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

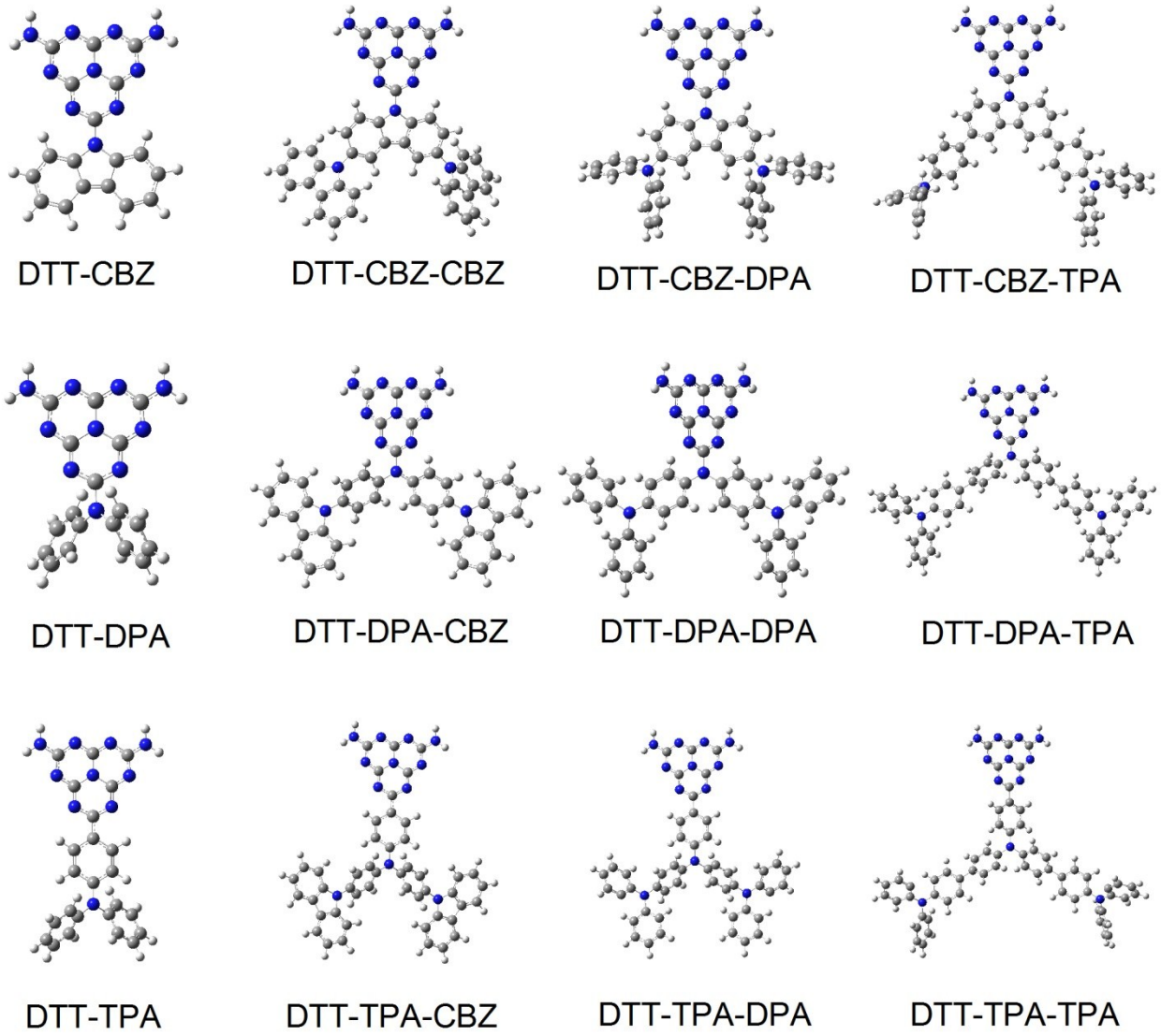

Figure SI1 The optimized structures of primary designed host molecules in ground states (S_0) at B3LYP/6-31G* level of theory

Figure SI2 The optimized structures of primary designed host molecules in exited state (T_1) at B3LYP/6-31G* level of theory

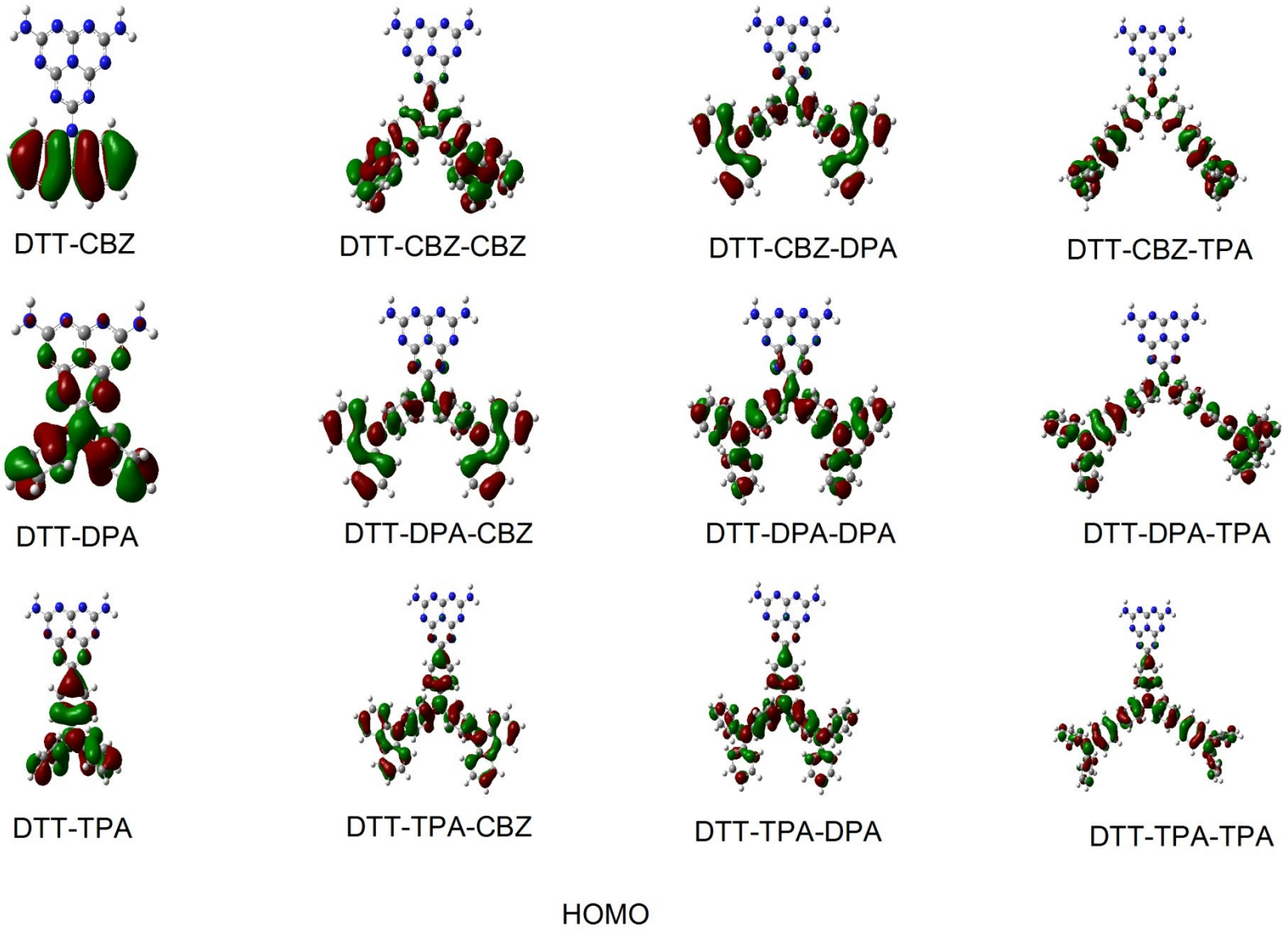

Figure SI3 The spatial distribution of frontier molecular orbitals(HOMO) for primary designed host molecules

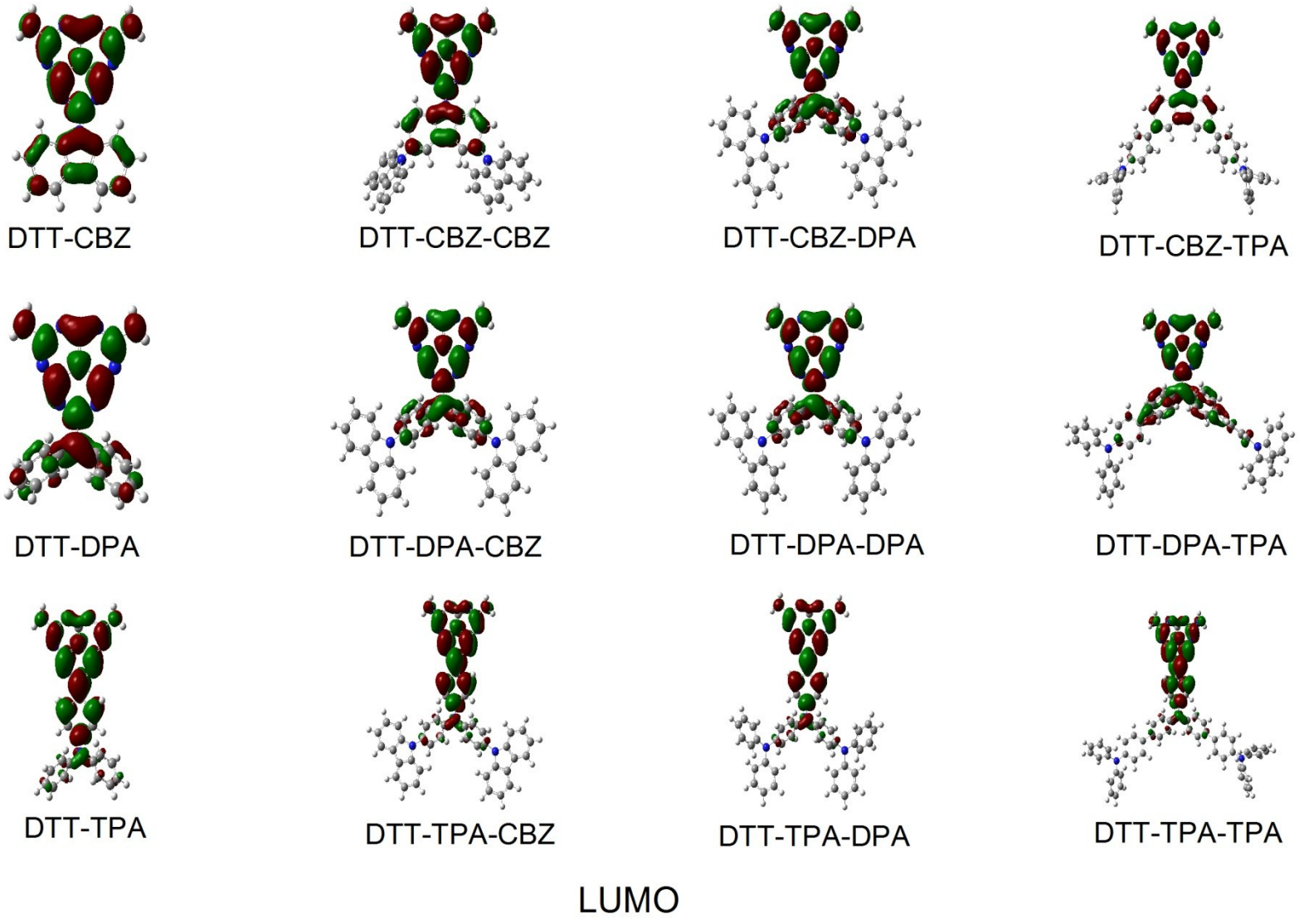

Figure SI4 The spatial distribution of frontier molecular orbitals(LUMO) for primary designed host molecules

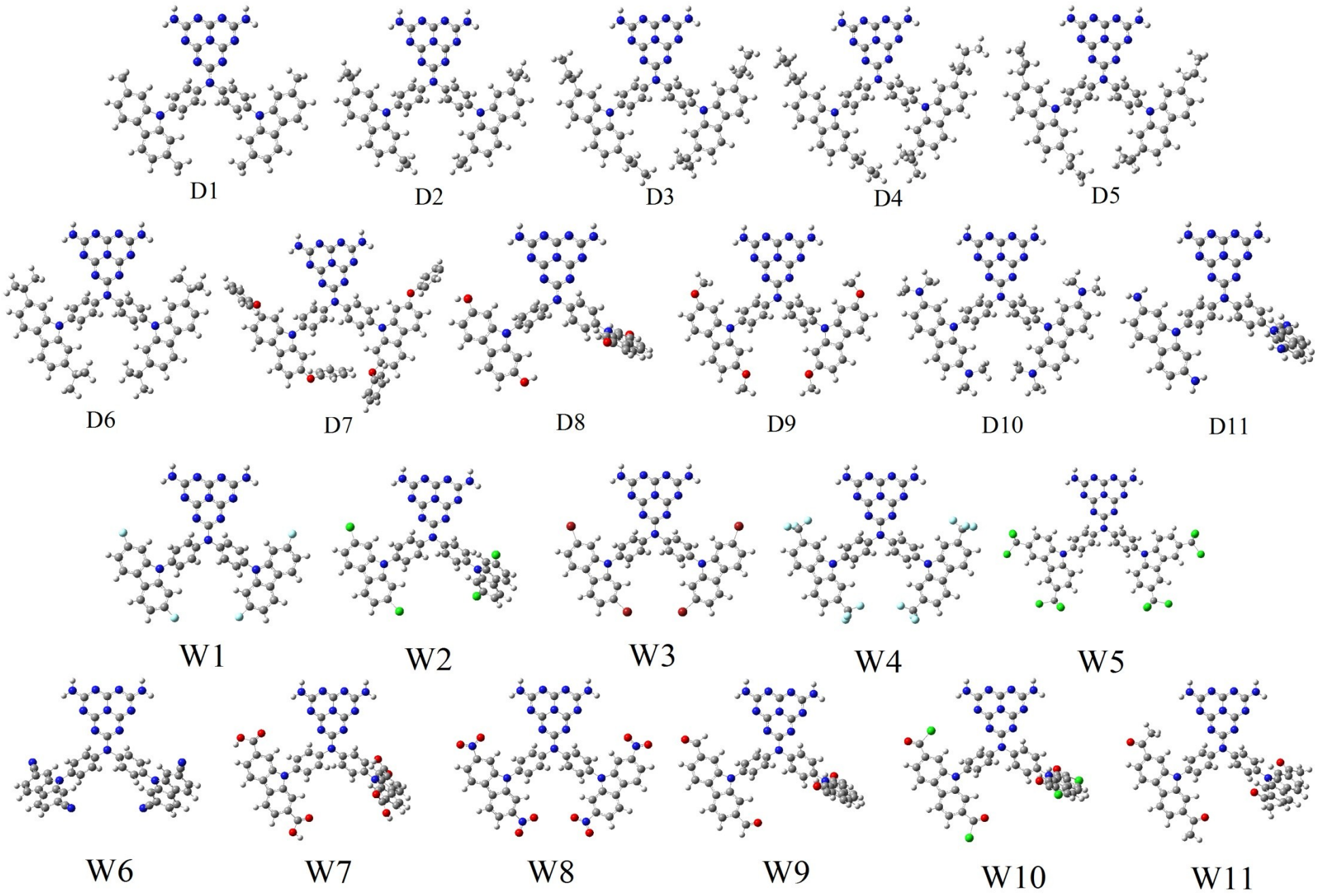

Figure SI5 The optimized structures of EDG and EWG substituted DTT-DPA-CBZ in ground states (S_0) at B3LYP/6-31G* level of theory

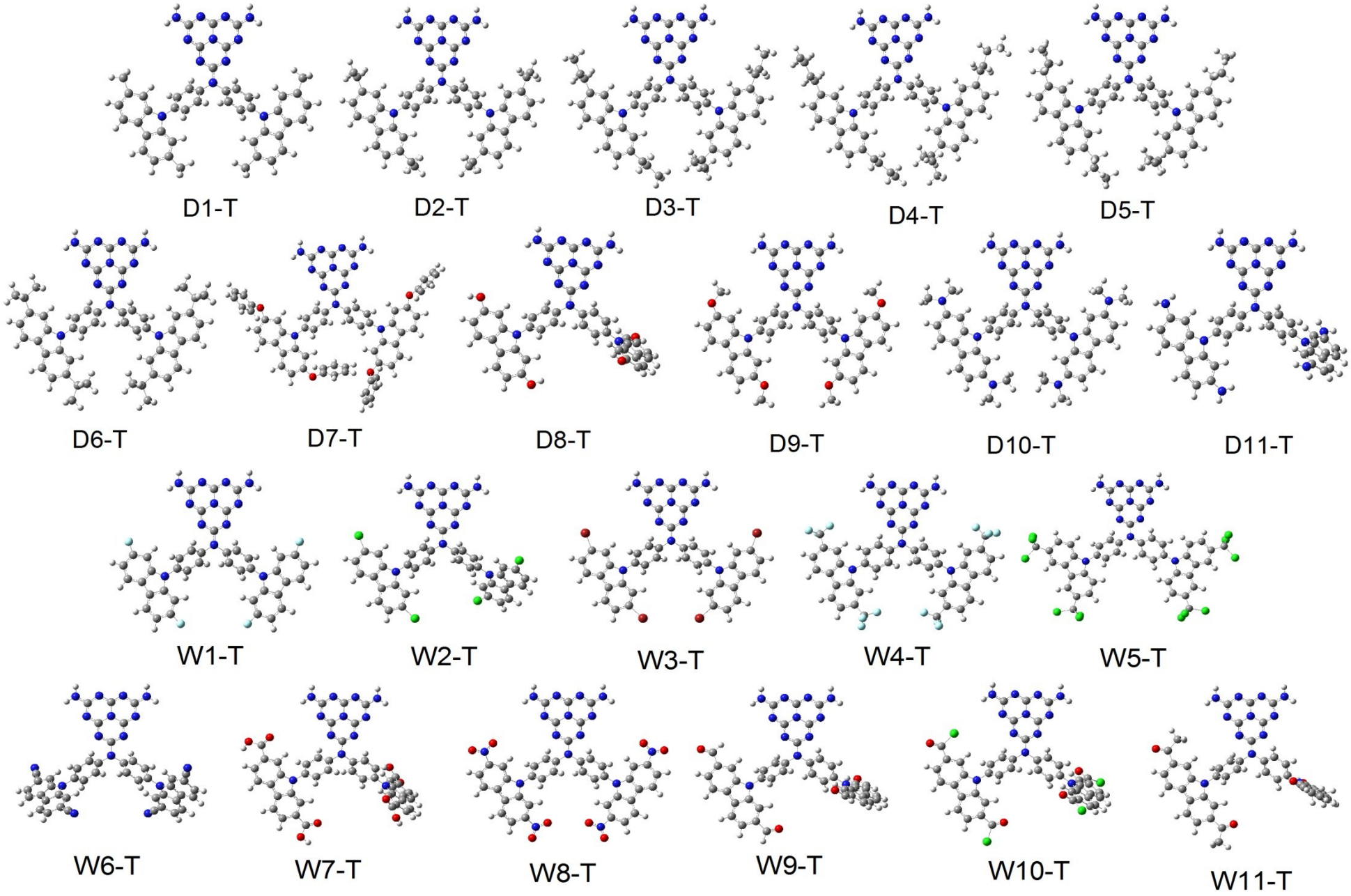

Figure SI6 The optimized structures of EDG and EWG substituted DTT-DPA-CBZ in exited states (T_1) at B3LYP/6-31G* level of theory

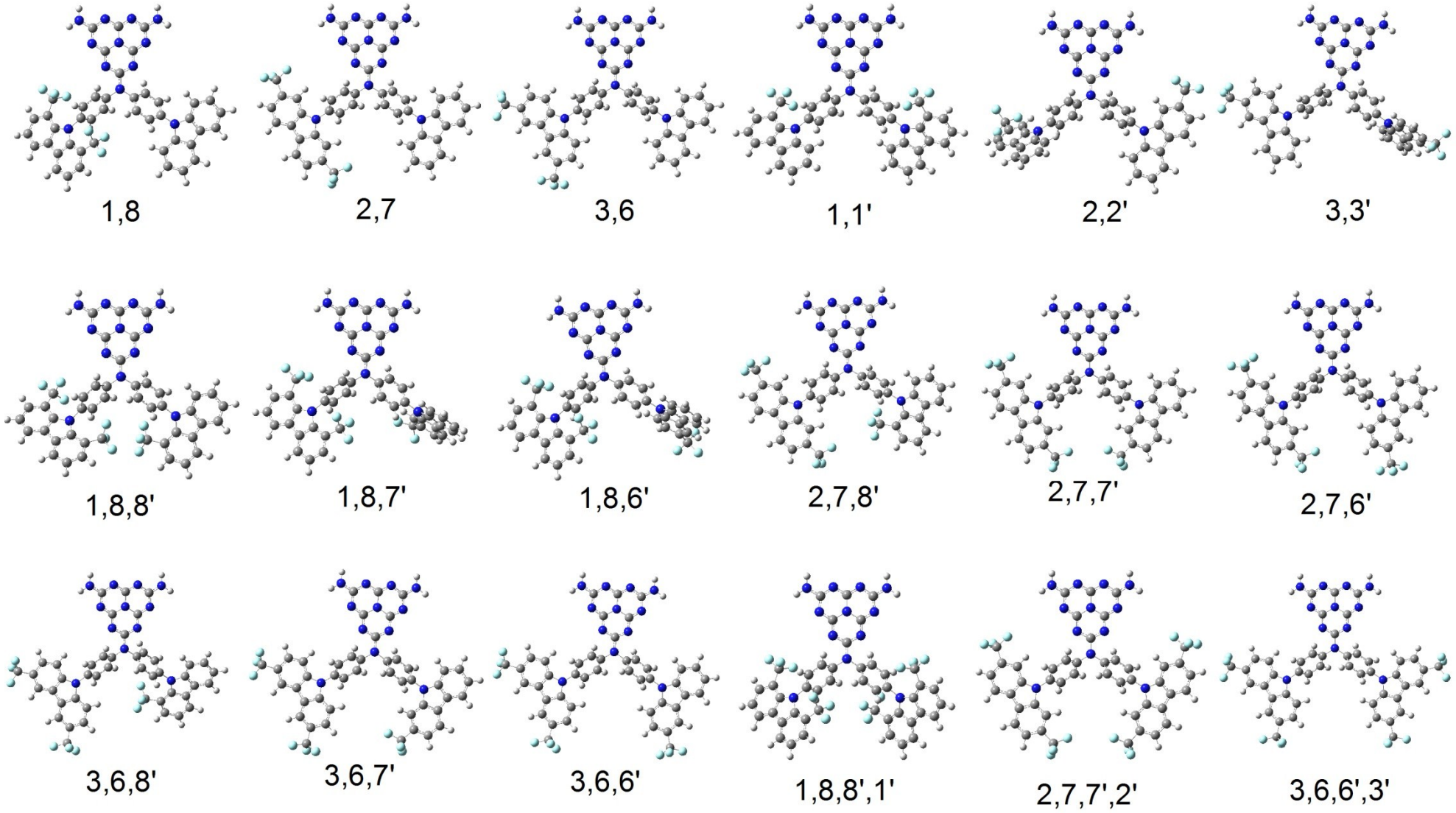

Figure SI7 The optimized structures for the trifluoromethyl substituted DTT-DPA-CBZ in ground states (S_0) at B3LYP/6-31G* level of theory

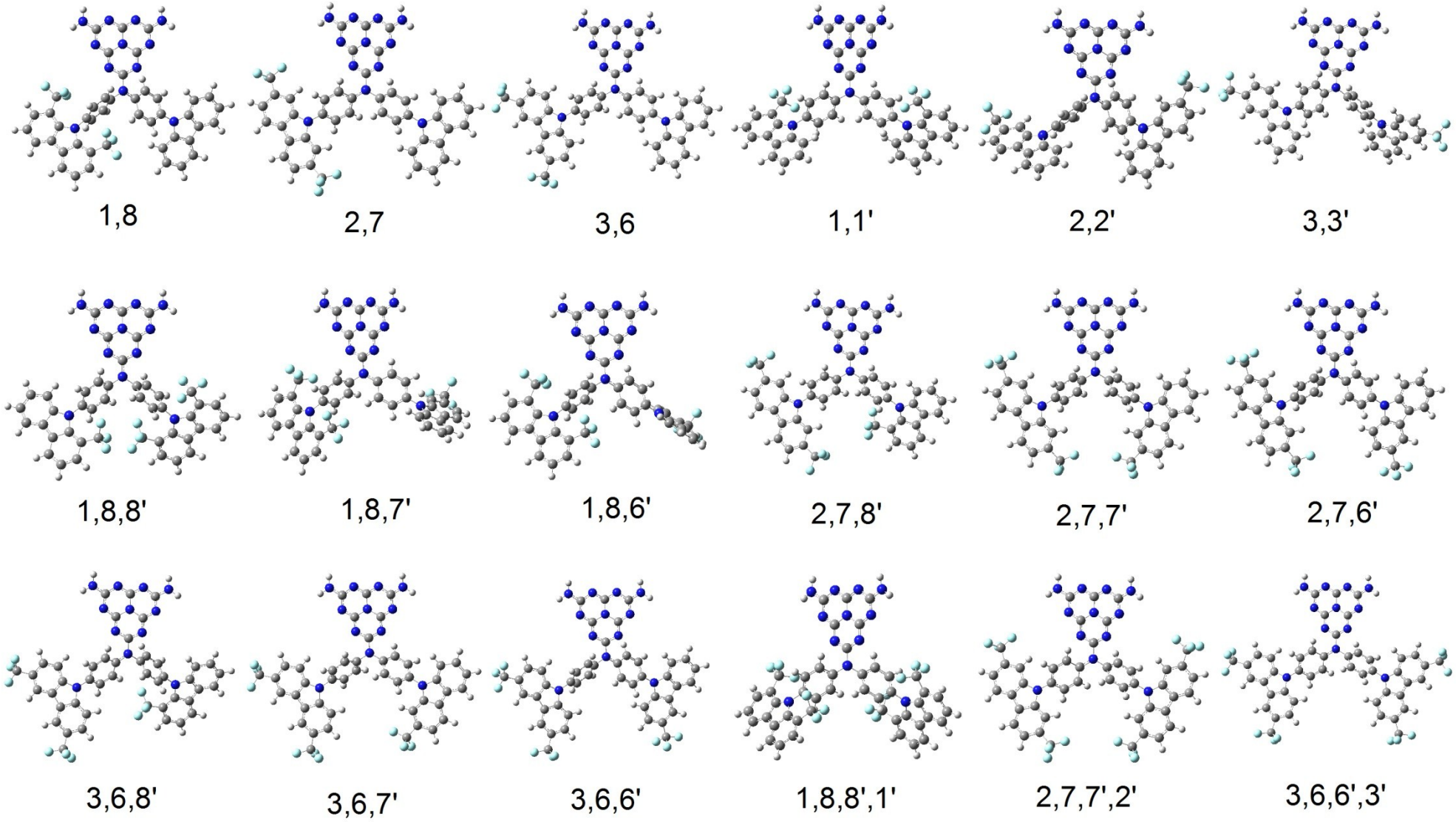

Figure SI8 The optimized structures for the trifluoromethyl substituted DTT-DPA-CBZ in exited states (T_1) at B3LYP/6-31G* level of theory

Table SI1 The triplet energies E_T, FMO energies (E_{HOMO} and E_{LUMO}), ΔE_{L-H}, IP , EA and reorganization energies of substituted DTT-DPA-CBZ (unit: eV)

Molecule	Substituent	E_T	ΔE_{L-H}	E_{HOMO}	E_{LUMO}	IP	EA	λ_h	λ_e
DTT-DPA-CBZ	H	2.92	3.78	-5.22	-1.44			0.23	0.41
D1	CH_3	3.45	3.73	-5.15	-1.42	6.09	-0.19	0.22	0.86
D2	C_2H_5	3.44	3.73	-5.16	-1.43	6.09	-0.21	0.22	0.85
D3	C_3H_7	3.45	3.74	-5.16	-1.42	6.08	-0.21	0.22	0.87
D4	C_4H_9	3.45	3.73	-5.15	-1.42	6.07	-0.21	0.21	0.88
D5	$C(CH_3)HC_2H_5$	3.45	3.73	-5.15	-1.42	6.06	-0.21	0.21	0.85
D6	$C(CH_3)_3$	3.43	3.71	-5.13	-1.42	6.04	-0.22	0.21	0.85
D7	OC_6H_5	3.32	3.72	-5.20	-1.48	6.04	-0.20	0.37	0.68
D8	OH	3.32	3.6	-5.03	-1.43	6.02	-0.38	0.19	0.45
D9	OCH_3	3.42	3.46	-4.92	-1.46	5.88	-0.22	0.22	0.89
D10	$N(CH_3)_2$	3.03	2.94	-4.27	-1.33	5.18	-0.08	0.31	0.95
D11	NH_2	3.12	3.15	-4.52	-1.37	5.51	-0.13	0.40	0.92

Table SI2 The triplet energies E_T, FMO energies (E_{HOMO} and E_{LUMO}), ΔE_{L-H}, IP , EA and reorganization energies of substituted DTT-DPA-CBZ (unit: eV)

Molecule	Substituent	E_T	ΔE_{L-H}	E_{HOMO}	E_{LUMO}	IP	EA	λ_h	λ_e
DTT-DPA-CBZ	H	2.92	3.78	-5.22	-1.44			0.23	0.41
W1	F	3.55	4.00	-5.53	-1.53	6.48	-0.33	0.31	0.83
W2	Cl	3.56	4.10	-5.68	-1.58	6.60	-0.48	0.32	0.72
W3	Br	3.57	4.08	-5.65	-1.57	6.57	-0.48	0.34	0.71
W4	CF_3	3.03	4.15	-5.76	-1.61	6.69	-0.68	0.37	0.38
W5	CCl_3	3.04	4.19	-5.99	-1.80	6.86	-0.78	0.35	0.60
W6	CN	3.02	3.94	-6.13	-2.19	7.04	-1.26	0.39	0.17
W7	COOH	2.95	3.75	-5.74	-1.99	6.67	-1.04	0.44	0.26
W8	NO_2	2.88	3.29	-6.13	-2.84	7.06	-1.88	0.50	0.25
W9	COH	2.66	3.45	-5.72	-2.27	6.65	-1.31	0.36	0.19
W10	COCl	2.56	3.31	-6.02	-2.71	6.93	-1.80	0.42	0.26
W11	$COCH_3$	2.59	3.58	-5.54	-1.96	6.45	-1.04	0.33	0.20

Table SI3 The calculated total energies and crystal cell parameters of 1,8,7' -substituted DTT-DPA-CBZ in different space groups

Space group	Total energy	Length a(Å)	Length b(Å)	Length c(Å)	Angle alpha((deg))	Angle beta(deg)	Angle gamma(deg)
C2	132.544051	23.07	6.98	26.52	90	76.69	90
C2/c	137.7817158	22.70	17.39	23.39	90	115.80	90
Cc	132.7195567	6.92	50.83	11.57	90	99.34	90
P1	135.4483765	15.55	10.63	8.93	72.36	79.43	47.84
$P\bar{1}$	129.0283163	12.55	11.57	27.10	70.63	69.23	32.92
$P2_1$	132.1734216	21.98	6.88	16.21	90	122.36	90
$P2_1/C$	133.7690718	13.25	11.49	26.78	90	83.21	90
Pbca	136.383321	22.71	19.62	17.99	90	90	90
Pbcn	138.1975572	8.63	19.18	51.69	90	90	90
$Pna2_1$	134.1406131	27.06	22.13	6.97	90	90	90