Electronic Supplementary Informations

Theoretical investigations of the realization of sky-blue to blue TADF Materials via CH/N & H/CN substitution at the Diphenylsulphone acceptor

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Table S1 Calculated structural parameters like bond lengths, bond angles and dihedral angles in the S_0 and S_1 optimized geometries using B3LYP/6-31g(d) and MPW1B95/6-31g(d) methods, respectively.

1a	**S_0**	**S_1**	**Diff.**
R(1,2)	1.462	1.469	0.007
R(1,4)	1.788	1.752	0.036
R(4,6)	1.393	1.413	0.020
R(4,14)	1.392	1.413	0.021
R(6,8)	1.390	1.380	0.010
R(8,10)	1.396	1.406	0.010
R(10,12)	1.395	1.406	0.011
R(12,14)	1.391	1.380	0.011
R(10,16)	1.427	1.437	0.010
R(16,18)	1.394	1.386	0.008
R(18,20)	1.403	1.410	0.007
R(20,22)	1.523	1.516	0.007
R(22,24)	1.523	1.515	0.008
R(24,26)	1.404	1.410	0.006
R(16,26)	1.393	1.384	0.009
R(18,28)	1.401	1.406	0.005
R(28,30)	1.385	1.382	0.003
R(30,32)	1.333	1.338	0.005
R(32,34)	1.331	1.329	0.002
R(20,34)	1.395	1.396	0.001
R(26,36)	1.402	1.407	0.005
R(36,38)	1.385	1.381	0.004
R(38,40)	1.333	1.338	0.005
R(40,42)	1.332	1.330	0.002
R(24,42)	1.395	1.396	0.001
α(1,3,2)	122.4	121.9	0.5
α(4,3,5)	104.4	105.5	1.1
α(3,4,6)	119.3	119.9	0.6
α(8,10,16)	119.7	119.8	0.1

α(10,16,18)	119.4	119.6	0.2
β(8,10,16,26)	92.6	90.4	2.2

1b	**S_0**	**S_1**	**Diff.**
R(1,2)	1.470	1.459	0.011
R(1,4)	1.822	1.760	0.062
R(4,6)	1.392	1.402	0.010
R(4,14)	1.328	1.348	0.020
R(6,8)	1.395	1.373	0.022
R(8,10)	1.396	1.409	0.013
R(10,12)	1.401	1.399	0.002
R(12,14)	1.335	1.313	0.022
R(10,16)	1.431	1.425	0.006
R(16,18)	1.405	1.385	0.020
R (16,26)	1.404	1.383	0.021
R (18,20)	1.408	1.403	0.005
R (18,30)	1.406	1.401	0.005
R (20,22)	1.532	1.510	0.022
R (20,42)	1.400	1.392	0.008
R (22,24)	1.532	1.510	0.022
R (22,44)	1.553	1.540	0.013
R (22,46)	1.553	1.540	0.013
R (24,26)	1.408	1.404	0.004
R (24,40)	1.400	1.391	0.009
R (26,28)	1.406	1.402	0.004
R (28,32)	1.389	1.378	0.011
R (30,34)	1.389	1.378	0.011
R (32,36)	1.338	1.334	0.004
R (34,38)	1.338	1.334	0.004
R (36,40)	1.337	1.326	0.011

R (38,42)	1.337	1.325	0.012
α(2,1,3)	120.8	121.6	0.8
α(4,1,5)	102.9	102.9	0.0
α(1,4,6)	119.0	118.9	0.1
α(8,10,16)	121.2	121.1	0.1
α(10,16,18)	119.4	119.6	0.2
β(8,10,16,26)	89.1	86.95	2.2

1c	**S_0**	**S_1**	**Diff.**
R(1,2)	1.469	1.461	0.008
R(1,4)	1.803	1.744	0.059
R(4,6)	1.395	1.410	0.015
R(4,14)	1.398	1.406	0.008
R(6,8)	1.392	1.376	0.014
R(8,10)	1.399	1.395	0.004
R(10,12)	1.336	1.341	0.005
R(12,14)	1.336	1.318	0.018
R(10,16)	1.431	1.436	0.005
R(16,18)	1.403	1.380	0.023
R (16,26)	1.402	1.379	0.023
R (18,20)	1.407	1.404	0.003
R (18,30)	1.405	1.402	0.003
R (20,22)	1.532	1.509	0.023
R (20,42)	1.400	1.391	0.009
R (22,24)	1.532	1.509	0.023
R (22,44)	1.553	1.540	0.013
R (22,46)	1.552	1.541	0.011
R (24,26)	1.407	1.404	0.003
R (24,40)	1.400	1.391	0.009
R (26,28)	1.405	1.402	0.003

R (28,32)	1.388	1.377	0.011
R (30,34)	1.388	1.378	0.010
R (32,36)	1.338	1.334	0.004
R (34,38)	1.338	1.334	0.004
R (36,40)	1.337	1.326	0.011
R (38,42)	1.337	1.326	0.011
α(2,1,3)	122.6	122.4	0.2
α(4,1,5)	104.7	105.2	0.5
α(1,4,6)	120.0	120.96	0.96
α(8,10,16)	119.4	119.9	0.5
α(10,16,18)	119.2	119.5	0.3
β(8,10,16,26)	86.7	91.4	4.7

1d	**S_0**	**S_1**	**Diff.**
R(1,2)	1.464	1.451	0.013
R(1,4)	1.839	1.773	0.066
R(4,6)	1.324	1.345	0.021
R(4,14)	1.329	1.345	0.016
R(6,8)	1.338	1.309	0.029
R(8,10)	1.397	1.406	0.009
R(10,12)	1.399	1.406	0.007
R(12,14)	1.336	1.309	0.027
R(10,16)	1.425	1.416	0.009
R(16,18)	1.407	1.388	0.019
R (16,26)	1.407	1.387	0.020
R (18,20)	1.407	1.402	0.005
R (18,30)	1.405	1.400	0.005
R (20,22)	1.531	1.510	0.021
R (20,42)	1.400	1.392	0.008
R (22,24)	1.531	1.509	0.022

R (22,44)	1.553	1.540	0.013
R (22,46)	1.552	1.540	0.012
R (24,26)	1.407	1.403	0.004
R (24,40)	1.400	1.391	0.009
R (26,28)	1.405	1.400	0.005
R (28,32)	1.389	1.378	0.011
R (30,34)	1.389	1.378	0.011
R (32,36)	1.338	1.332	0.006
R (34,38)	1.338	1.333	0.005
R (36,40)	1.336	1.326	0.010
R (38,42)	1.336	1.325	0.011
α(2,1,3)	121.9	122.3	0.4
α(4,1,5)	101.6	100.8	0.8
α(1,4,6)	115.7	116.8	1.1
α(8,10,16)	121.7	121.8	0.1
α(10,16,18)	119.4	119.9	0.5
β(8,10,16,26)	87.0	88.9	1.9

1e	**S_0**	**S_1**	**Diff.**
R(1,2)	1.468	1.460	0.008
R(1,4)	1.795	1.740	0.055
R(4,6)	1.397	1.408	0.011
R(4,14)	1.396	1.408	0.012
R(6,8)	1.332	1.318	0.014
R(8,10)	1.342	1.334	0.008
R(10,12)	1.341	1.333	0.008
R(12,14)	1.336	1.319	0.017
R(10,16)	1.415	1.435	0.020
R(16,18)	1.415	1.378	0.037
R (16,26)	1.415	1.377	0.038

R (18,20)	1.405	1.403	0.002
R (18,30)	1.406	1.401	0.005
R (20,22)	1.528	1.510	0.018
R (20,42)	1.402	1.391	0.011
R (22,24)	1.529	1.509	0.020
R (22,44)	1.553	1.541	0.012
R (22,46)	1.553	1.540	0.013
R (24,26)	1.406	1.404	0.004
R (24,40)	1.402	1.391	0.011
R (26,28)	1.406	1.401	0.005
R (28,32)	1.387	1.377	0.010
R (30,34)	1.387	1.377	0.010
R (32,36)	1.338	1.334	0.004
R (34,38)	1.339	1.334	0.005
R (36,40)	1.334	1.326	0.008
R (38,42)	1.334	1.325	0.009
α(2,1,3)	122.99	122.8	0.19
α(4,1,5)	104.98	105.2	0.22
α(1,4,6)	121.5	121.7	0.2
α(8,10,16)	116.6	115.5	1.1
α(10,16,18)	119.3	119.4	0.1
β(8,10,16,26)	59.5	93.1	33.6

1f	**S_0**	**S_1**	**Diff.**
R(1,2)	1.467	1.460	0.007
R(1,4)	1.814	1.763	0.051
R(4,6)	1.391	1.387	0.004
R(4,14)	1.410	1.425	0.015
R(6,8)	1.395	1.380	0.015
R(8,10)	1.396	1.406	0.010

R(10,12)	1.397	1.375	0.022
R(12,14)	1.403	1.401	0.002
R(10,16)	1.432	1.432	0.000
R(16,18)	1.405	1.382	0.023
R (16,26)	1.406	1.383	0.023
R (18,20)	1.408	1.403	0.005
R (18,30)	1.405	1.402	0.003
R (20,22)	1.532	1.509	0.023
R (20,42)	1.400	1.392	0.008
R (22,24)	1.532	1.510	0.022
R (22,44)	1.553	1.541	0.012
R (22,46)	1.552	1.540	0.012
R (24,26)	1.407	1.404	0.003
R (24,40)	1.400	1.391	0.009
R (26,28)	1.406	1.402	0.004
R (28,32)	1.389	1.379	0.010
R (30,34)	1.389	1.378	0.011
R (32,36)	1.338	1.334	0.004
R (34,38)	1.338	1.334	0.004
R (36,40)	1.336	1.325	0.011
R (38,42)	1.337	1.326	0.011
α(2,1,3)	121.2	119.5	1.7
α(4,1,5)	105.2	103.8	1.4
α(1,4,6)	116.7	116.6	0.1
α(8,10,16)	120. 4	119.0	1.6
α(10,16,18)	119.5	119.0	0.5
β(8,10,16,26)	84.7	88.2	3.5

1g	**S_0**	**S_1**	**Diff.**
R(1,2)	1.469	1.459	0.010

R(1,4)	1.808	1.759	0.049
R(4,6)	1.395	1.411	0.016
R(4,14)	1.392	1.387	0.005
R(6,8)	1.395	1.379	0.016
R(8,10)	1.396	1.390	0.006
R(10,12)	1.413	1.424	0.011
R(12,14)	1.402	1.390	0.012
R(10,16)	1.428	1.426	0.002
R(16,18)	1.407	1.385	0.022
R (16,26)	1.406	1.383	0.023
R (18,20)	1.406	1.403	0.003
R (18,30)	1.404	1.401	0.003
R (20,22)	1.532	1.509	0.023
R (20,42)	1.400	1.392	0.008
R (22,24)	1.532	1.509	0.023
R (22,44)	1.552	1.539	0.013
R (22,46)	1.553	1.542	0.011
R (24,26)	1.406	1.403	0.003
R (24,40)	1.400	1.392	0.008
R (26,28)	1.405	1.401	0.004
R (28,32)	1.389	1.377	0.012
R (30,34)	1.389	1.378	0.011
R (32,36)	1.332	1.334	0.002
R (34,38)	1.337	1.334	0.003
R (36,40)	1.337	1.325	0.012
R (38,42)	1.336	1.325	0.011
α(2,1,3)	122.7	122.4	0.3
α(4,1,5)	104.7	105.4	0.7
α(1,4,6)	119.2	119.9	0.7
α(8,10,16)	120. 4	121.1	0.7
α(10,16,18)	119.3	119.1	0.2

β(8,10,16,26)	89.1	91.9	2.8

1h	**S_0**	**S_1**	**Diff.**
R(1,2)	1.461	1.454	0.007
R(1,4)	1.827	1.764	0.063
R(4,6)	1.407	1.409	0.002
R(4,14)	1.410	1.426	0.016
R(6,8)	1.407	1.385	0.022
R(8,10)	1.392	1.400	0.008
R(10,12)	1.395	1.381	0.014
R(12,14)	1.402	1.392	0.010
R(10,16)	1.427	1.428	0.001
R(16,18)	1.407	1.384	0.023
R (16,26)	1.409	1.384	0.025
R (18,20)	1.407	1.403	0.004
R (18,30)	1.405	1.401	0.004
R (20,22)	1.531	1.508	0.023
R (20,42)	1.400	1.392	0.008
R (22,24)	1.532	1.509	0.023
R (22,44)	1.553	1.541	0.012
R (22,46)	1.552	1.540	0.012
R (24,26)	1.407	1.404	0.003
R (24,40)	1.400	1.392	0.008
R (26,28)	1.405	1.402	0.003
R (28,32)	1.389	1.379	0.010
R (30,34)	1.389	1.378	0.011
R (32,36)	1.338	1.335	0.003
R (34,38)	1.337	1.334	0.003
R (36,40)	1.336	1.325	0.011
R (38,42)	1.336	1.325	0.011

α(2,1,3)	122.2	121.1	1.1
α(4,1,5)	105.3	104.5	0.8
α(1,4,6)	119.8	120.2	0.4
α(8,10,16)	120.3	119.5	0.8
α(10,16,18)	119.4	118.9	0.5
β(8,10,16,26)	81.8	88.3	6.5

1i	**S_0**	**S_1**	**Diff.**
R(1,2)	1.467	1.459	0.008
R(1,4)	1.812	1.757	0.055
R(4,6)	1.392	1.399	0.007
R(4,14)	1.392	1.400	0.008
R(6,8)	1.404	1.384	0.020
R(8,10)	1.409	1.413	0.004
R(10,12)	1.410	1.414	0.004
R(12,14)	1.403	1.383	0.020
R(10,16)	1.421	1.420	0.001
R(16,18)	1.411	1.387	0.024
R (16,26)	1.410	1.385	0.025
R (18,20)	1.405	1.402	0.003
R (18,30)	1.404	1.400	0.004
R (20,22)	1.531	1.508	0.023
R (20,42)	1.400	1.392	0.008
R (22,24)	1.531	1.508	0.023
R (22,44)	1.553	1.541	0.012
R (22,46)	1.553	1.541	0.012
R (24,26)	1.405	1.402	0.003
R (24,40)	1.400	1.392	0.008
R (26,28)	1.404	1.400	0.004
R (28,32)	1.389	1.377	0.012

R (30,34)	1.389	1.378	0.011
R (32,36)	1.337	1.334	0.003
R (34,38)	1.337	1.334	0.003
R (36,40)	1.336	1.325	0.011
R (38,42)	1.336	1.325	0.011
α(2,1,3)	123.2	123.1	0.1
α(4,1,5)	104.7	105.7	1.0
α(1,4,6)	118.9	119.4	0.5
α(8,10,16)	120.5	120.1	0.4
α(10,16,18)	119.3	119.2	0.1
β(8,10,16,26)	88.93	88.99	0.06

Table S2 HOMO-LUMO Energy gap ($\Delta E_{L\text{-}H}$) in the S_0 and S_1 state optimized geometries using B3LYP/6-31g(d) and MPW1B95/6-31g(d) methods, respectively.

Sr. No.	S_0 geometry			S_1 geometry		
	E_{HOMO}	E_{LUMO}	$\Delta E_{L\text{-}H}$	E_{HOMO}	E_{LUMO}	$\Delta E_{L\text{-}H}$
1a	-6.31	-2.09	4.22	-6.28	-2.44	3.84
1b	-6.14	-2.19	3.95	-6.52	-2.41	4.11
1c	-6.10	-2.64	3.46	-6.44	-2.61	3.83
1d	-6.30	-2.46	3.84	-6.75	-3.33	3.42
1e	-6.24	-2.94	3.30	-6.49	-3.08	3.41
1f	-6.20	-2.83	3.37	-6.48	-2.76	3.72
1g	-6.27	-2.93	3.34	-6.59	-2.80	3.79
1h	-6.43	-3.35	3.08	-6.75	-3.33	3.42
1i	-6.49	-3.53	2.96	-6.82	-3.41	3.41

Table S3 Calculated absorption Wavelength (λ_{ab}) values and main configuration for the investigated molecules using TD-MPW1B95/6-31g(d) method based on optimized S_0 geometry in Toluene media using PCM Model.

Sr. No.	Excited State	Main Configuration/ Transition (%T=T*100)	Wavelength λ_{ab} (nm)	E_S@S_0 (eV)	Oscillator Strength (f)
1a	S_1	HOMO→LUMO (87%)	336	3.6914	0.0002

f_{max}	S_6	H-1→L+4 (47%), HOMO→L+5 (40%)	270	4.5847	0.2594
1b	S_1	HOMO→LUMO (62%) H-1→L+1 (34%)	347	3.5761	0.0011
f_{max}	S_7	H-1→L+5 (47%) HOMO→L+4 (48%)	271	4.5703	0.2676
1c	S_1	HOMO→LUMO (85%) H-1→L+1, 2 (5%, 9%)	376	3.2959	0.0086
f_{max}	S_{12}	H-1→L+5 (23%) HOMO→L+4 (22%)	269	4.6105	0.1242
1d	S_1	H-1→LUMO (45%) HOMO→L+2 (40%)	361	3.4330	0.0034
f_{max}	S_9	H-1→L+4 (35%) HOMO→L+5 (34%)	271	4.5785	0.1754
1e	S_1	HOMO→LUMO (86%) H-1→L+3 (12%)	400	3.0969	0.2640
f_{max}	S_{19}	HOMO→L+5 (41%) H-1→L+4 (37%)	266	4.6582	0.1702
1f	S_1	H-1→LUMO (65%) HOMO→L+1 (32%)	396	3.1292	0.0065
f_{max}	S_{15}	H-1→L+4 (42%) HOMO→L+5 (43%)	270	4.5890	0.2423
1g	S_1	HOMO->LUMO (74%) H-1->L+1 (20%)	401	3.0899	0.0002
f_{max}	S_{16}	H-1->L+5 (46%) HOMO->L+4 (46%)	268	4.6222	0.2419
1h	S_1	H-1→LUMO (67%) HOMO→L+1 (29%)	439	2.8260	0.0182
f_{max}	S_{19}	H-7→L+3 (22%) H-6→L+2 (60%)	285	4.3464	0.0222
1i	S_1	HOMO->LUMO (77%)	456	2.7163	0.0001

		H-1->L+3 (20%)			
f_{max}	S_{19}	H-7->L+2 (26%)	295	4.2025	0.0092
		H-6->L+1 (73%)			

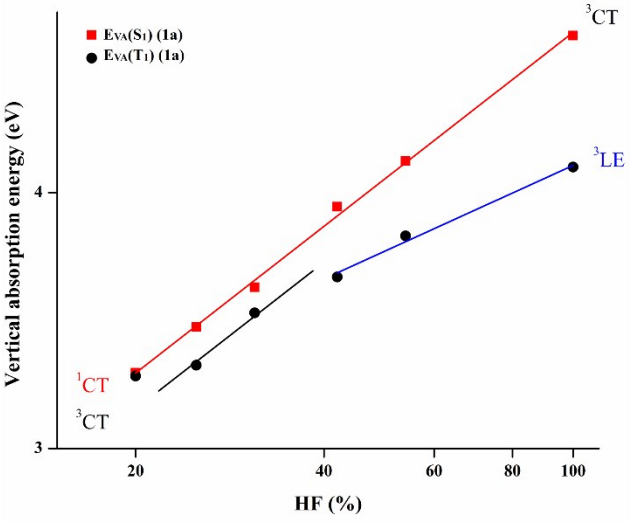
Table S4 Calculated emission Wavelength (λ_{em}) values and main configuration for the investigated molecules using TD-MPW1B95/6-31g(d) method based on optimized S_1 geometry in Toluene media using PCM Model.

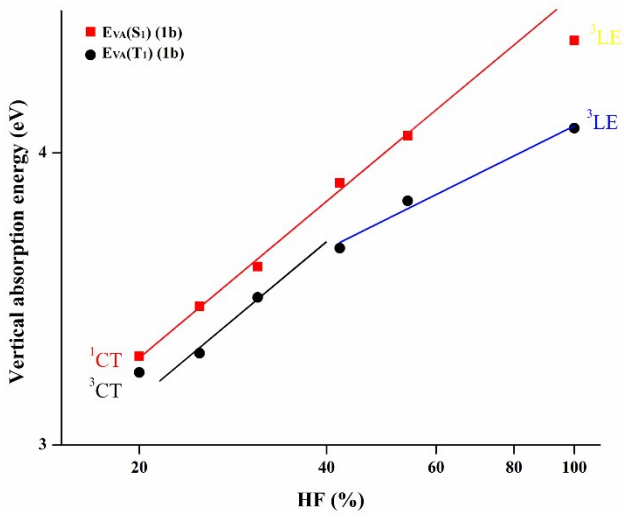
Sr. No.	Excited State	Main Configuration/ Transition (%T=T*100)	Wavelength λ_{em} (nm)	E_S@S_0 (eV)	Oscillator Strength (f)
1a	S_1	LUMO → HOMO -1 (90)	366	3.39	0.0028
f_{max}	S_{17}	LUMO→H-10 (93)	249	4.98	0.6774
1b	S_1	LUMO → HOMO (87)	397	3.12	0.0052
f_{max}	S_{12}	L+4→H-1 (48), L+5→H (47)	272	4.56	0.2190
1c	S_1	LUMO → HOMO (89)	416	2.98	0.0001
f_{max}	S_{17}	L+4→H-1 (32), L+3→H (21)	270	4.59	0.1361
1d	S_1	LUMO → HOMO (88)	447	2.78	0.0001
f_{max}	S_{20}	L+4→H-1 (37), L+4→H (37)	271	4.57	0.1345
1e	S_1	LUMO → H-1 (89)	482	2.57	0.0025
f_{max}	S_{20}	L+1→H-13 (27), L+1→H-5 (36)	276	4.49	0.0031
1f	S_1	LUMO → HOMO (70)	437	2.84	0.0003
f_{max}	S_{11}	L→H-6 (78), L+1→H-7 (20)	289	4.29	0.0199
1g	S_1	LUMO → HOMO (77)	432	2.87	0.0002
f_{max}	S_{18}	L+4→H (43), L+5→H-1 (43)	270	4.60	0.2131
1h	S_1	LUMO → H-1 (73)	494	2.51	0.0009
f_{max}	S_{13}	L→H-6 (83), L+1→H-7 (16)	318	3.90	0.0068
1i	S_1	LUMO → HOMO (81)	497	2.49	0.0002
f_{max}	S_{17}	L+1→H-4 (68), L+2→H-5 (21)	302	4.10	0.0036

Table S5 Calculated $E_{VA}(S_1)$ and $E_{VA}(T_1)$ using various exchange-correlation functionals and 6-31G(d) basis set based on B3LYP optimized geometries, and calculated CT amount (q), optimal HF% (OHF), $E_{0\text{-}0}$ (^{3}LE), $E_{0\text{-}0}$ (^{1}CT) and $E_{0\text{-}0}$ (^{3}CT) of investigated molecules **1a-1e**.

Parameter	Functionals	**1a**	**1b**	**1c**	**1d**	**1e**

E_{VA} (S_1) eV	B3LYP	3.2664	3.2739	2.9611	3.1282	2.8064
	PBE1PBE	3.4393	3.4387	3.1413	3.2998	2.9740
	MPWB95	3.5962	3.5761	3.2959	3.4330	3.0969
	BMK	3.9372	3.8833	3.6213	3.7140	3.3508
	M062X	4.1448	4.0679	3.8457	3.8883	3.5521
	M06HF	4.7723	4.4685	4.4807	4.3071	4.0925
E_{VA} (T_1) eV	B3LYP	3.2548	3.2224	2.9410	3.0382	2.6252
	PBE1PBE	3.2943	3.2839	3.1101	3.1624	2.7471
	MPWB95	3.4944	3.4694	3.2695	3.3173	2.8833
	BMK	3.6379	3.6420	3.5841	3.5478	3.1055
	M062X	3.8103	3.8157	3.8040	3.7084	3.3120
	M06HF	4.1166	4.0986	4.1430	3.9389	3.7979
CT amount (q)		0.8544	0.8565	0.8484	0.8816	0.7852
Optimal HF%		36	36	36	37	33
E_{VA} (S_1, OHF) (eV)		3.75	3.72	3.44	3.59	3.16
$E_{0\text{-}0}$ (^{1}CT) (eV)		3.51	3.48	3.20	3.35	2.92
$E_{0\text{-}0}$ (^{3}CT) (eV)		3.50	3.42	3.18	3.25	2.72
$E_{0\text{-}0}$ (^{3}LE) (eV)		3.15	3.14	3.13	3.07	2.76





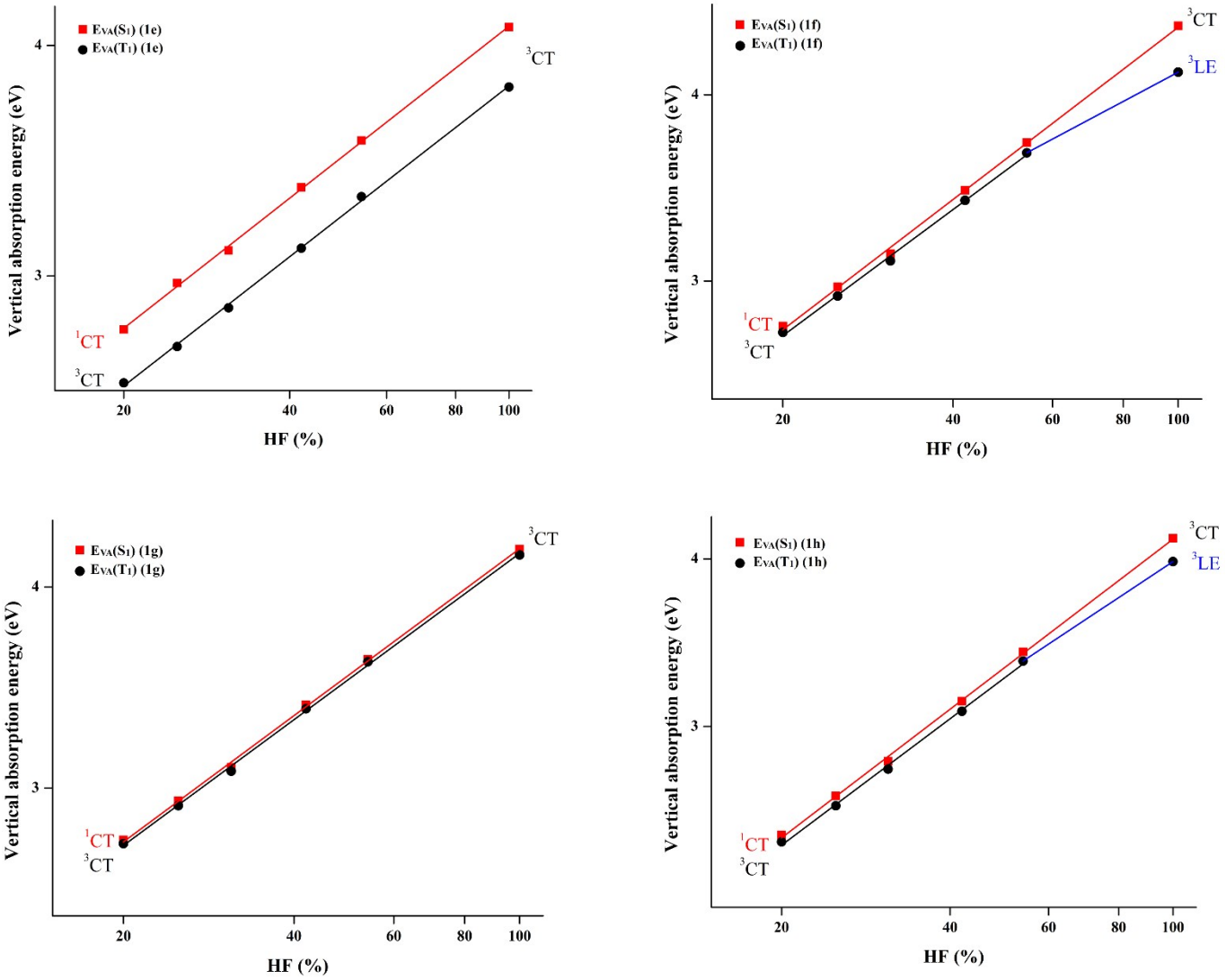
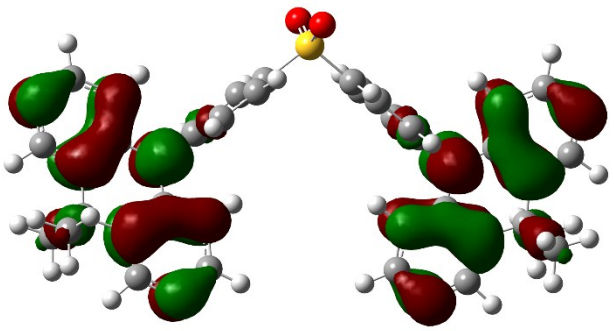
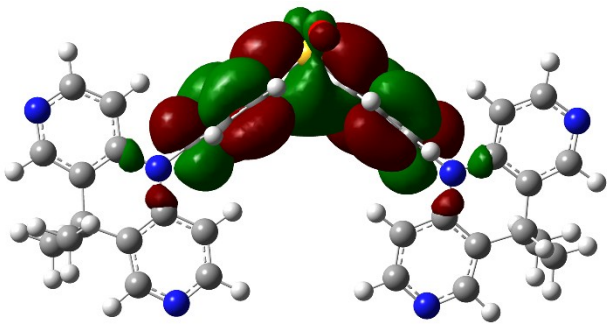
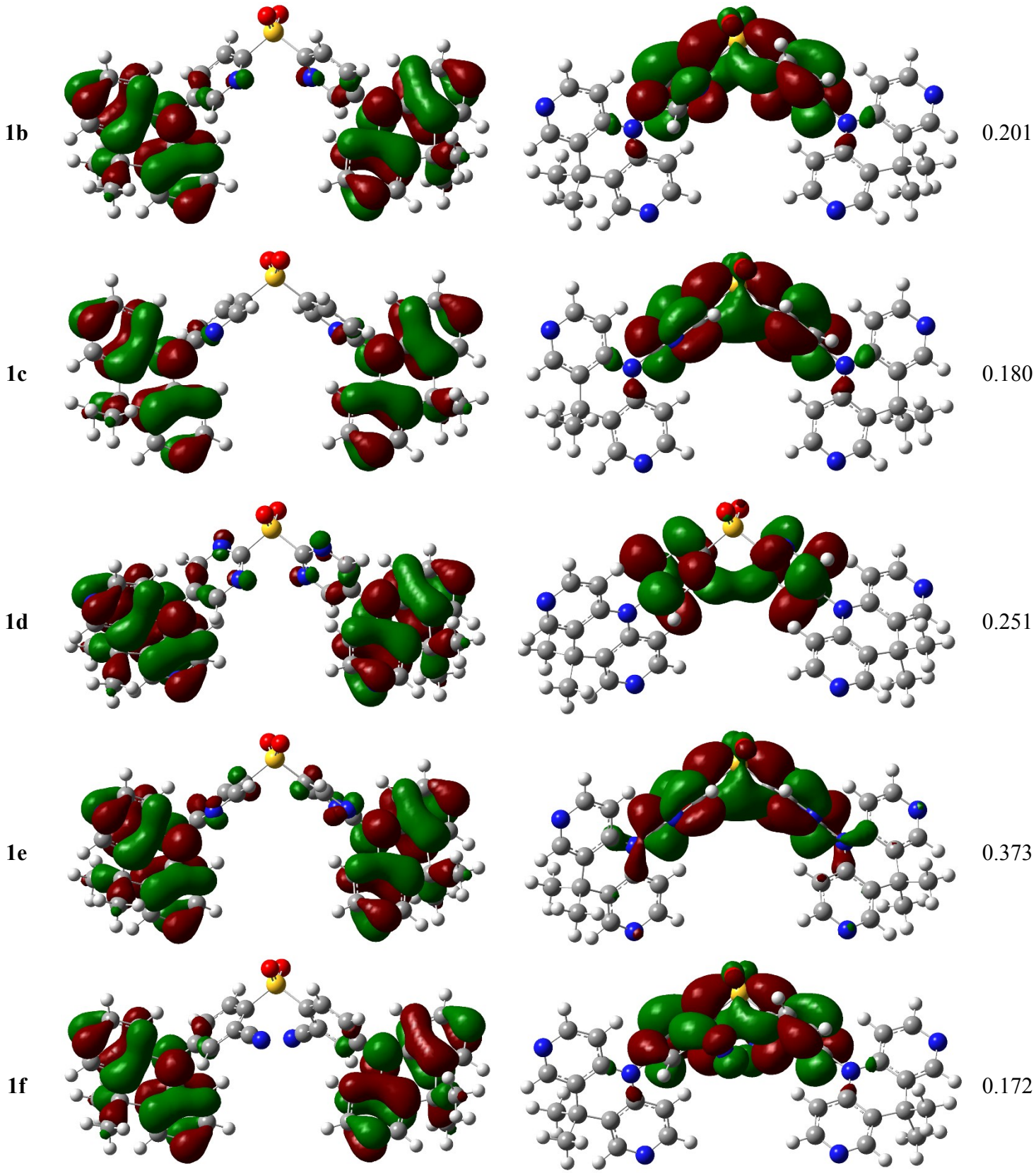


Figure S1 Dependence of $E_{VA}(S_1)$ and $E_{VA}(T_1)$ on the HF% in TD-DFT plotted on a log-log scale for **1a-1h**.

Sr. No.	HOMO	LUMO	ρ
1a			0.167


1b
0.201
1c
0.180
1d
0.251
1e
0.373
1f
0.172

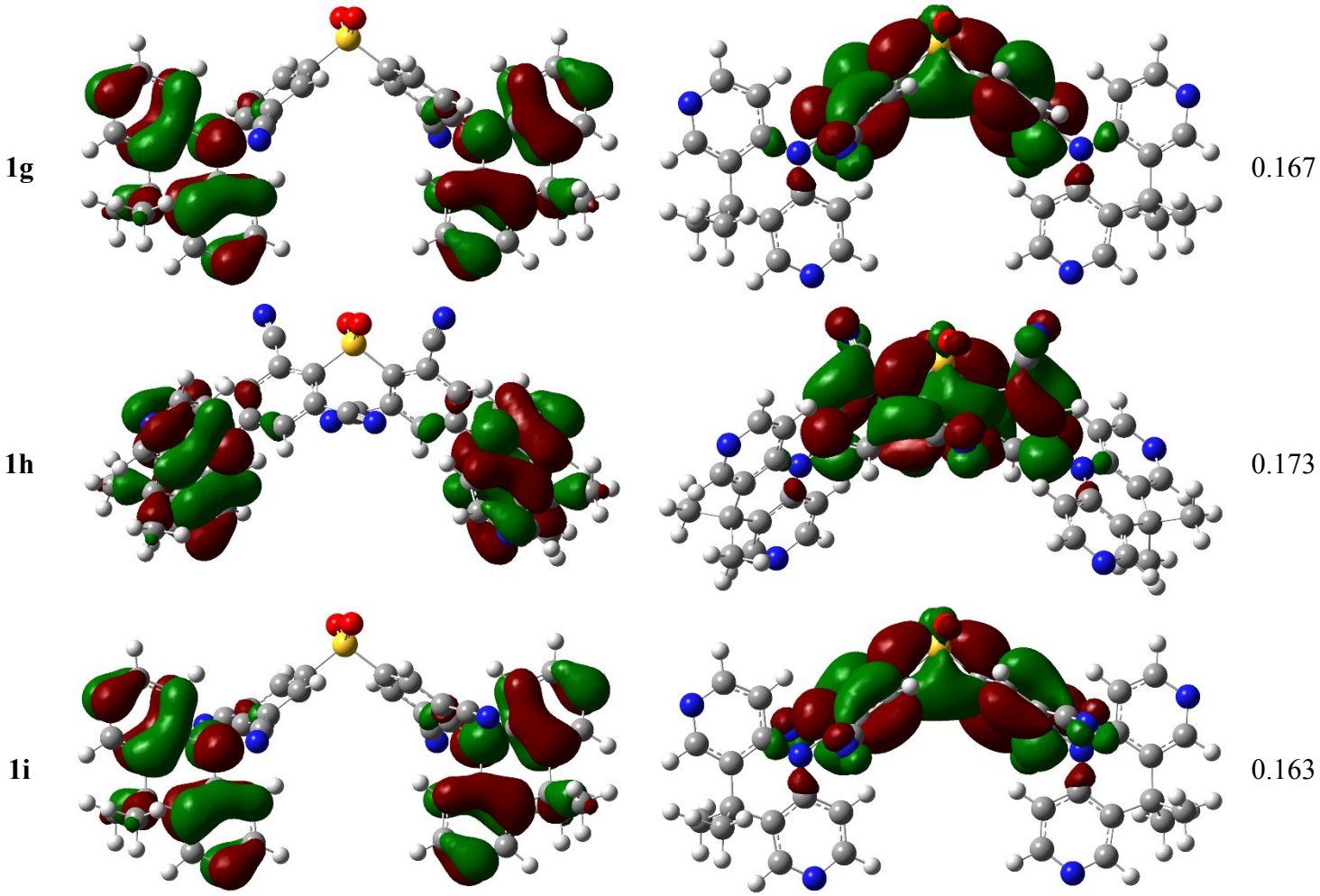


Figure S2 The electron density plots of the HOMOs and LUMOs and the overlap between them in whole space for these investigated compounds in S_0 geometries.