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

Electronic Supporting Information

for

The role of excited-state character, structural relaxation, and symmetry breaking in enabling delayed fluorescence activity in push-pull chromophores

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Table S1 - Relative electronic + zero point vibrational energies of the C_i and C_2 symmetries of BDT and AQ calculated at the ωB97X-V/def2-SVP level of theory.

Molecule	Rel.energy (eV)	Molecule	Rel.energy (eV)
AQ (C_i)	0.028	BDT (C_i)	0
AQ (C_2)	0	BDT (C_2)	0.001

Table S2 - Vertical excited state energies, oscillator strengths and state characters for Cz-BDT calculated at the ri-ADC(2)/def2-TZVP level of theory

State	Energy (eV)	f	O→BDT	BDT	Ph→BDT	Cz→BDT	Ph/Cz
T_1	2.64	0.00	0.02	0.61	0.18	0.07	0.08
T_2	2.84	0.00	0.29	0.35	0.12	0.07	0.10
T_3	2.88	0.00	0.48	0.28	0.06	0.04	0.06
T_4	3.01	0.00	0.69	0.20	0.01	0.01	0.03
S_1	3.06	0.00	0.01	0.44	0.24	0.24	0.05
S_2	3.14	0.01	0.68	0.22	0.01	0.01	0.03
S_3	3.27	0.00	0.71	0.20	0.01	0.00	0.02
S_4	3.28	0.45	0.03	0.13	0.23	0.50	0.07
T_5	3.46	0.00	0.00	0.21	0.09	0.25	0.37
T_6	3.51	0.00	0.09	0.21	0.06	0.25	0.32

Table S3 - Vertical excited state energies, oscillator strengths and state characters for Cz-AQ calculated at the ri-ADC(2)/def2-TZVP level of theory

State	Energy (eV)	f	O→AQ	AQ	Ph→AQ	Cz→AQ	Ph/Cz
T_1	2.86	0.00	0.66	0.24	0.01	0.00	0.06
T_2	3.08	0.00	0.66	0.23	0.00	0.00	0.07
S_1	3.13	0.00	0.67	0.24	0.01	0.00	0.05
T_3	3.21	0.00	0.02	0.39	0.18	0.17	0.05
T_4	3.24	0.00	0.06	0.35	0.16	0.16	0.07
S_2	3.36	0.00	0.68	0.22	0.00	0.00	0.06
S_3	3.52	0.00	0.01	0.13	0.21	0.53	0.04
S_4	3.55	0.47	0.01	0.07	0.18	0.57	0.04
T_5	3.69	0.00	0.06	0.19	0.02	0.12	0.13
T_6	3.70	0.00	0.00	0.07	0.01	0.03	0.09

Table S4 - Vertical excited state energies, oscillator strengths, exciton sizes, and state characters for Cz-BDT evaluated with TDDFT/TDA using the functional specified and the def2-SV(P) basis set

Functional	State	Energy (eV)	f	d_{exc}	O→BDT	BDT	Ph→BDT	Cz→BDT	Ph/Cz
PBE	T_1	1.22	0.00	10.66	0.00	0.06	0.10	0.79	0.04
	T_2	1.25	0.00	10.89	0.01	0.02	0.09	0.84	0.04
	S_1	1.29	0.07	11.09	0.00	0.01	0.08	0.86	0.04
	S_2	1.29	0.00	11.05	0.00	0.02	0.09	0.85	0.04
	T_3	1.66	0.00	11.73	0.00	0.00	0.00	0.96	0.04
	T_4	1.66	0.00	11.73	0.00	0.00	0.00	0.96	0.04
	S_3	1.66	0.00	11.74	0.00	0.00	0.00	0.96	0.04
	S_4	1.66	0.00	11.74	0.00	0.00	0.00	0.96	0.04
	T_5	2.00	0.00	6.29	0.02	0.58	0.23	0.12	0.05
	S_5	2.36	0.00	7.09	0.01	0.48	0.31	0.13	0.07
PBE0	T_1	2.06	0.00	7.10	0.02	0.46	0.19	0.28	0.06
	T_2	2.23	0.00	8.72	0.06	0.20	0.16	0.51	0.07
	S_1	2.33	0.00	10.14	0.00	0.10	0.14	0.71	0.05
	S_2	2.37	0.13	10.61	0.00	0.03	0.11	0.80	0.05
	T_3	2.60	0.00	9.30	0.01	0.29	0.06	0.59	0.05
	T_4	2.61	0.00	3.60	0.70	0.26	0.00	0.01	0.02
	T_5	2.70	0.00	7.65	0.13	0.37	0.07	0.35	0.07
	S_3	2.81	0.00	11.56	0.00	0.00	0.00	0.95	0.05
	S_4	2.81	0.00	11.56	0.00	0.00	0.00	0.95	0.05
	S_5	2.99	0.00	6.65	0.01	0.59	0.18	0.19	0.03
ωPBEh	T_1	2.22	0.00	4.83	0.02	0.69	0.17	0.06	0.06
	T_2	2.48	0.00	4.94	0.17	0.48	0.16	0.09	0.10
	T_3	2.59	0.00	3.39	0.70	0.27	0.00	0.00	0.02
	T_4	2.76	0.00	3.29	0.76	0.22	0.00	0.00	0.02
	S_1	2.80	0.00	6.89	0.01	0.49	0.22	0.24	0.04
	S_2	3.01	0.26	7.31	0.29	0.18	0.13	0.34	0.07
	S_3	3.06	0.17	6.51	0.42	0.20	0.07	0.26	0.06
	T_5	3.14	0.00	6.35	0.03	0.43	0.05	0.26	0.23
	S_4	3.36	0.00	8.69	0.00	0.28	0.06	0.55	0.11
	S_5	3.66	0.00	10.95	0.00	0.00	0.00	0.89	0.11
CAM-B3LYP	T_1	2.42	0.00	4.12	0.02	0.75	0.13	0.03	0.07
	T_2	2.64	0.00	3.93	0.16	0.57	0.12	0.03	0.11
	T_3	2.90	0.00	3.10	0.72	0.27	0.00	0.00	0.01
	T_4	3.08	0.00	3.03	0.76	0.22	0.00	0.00	0.01
	S_1	3.20	0.00	5.56	0.01	0.66	0.19	0.11	0.04
	S_2	3.38	0.01	3.29	0.70	0.28	0.01	0.00	0.02
	T_5	3.39	0.00	3.64	0.06	0.65	0.03	0.02	0.24
	S_3	3.57	0.00	3.15	0.76	0.23	0.00	0.00	0.02
	S_4	3.60	0.80	8.07	0.02	0.20	0.20	0.43	0.14
	S_5	3.94	0.00	9.05	0.00	0.17	0.05	0.62	0.17
ωB97X-V	T_1	2.63	0.00	3.66	0.02	0.79	0.10	0.01	0.08
	T_2	2.81	0.00	3.46	0.17	0.62	0.09	0.01	0.11
	T_3	3.07	0.00	2.96	0.72	0.27	0.00	0.00	0.01
	T_4	3.24	0.00	2.89	0.76	0.22	0.00	0.00	0.01
	S_1	3.55	0.00	3.06	0.70	0.28	0.00	0.00	0.01
	S_2	3.57	0.00	4.35	0.01	0.79	0.14	0.03	0.04
	T_5	3.59	0.00	3.32	0.05	0.61	0.04	0.01	0.29
	S_3	3.73	0.00	2.98	0.76	0.23	0.00	0.00	0.01
	S_4	4.16	1.83	5.11	0.03	0.43	0.20	0.10	0.24
	S_5	4.66	0.00	5.40	0.00	0.09	0.06	0.17	0.69

Table S5 - Vertical excited state energies, oscillator strengths, exciton sizes, and state characters for Cz-AQ evaluated with TDDFT/TDA using the functional specified and the def2-SV(P) basis set

Functional	State	Energy (eV)	f	d_{exc}	O→AQ	AQ	Ph→AQ	Cz→AQ	Ph/Cz
PBE	T_1	1.35	0.00	11.06	0.00	0.02	0.09	0.84	0.05
	T_2	1.36	0.00	11.11	0.00	0.01	0.09	0.85	0.05
	S_1	1.38	0.09	11.23	0.00	0.01	0.08	0.86	0.05
	S_2	1.40	0.00	11.24	0.00	0.01	0.08	0.86	0.04
	T_3	1.77	0.00	11.87	0.00	0.00	0.00	0.95	0.05
	T_4	1.77	0.00	11.87	0.00	0.00	0.00	0.95	0.05
	S_3	1.77	0.00	11.87	0.00	0.00	0.00	0.95	0.05
	S_4	1.77	0.00	11.87	0.00	0.00	0.00	0.95	0.05
	T_5	2.03	0.00	3.90	0.68	0.27	0.01	0.00	0.04
	S_5	2.35	0.00	4.15	0.66	0.28	0.01	0.00	0.05
PBE0	T_1	2.47	0.00	9.66	0.01	0.13	0.15	0.62	0.08
	T_2	2.50	0.00	9.89	0.03	0.08	0.14	0.67	0.08
	S_1	2.57	0.15	10.80	0.00	0.02	0.11	0.81	0.06
	S_2	2.57	0.00	10.77	0.00	0.03	0.11	0.80	0.06
	T_3	2.63	0.00	3.66	0.68	0.27	0.00	0.02	0.02
	T_4	3.00	0.00	11.66	0.00	0.00	0.00	0.94	0.06
	T_5	3.00	0.00	11.66	0.00	0.00	0.00	0.94	0.06
	S_3	3.00	0.00	11.69	0.00	0.00	0.00	0.94	0.06
	S_4	3.00	0.00	11.69	0.00	0.00	0.00	0.94	0.06
	S_5	3.09	0.00	3.55	0.68	0.29	0.01	0.00	0.03
ωPBEh	T_1	2.60	0.00	3.30	0.69	0.28	0.00	0.00	0.02
	T_2	2.82	0.00	5.81	0.03	0.50	0.19	0.15	0.12
	T_3	2.89	0.00	3.20	0.74	0.24	0.00	0.00	0.02
	T_4	2.90	0.00	5.82	0.12	0.40	0.17	0.16	0.15
	S_1	3.06	0.01	3.64	0.67	0.29	0.01	0.01	0.02
	S_2	3.22	0.00	9.16	0.01	0.14	0.20	0.57	0.09
	S_3	3.25	0.39	9.45	0.02	0.07	0.17	0.63	0.12
	T_5	3.34	0.00	4.01	0.11	0.83	0.01	0.03	0.03
	S_4	3.37	0.00	3.39	0.74	0.23	0.00	0.00	0.02
	S_5	3.80	0.00	6.60	0.01	0.54	0.14	0.21	0.11
CAM-B3LYP	T_1	2.93	0.00	3.02	0.71	0.28	0.00	0.00	0.01
	T_2	3.08	0.00	4.34	0.03	0.64	0.13	0.04	0.16
	T_3	3.10	0.00	3.97	0.16	0.55	0.10	0.03	0.15
	T_4	3.17	0.00	2.90	0.75	0.23	0.00	0.00	0.01
	S_1	3.41	0.00	3.16	0.69	0.29	0.00	0.00	0.01
	T_5	3.57	0.00	3.48	0.13	0.82	0.01	0.01	0.03
	S_2	3.68	0.00	3.05	0.74	0.24	0.00	0.00	0.01
	S_3	3.81	0.00	7.88	0.01	0.30	0.20	0.37	0.11
	S_4	3.87	0.76	8.65	0.01	0.13	0.18	0.50	0.18
	S_5	4.30	0.00	7.22	0.00	0.48	0.06	0.32	0.14
ωB97X-V	T_1	3.08	0.00	2.87	0.71	0.28	0.00	0.00	0.01
	T_2	3.29	0.00	3.35	0.17	0.61	0.07	0.01	0.14
	T_3	3.30	0.00	3.54	0.09	0.65	0.09	0.01	0.16
	T_4	3.32	0.00	2.84	0.69	0.28	0.01	0.00	0.03
	S_1	3.56	0.00	2.97	0.70	0.29	0.00	0.00	0.01
	T_5	3.67	0.00	3.06	0.00	0.00	0.00	0.00	1.00
	S_2	3.81	0.00	2.84	0.75	0.24	0.00	0.00	0.01
	S_3	4.34	0.00	4.85	0.01	0.66	0.16	0.06	0.10
	S_4	4.48	1.67	5.10	0.01	0.46	0.16	0.10	0.26
	S_5	4.71	0.14	3.58	0.00	0.07	0.01	0.00	0.92

Table S6 - Optimal (IP-EA) tuning of the range separation parameter, ω, using the ωPBEh functional with the def2-SV(P) basis set and the S_0 geometries in vacuo for Cz-BDT and Cz-AQ, EA and IP are the electron affinity and ionisation potential. All energies are given in Hartree atomic units. ϵ_{HOMO} and ϵ_{LUMO} refer to the singlet species

Molecule	Omega (Bohr^{-1})	$E_{Singlet}$	E_{Cation}	E_{Anion}	EA	IP	ϵ_{HOMO}	ϵ_{LUMO}
Cz-BDT	0.001	-2820.573	-2820.328	-2820.648	-0.075	0.245	-0.214	-0.124
	0.025	-2820.577	-2820.331	-2820.652	-0.075	0.246	-0.224	-0.113
	0.050	-2820.595	-2820.345	-2820.670	-0.075	0.250	-0.235	-0.103
	0.075	-2820.629	-2820.373	-2820.704	-0.075	0.256	-0.245	-0.094
	0.100	-2820.676	-2820.415	-2820.750	-0.074	0.261	-0.254	-0.086
	0.125	-2820.731	-2820.465	-2820.805	-0.074	0.266	-0.262	-0.079
	0.150	-2820.791	-2820.521	-2820.865	-0.074	0.270	-0.269	-0.074
	0.175	-2820.854	-2820.580	-2820.928	-0.074	0.274	-0.275	-0.069
	0.200	-2820.917	-2820.639	-2820.991	-0.074	0.278	-0.281	-0.066
	0.225	-2820.979	-2820.697	-2821.053	-0.074	0.281	-0.286	-0.062
	0.250	-2821.037	-2820.753	-2821.112	-0.074	0.284	-0.290	-0.060
Cz-AQ	0.001	-2179.274	-2179.030	-2179.341	-0.067	0.244	-0.212	-0.116
	0.025	-2179.278	-2179.033	-2179.345	-0.067	0.245	-0.223	-0.105
	0.050	-2179.297	-2179.047	-2179.364	-0.067	0.250	-0.234	-0.095
	0.075	-2179.332	-2179.077	-2179.399	-0.067	0.255	-0.244	-0.085
	0.100	-2179.380	-2179.120	-2179.447	-0.066	0.260	-0.253	-0.077
	0.125	-2179.438	-2179.173	-2179.504	-0.065	0.265	-0.261	-0.070
	0.150	-2179.501	-2179.232	-2179.566	-0.065	0.269	-0.268	-0.065
	0.175	-2179.567	-2179.294	-2179.631	-0.064	0.273	-0.274	-0.060
	0.200	-2179.633	-2179.356	-2179.697	-0.064	0.277	-0.280	-0.055
	0.225	-2179.697	-2179.417	-2179.760	-0.063	0.280	-0.285	-0.052
	0.250	-2179.758	-2179.475	-2179.821	-0.063	0.283	-0.289	-0.049

Table S7 - Optimal (IP-EA) tuning of the range separation parameter, ω, using the ωPBEh functional with the def2-SV(P) basis set and the S_0 geometries in toluene for Cz-BDT and Cz-AQ EA and IP are the electron affinity and ionisation potential. All energies are given in Hartree atomic units. ϵ_{HOMO} and ϵ_{LUMO} refer to the singlet species

Molecule	Omega (Bohr^{-1})	$E_{Singlet}$	E_{Cation}	E_{Anion}	EA	IP	ϵ_{HOMO}	ϵ_{LUMO}
Cz-BDT	0.001	-2820.588	-2820.364	-2820.693	-0.106	0.224	-0.214	-0.124
	0.025	-2820.592	-2820.367	-2820.697	-0.106	0.225	-0.224	-0.114
	0.030	-2820.594	-2820.369	-2820.700	-0.106	0.226	-0.227	-0.111
	0.035	-2820.597	-2820.371	-2820.703	-0.106	0.226	-0.229	-0.109
	0.040	-2820.601	-2820.373	-2820.706	-0.106	0.227	-0.231	-0.107
	0.045	-2820.605	-2820.377	-2820.711	-0.106	0.228	-0.233	-0.105
	0.050	-2820.610	-2820.381	-2820.716	-0.106	0.229	-0.235	-0.103
	0.075	-2820.644	-2820.409	-2820.750	-0.106	0.235	-0.245	-0.094
	0.100	-2820.691	-2820.450	-2820.796	-0.106	0.240	-0.254	-0.086
	0.125	-2820.746	-2820.501	-2820.852	-0.106	0.245	-0.262	-0.080
	0.150	-2820.807	-2820.557	-2820.912	-0.106	0.250	-0.269	-0.074
	0.175	-2820.869	-2820.615	-2820.975	-0.106	0.254	-0.275	-0.069
	0.200	-2820.933	-2820.675	-2821.039	-0.106	0.257	-0.281	-0.066
	0.225	-2820.994	-2820.733	-2821.101	-0.107	0.261	-0.286	-0.063
	0.250	-2821.053	-2820.789	-2821.160	-0.107	0.264	-0.290	-0.060
Cz-AQ	0.001	-2179.289	-2179.066	-2179.386	-0.097	0.223	-0.213	-0.115
	0.025	-2179.293	-2179.068	-2179.390	-0.097	0.225	-0.224	-0.105
	0.030	-2179.296	-2179.070	-2179.393	-0.097	0.226	-0.226	-0.102
	0.035	-2179.299	-2179.072	-2179.396	-0.097	0.226	-0.228	-0.100
	0.040	-2179.302	-2179.075	-2179.400	-0.097	0.227	-0.231	-0.098
	0.045	-2179.307	-2179.079	-2179.404	-0.097	0.228	-0.233	-0.096
	0.050	-2179.312	-2179.083	-2179.409	-0.097	0.229	-0.235	-0.094
	0.075	-2179.347	-2179.113	-2179.444	-0.097	0.235	-0.245	-0.085
	0.100	-2179.396	-2179.156	-2179.492	-0.096	0.240	-0.254	-0.077
	0.125	-2179.454	-2179.209	-2179.550	-0.096	0.245	-0.262	-0.070
	0.150	-2179.517	-2179.268	-2179.613	-0.096	0.249	-0.269	-0.064
	0.175	-2179.583	-2179.330	-2179.678	-0.095	0.253	-0.275	-0.059
	0.200	-2179.649	-2179.392	-2179.744	-0.095	0.257	-0.281	-0.055
	0.225	-2179.713	-2179.453	-2179.807	-0.095	0.260	-0.286	-0.052
	0.250	-2179.774	-2179.511	-2179.868	-0.095	0.263	-0.290	-0.049

Table S8 - Adiabatic excited state energies, oscillator strengths, exciton sizes, and state characters for Cz-BDT evaluated at the ωPBEh/def2-SV(P) level of theory using the specified toluene solvent model and state geometry

Method	State	Energy (eV)	f	d_{exc}	O→BDT	BDT	Ph→BDT	Cz→BDT	Ph/Cz
LR-PCM	T_1	1.81	0.00	6.73	0.02	0.48	0.22	0.22	0.07
RKS/PCM(S_0)	T_2	2.03	0.00	8.22	0.06	0.23	0.20	0.43	0.08
	S_1	2.14	0.00	9.46	0.01	0.17	0.19	0.59	0.05
	S_2	2.21	0.23	10.30	0.00	0.04	0.14	0.75	0.06
	T_3	2.46	0.00	9.51	0.01	0.23	0.06	0.63	0.07
	T_4	2.50	0.00	3.83	0.69	0.25	0.01	0.02	0.03
	S_3	2.69	0.00	11.48	0.00	0.00	0.00	0.94	0.06
ptSS	T_1	1.75	0.00	6.73	0.02	0.48	0.22	0.22	0.07
RKS/PCM(S_0)	T_2	1.91	0.00	8.22	0.06	0.23	0.20	0.43	0.08
	S_1	1.94	0.17	10.37	0.00	0.04	0.14	0.76	0.06
	S_2	1.95	0.00	9.60	0.01	0.16	0.18	0.61	0.05
	T_3	2.27	0.00	9.51	0.01	0.23	0.06	0.63	0.07
	S_3	2.28	0.00	11.48	0.00	0.00	0.00	0.94	0.06
	S_4	2.28	0.00	11.48	0.00	0.00	0.00	0.94	0.06
LR-PCM	T_1	1.63	0.00	6.69	0.02	0.48	0.23	0.21	0.06
TD/LR-PCM(S_1)	T_2	1.89	0.00	8.18	0.08	0.22	0.21	0.42	0.07
	S_1	1.99	0.00	9.06	0.01	0.22	0.21	0.51	0.05
	S_2	2.09	0.28	10.20	0.01	0.05	0.16	0.72	0.06
	T_3	2.37	0.00	9.53	0.00	0.24	0.07	0.63	0.06
	T_4	2.42	0.00	3.63	0.74	0.23	0.00	0.00	0.03
	S_3	2.62	0.00	7.96	0.01	0.45	0.14	0.36	0.04
SS-PCM	T_1	1.53	0.00	7.48	0.02	0.39	0.23	0.30	0.06
TD/LR-PCM(S_1)	T_2	1.75	0.00	9.09	0.04	0.15	0.20	0.55	0.07
	S_1	1.83	0.00	9.65	0.01	0.15	0.18	0.61	0.05
	S_2	1.89	0.28	10.37	0.00	0.04	0.15	0.75	0.06
	T_3	2.22	0.00	9.09	0.00	0.31	0.08	0.55	0.06
	T_4	2.40	0.00	11.51	0.00	0.00	0.00	0.94	0.06
	S_3	2.41	0.00	11.53	0.00	0.00	0.00	0.94	0.06
LR-PCM	T_1	1.59	0.00	6.36	0.03	0.50	0.23	0.17	0.07
TD/LR-PCM(T_1)	T_2	1.89	0.00	7.56	0.09	0.27	0.22	0.33	0.09
	S_1	2.02	0.00	8.61	0.01	0.27	0.23	0.43	0.05
	S_2	2.16	0.37	9.99	0.01	0.07	0.19	0.67	0.07
	T_3	2.45	0.00	9.62	0.00	0.21	0.07	0.64	0.08
	T_4	2.49	0.00	3.84	0.72	0.23	0.00	0.01	0.04
	S_3	2.67	0.00	8.38	0.01	0.40	0.12	0.42	0.06
SS-PCM	T_1	1.34	0.00	6.65	0.03	0.47	0.23	0.20	0.07
TD/LR-PCM(T_1)	T_2	1.63	0.00	8.08	0.07	0.23	0.23	0.39	0.08
	S_1	1.75	0.00	8.91	0.01	0.23	0.22	0.48	0.06
	S_2	1.85	0.38	10.08	0.01	0.06	0.18	0.68	0.07
	T_3	2.16	0.00	9.52	0.00	0.23	0.07	0.62	0.07
	T_4	2.28	0.00	8.36	0.11	0.29	0.09	0.42	0.09
	S_3	2.39	0.00	11.50	0.00	0.00	0.00	0.93	0.07
SS-PCM	T_1	1.48	0.00	6.61	0.03	0.47	0.23	0.19	0.07
UKS/LR-PCM(T_1)	T_2	1.77	0.00	8.05	0.07	0.23	0.23	0.39	0.08
	S_1	1.89	0.00	8.87	0.01	0.24	0.22	0.47	0.06
	S_2	2.00	0.39	10.08	0.01	0.06	0.18	0.68	0.07
	T_3	2.30	0.00	9.55	0.00	0.22	0.07	0.63	0.07
	T_4	2.42	0.00	8.38	0.11	0.29	0.09	0.42	0.09
	S_3	2.54	0.00	11.50	0.00	0.00	0.00	0.93	0.07

Table S9 - Adiabatic excited state energies, oscillator strengths, exciton sizes, and state characters for Cz-AQ evaluated at the ωPBEh/def2-SV(P) level of theory using the specified toluene solvent model and state geometry

Method	State	Energy (eV)	f	d_{exc}	O→AQ	AQ	Ph→AQ	Cz→AQ	Ph/Cz
LR-PCM	T_1	2.30	0.00	9.01	0.01	0.19	0.20	0.51	0.09
RKS/PCM(S_0)	T_2	2.35	0.00	9.45	0.03	0.11	0.18	0.59	0.09
	S_1	2.44	0.00	10.40	0.00	0.05	0.15	0.73	0.06
	S_2	2.44	0.25	10.50	0.00	0.03	0.14	0.76	0.07
	T_3	2.54	0.00	3.64	0.69	0.27	0.00	0.01	0.03
	T_4	2.88	0.00	7.80	0.02	0.45	0.11	0.34	0.07
	S_3	2.93	0.00	11.62	0.00	0.00	0.00	0.94	0.06
ptSS	T_1	2.12	0.00	9.01	0.01	0.19	0.20	0.51	0.09
RKS/PCM(S_0)	T_2	2.13	0.00	9.45	0.03	0.11	0.18	0.59	0.09
	S_1	2.14	0.18	10.56	0.00	0.03	0.14	0.76	0.06
	S_2	2.15	0.00	10.48	0.00	0.05	0.15	0.74	0.06
	S_3	2.50	0.00	11.62	0.00	0.00	0.00	0.94	0.06
	S_4	2.50	0.00	11.62	0.00	0.00	0.00	0.94	0.06
	T_3	2.53	0.00	3.64	0.69	0.27	0.00	0.01	0.03
LR-PCM	T_1	2.17	0.00	9.45	0.02	0.15	0.19	0.58	0.07
TD/LR-PCM(S_1)	T_2	2.28	0.00	9.68	0.03	0.12	0.16	0.63	0.07
	S_1	2.28	0.11	10.52	0.00	0.04	0.14	0.76	0.05
	S_2	2.37	0.10	10.64	0.00	0.03	0.12	0.79	0.06
	T_3	2.49	0.00	3.64	0.72	0.24	0.00	0.01	0.03
	T_4	2.73	0.00	3.44	0.78	0.19	0.00	0.00	0.03
	S_3	2.82	0.00	11.64	0.00	0.00	0.00	0.94	0.06
SS-PCM	T_1	1.95	0.00	10.46	0.01	0.05	0.14	0.75	0.06
TD/LR-PCM(S_1)	S_1	2.02	0.11	10.84	0.00	0.02	0.11	0.81	0.05
	T_2	2.54	0.00	9.85	0.01	0.11	0.16	0.66	0.07
	T_3	2.58	0.00	11.71	0.00	0.00	0.00	0.95	0.05
	S_2	2.58	0.00	11.72	0.00	0.00	0.00	0.95	0.05
	S_3	2.62	0.10	10.67	0.00	0.03	0.11	0.80	0.06
	T_4	2.89	0.00	5.54	0.37	0.36	0.14	0.09	0.05
LR-PCM	T_1	2.09	0.00	7.65	0.04	0.26	0.26	0.32	0.12
TD/LR-PCM(T_1)	S_1	2.39	0.31	9.53	0.01	0.11	0.23	0.58	0.08
	T_2	2.39	0.00	9.85	0.02	0.12	0.17	0.61	0.08
	S_2	2.47	0.11	10.84	0.00	0.03	0.13	0.77	0.07
	T_3	2.58	0.00	3.72	0.71	0.24	0.00	0.01	0.04
	T_4	2.88	0.00	8.55	0.03	0.33	0.09	0.45	0.09
	S_3	2.93	0.00	11.87	0.00	0.00	0.00	0.93	0.07
SS-PCM	T_1	1.91	0.00	8.48	0.03	0.19	0.25	0.43	0.10
TD/LR-PCM(T_1)	S_1	2.16	0.30	9.89	0.01	0.08	0.21	0.64	0.07
	T_2	2.41	0.00	9.94	0.02	0.11	0.16	0.63	0.08
	S_2	2.50	0.09	10.81	0.00	0.03	0.12	0.77	0.07
	T_3	2.69	0.00	3.77	0.71	0.24	0.00	0.01	0.04
	T_4	2.74	0.00	11.43	0.00	0.00	0.00	0.91	0.09
	S_3	2.75	0.00	11.48	0.00	0.00	0.00	0.92	0.08
SS-PCM	T_1	1.99	0.00	8.77	0.02	0.20	0.23	0.46	0.09
UKS/LR-PCM(T_1)	T_2	2.06	0.00	9.36	0.03	0.12	0.21	0.55	0.09
	S_1	2.19	0.32	10.34	0.00	0.05	0.17	0.70	0.07
	S_2	2.20	0.09	10.25	0.01	0.07	0.17	0.68	0.07
	T_3	2.72	0.00	11.62	0.00	0.00	0.00	0.92	0.08
	S_3	2.73	0.00	11.65	0.00	0.00	0.00	0.93	0.07
	T_4	2.73	0.00	11.62	0.00	0.00	0.00	0.92	0.08

Table S10 - Adiabatic excited state energies, oscillator strengths, exciton sizes, and state characters for Cz-BDT-SO_2 evaluated at the ωPBEh/def2-SV(P) level of theory using the specified toluene solvent model and state geometry

Method	State	Energy (eV)	f	d_{exc}	O→Core	BDT-SO_2	Ph→Core	Cz→Core	Ph/Cz
ptSS	T_1	0.92	0.00	8.05	0.04	0.29	0.18	0.37	0.13
RKS/PCM(S_0)	T_2	1.01	0.00	9.08	0.02	0.14	0.18	0.52	0.14
	S_1	1.21	0.55	10.60	0.00	0.05	0.12	0.71	0.12
	T_3	1.26	0.00	11.46	0.00	0.00	0.00	0.87	0.13
	S_2	1.27	0.00	11.50	0.00	0.00	0.00	0.87	0.12
	S_3	1.27	0.00	11.50	0.00	0.00	0.00	0.87	0.12
	S_4	1.35	0.00	10.75	0.02	0.07	0.10	0.70	0.11
SS-PCM	T_1	0.75	0.00	11.20	0.00	0.00	0.02	0.88	0.10
TD/LR-PCM(S_1)	S_1	0.75	0.00	11.21	0.00	0.00	0.02	0.88	0.10
	T_2	1.25	0.00	11.63	0.00	0.00	0.00	0.90	0.10
	S_2	1.25	0.00	11.63	0.00	0.00	0.00	0.90	0.10
	T_3	1.41	0.00	9.67	0.03	0.12	0.13	0.62	0.10
	S_3	1.65	0.28	10.79	0.01	0.03	0.08	0.78	0.10
	T_4	1.81	0.00	5.86	0.05	0.53	0.23	0.09	0.10
SS-PCM	T_1	0.71	0.00	8.37	0.06	0.25	0.16	0.38	0.15
TD/LR-PCM(T_1)	T_2	0.84	0.00	9.49	0.02	0.12	0.16	0.54	0.16
	S_1	1.09	0.93	10.64	0.00	0.05	0.12	0.67	0.15
	S_2	1.25	0.00	10.70	0.03	0.08	0.09	0.65	0.15
	T_3	1.41	0.00	8.21	0.01	0.39	0.09	0.34	0.16
	T_4	1.47	0.00	11.57	0.00	0.00	0.00	0.84	0.16
	S_3	1.48	0.00	11.61	0.00	0.00	0.00	0.84	0.16

Table S11 - Adiabatic excited state energies, oscillator strengths, exciton sizes, and state characters for Cz-BDF evaluated at the ωPBEh/def2-SV(P) level of theory using the specified toluene solvent model and state geometry

Method	State	Energy (eV)	f	d_{exc}	O→BDF	BDF	Ph→BDF	Cz→BDF	Ph/Cz
ptSS	T_1	1.67	0.00	6.04	0.03	0.54	0.21	0.16	0.06
RKS/PCM(S_0)	T_2	1.91	0.00	7.73	0.08	0.26	0.20	0.39	0.07
	S_1	1.95	0.17	10.12	0.00	0.04	0.14	0.76	0.05
	S_2	1.96	0.00	9.02	0.01	0.20	0.19	0.56	0.04
	T_3	2.22	0.00	9.61	0.00	0.18	0.06	0.69	0.06
	S_3	2.30	0.00	11.23	0.00	0.00	0.00	0.95	0.05
	S_4	2.30	0.00	11.22	0.00	0.00	0.00	0.94	0.05
SS-PCM	T_1	1.46	0.00	6.73	0.03	0.46	0.23	0.24	0.05
TD/LR-PCM(S_1)	T_2	1.74	0.00	8.71	0.06	0.17	0.20	0.52	0.05
	S_1	1.83	0.00	9.15	0.01	0.18	0.19	0.58	0.04
	S_2	1.90	0.22	10.10	0.01	0.04	0.15	0.76	0.05
	T_3	2.19	0.00	9.23	0.00	0.25	0.07	0.62	0.05
	T_4	2.39	0.00	7.46	0.15	0.35	0.11	0.34	0.05
	S_3	2.42	0.00	11.26	0.00	0.00	0.00	0.95	0.04
SS-PCM	T_1	1.40	0.00	6.06	0.04	0.52	0.22	0.16	0.06
TD/LR-PCM(T_1)	T_2	1.77	0.00	7.78	0.08	0.24	0.23	0.38	0.07
	S_1	1.89	0.00	8.41	0.02	0.27	0.22	0.45	0.05
	S_2	2.01	0.32	9.88	0.01	0.06	0.18	0.70	0.06
	T_3	2.27	0.00	9.54	0.00	0.19	0.07	0.67	0.06
	T_4	2.42	0.00	8.25	0.12	0.28	0.08	0.45	0.07
	S_3	2.50	0.00	8.07	0.01	0.41	0.12	0.41	0.05

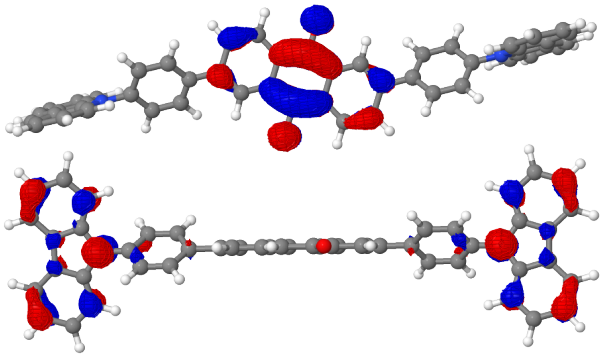
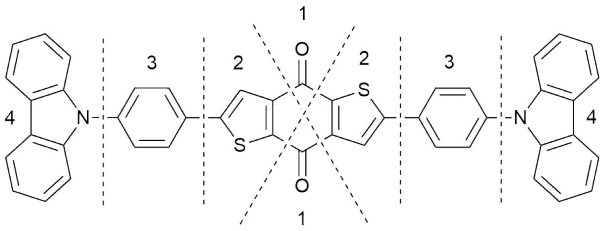


Figure S1 - The HOMO (bottom) and LUMO (top) frontier orbitals for AQ calculated at the ωB97X-V/def2-SVP level of theory



Character	Hole fragment	Electron fragment
O→Core	1	1
	1	2
Core	2	1
	2	2
Ph→Core	3	1
	3	2
Cz→Core	4	1
	4	2
Cz/Ph	3	3
	4	4
	3	4
	4	3
	1	3
	1	4
	2	3
	2	4

Figure S2 - Assignment of molecular fragments to deconstruct excited state character into local and charge transfer contributions. 'O→Core' character is analogous to local $n\pi^*$ character and 'Core' denotes local $\pi\pi^*$ character on the acceptor core. 'Ph→Core' and 'Cz→Core' are charge transfer contributions where the hole and electron are spatially separated.

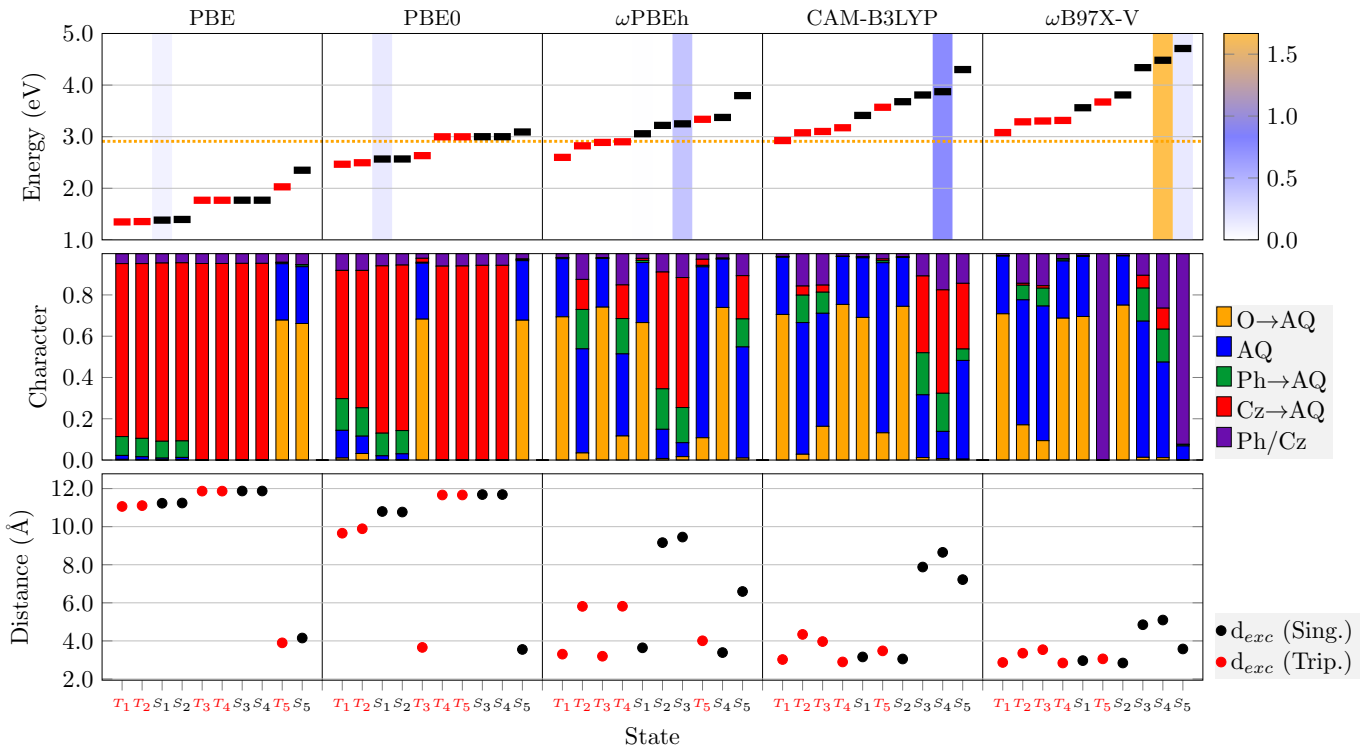


Figure S3 - Excited state energies and characters of the first five singlet and triplet states of AQ in C_2 symmetry computed at the functionals displayed (top)/def2-SV(P) level of theory in vacuum.

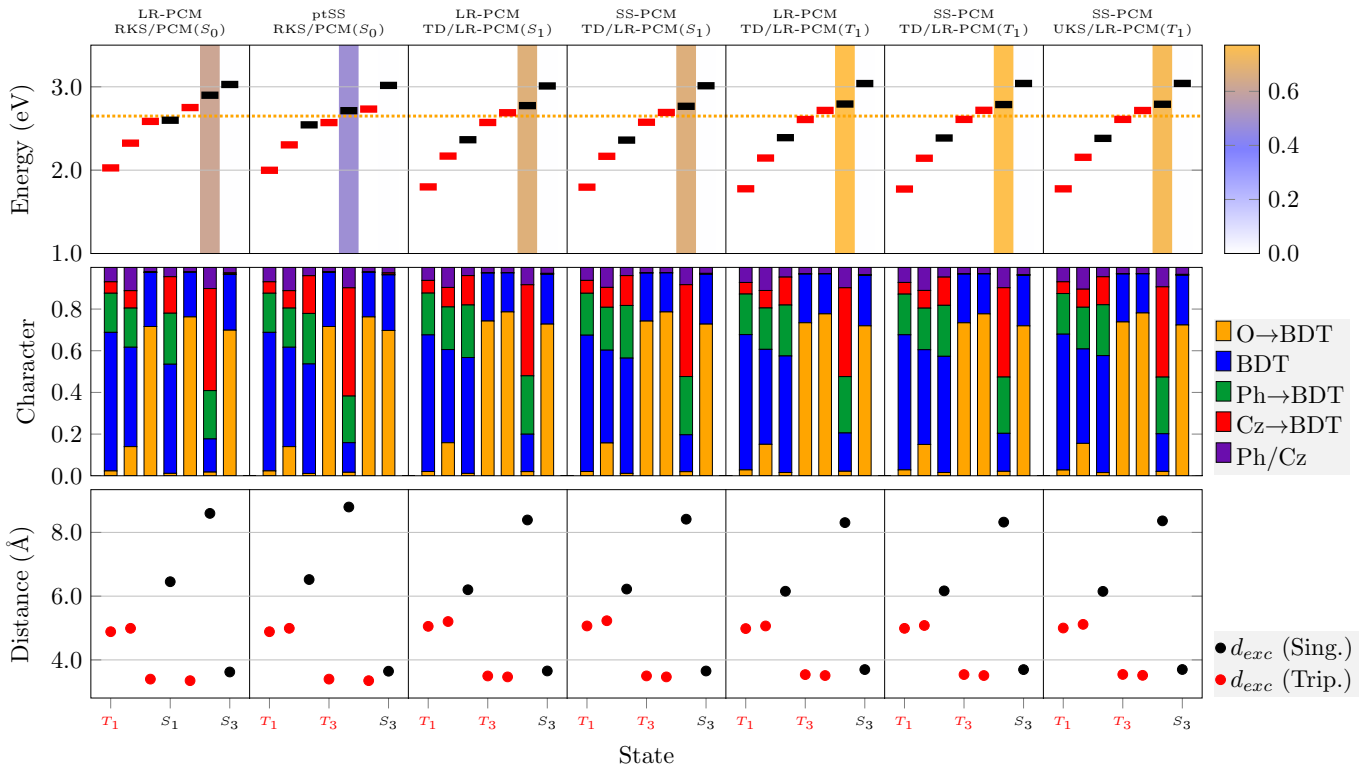


Figure S4 - Analysis of the lowest singlet and triplet states of Cz-BDT at the S_0, T_1 and S_1 minimum geometries: Adiabatic energies and oscillator strengths (top), excited-state characters (middle), and charge transfer measures (d_{exc}, d_{he}, bottom). The excited-state solvation model and method for computing the geometry are given in the top two lines, always in connection with the ωPBEh/def2-SVP level of theory with ω = 0.100 Bohr^{-1}.

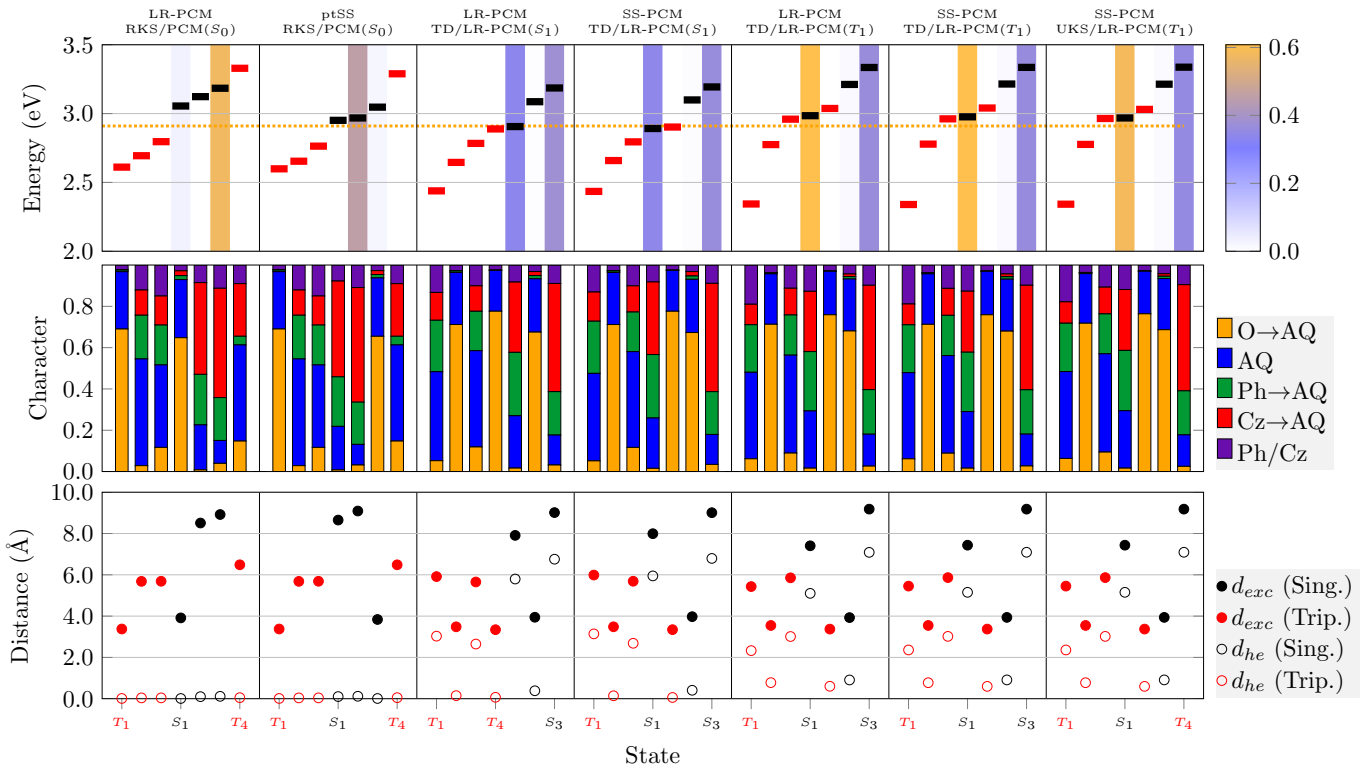


Figure S5 - Analysis of the lowest singlet and triplet states of Cz-AQ at the S_0, T_1 and S_1 minimum geometries: Adiabatic energies and oscillator strengths (top), excited-state characters (middle), and charge transfer measures (d_{exc}, d_{he}, bottom). The excited-state solvation model and method for computing the geometry are given in the top two lines, always in connection with the ωPBEh/def2-SVP level of theory with ω = 0.100 Bohr^{-1}.

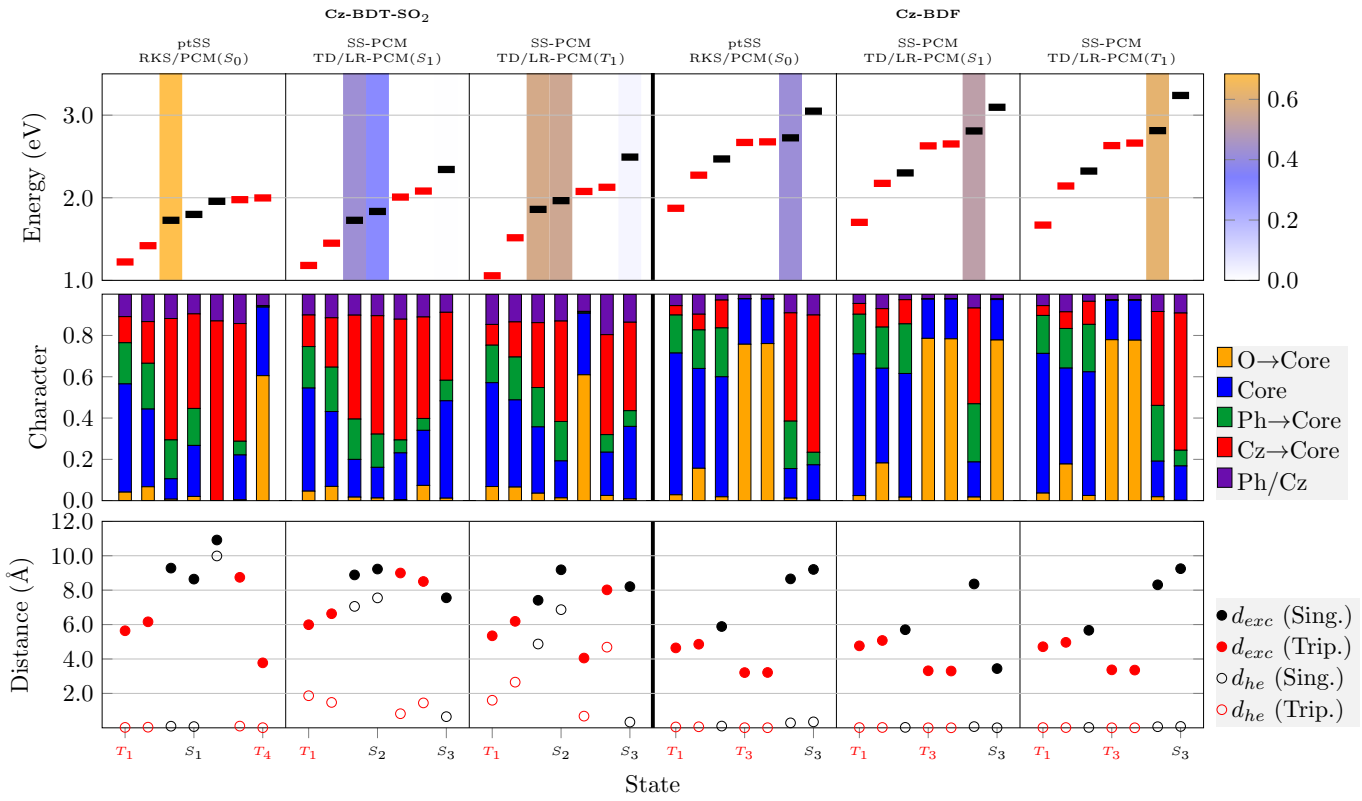


Figure S6 - Analysis of the lowest singlet and triplet states of Cz-BDT-SO2 (left) and Cz-BDF (right) at the S_0, T_1 and S_1 minimum geometries: Adiabatic energies and oscillator strengths (top), excited-state characters (middle), and charge transfer measures (d_{exc}, d_{he}, bottom), using the ωPBEh/def2-SVP level of theory with ω = 0.100 Bohr^{-1}.