Quantum Chemical Design of Carbazole- and Pyridoindole-Based Ambipolar Host Materials for Blue Phosphorescent OLEDs

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Supporting Information

(25 pages including this page)

Table S1: Calculated HOMO and LUMO Energies (E_H and E_L) and Available Experimental Values for the Reference Molecules (Units in eV).

Table S2: DFT/B3LYP Calculated FMO Energy Levels (in eV), Adiabatic IPs/EAs (in eV), and Relaxation Energy (λ_1, λ_2, λ_3 and λ_4) for the Designed Host Molecules at B3LYP/6-31+G* level.

Table S3: Calculated HOMO, HOMO-1, LUMO, LUMO+1 and LUMO+2 Energies of the subunits at the B3LYP/6-31+G* method.

Table S4: Torsional angles (ω) between core moieties (Ph-Cb1, Ph-Cbz) and substituted host molecules in the ground state.

Table S5: The % Molecular Orbital Contribution of the HOMO and LUMO of the Ph-Cb1 based host.

Table S6: The % Molecular Orbital Contribution of the HOMO and LUMO of the Ph-Cbz based host.

Figure S1: The calculated and experimentally reported HOMO and IP energy values of reference systems at B3LYP/6-31+G* level of theory.

Figure S2: The calculated and experimentally reported LUMO and EA energy values of reference systems at B3LYP/6-31+G* level of theory.

Figure S3: Evolution of ΔE_{ST} for experimentally reported host materials using different density functional with 6-31G* basis set.

Figure S4: Evolution of ΔEST for experimentally reported systems in B3LYP functional with 6-31G* and 6-31+G** basis sets.

Figure S5: The M06-2X/6-31G* Optimized Geometries of hosts Dimer.

Figure S6: Contour plots (isosurface value = 0.03 au) of the HOMO and LUMO levels of the Ph-Cb1-based host molecules. The hydrogen atoms are omitted here for clarity.

Figure S7: HOMO and LUMO Contour Plots of core units.

Figure S8: Hole-particle pairs of natural transition orbitals (NTOs) of the Ph-cb1 based host materials for the T_1 state (isosurface value = 0.030 au). The hydrogen atoms are omitted here for clarity.

Figure S9: Contour plots (isosurface value = 0.03 au) of the HOMO and LUMO levels of the Ph-Cbz-based host molecules. The hydrogen atoms are omitted here for clarity.

Figure S10: Hole-particle pairs of natural transition orbitals (NTOs) of the Ph-Cbz-based host materials for the T_1 state (isosurface value = 0.030 au). The hydrogen atoms are omitted here for clarity.

Benchmarking the theoretical methods

We have addressed the accuracy of a quantum chemical method to calculate the vertical singlet (S_1) and triplet (T_1) excitation energies in the studied host materials. It is evident from the previous reports that, the TD-DFT energies of the excited states depend on the choice of the DFT functional.[1,2] In order to analyze how the variation in the choice of functional can alter the vertical E_{S1}/E_{T1} excitation energies, we carried out excited state calculations with functionals like CAM-B3LYP, M06, M06-2X, PBE0,ωB97X and LCω-PBE in conjunction with the 6-31G* basis set. The B3LYP/6-31G* optimized geometries were used for benchmarking various functionals. Evolution of ΔE_{ST} values along with the available experimental data are shown in Figure S3. The long range corrected functionals overestimated the ΔE_{ST} values when compared with experimental reported values. Moreover, when B3LYP and M06-2X functionals are employed, the ΔE_{ST} values are underestimated for few host molecules due to overestimation of π-delocalization. However, B3LYP and M06-2X functionals exhibit good correlation with experimental data. Hence, we have restricted our calculation with B3LYP functional. Note that these calculations do not account for geometry relaxations in the excited state.

Direct comparison of singlet (S_1) and triplet (T_1) energies with the experimental ΔE_{ST} requires calculating the S_1 and T_1 energies at the minimum energy geometries of these states (adiabatic states). The adiabatic E_S and E_T energies were calculated by means of the ΔSCF method using the B3LYP/6-31G* optimized geometries of S_1, T_1, and S_0 states. To further investigate the effect of basis sets on adiabatic ΔE_{ST} values, we have calculated the adiabatic E_S and E_T energies with 6-31G* and 6-31+G* basis set along with and compared in Figure S4 (supporting information). As shown in the Figure S4, both basis sets give the similar trends of the ΔE_{ST} values for five experimentally reported host materials. Thus, for all the adiabatic E_S and E_T values are calculated using 6-31G* basis set.

References

1) D. Jacquemin, E. A. Perpète, I. Ciofini and C. J. Adamo, *J. Chem. Theory Comput*, 2010, **6**, 1532.
2) D. Jacquemin, V. Wathelet, E. A. Perpète and C. Adamo, *J. Chem. Theory Comput.*, 2009, **5**, 2420.

Table S1: Calculated HOMO and LUMO Energies (E_H and E_L) and Available Experimental Values for the Reference Molecules (Units in eV)

	E_H											
	BP86	**O3LYP**	**B3LYP**	**PBE0**	**M06**	**BMK**	**BH&HLYP**	**M06-2X**	**M06-HF**	**CAM-B3LYP**	**LC-ωPBE**	**ω-B97XD**	**Exp**
1	-5.28	-5.56	-5.89	-6.09	-6.17	-6.55	-6.84	-7.08	-8.66	-7.19	-8.38	-7.73	−6.08[a]
2	-5.28	-5.57	-5.89	-6.08	-6.11	-6.55	-6.81	-7.06	-8.67	-7.18	-8.37	-7.72	−6.06[a]
3	-4.99	-5.25	-5.56	-5.75	-5.81	-6.19	-6.45	-6.72	-8.31	-6.81	-7.98	-7.36	−5.75[a]
13	-5.03	-5.27	-5.63	-5.83	-5.91	-6.29	-6.57	-6.83	-6.83	-6.92	-8.10	-7.45	-5.90[b]
16	-5.09	-5.33	-5.69	-5.89	-5.97	-6.35	-6.63	-6.89	-8.45	-6.98	-8.15	-7.51	-6.10[c]
FIrpic	-5.13	-5.46	-5.91	-6.10	-6.07	-6.81	-7.08	-7.36	-9.29	-7.31	-8.49	-7.78	−5.70[d]
mCP	-5.10	-5.36	-5.71	-5.90	-5.96	-6.35	-6.62	-6.88	-8.45	-6.97	-8.15	-7.50	−6.10[e]
TAPC	-4.32	-4.56	-4.91	-5.07	-5.18	-5.51	-5.81	-6.06	-7.60	-6.15	-7.29	-6.66	-5.50[f]
TmPyPB	-5.82	-6.11	-6.43	-6.66	-6.65	-7.15	-7.35	-	-	-7.77	-9.04	-8.34	-6.70[f]
	E_L												
1	-2.19	-1.58	-1.43	-1.28	-1.28	-0.70	-0.29	-0.59	0.30	-0.24	0.69	0.38	−2.40[a]
2	-2.20	-1.58	-1.44	-1.29	-1.30	-0.72	-0.29	-0.60	0.26	-0.25	0.68	0.37	−2.43[a]
3	-2.12	-1.50	-1.35	-1.21	-1.22	-0.63	-0.21	-0.52	0.23	-0.17	0.76	0.49	−2.31[a]
13	-2.21	-1.64	-1.46	-1.30	-1.30	-0.74	-0.32	-0.62	-0.62	-0.27	0.66	0.36	-2.45[b]
16	-2.58	-2.00	-1.82	-1.65	-1.65	-1.08	-0.66	-0.95	0.06	-0.61	0.33	0.01	-2.52[c]
FIrpic	-2.96	-2.32	-2.16	-1.96	-1.96	-1.35	-0.92	-1.19	-0.14	-0.91	0.02	-0.28	−2.70[d]
mCP	-1.98	-1.42	-1.73	-1.02	-1.04	-0.47	-0.05	-0.37	0.12	0.00	0.93	0.62	−2.40[e]
TAPC	-1.51	-0.88	-0.73	-0.56	-0.92	0.03	0.34	-0.04	0.14	0.42	1.33	1.10	-2.00[f]
TmPyPB	-2.32	-1.65	-1.52	-1.37	-1.39	-0.81	-0.34	-	-	-0.30	0.68	0.34	-2.70[f]

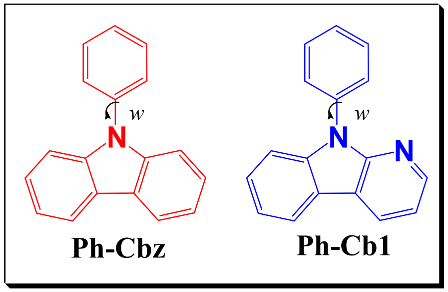
[a] Data from ref 46. [b]Data from ref 56. [c] Data from ref 59. [d] Data from ref 5. [e] Data from ref 9. [f] Data from ref *J. Phys. Chem. C* 2014, ***118***, 28757.

Table S2: DFT/B3LYP Calculated FMO Energy Levels (in eV), Adiabatic IPs/EAs (in eV), and Relaxation Energy (λ_1, λ_2, λ_3 and λ_4) for the Designed Host Molecules at B3LYP/6-31+G* level.

Hosts	HOMO	LUMO	IP	EA	λ_1	λ_2	λ_3	λ_4
1	-5.89	-1.43	7.01	0.38	0.10	0.10	0.06	0.06
2	-5.89	-1.44	6.94	0.39	0.07	0.08	0.06	0.07
3	-5.56	-1.35	6.61	0.29	0.09	0.09	0.05	0.05
4	-5.96	-1.73	7.13	0.59	0.11	0.10	0.06	0.06
5	-5.95	-1.69	7.06	0.59	0.08	0.08	0.07	0.07
6	-5.77	-1.47	6.75	0.47	0.09	0.10	0.07	0.08
7	-5.80	-1.44	6.79	0.42	0.18	0.17	0.06	0.06
8	-5.77	-1.45	6.73	0.43	0.15	0.14	0.06	0.07
9	-5.50	-1.37	6.41	0.32	0.16	0.17	0.05	0.06
10	-5.88	-1.75	6.90	0.63	0.18	0.18	0.06	0.06
11	-5.86	-1.71	6.84	0.63	0.16	0.15	0.07	0.07
12	-5.66	-1.49	6.55	0.51	0.17	0.18	0.07	0.07
13	-5.63	-1.46	6.90	0.31	0.06	0.05	0.08	0.11
14	-5.64	-1.44	6.85	0.36	0.04	0.05	0.13	0.24
15	-5.54	-1.22	6.59	0.24	0.05	0.05	0.10	0.21
16	-5.69	-1.82	6.99	0.55	0.07	0.06	0.08	0.09
17	-5.69	-1.78	6.95	0.54	0.05	0.05	0.09	0.10
18	-5.60	-1.55	6.72	0.41	0.05	0.06	0.09	0.10
19	-5.61	-1.48	6.74	0.35	0.12	0.11	0.07	0.14
20	-5.61	-1.46	6.69	0.41	0.10	0.10	0.15	0.24
21	-5.48	-1.25	6.41	0.28	0.12	0.12	0.11	0.12
22	-5.66	-1.84	6.84	0.56	0.12	0.11	0.06	0.13
23	-5.67	-1.80	6.79	0.57	0.11	0.10	0.09	0.10
24	-5.55	-1.57	6.53	0.44	0.12	0.13	0.08	0.10
FIrpic	-5.91	-2.16	6.96	1.06	-	-	-	-
TAPC	-4.91	-0.73	5.80	-0.11	-	-	-	-
TmpyPB	-6.43	-1.52	7.41	0.68	-	-	-	-

Table S3: Calculated HOMO, HOMO-1, LUMO, LUMO+1 and LUMO+2 Energies of the subunits at the B3LYP/6-31+G* method.

Subunits	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
Ph-Cbz	-5.98	-5.62	-1.05	-0.86	-0.77
Ph-Cb1	-6.25	-5.88	-1.42	-0.74	-0.56
DBF	-6.43	-6.30	-1.32	-0.35	-0.16
DBT	-6.34	-6.06	-1.32	-0.55	-0.46
BFP	-6.78	-6.57	-1.71	-0.66	-0.31
BTP	-6.61	-6.33	-1.68	-0.86	-0.65



Ph-Cbz **Ph-Cb1**

Table S4: Torsional angles (ω) between core moieties (Ph-Cb1, Ph-Cbz) and substituted host molecules in the ground state.

	Ph-Cb1	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
ω	51.55	52.09	51.51	52.40	51.64	51.31	51.80	50.03	50.03	51.19	49.67	49.74	50.80
	Ph-Cbz	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**
ω	56.07	56.09	55.70	56.55	56.55	55.51	56.08	55.24	54.95	55.76	54.63	54.60	55.16

The torsional angle ω is defined as an angle between the mean plane of carbazole moiety and the phenyl moiety.

Table S5: The % Molecular Orbital Contribution of the HOMO and LUMO of the Ph-Cb1 based host.

		PhCb1-Based Hosts			
Hosts		E (eV)	(%) PhCb1	(%) R_1	(%) R_2
1	HOMO	-5.59	97.47	-	2.53
	LUMO	-1.05	99.74	-	0.26
2	HOMO	-5.59	89.77	-	10.23
	LUMO	-1.06	99.77	-	0.23
3	HOMO	-5.27	13.60	-	86.40
	LUMO	-0.98	99.81	-	0.19
4	HOMO	-5.65	98.43	-	1.57
	LUMO	-1.35	6.09	-	93.91
5	HOMO	-5.66	97.09	-	2.91
	LUMO	-1.33	6.20	-	93.80
6	HOMO	-5.46	24.99	-	75.01
	LUMO	-1.09	6.23	-	93.77
7	HOMO	-5.48	83.69	16.31	-
	LUMO	-1.07	99.97	0.03	-
8	HOMO	-5.47	70.94	29.06	-
	LUMO	-1.08	99.94	0.06	-
9	HOMO	-5.19	37.50	62.50	-
	LUMO	-1.00	99.98	0.02	-
10	HOMO	-5.56	88.32	11.68	-
	LUMO	-1.37	5.56	94.44	-
11	HOMO	-5.55	81.03	18.97	-
	LUMO	-1.35	5.50	94.50	-
12	HOMO	-5.34	53.67	46.33	-
	LUMO	-1.12	5.70	94.30	-

Table S6: The % Molecular Orbital Contribution of the HOMO and LUMO of the Ph-Cbz based host.

		PhCbz-Based Hosts			
Hosts		E (eV)	(%) PhCbz	(%) R_1	(%) R_2
13	HOMO	-5.33	99.43	-	0.57
	LUMO	-1.07	9.96	-	90.04
14	HOMO	-5.35	99.36	-	0.64
	LUMO	-1.08	9.95	-	90.05
15	HOMO	-5.25	97.89	-	2.11
	LUMO	-0.84	15.68	-	84.32
16	HOMO	-5.40	99.45	-	0.55
	LUMO	-1.45	6.58	-	93.42
17	HOMO	-5.40	99.40	-	0.60
	LUMO	-1.42	6.19	-	93.81
18	HOMO	-5.31	99.14	-	0.86
	LUMO	-1.19	6.73	-	93.27
19	HOMO	-5.31	94.97	5.03	-
	LUMO	-1.09	9.66	90.34	-
20	HOMO	-5.31	92.43	7.57	-
	LUMO	-1.10	8.97	91.03	-
21	HOMO	-5.16	73.89	26.11	-
	LUMO	-0.86	21.75	78.25	-
22	HOMO	-5.37	95.95	4.05	-
	LUMO	-1.46	5.76	94.24	-
23	HOMO	-5.37	94.41	5.59	-
	LUMO	-1.44	5.67	94.33	-
24	HOMO	-5.25	85.61	14.39	-
	LUMO	-1.20	5.97	94.03	-

Table S7: DFT/B3LYP Calculated FMO Energy Levels (in eV), Adiabatic IPs/EAs (in eV), and Relaxation Energy (λ_1, λ_2, λ_3 and λ_4) for the Designed Host Molecules at B3LYP/6-31+G* level.

Hosts	HOMO	LUMO	IP	EA	λ_1	λ_2	λ_3	λ_4
25	-5.57	-1.83	6.36	0.79	0.06	0.06	0.11	0.13
26	-5.54	-1.95	6.38	0.86	0.13	0.09	0.07	0.07
27	-5.54	-1.90	6.38	0.85	0.12	0.09	0.07	0.07
28	-5.49	-1.68	6.32	0.73	0.14	0.10	0.08	0.08
29	-5.50	-1.61	6.33	0.70	0.12	0.09	0.07	0.08
30	-5.53	-1.96	6.37	0.89	0.12	0.09	0.07	0.07
31	-5.53	-1.92	6.37	0.88	0.12	0.09	0.07	0.07
32	-5.48	-1.69	6.30	0.76	0.09	0.12	0.08	0.08

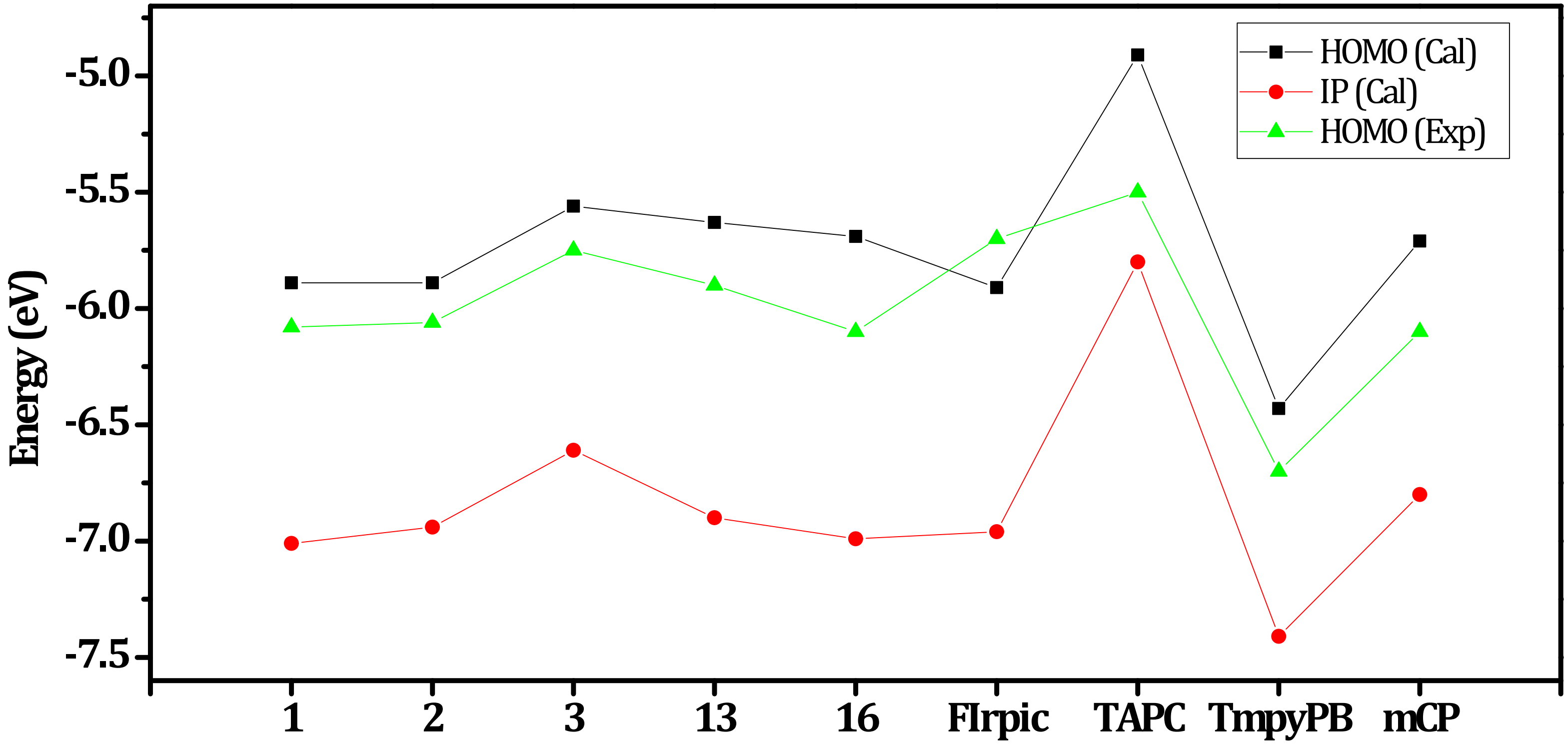


Figure S1: The calculated HOMO and IP energy values of experimentally reported reference systems at B3LYP/6-31+G* level of theory.

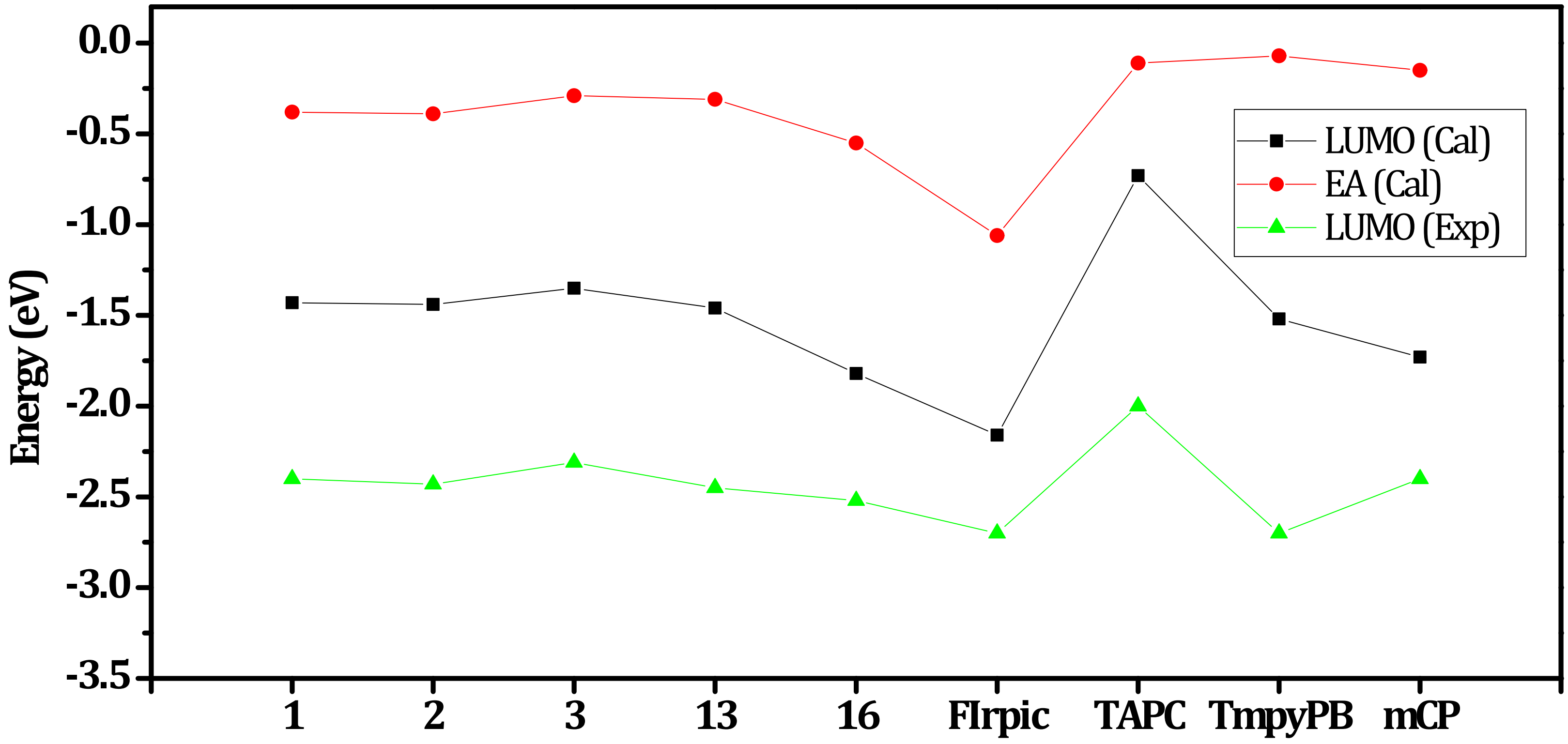


Figure S2: The calculated and experimentally reported LUMO and EA energy values of reference systems at B3LYP/6-31+G* level of theory.

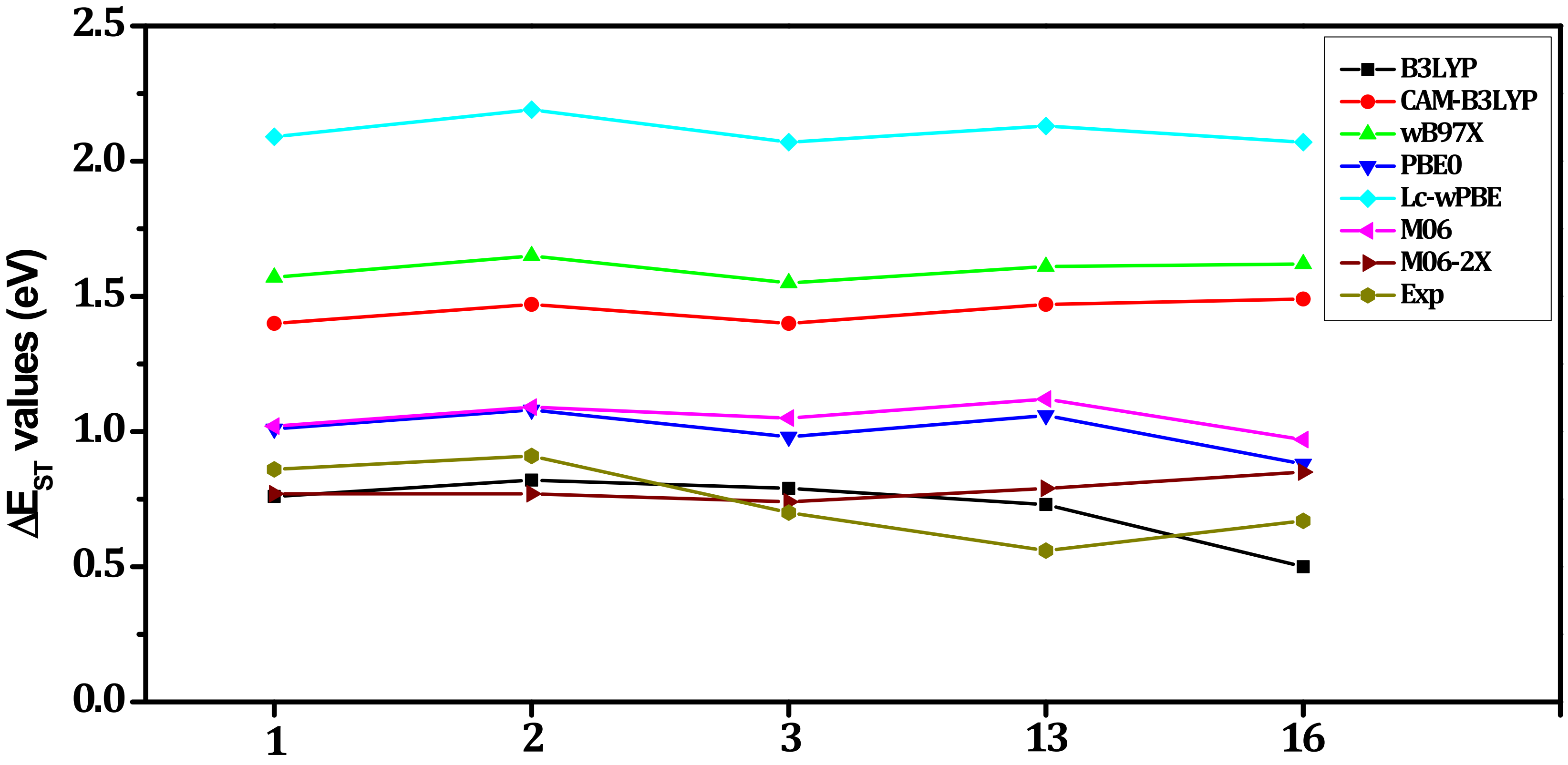


Figure S3: Evolution of ΔE_{ST} for experimentally reported host materials using different density functional with 6-31G* basis set.

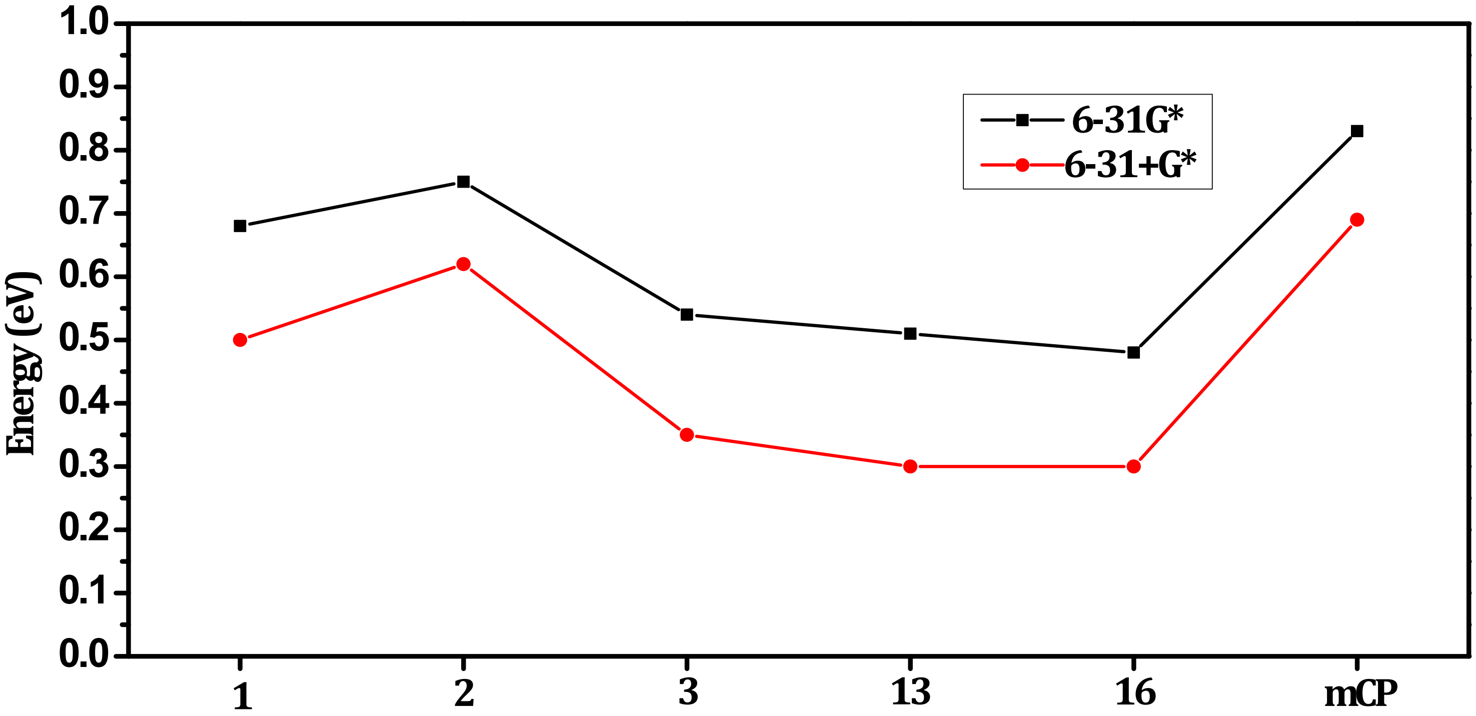
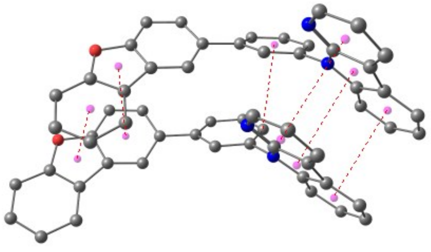
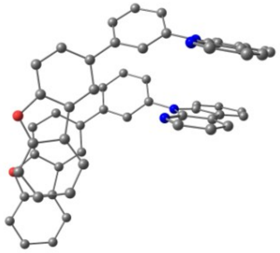
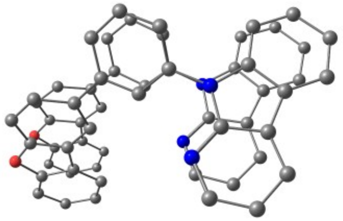
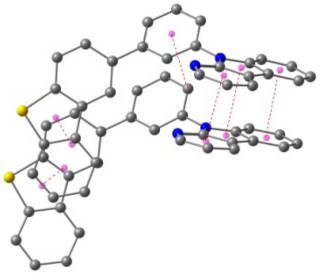
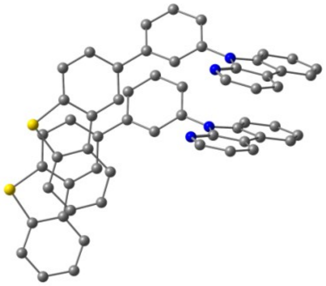
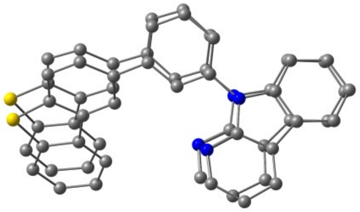
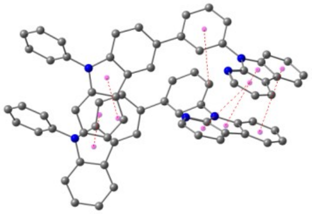
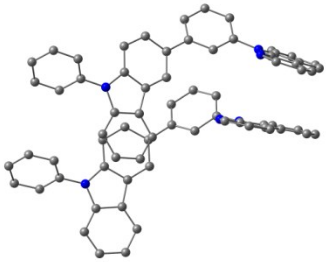
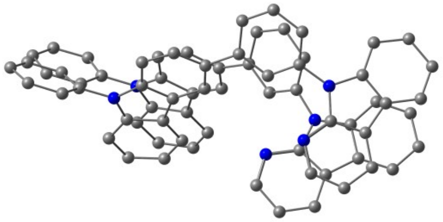
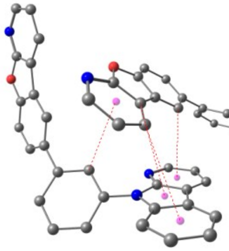
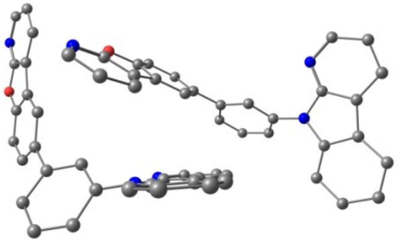
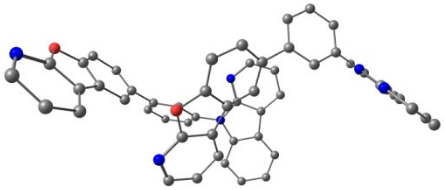
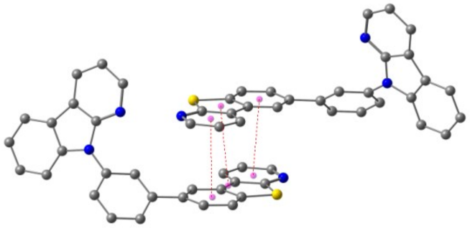
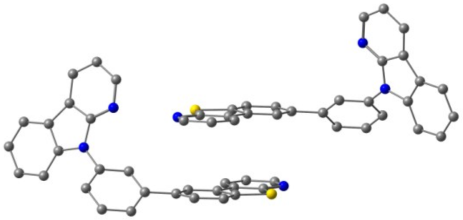
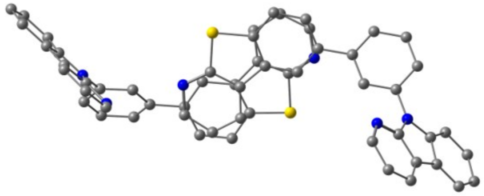
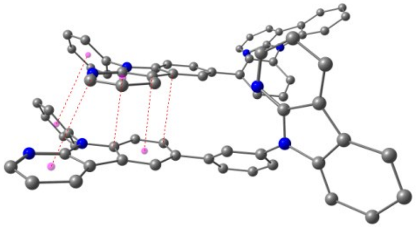
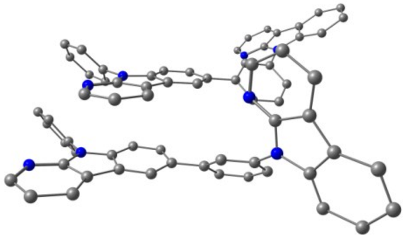
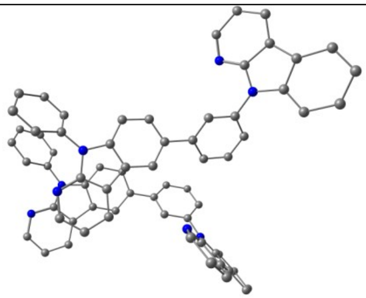
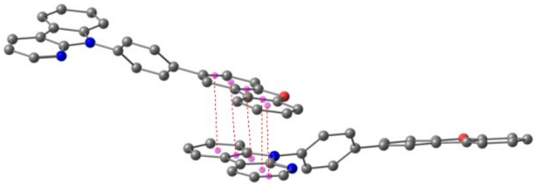
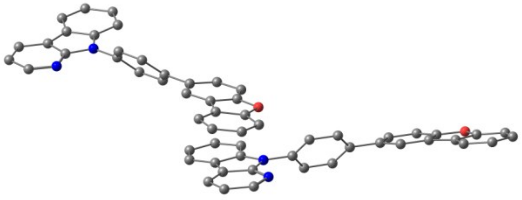
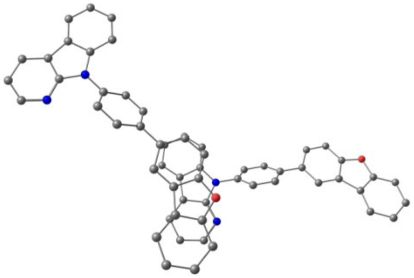
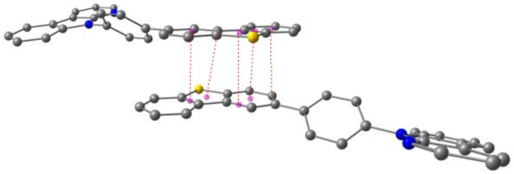
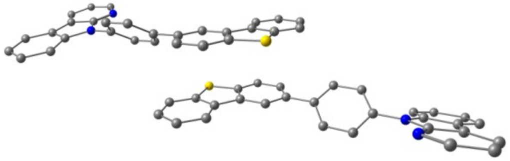
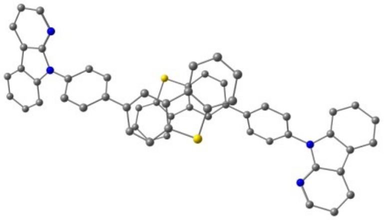
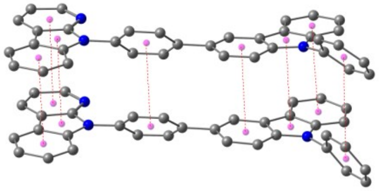
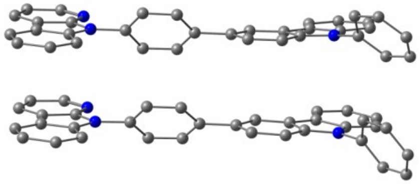
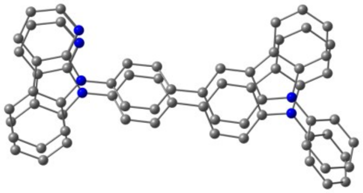
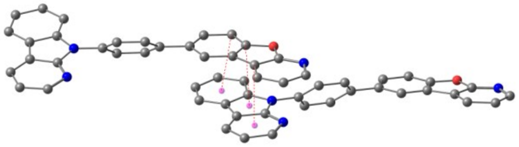
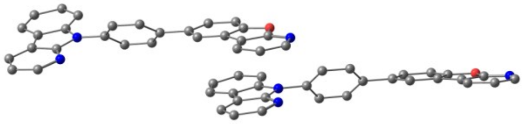
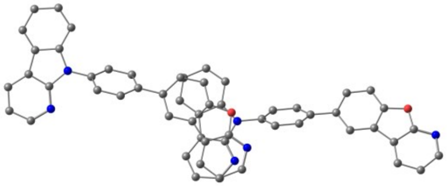
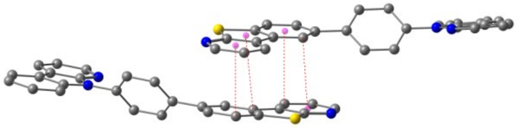
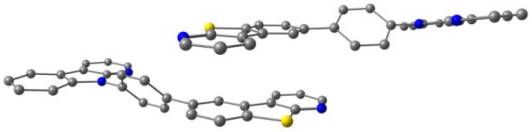
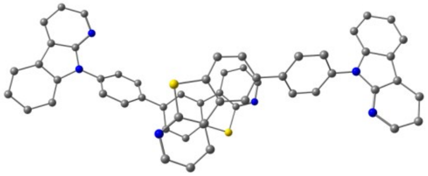
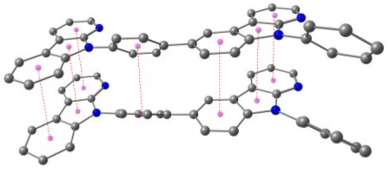
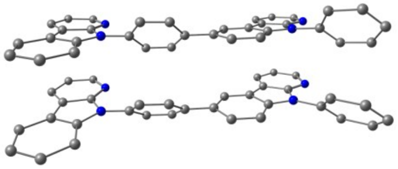
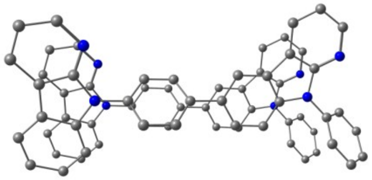
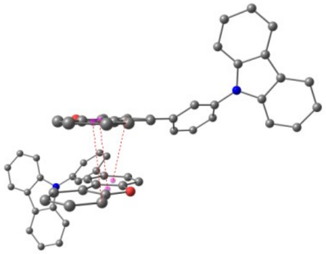
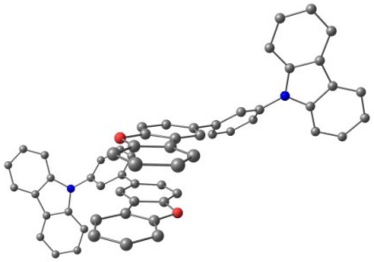
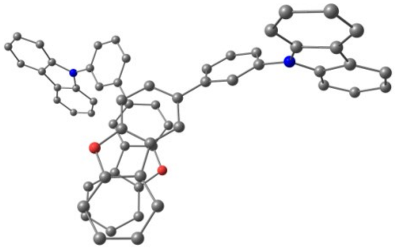
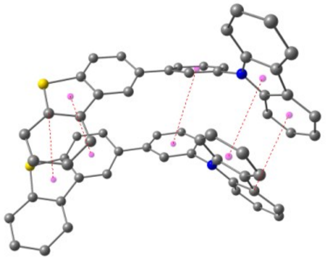
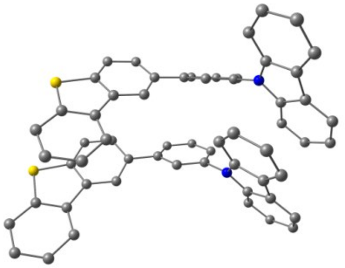
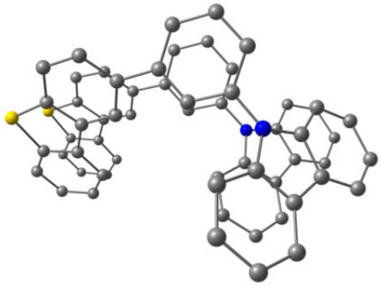
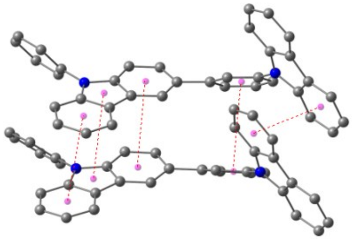
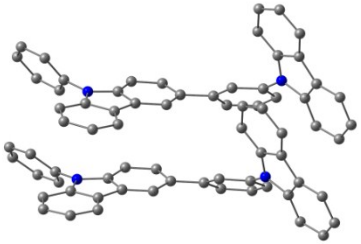
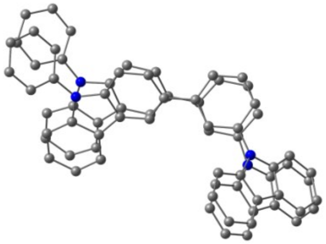
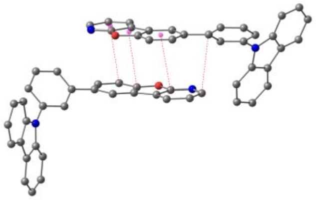
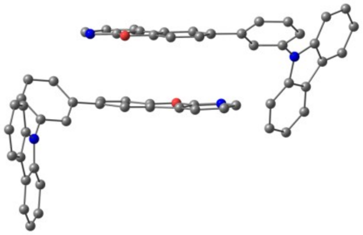
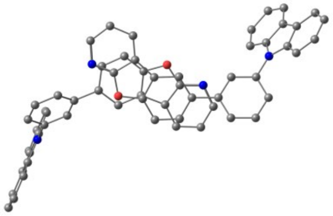
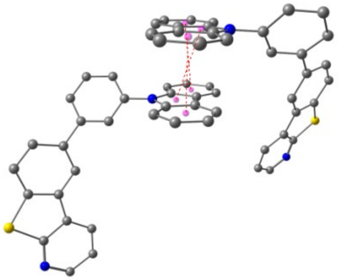
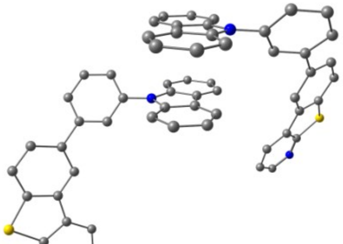
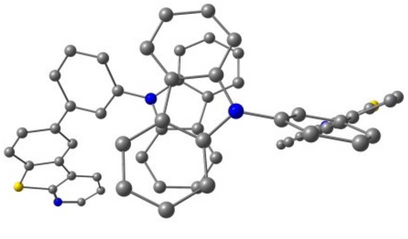


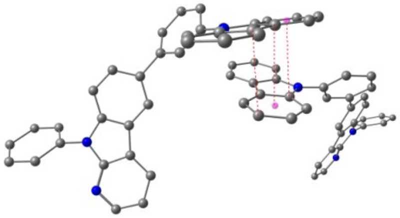
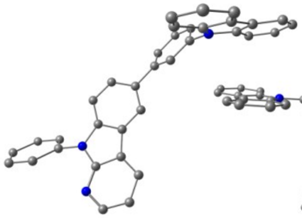
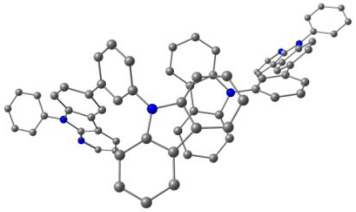
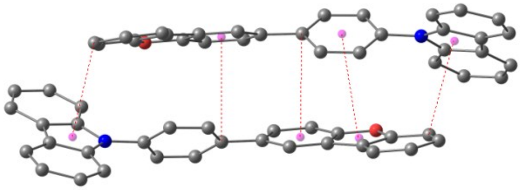
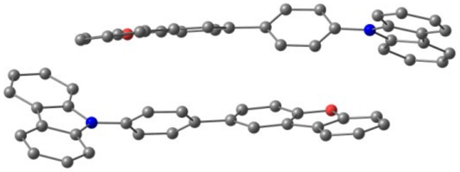
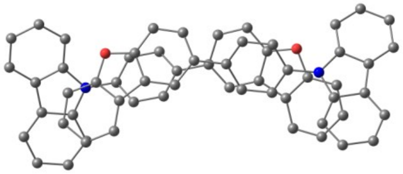
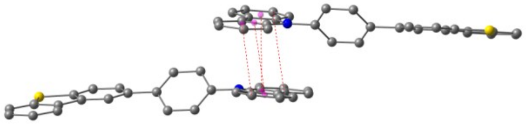
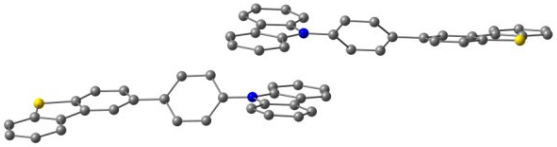
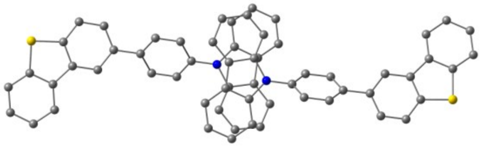
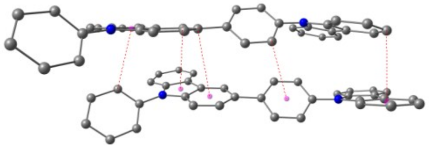
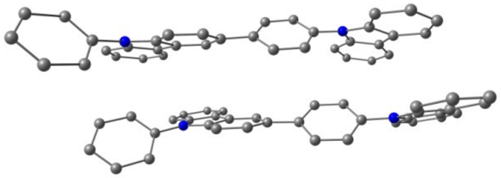
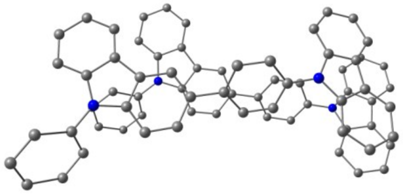
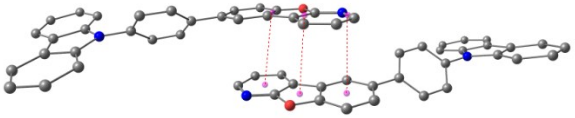
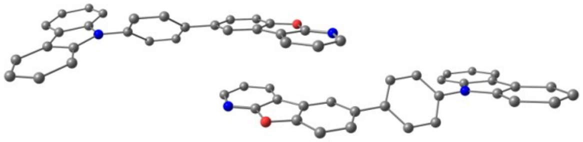
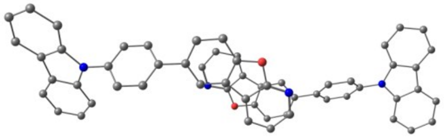
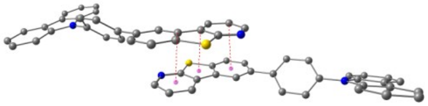
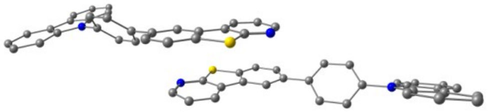
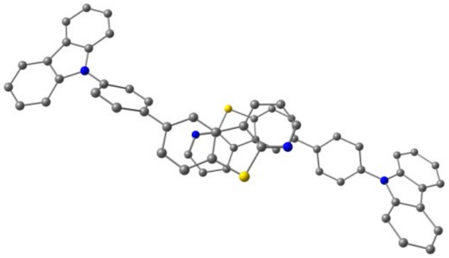
Figure S4: Evolution of ΔEST for experimentally reported systems in B3LYP functional with 6-31G* and 6-31+G** basis sets.

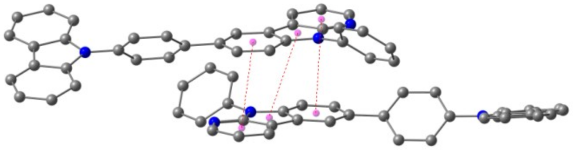
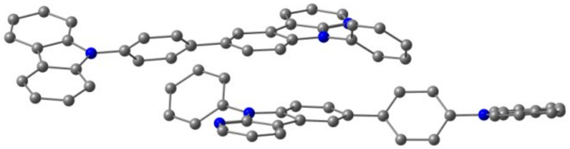
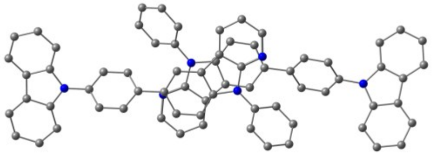
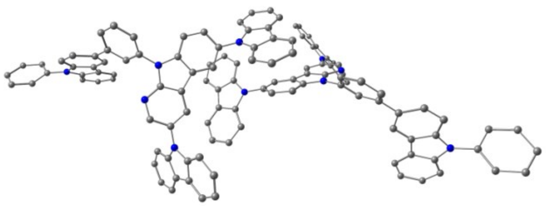
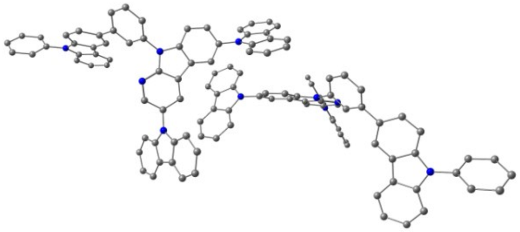
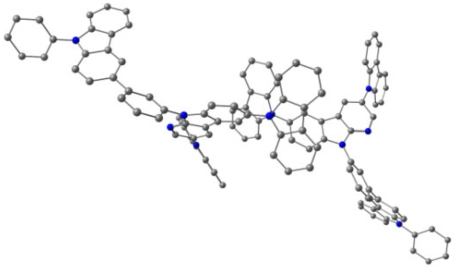
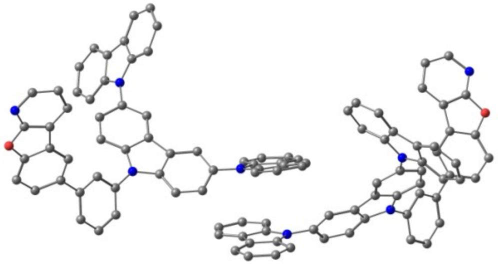
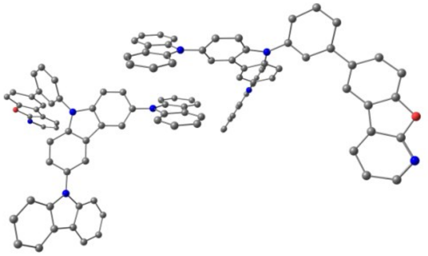
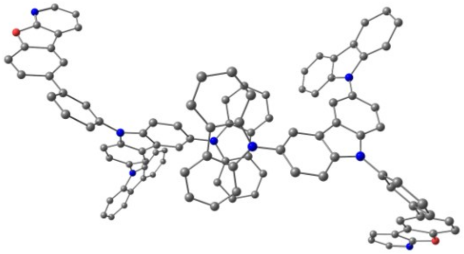
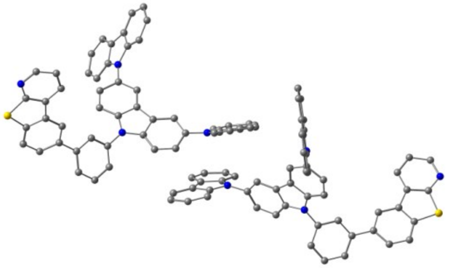
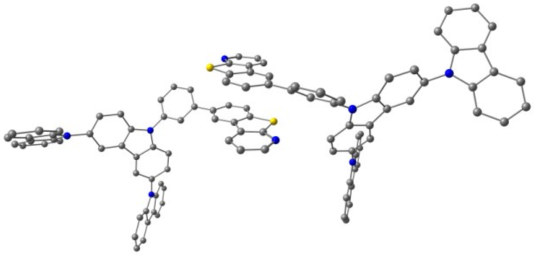
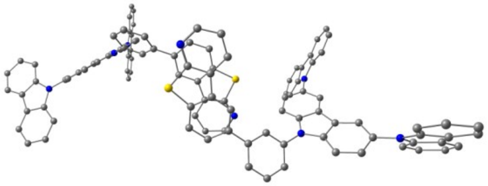
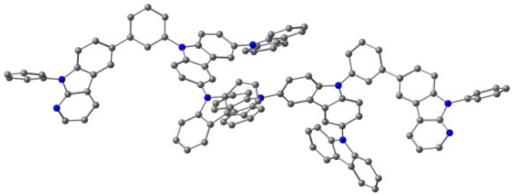
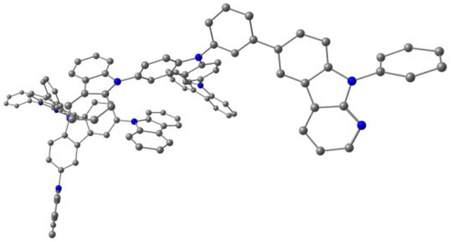
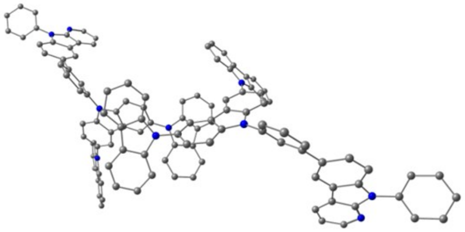
Hosts	Dimer structure	Side view	Top view
1			
2			
3			

4			
5			
6			
7			

8			
9			
10			
11			
12			
13			

14			
15			
16			
17			

18			
19			
20			
21			
22			
23			

24			
25			
26			
27			
28			

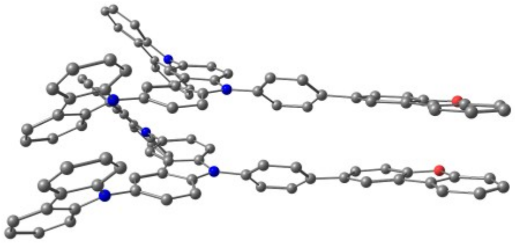
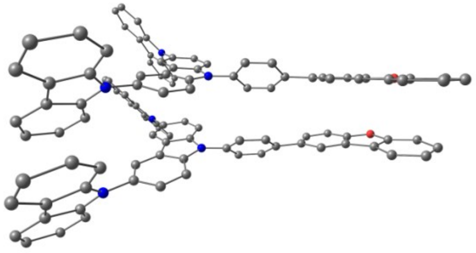
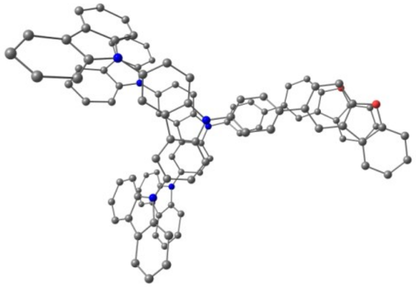
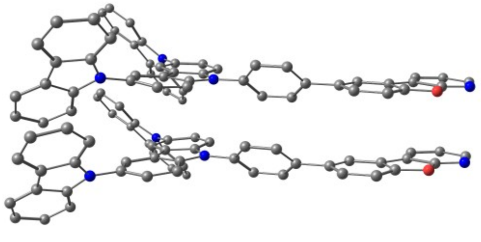
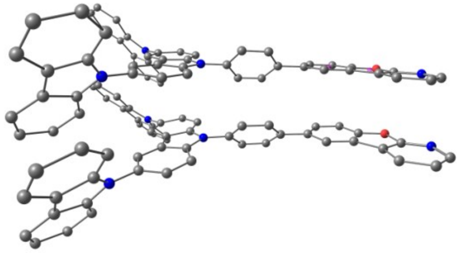
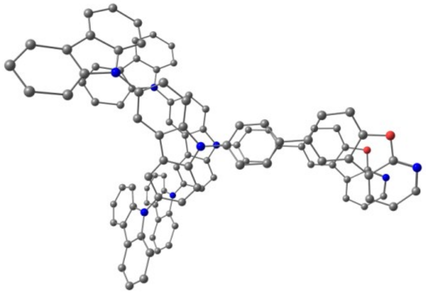
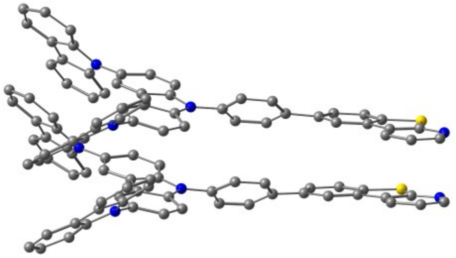
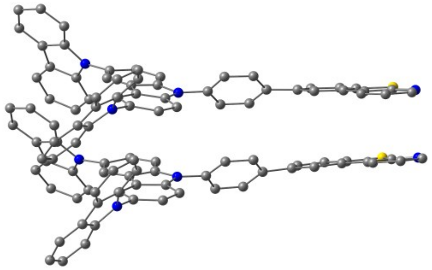
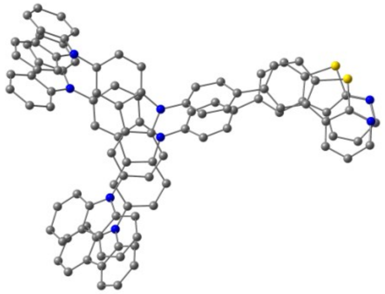
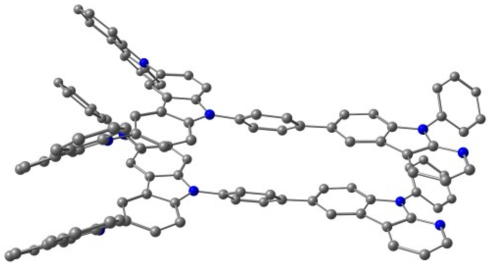
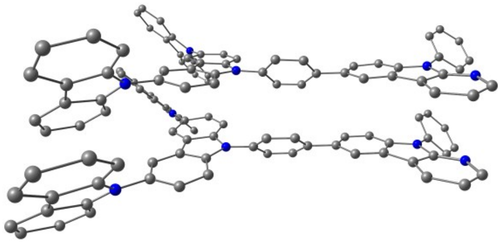
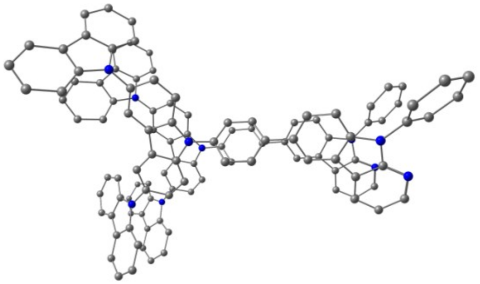
29			
30			
31			
32			

Figure S5: The M06-2X/6-31G* Optimized Geometries of hosts Dimer.

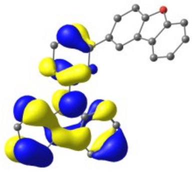
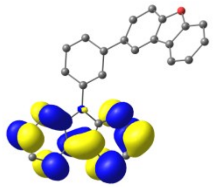
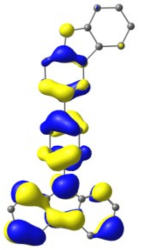
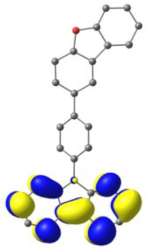
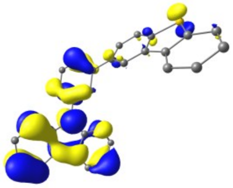
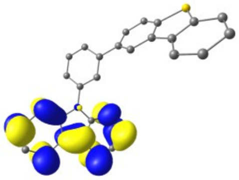
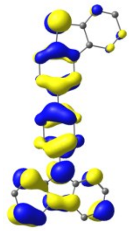
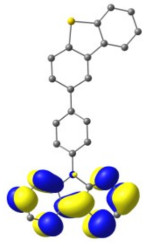
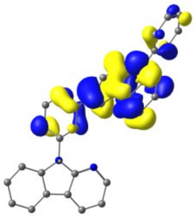
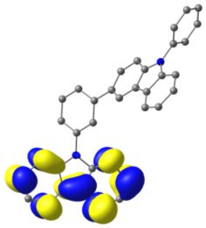
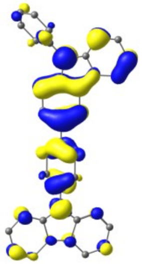
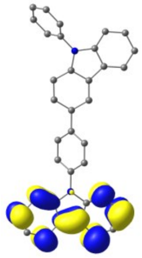
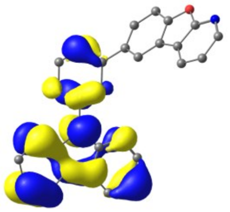
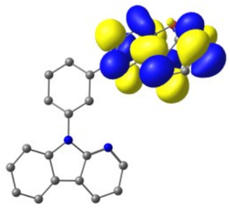
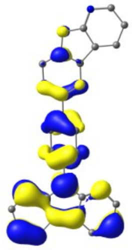
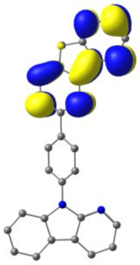
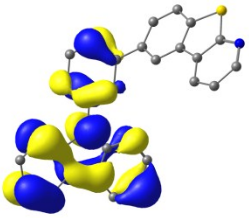
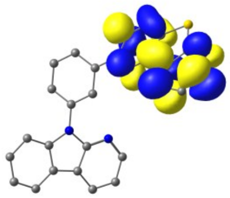
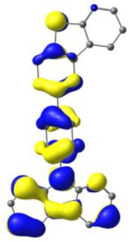
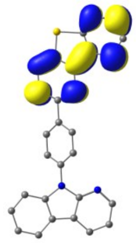
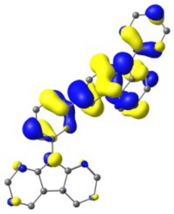
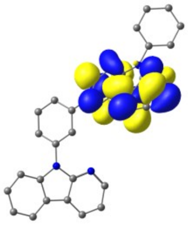
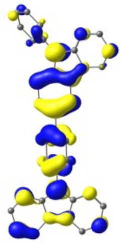
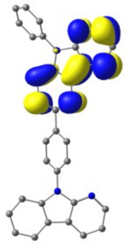
Hosts	HOMO	LUMO	Hosts	HOMO	LUMO
1			**7**		
2			**8**		
3			**9**		
4			**10**		
5			**11**		
6			**12**		

Figure S6**:** Contour plots (isosurface value = 0.03 au) of the HOMO and LUMO levels of the Ph-Cb1-based host molecules. The hydrogen atoms are omitted here for clarity.

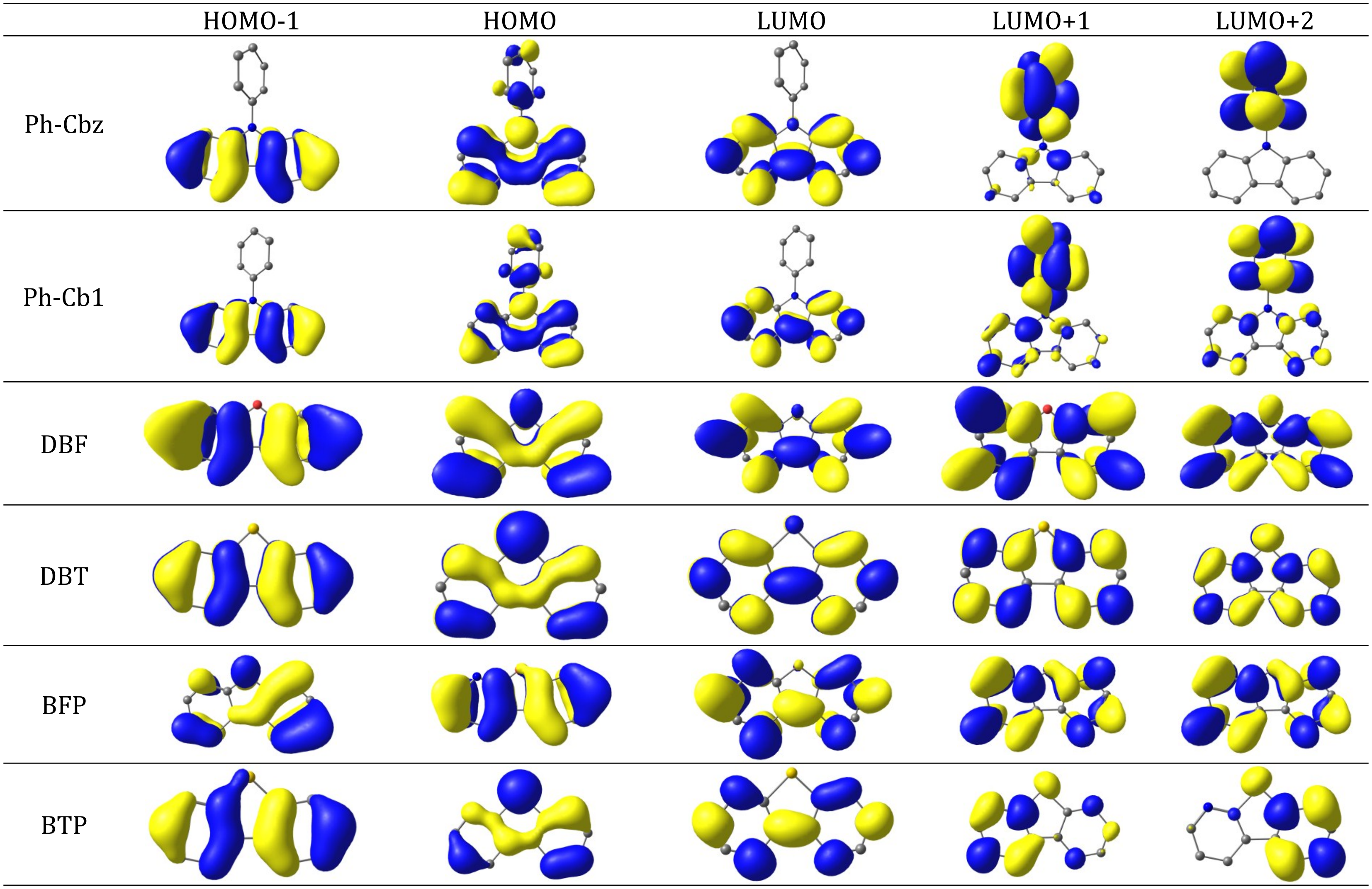


Figure S7: HOMO and LUMO Contour Plots of core units.

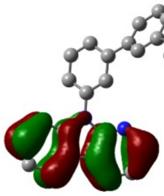
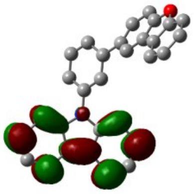
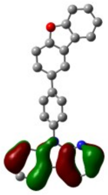
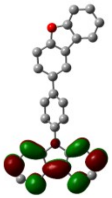
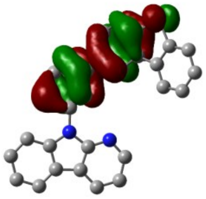
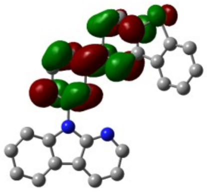
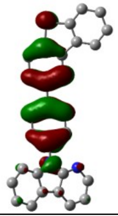
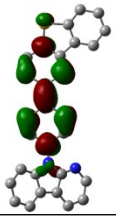
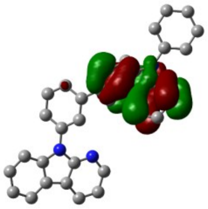
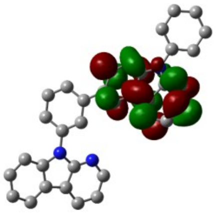
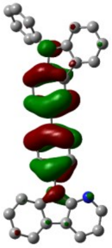
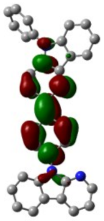
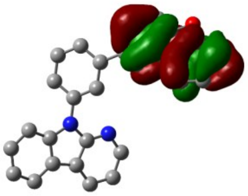
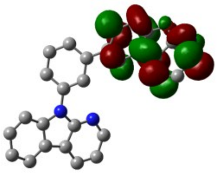
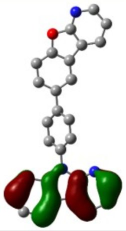
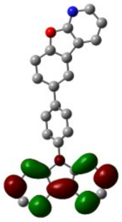
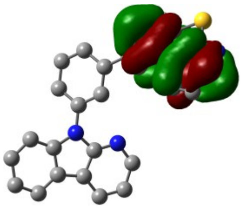
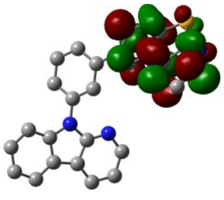
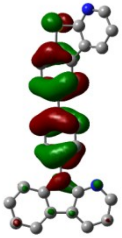
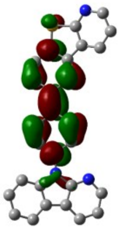
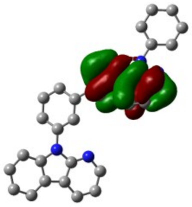
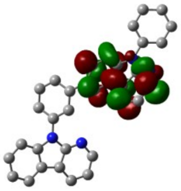
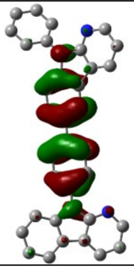
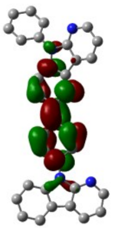
Hosts	Hole	Electron	λ	Hosts	Hole	Electron	λ
1			0.96	**7**			0.96
2			0.95	**8**			0.96
3			0.93	**9**			0.96
4			0.96	**10**			0.96
5			0.96	**11**			0.96
6			0.95	**12**			0.96

Figure S8: Hole-particle pairs of natural transition orbitals (NTOs) of the Ph-cb1 based host materials for the T_1 state (isosurface value = 0.030 au). The hydrogen atoms are omitted here for clarity.

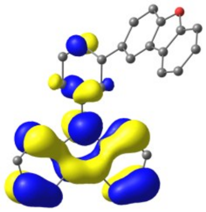
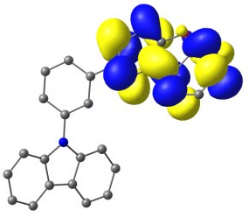
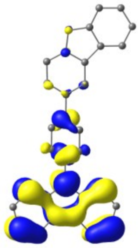
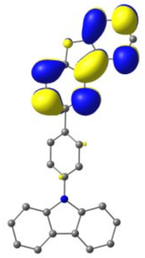
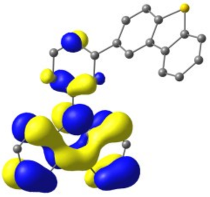
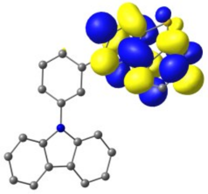
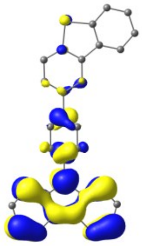
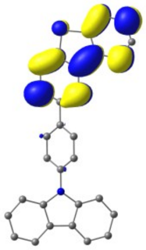
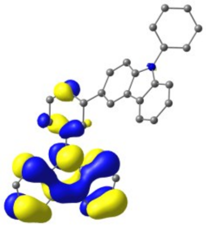
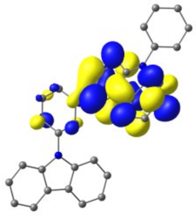
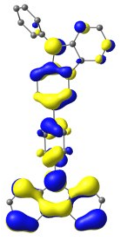
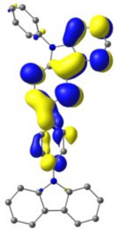
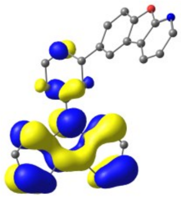
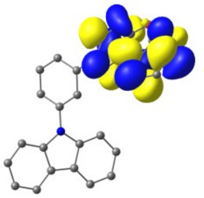
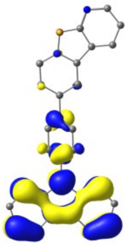
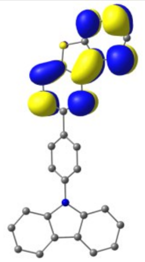
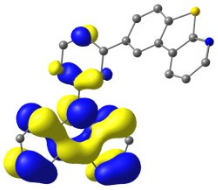
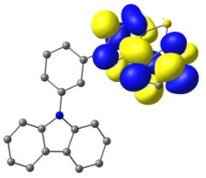
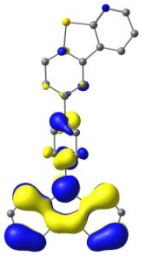
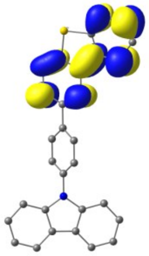
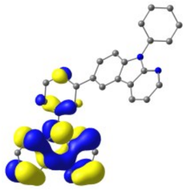
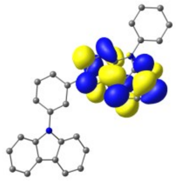
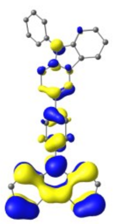
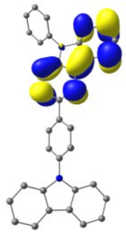
Hosts	HOMO	LUMO	Hosts	HOMO	LUMO
13			**19**		
14			**20**		
15			**21**		
16			**22**		
17			**23**		
18			**24**		

Figure S9**:** Contour plots (isosurface value = 0.03 au) of the HOMO and LUMO levels of the Ph-Cbz-based host molecules. The hydrogen atoms are omitted here for clarity.

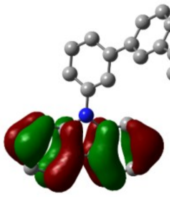
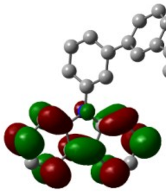
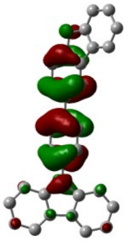
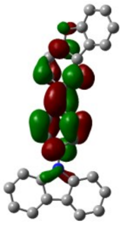
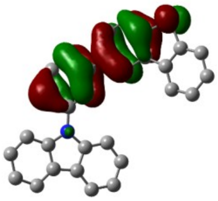
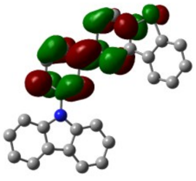
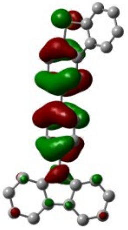
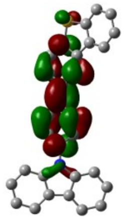
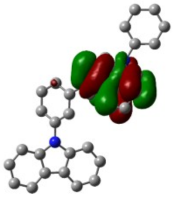
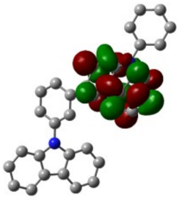
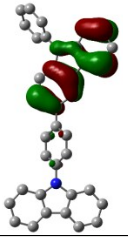
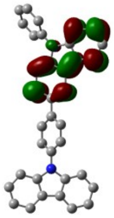
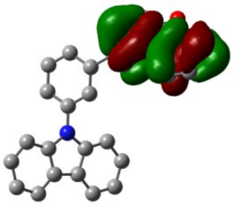
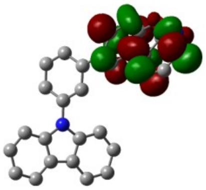
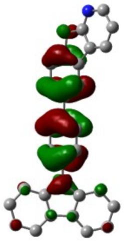
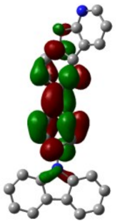
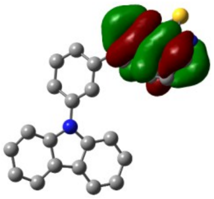
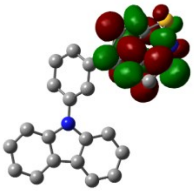
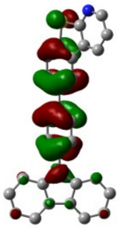
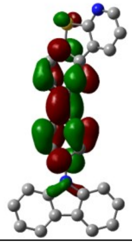
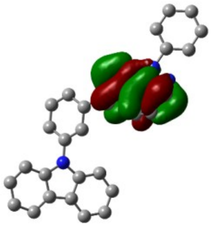
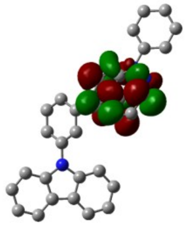
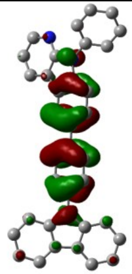
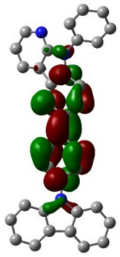
Hosts	Hole	Electron	λ	Hosts	Hole	Electron	λ
13			0.94	**19**			0.96
14			0.95	**20**			0.96
15			0.93	**21**			0.92
16			0.96	**22**			0.96
17			0.94	**23**			0.96
18			0.94	**24**			0.96

Figure S10: Hole-particle pairs of natural transition orbitals (NTOs) of the Ph-Cbz-based host materials for the T_1 state (isosurface value = 0.030 au). The hydrogen atoms are omitted here for clarity.