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Efficient Phenanthroimidazole–Styryl–Triphenylamine Derivatives for Blue OLEDs : A Combined Experimental and Theoretical Study

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Table S1. Photophysical properties of TPA–BDIS in different solvents

Solvents	ε	n	f(ε,n)	ET(30)	λ_{ab} (nm)	ν_{ab} (cm^{-1})	λ_{flu} (nm)	ν_{flu} (cm^{-1})	ν_{ss} (cm^{-1})	ΔG (kcal/mol)	$\Delta(\Delta G_{hex}-\Delta G_{sol})$ (kcal/mol)	λ (kcal/mol)
Hexane	1.88	1.370	0.0012	32.4	366	27322.40	379	26385.22	937.1801	76.76	0.00	1.34
Dioxane	2.22	1.423	0.0214	36.0	367	27247.96	382	26178.01	1069.946	76.36	0.40	1.53
Toluene	2.38	1.494	0.0140	33.9	367	27247.96	383	26109.66	1138.296	76.26	0.50	1.63
Carbontetrachloride	2.24	1.460	0.0111	39.1	365	27397.26	384	26041.67	1355.594	76.38	0.38	1.94
Benzene	2.28	1.426	0.0027	34.3	368	27173.91	387	25839.79	1334.12	75.77	0.99	1.91
Triethylamine	3.13	1.432	0.0480	31.2	367	27247.96	389	25706.94	1541.016	75.69	1.07	2.20
Butylether	3.57	1.421	0.0960	33.4	365	27397.26	390	25641.03	1756.235	75.81	0.95	2.51
Ether	4.27	1.353	0.1670	34.4	365	27397.26	393	25445.29	1951.968	75.53	1.23	2.79
Isopropylether	3.88	1.368	0.1450		366	27322.40	394	25380.71	1941.694	75.33	1.43	2.78
Chloroform	4.81	1.446	0.1492	39.1	367	27247.96	395	25316.46	1931.501	75.13	1.63	2.76
Ethyl acetate	6.09	1.413	0.2000	38.1	362	27624.31	398	25125.63	2498.681	75.39	1.37	3.57
THF	7.52	1.405	0.2106	37.4	366	27322.40	421	23752.97	3569.435	73.00	3.76	5.10
Methylenechloride	7.98	1.427	0.0111	39.1	367	27247.96	423	23640.66	3607.294	72.73	4.03	5.16
Dimethylformamide	8.36	1.413	0.2766	39.8	365	27397.26	426	23474.18	3923.082	72.71	4.05	5.61
Dichloromethane	9.08	1.424	0.2173	40.7	369	27100.27	428	23364.49	3735.785	72.13	4.63	5.34
Acetone	21.01	1.359	0.2848	42.2	365	27397.26	431	23201.86	4195.404	72.32	4.44	6.00
Acetonitrile	37.50	1.344	0.3054	45.6	362	27624.31	434	23041.47	4582.835	72.41	4.35	6.55

Table S2. Photophysical properties of TPA–BPIS in different solvents

Solvents	ε	n	f(ε,n)	ET(30)	λ_{ab} (nm)	ν_{ab} (cm^{-1})	λ_{flu} (nm)	ν_{flu} (cm^{-1})	ν_{ss} (cm^{-1})	ΔG (kcal/mol)	$\Delta(\Delta G_{hex}-\Delta G_{sol})$ (kcal/mol)	λ (kcal/mol)
Hexane	1.88	1.370	0.0012	32.4	373	26809.65	414	24154.59	2655.062	72.84	0.04	3.79
Dioxane	2.22	1.423	0.0214	36.0	371	26954.18	416	24038.46	2915.716	72.88	0.00	4.17
Toluene	2.38	1.494	0.0140	33.9	374	26737.97	417	23980.82	2757.153	72.49	0.39	3.94
Carbontetrachloride	2.24	1.460	0.0111	39.1	372	26881.72	417	23980.82	2900.905	72.70	0.18	4.15
Benzene	2.28	1.426	0.0027	34.3	373	26809.65	419	23866.35	2943.303	72.43	0.45	4.21
Triethylamine	3.13	1.432	0.0480	31.2	373	26809.65	421	23752.97	3056.682	72.27	0.61	4.37
Butylether	3.57	1.421	0.0960	33.4	373	26809.65	423	23640.66	3168.99	72.11	0.77	4.53
Ether	4.27	1.353	0.1670	34.4	372	26881.72	426	23474.18	3407.542	71.97	0.91	4.87
Isopropylether	3.88	1.368	0.1450		373	26809.65	426	23474.18	3335.473	71.87	1.01	4.77
Chloroform	4.81	1.446	0.1492	39.1	374	26737.97	427	23419.20	3318.764	71.69	1.19	4.74
Ethyl acetate	6.09	1.413	0.2000	38.1	369	27100.27	429	23310.02	3790.248	72.05	0.83	5.42
THF	7.52	1.405	0.2106	37.4	374	26737.97	430	23255.81	3482.154	71.45	1.43	4.98
Methylenechloride	7.98	1.427	0.0111	39.1	374	26737.97	434	23041.47	3696.493	71.15	1.73	5.28
Dimethylformamide	8.36	1.413	0.2766	39.8	371	26954.18	438	22831.05	4123.128	71.16	1.72	5.89
Dichloromethane	9.08	1.424	0.2173	40.7	376	26595.74	439	22779.04	3816.701	70.57	2.31	5.46
Acetone	21.01	1.359	0.2848	42.2	377	26525.2	440	22727.27	3797.926	70.39	2.49	5.43
Acetonitrile	37.50	1.344	0.3054	45.6	369	27100.27	444	22522.52	4577.748	70.92	1.96	6.54

Table S3. Photophysical properties of Cz–BPIS in different solvents

Solvents	ε	n	f(ε,n)	ET(30)	λ_{ab} (nm)	ν_{ab} (cm^{-1})	λ_{flu} (nm)	ν_{flu} (cm^{-1})	ν_{ss} (cm^{-1})	ΔG (kcal/mol)	$\Delta(\Delta G_{hex}-\Delta G_{sol})$ (kcal/mol)	λ (kcal/mol)
Hexane	1.88	1.370	0.001	32.4	357	28011.20	404	24752.48	3258.729	75.41	0.00	4.66
Dioxane	2.22	1.423	0.021	36.0	358	27932.96	405	24691.36	3241.603	75.21	0.20	4.63
Toluene	2.38	1.494	0.014	33.9	356	28089.89	406	24630.54	3459.346	75.35	0.06	4.94
Carbontetrachloride	2.24	1.460	0.011	39.1	356	28089.89	406	24630.54	3459.346	75.35	0.06	4.94
Benzene	2.28	1.426	0.003	34.3	359	27855.15	407	24570.02	3285.129	74.93	0.48	4.70
Triethylamine	3.13	1.432	0.048	31.2	357	28011.20	409	24449.88	3561.327	74.98	0.43	5.09
Butylether	3.57	1.421	0.096	33.4	356	28089.89	410	24390.24	3699.644	75.01	0.40	5.29
Ether	4.27	1.353	0.167	34.4	356	28089.89	412	24271.84	3818.043	74.84	0.57	5.46
Isopropylether	3.88	1.368	0.145		356	28089.89	412	24271.84	3818.043	74.84	0.57	5.46
Chloroform	4.81	1.446	0.149	39.1	359	27855.15	413	24213.08	3642.078	74.42	0.99	5.21
Ethyl acetate	6.09	1.413	0.200	38.1	353	28328.61	415	24096.39	4232.226	74.93	0.48	6.05
THF	7.52	1.405	0.211	37.4	357	28011.20	417	23980.82	4030.389	74.31	1.10	5.76
Methylenechloride	7.98	1.427	0.011	39.1	358	27932.96	418	23923.44	4009.516	74.12	1.29	5.73
Dimethylformamide	8.36	1.413	0.277	39.8	354	28248.59	421	23752.97	4495.618	74.32	1.09	6.43
Dichloromethane	9.08	1.424	0.217	40.7	360	27777.78	422	23696.68	4081.095	73.57	1.84	5.83
Acetone	21.01	1.359	0.285	42.2	355	28169.01	426	23474.18	4694.836	73.81	1.60	6.71
Acetonitrile	37.50	1.344	0.305	45.6	353	28328.61	427	23419.2	4909.408	73.96	1.45	7.02

Table S4. Analysis of hole (H), electron (E), their overlap, dipolemoment (D) and charge density difference (D_{H-E}) of TPA-BDIS.

States	Integral of hole	Integral of electron	Integral of transition density	Integral overlap of H-E	Centeroid of hole (A˚)			Centeroid of electron (A˚)			D_{H-E} (A˚)	D (a.u.)
					X	Y	Z	X	Y	Z		
S1	0.4472	0.7093	0.0034	0.1420	8.6129	-1.7891	0.3327	7.7987	-0.9982	-0.1147	1.2201	1.3334
S2	0.4577	0.7205	0.0026	0.1635	8.6129	-1.7891	0.3327	8.1322	-2.3283	0.6208	0.7777	0.8658
S3	0.4325	0.6631	-0.0007	0.0998	8.6129	-1.7891	0.3327	7.4861	-1.5619	0.2339	1.1536	1.1842
S4	0.4469	0.6862	-0.0001	0.0871	8.6129	-1.7891	0.3327	7.8787	-2.3688	0.6387	0.9843	1.0539
S5	0.4591	0.7624	0.0027	0.0158	8.6129	-1.7891	0.3327	2.2346	-1.2372	0.1320	6.4189	7.4090
S6	0.4234	0.7057	0.0384	0.0996	8.2317	-1.7543	0.3072	6.9380	-1.1172	-0.0671	1.4899	0.8856
S7	0.4525	0.6242	-0.0028	0.0540	8.6129	-1.7891	0.3327	5.9075	-1.5935	0.1567	2.7182	2.7657
S8	0.4016	0.7115	-0.0730	0.0631	8.6129	-1.7891	0.3327	6.1889	-1.6230	0.1804	2.4343	1.4104
S9	0.4425	0.6794	-0.0038	0.0096	8.6129	-1.7891	0.3327	-1.2925	-1.1418	-0.1767	9.9396	10.5369
S10	0.4431	0.5286	-0.0045	0.0736	8.6129	-1.7891	0.3327	8.1509	-0.2232	-0.5226	1.8431	1.6922

Table S5. Analysis of hole (H), electron (E), their overlap, dipolemoment (D) and charge density difference (D_{H-E}) of TPA-BPIS

States	Integral of hole	Integral of electron	Integral of transition density	Integral overlap of H-E	Centeroid of hole (A°)			Centeroid of electron (A°			D_{H-E} (A°)	D (a.u.)
					X	Y	Z	X	Y	Z		
S1	0.8604	0.6702	0.0036	0.4249	-3.6960	-1.7061	0.1823	-3.4463	-1.5785	0.2043	0.2812	0.4068
S2	0.9026	0.6690	0.0012	0.5249	-5.5298	-2.0682	0.1874	-6.6843	-2.0224	0.3783	1.1710	1.7390
S3	0.9092	0.6863	0.0138	0.5273	-1.7058	-1.5927	0.1716	-2.3238	-1.5149	0.2860	0.6336	0.9553
S4	0.8129	0.6065	0.0042	0.3702	-3.6357	-1.8358	0.1709	-1.7380	-1.8401	0.0367	1.9024	2.5516
S5	0.7886	0.5696	0.0006	0.2541	6.4788	-0.7468	0.1458	5.8442	-0.7686	0.2063	0.6378	0.8186
S6	0.8581	0.6255	0.0001	0.3437	8.3308	-0.6598	0.1038	9.6999	-0.4626	0.2096	1.3872	1.9448
S7	0.9179	0.6261	0.0005	0.5228	1.8069	-0.9789	0.2395	1.5428	-1.0037	0.2869	0.2694	0.3931
S8	0.8300	0.5717	0.0002	0.3740	7.3250	-0.6942	0.1411	8.6124	-0.7174	0.0143	1.2938	1.7138
S9	0.8945	0.6132	0.0041	0.4420	8.5974	-0.6482	0.0958	9.1595	-0.6080	0.1182	0.5640	0.8035
S10	0.7962	0.5762	-0.0125	0.3807	2.1754	-1.1935	0.1409	1.8447	-1.2079	0.0199	0.3524	0.4570

Table S6. Analysis of hole (H), electron (E), their overlap, dipolemoment (D) and charge density difference (D_{H-E}) of Cz-BPIS.

States	Integral of hole	Integral of electron	Integral of transition density	Integral overlap of H-E	Centeroid of hole (A˚)			Centeroid of electron (A˚)			D_{H-E} (A˚)	D (a.u.)
					X	Y	Z	X	Y	Z		
S1	0.454	0.603	0.014	0.171	4.406	0.660	0.024	4.875	-0.695	0.307	1.462	1.461
S2	0.454	0.624	0.099	0.099	4.406	0.660	0.024	3.384	-1.485	-0.088	2.379	2.424
S3	0.439	0.556	0.627	0.096	4.406	0.660	0.024	4.464	-1.437	0.193	2.105	1.981
S4	0.470	0.725	-0.012	0.056	4.406	0.660	0.024	1.029	-1.816	-0.522	4.224	4.773
S5	0.428	0.591	-0.003	0.047	4.406	0.660	0.024	3.992	-3.301	-0.006	3.983	3.840
S6	0.475	0.703	-0.010	0.017	4.406	0.660	0.024	4.666	5.779	0.069	5.125	5.709
S7	0.484	0.724	0.012	0.008	4.406	0.660	0.024	4.750	5.855	0.067	5.206	5.984
S8	0.451	0.644	0.008	0.041	4.406	0.660	0.024	-0.173	-1.689	-0.618	5.188	5.266
S9	0.415	0.559	-0.005	0.056	4.406	0.660	0.024	3.504	-3.187	0.040	3.952	3.640
S10	0.475	0.713	0.005	0.005	4.406	0.660	0.024	-4.420	-0.886	-0.684	8.989	10.100

	TPA-BDIS			TPA-BDIS			Cz-BDIS		
Transition	**D (a.u.)**	**ΔE (eV)**	**Transition**	**D (a.u.)**	**ΔE (eV)**	**Transition**	**D (a.u.)**	**ΔE (eV)**	**Transition**
S3→S4	1.9459	0.30490	0.02828	0.8222	0.29430	0.00487	2.041	0.406	0.041
S3→S5	0.1280	1.17570	0.00047	0.0887	0.34780	0.00007	1.710	1.025	0.073
S3→S6	0.0932	1.87940	0.00039	0.4430	0.47890	0.00230	5.106	1.283	0.849
S3→S7	1.7098	1.90250	0.13626	0.1517	0.51950	0.00029	0.741	1.347	0.081
S3→S8	0.0838	2.06200	0.00035	0.2146	0.55850	0.00063	0.411	1.655	0.006
S3→S9	3.9061	2.35310	0.87959	0.4068	0.61740	0.00250	1.654	1.812	0.121
S3→S10	1.2163	2.57080	0.09318	2.8876	0.70260	0.14353	2.90	1.862	0.385
S4→S5	2.6124	0.87080	0.14559	0.1058	0.05350	0.00001	3.236	0.619	0.158
S4→S6	0.0885	1.52450	0.00029	0.7066	0.18460	0.00226	0.311	0.877	0.002
S4→S7	1.2172	1.59760	0.05799	0.1268	0.22520	0.00009	0.199	0.941	0.001
S4→S8	0.1264	1.75710	0.00069	0.1595	0.26420	0.00016	1.797	1.249	0.098
S4→S9	4.6383	2.04820	1.07954	0.0973	0.32310	0.00007	0.499	1.405	0.008
S4→S10	1.0582	2.26590	0.06216	1.9834	0.40830	0.03935	1.489	1.456	0.079
S2→S3	1.0193	0.09340	0.00658	1.6957	0.58510	0.01489	4.994	0.449	0.274
S2→S4	0.933	0.38770	0.01260	1.1516	0.89000	0.02151	1.466	0.855	0.045
S2→S5	0.4850	0.44120	0.00005	0.0666	1.76080	0.01015	3.705	1.474	0.496
S2→S6	0.0851	0.57230	0.00059	0.2057	2.41450	0.00043	1.922	1.732	0.156
S2→S7	1.4730	0.61290	0.00006	0.0621	2.48760	0.13223	0.234	1.796	0.002
S2→S8	0.1548	0.65190	0.00015	0.0985	2.64710	0.00155	1.800	2.104	0.167
S2→S9	0.7139	0.71080	0.00075	0.2071	2.93820	0.03669	9.487	2.261	4.986
S2→S10	0.9738	0.79600	0.00452	0.4814	3.15590	0.07332	1.971	2.311	0.220
S1→S2	1.6322	0.2491	0.00206	0.5803	0.11650	0.00760	4.026	0.594	0.235
S1→S3	0.2846	0.3425	0.23988	5.3468	0.70160	0.00139	3.539	1.043	0.320
S1→S4	0.7726	0.6368	0.15043	3.1051	1.00650	0.01472	1.312	1.449	0.061
S1→S5	0.9467	0.6903	0.00018	0.1046	1.87730	0.04123	4.030	1.068	0.823
S1→S6	0.0106	0.8214	0.00052	0.1612	2.53100	0.00001	2.943	2.326	0.493
S1→S7	1.1013	0.8620	0.00003	0.0386	2.60401	0.07739	0.164	2.390	0.001
S1→S8	0.0515	0.9010	0.00003	0.0346	2.76360	0.00018	3.663	2.698	0.887
S1→S9	1.6232	0.9599	0.00008	0.0567	3.05470	0.19719	3.299	2.855	0.761
S1→S10	1.7201	1.0451	0.17723	2.6309	3.27240	0.23720	1.250	2.855	0.111

Table S7. Transition dipole moment (D), oscillator strength (F) and energy (ΔE) difference between the transition states of TPA-BDIS, TPA-BPIS and Cz-BPIS.

Contd….

TPA-BDIS				TPA-BDIS			Cz-BDIS		
Transition	**D (a.u.)**	**ΔE (eV)**	**Transition**	**D (a.u.)**	**ΔE (eV)**	**Transition**	**D (a.u.)**	**ΔE (eV)**	**Transition**
S6→S7	1.3767	0.07310	0.00339	0.1265	0.04060	0.00002	1.392	0.064	0.003
S6→S8	2.0928	0.23260	0.02496	0.2276	0.07960	0.00010	3.521	0.372	0.113
S6→S9	1.7130	0.52370	0.03765	0.2482	0.13850	0.00021	0.768	0.528	0.007
S6→S10	0.1228	0.74140	0.00027	1.1587	0.22370	0.00736	0.167	0.579	0.001
S7→S8	0.4642	0.15950	0.00084	0.6040	0.03900	0.00035	0.224	0.308	0.0003
S7→S9	2.8372	0.45060	0.08887	0.1381	0.09790	0.00005	0.404	0.464	0.018
S7→S10	1.3537	0.66830	0.03000	0.0926	0.18310	0.00004	0.122	0.515	0.0001
S8→S9	0.6790	0.29110	0.00329	0.1279	0.05890	0.00002	2.284	0.156	0.020
S9→S10	1.2686	0.50880	0.02006	0.3442	0.14410	0.00042	2.475	0.207	0.311
S9→S10	1.2245	0.21770	0.00800	0.2328	0.08520	0.00011	3.153	0.508	0.123

Figure S1. MALDI–TOF mass spectra of BDIS, BPIS, TPA–BDIS, TPA–BPIS and Cz-BPIS.

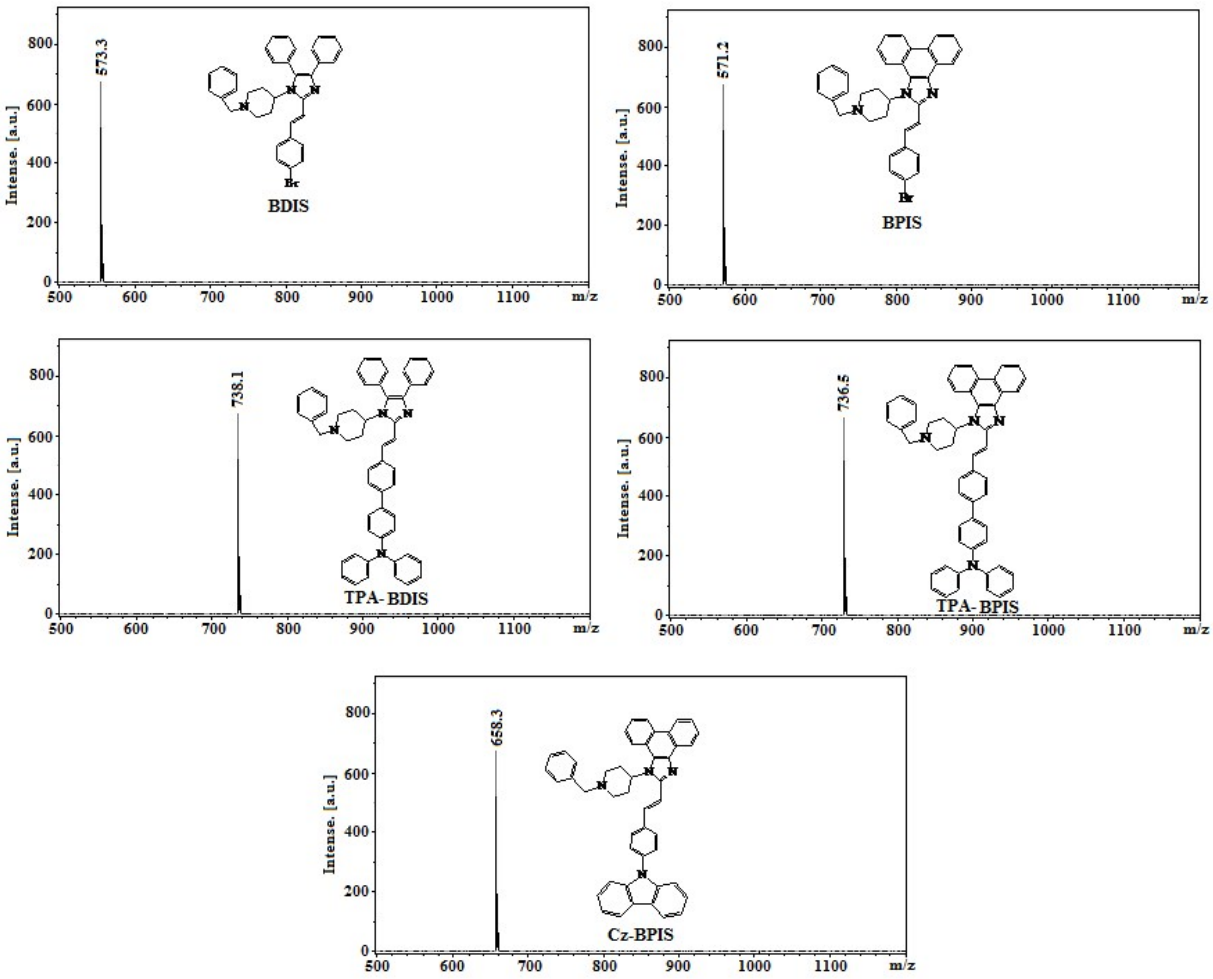

Figure S2. Normalized emission spectra of (a) TPA–BDIS, (b) TPA–BPIS and Cz–BPIS.

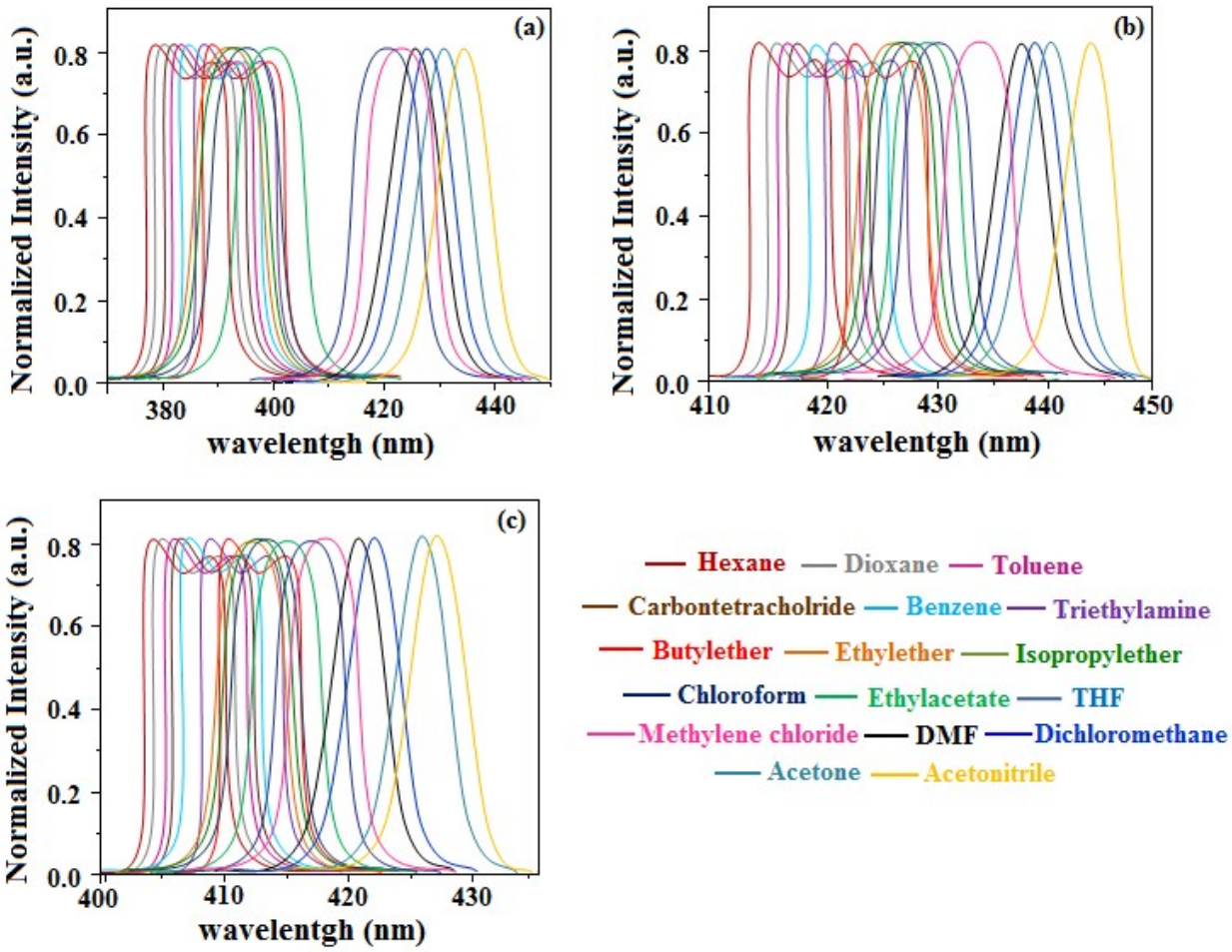

Figure S3. Normalized absorption spectra of (a) TPA–BDIS, (b) TPA–BPIS and Cz–BPIS.

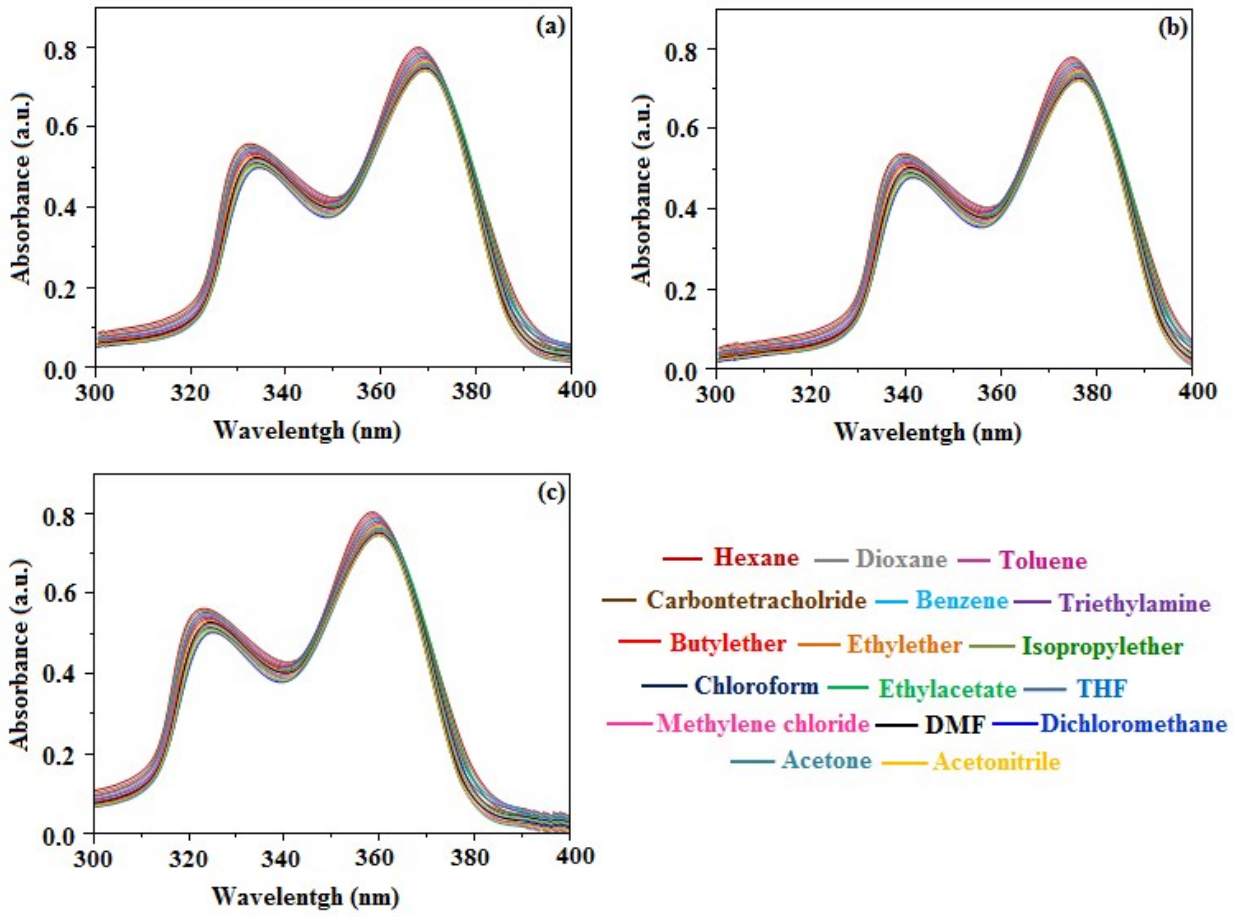

Figure S4. (a) Polt of $\Delta(\Delta G_{hex}-\Delta G_{sol})$ versus solvent polarity function f(ε, n) of TPA–BDIS, TPA–BPIS and Cz-BPIS; (b) Polt of λ (kcal/mol) depends of the solvent polarity function f(ε, n) of TPA–BDIS and TPA-BPIS and Cz-BPIS.

Estimation of free energy change of solvation (ΔG_{solv}) and reorganization energies (λ) in various solvents are displayed in Tables S1 & S2. Marcus shown that E (A) = $\Delta G_{solv} + \lambda_1$ and E (F) = $\Delta G_{solv} - \lambda_0$; E (A) + E (F) = $2\Delta G_{solv}$; E (A) - E (F) = 2 λ (under, $\lambda_0 \approx \lambda_1 \approx \lambda$), where E(A) and E(F) are absorption maxima and fluorescence maxima in cm^{-1}, respectively, ΔG_{solv} is difference in free energy of ground and excited states in a given solvent and λ is reorganization energy. The difference between ΔG_{hex} and ΔG_{sol} gives the free energy change required for hydrogen bond formation. The plot of $\Delta(\Delta G_{solv})$ against f(Ɛ,n) has been shown in Figure S4. The definite reorganization energies confirmed the interaction between low frequency motions such as reorientation of solvent cell with low and medium frequency nuclear motion of the solute.

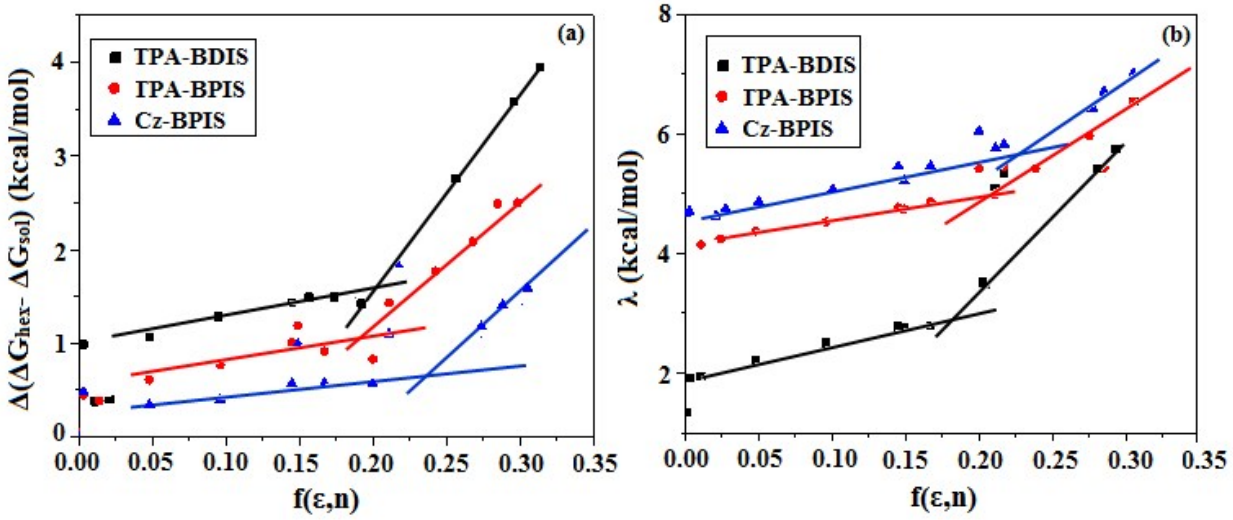

Figure S5. Natural transition orbital of TPA–BDIS for S_1-S_{10} transitions.

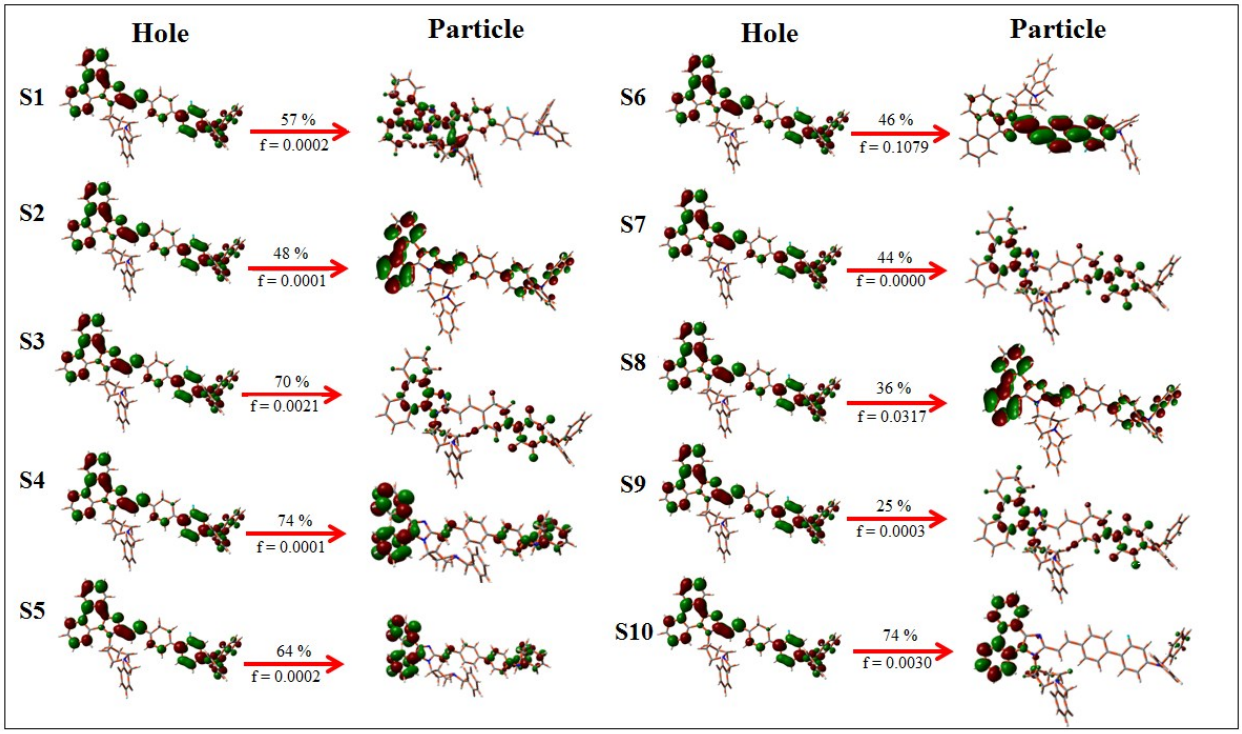

Figure S6. Natural transition orbital of TPA–BPIS for S_1-S_{10} transitions.

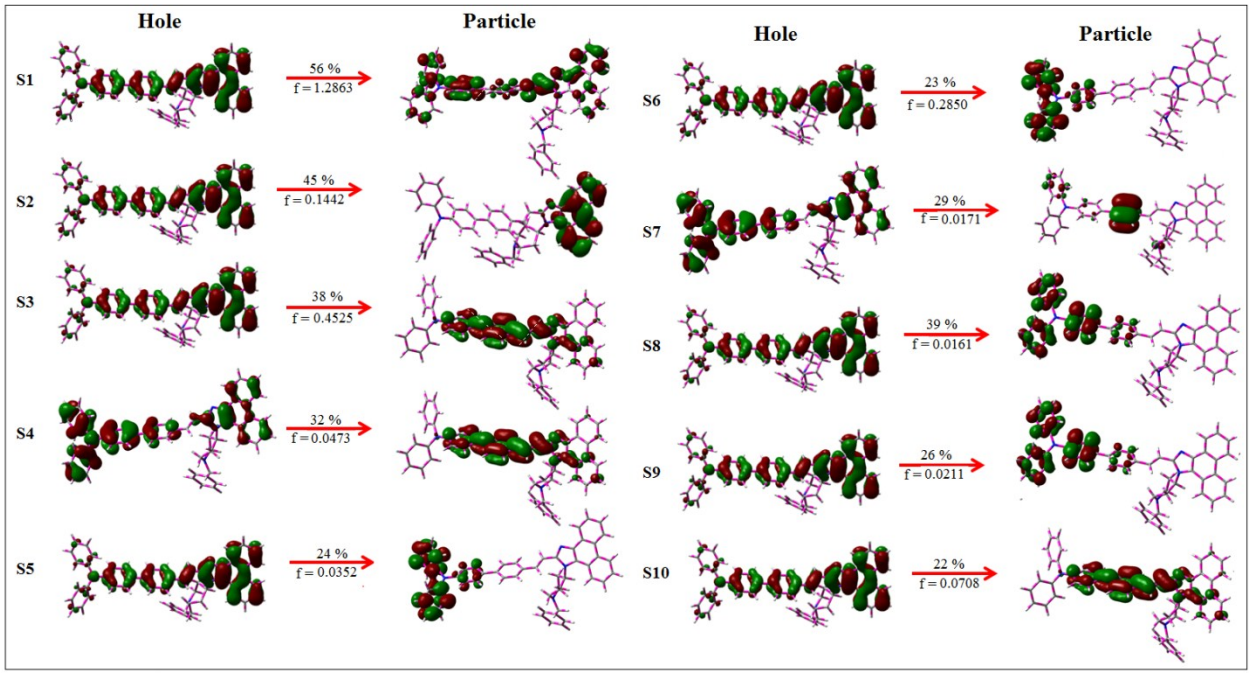

Figure S7. Natural transition orbital of Cz–BPIS for S_1-S_{10} transitions.

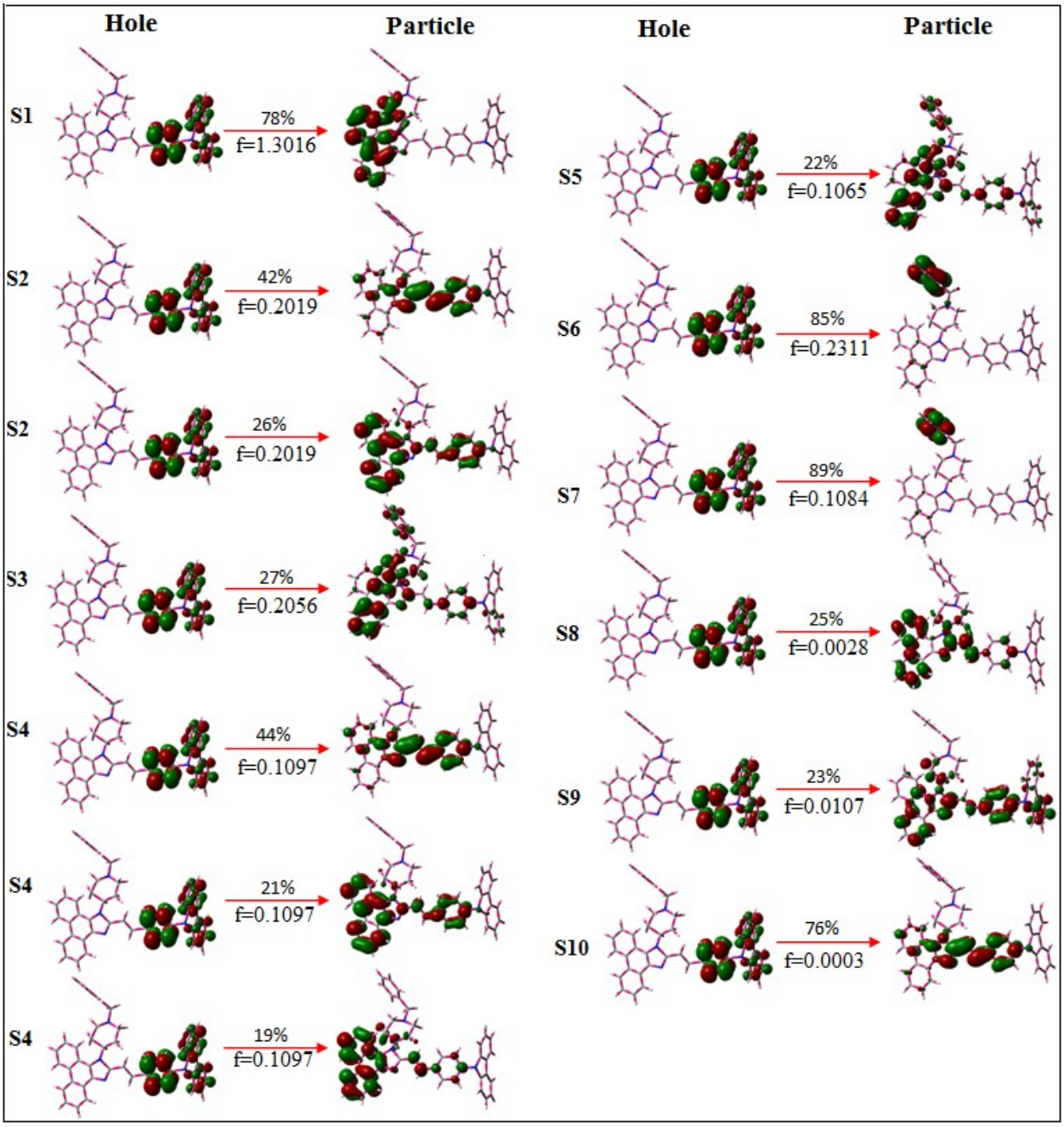

Figure S8. Hole-particle distribution of S_1-S_{10} transition TPA-BDIS. Green and blue areas refer to the zones where electron density increased and decreased respectively.

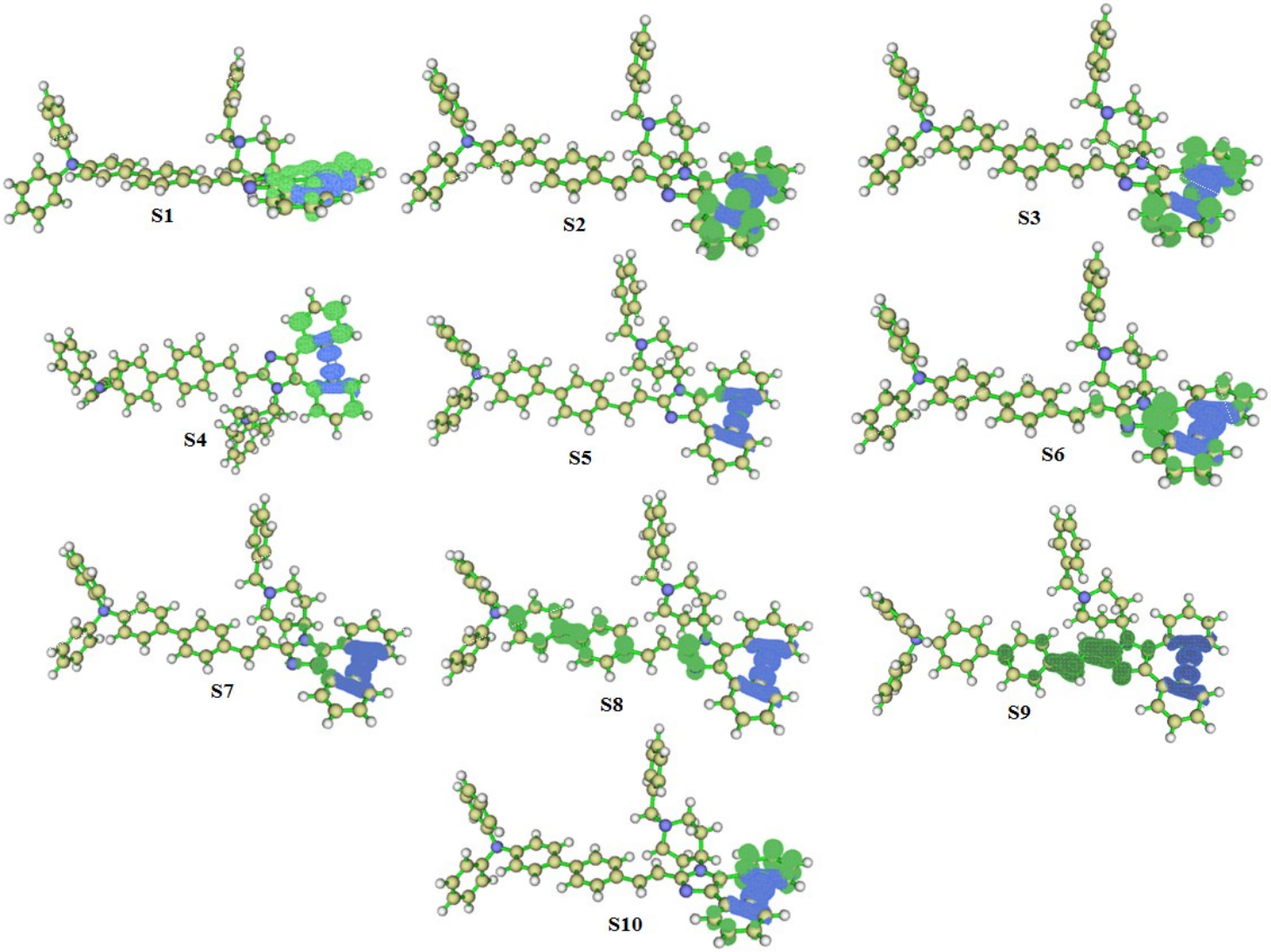

Figure S9. Hole-particle distribution of S_1-S_{10} transition TPA-BPIS. Green and blue areas refer to the zones where electron density increased and decreased respectively

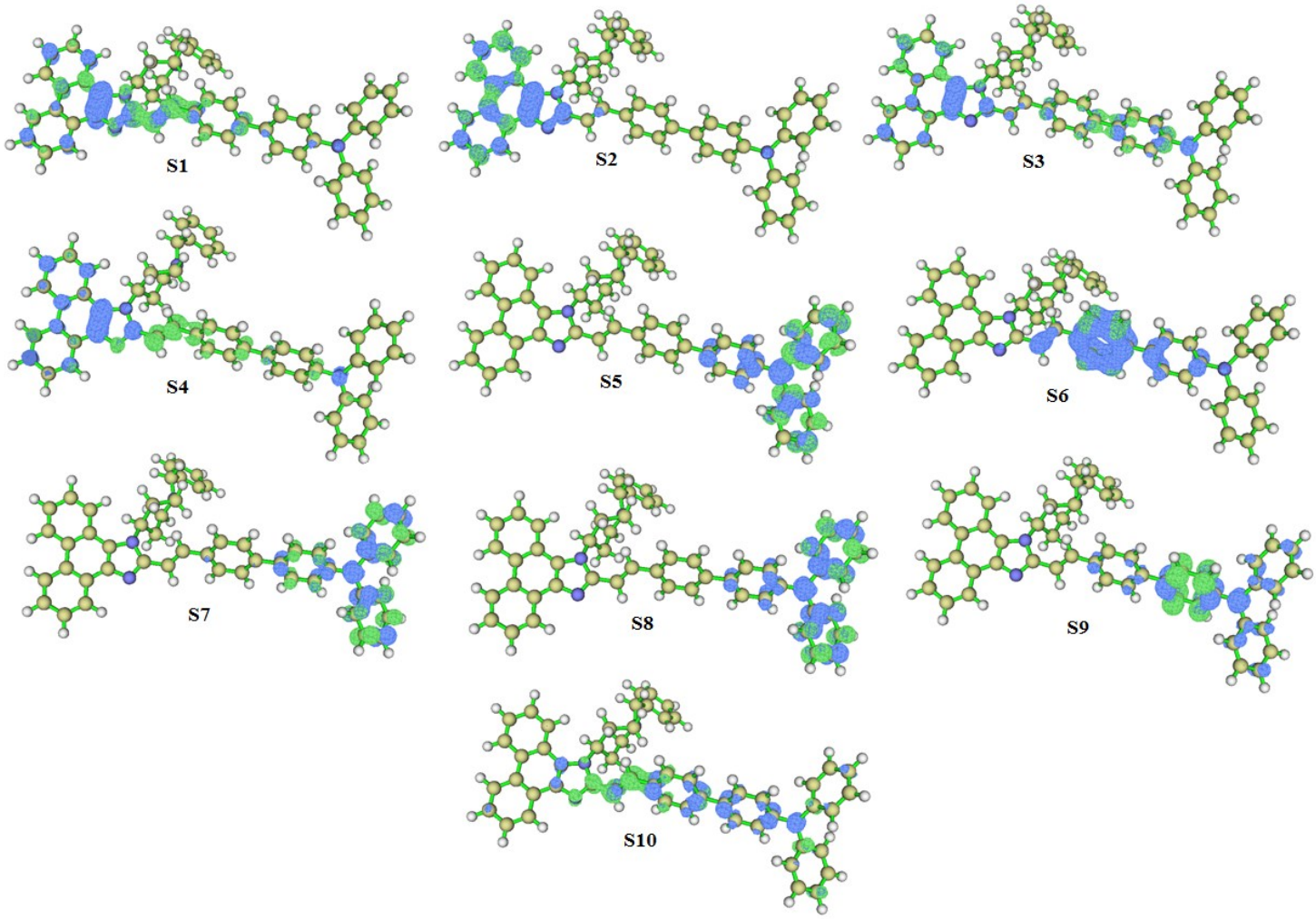

Figure S10. Hole-particle distribution of S_1-S_{10} transition Cz-BPIS. Green and blue areas refer to the zones where electron density increased and decreased respectively.

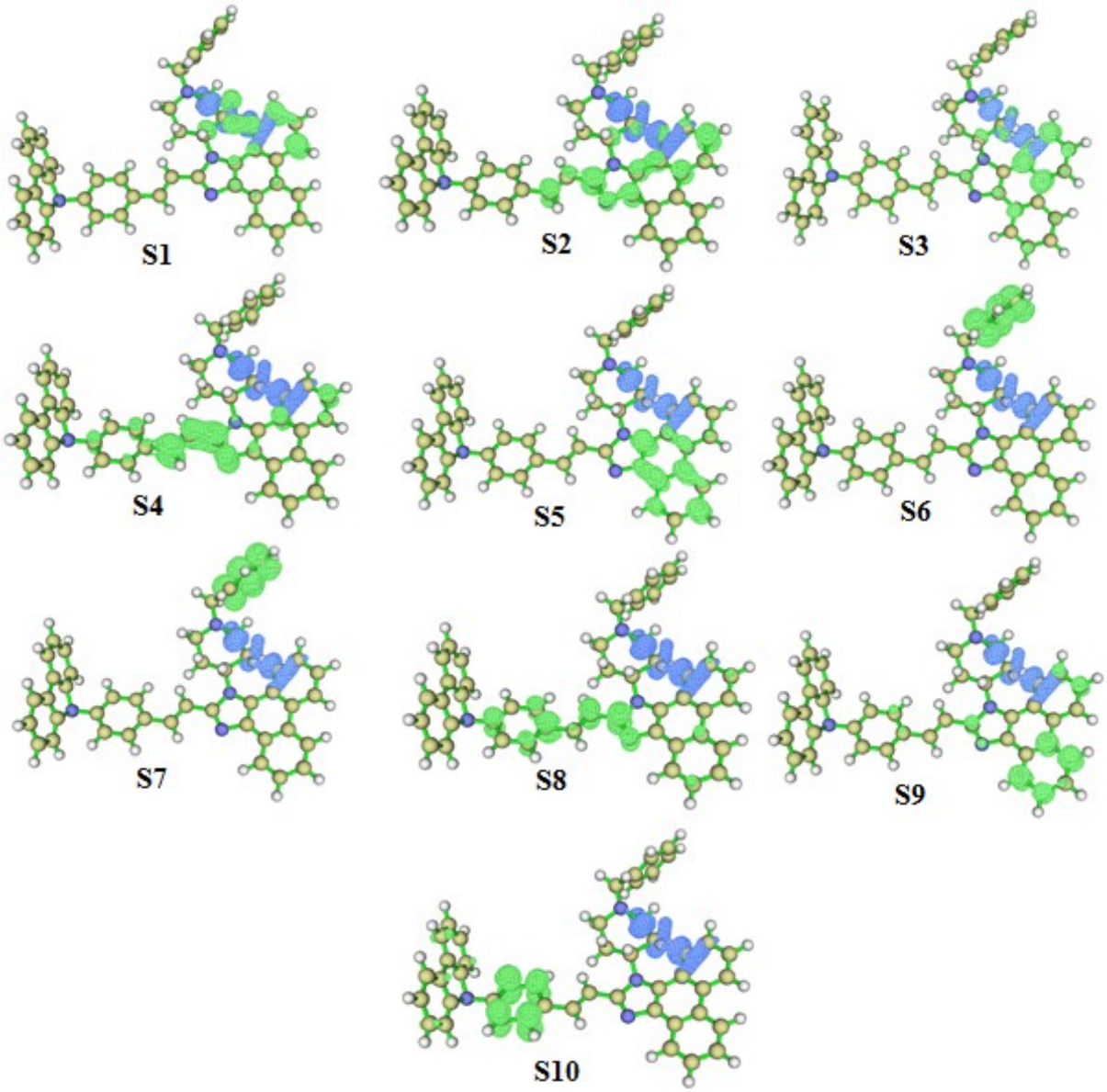

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Figure S11. Transition density matrix color-filled map of S0 and S5 states of TPA-BDIS

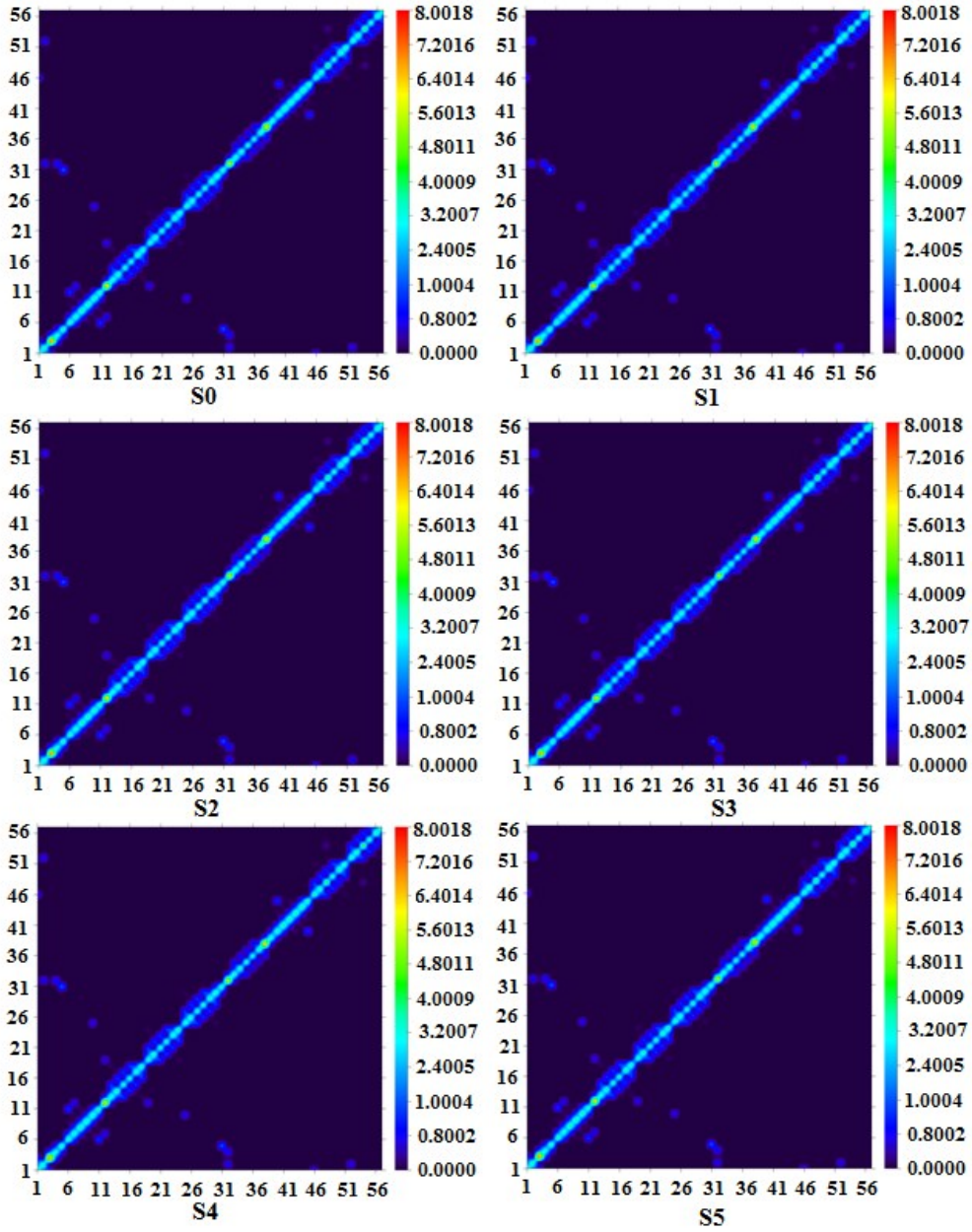

Figure S12. Transition density matrix color-filled map of S0 and S10 states of TPA-BPIS.

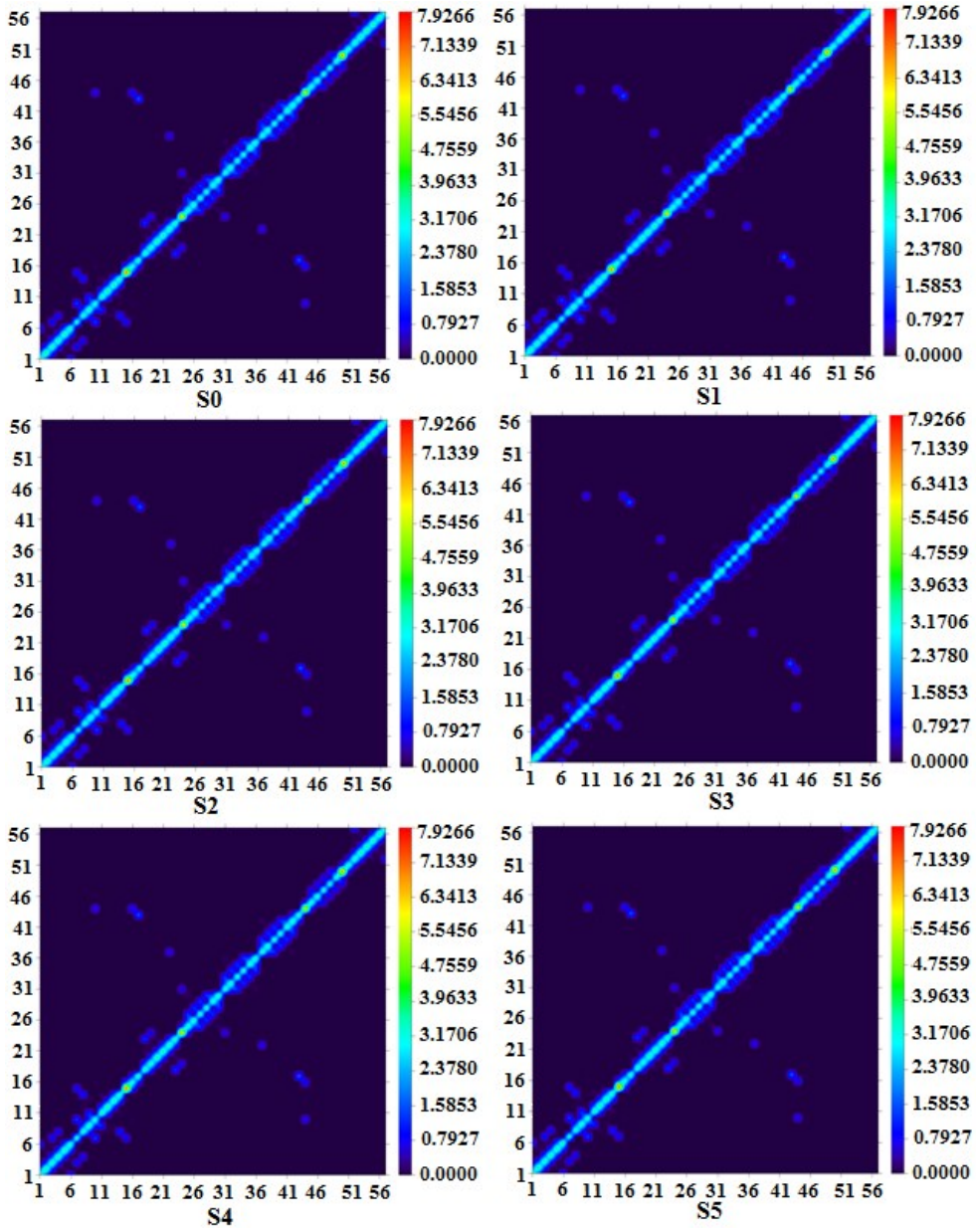

Figure S13. Transition density matrix color-filled map of S0 and S5 states of Cz-BPIS.