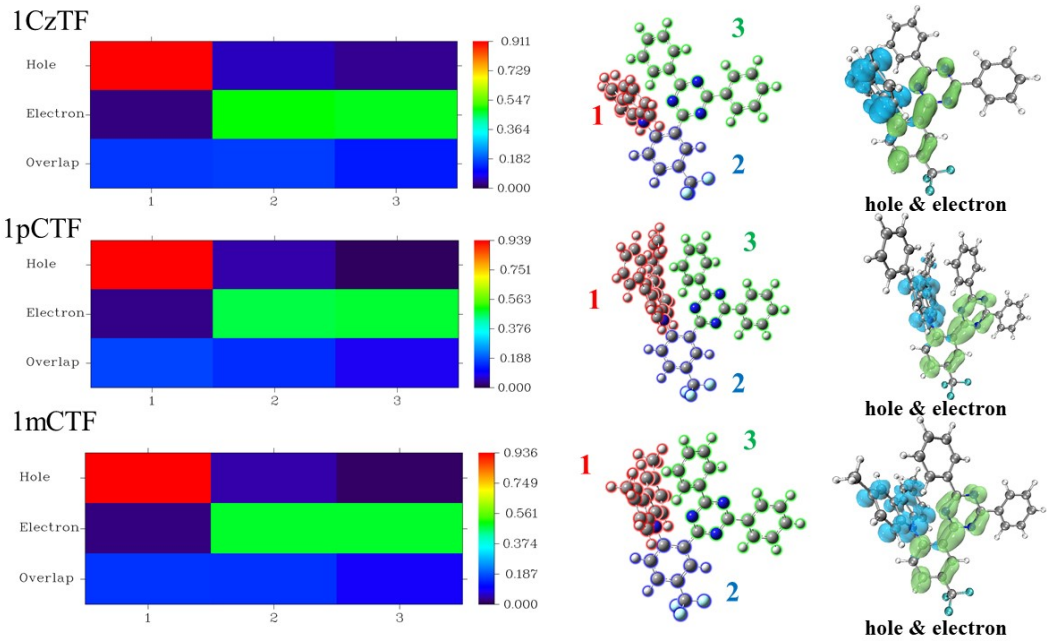

Figure S10. Heat maps and distributions of hole and electron in S_1 state for 1CzTF, 1pCTF and 1mCTF. (Iso-value = 0.002)

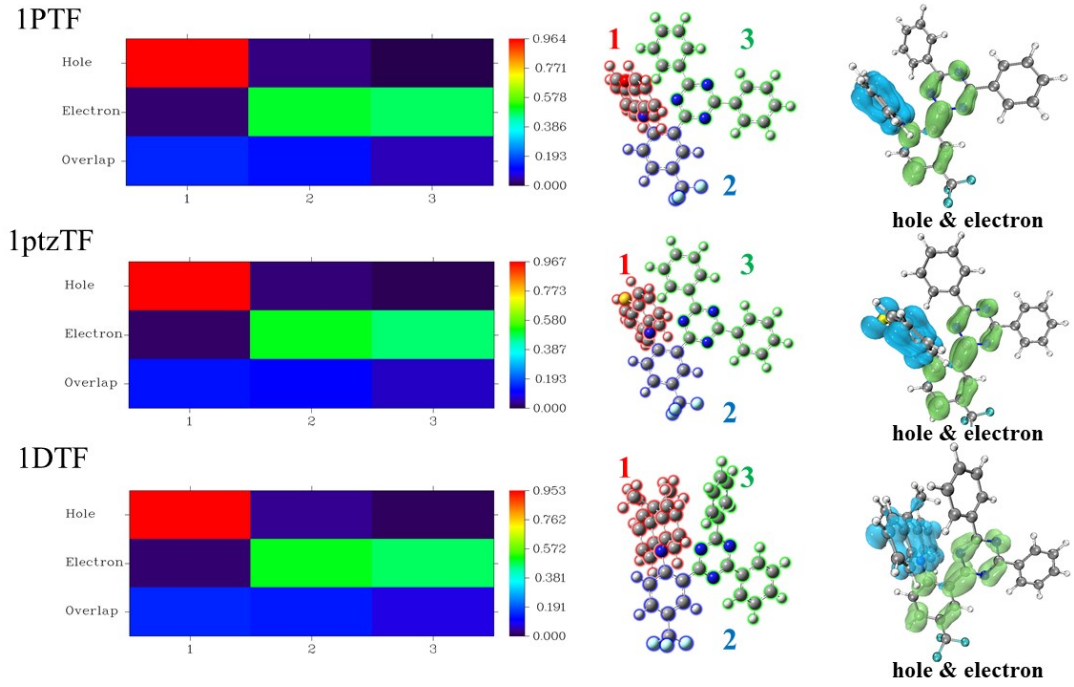

Figure S11. Heat maps and distributions of hole and electron in S_1 state for 1PTF, 1ptzTF and 1DTF. (Iso-value = 0.002)

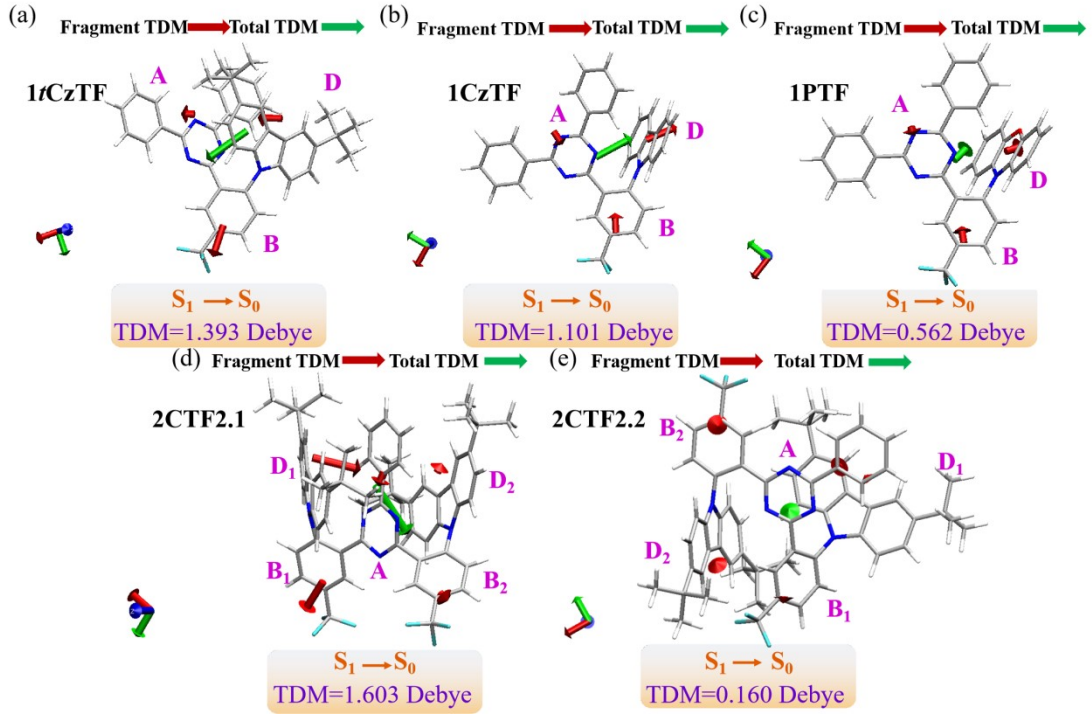

Figure S12. Transition dipole moment vector contributions from different fragments (red) and the whole molecules (green) for 1*t*CzTF (a), 1CzTF (b), 1PTF (c), 2CTF2.1 (d), and 2CTF2.2 (e), respectively.

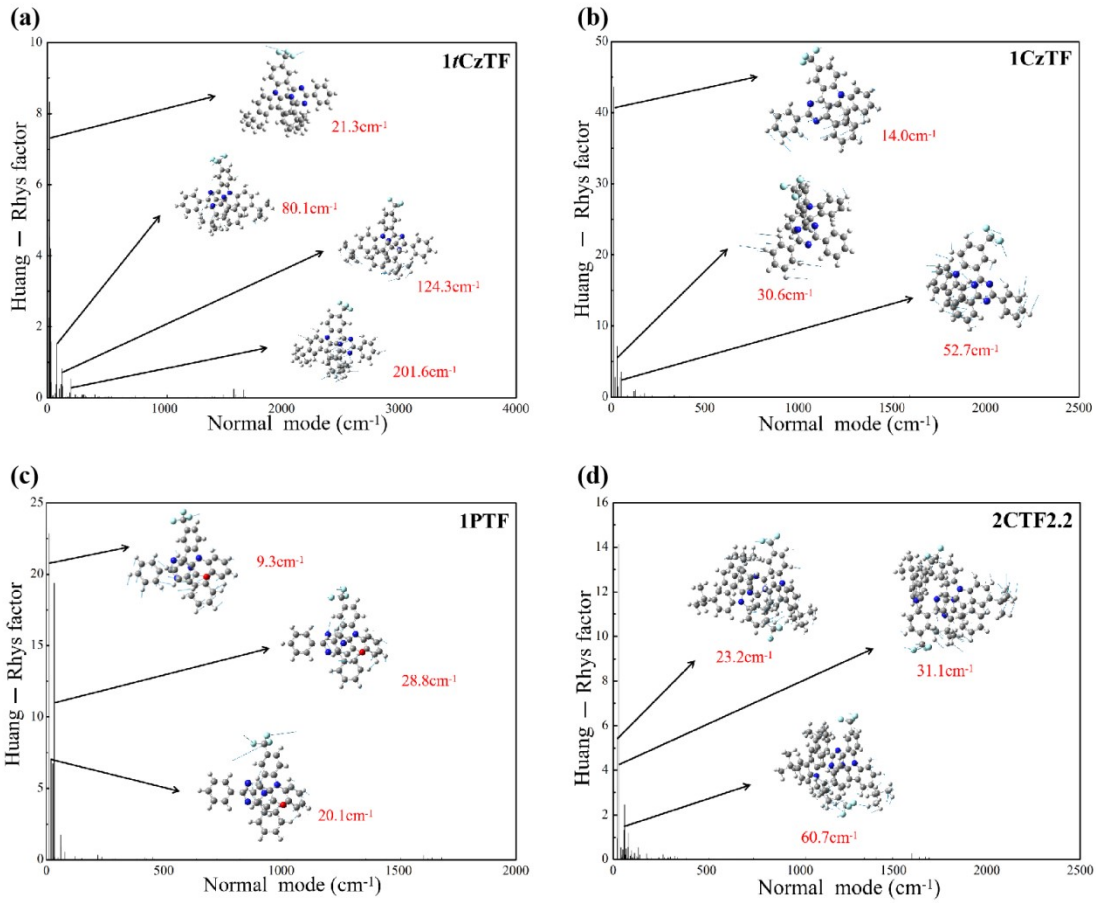

Figure S13. Calculated HR factors versus the normal-mode frequencies for 1*t*CzTF (a), 1CzTF (b), 1PTF (c) and 2CTF2.2 (d) and representative vibration modes are shown as insets.

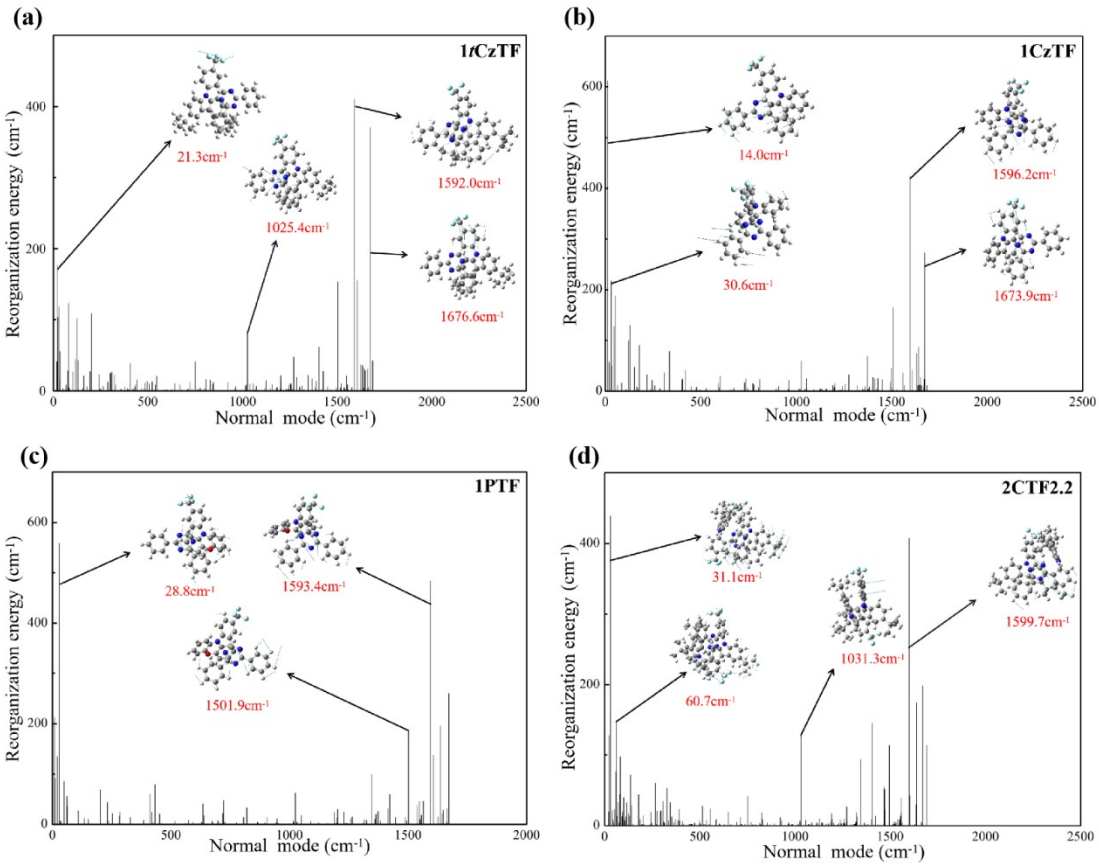

Figure S14. Calculated reorganization energies versus the normal-mode frequencies for 1*t*CzTF (a), 1CzTF (b), 1PTF (c) and 2CTF2.2 (d) and representative vibration modes are shown as insets.

Table S1. Calculated results of GCDA. Where d represents the charge transfer amount from donors to acceptors and bridges, b represents the charge transfer amount from acceptors and bridges to donors. d-b represents the net charge transfer calculated with GCDA.

Molecule	d	b	d-b
1*t*CzTF	0.167	0.027	0.140
1CzTF	0.154	0.007	0.147
1pCTF	0.157	0.012	0.145
1mCTF	0.156	0.008	0.148
1PTF	0.158	0.001	0.157
1ptzTF	0.157	0.006	0.151
1DFT	0.158	0.013	0.145

Table S2. Energies of HOMO and LUMO, ε_{gap} represents HOMO-LUMO energy gap.

Molecule	HOMO (eV)	LUMO (eV)	ε_{gap} (eV)
1*t*CzTF	-6.14	-1.33	4.81
1CzTF	-6.34	-1.35	4.99
1pCTF	-6.13	-1.34	4.79
1mCTF	-6.15	-1.31	4.84
1PTF	-5.66	-1.38	4.28
1ptzTF	-5.88	-1.62	4.26
1DFT	-5.78	-1.33	4.45
2CTF2.1	-6.19	-1.38	4.81
2CTF2.2	-6.12	-1.64	4.48

Table S3. Transition dipole moment (Debye) contribution from different fragments for 1*t*CzTF, 1CzTF, 1PTF, 2CTF2.1 and 2CTF2.2.

	Transition dipole moment				
	Fragment	X (a.u.)	Y(a.u.)	Z (a.u.)	Total* (Debye)
1*t*CzTF	D	0.175	-0.077	-0.152	0.621
	B	0.213	0.274	-0.031	0.886
	A	0.074	-0.034	-0.063	0.262
	All	0.462	0.163	-0.246	1.393
1CzTF	D	-0.275	-0.212	0.087	0.910
	B	-0.161	0.104	0.033	0.494
	A	0.065	-0.125	0.013	0.360
	All	-0.340	-0.233	0.133	1.101
1PTF	D	-0.118	-0.093	0.077	0.429
	B	-0.094	0.093	0.042	0.353
	A	0.032	-0.041	0.001	0.132
	All	-0.181	-0.041	0.120	0.562
2CTF2.1	D_1	-0.361	-0.114	-0.323	1.265
	D_2	0.002	-0.051	0.001	0.130
	B_1	-0.036	0.374	-0.041	0.961
	B_2	-0.068	0.004	0.000	0.173
	A	-0.020	0.103	0.003	0.267
	All	-0.411	0.316	-0.359	1.603
2CTF2.2	D_1	0.002	0.013	-0.031	0.086
	D_2	0.002	0.036	-0.036	0.130
	B_1	0.006	-0.009	0.000	0.027
	B_2	0.002	-0.007	-0.026	0.069
	A	-0.010	0.001	0.010	0.036
	All	0.002	0.034	-0.053	0.160

$* \ Total = \sqrt{x^2 + y^2 + z^2} \times 2.5417 \ Debye/a.u.$