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Quantum chemical investigation of the formation mechanism, structures and spectra of dibenzofuran excimer and dibenzofuran–fluorene exciplex

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COMPUTATIONAL PROCEDURE

Pairs of molecules in the starting complexes were placed in parallel planes at a distance between the planes 3.5 Å, typical of vdW dimers of organic molecules. We tested different mutual orientations and shifts of molecules in the DBF−FL and DBF−DBF pairs. Configurations with substantially nonparallel orientations of molecular planes of DBF and FL molecules were not considered, because, according to the data of QC calculations for similar small molecules, these configurations are higher in energy both in the ground and excited states. Totally, we considered sixteen structures for each of the DBF−FL exciplex and DBF_2 excimer, built as described above.

The geometries of the DBF−FL and DBF_2 pairs and of the isolated constituent monomers in the ground electronic state S_0 were optimized within the density functional theory (DFT). The binding energies were found as the differences between the total energy of the complex and the sum of total energies of isolated constituent molecules.

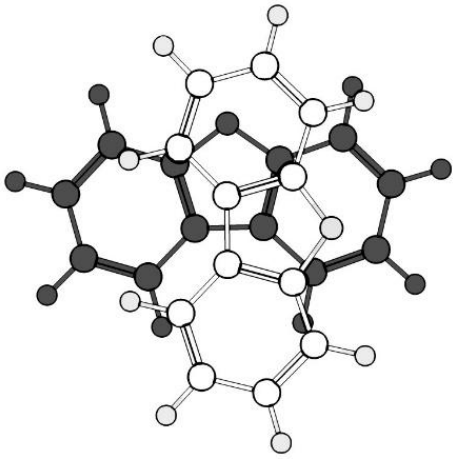
Next, energies of vertical excitations $S_0 \rightarrow S_1 \ldots S_0 \rightarrow S_5$ in the studied complexes were calculated within the TDDFT approach and low-lying charge-transfer (CT) states for the DBF−FL pairs and local-energy (LE) and CT states for the DBF_2 pairs were found.

Finally, the geometries of the DBF−FL and DBF_2 complexes in the first excited state (S_1) were optimized within the TDDFT approximation. The binding energies of exciplexes were found as the differences between the total energy of the exciplex and the sum of total energies of isolated constituent molecules, one in the ground and the other (FL) in the excited state.

All DFT and TDDFT calculations were performed using the standard BHandHLYPB functional with 50% of Hartree-Fock exchange[S1] with the Aldrich SVP[S2] basis set for geometry optimizations and TZVP[S3] basis set for single-point calculations at the optimized geometries, taking into account dispersion interactions within the Becke-Johnson damping (D3BJ) formalism.[S4,S5] The ORCA 5.0.3 software package was used.[S6]

Charge transfer between the molecules in the vdW complexes and exciplexes was estimated by calculating Mulliken charges on atoms, their summation over constituent molecules, and subtracting charges on molecules from zero. The resulting values characterized the degree of charge transfer from the donor to the acceptor in the complexes.

The minimum energy pathway between the structures corresponding to local and global minima on the potential energy surfaces of the S_0 and S_1 states were calculated by the Nudged Elastic Band (NEB) method[S7] and heights of potentil energy barriers were estimated.



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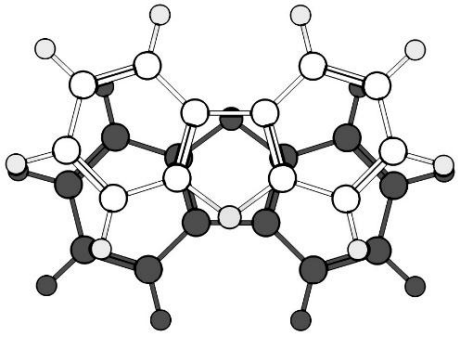

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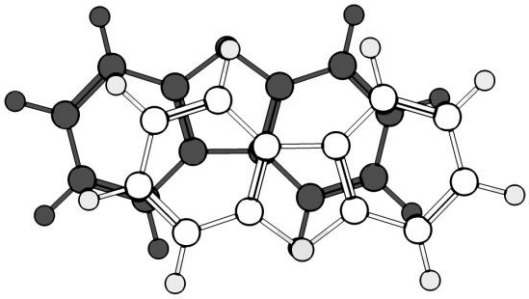

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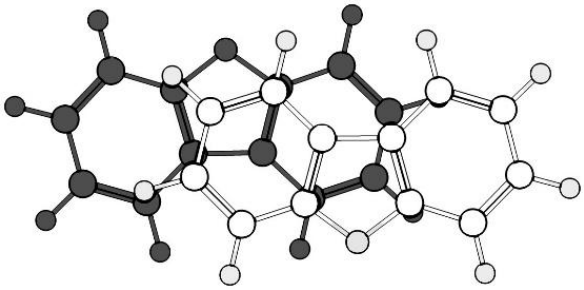

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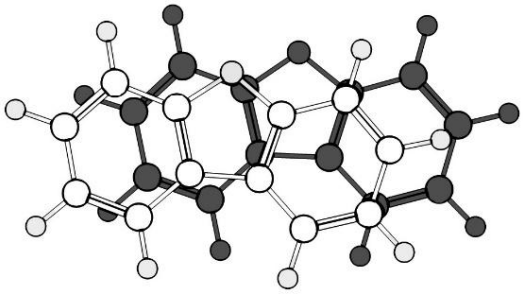

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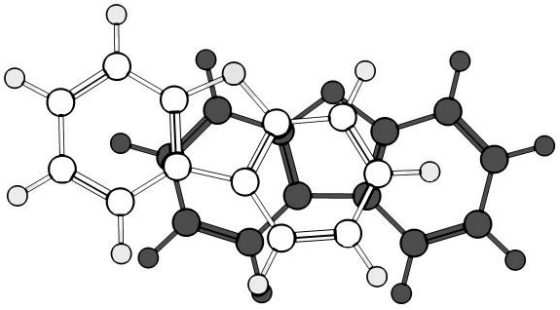

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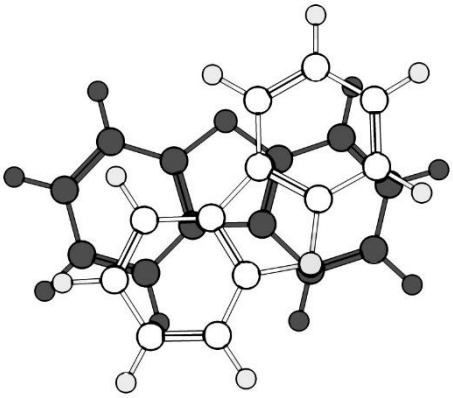

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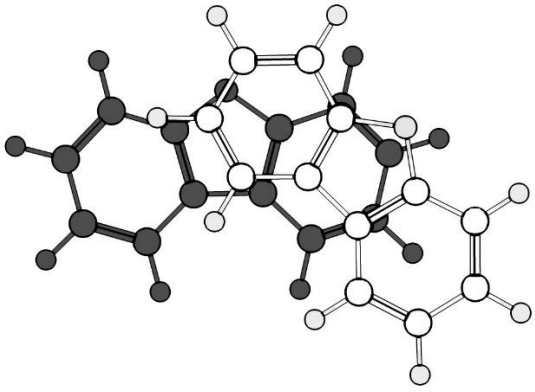
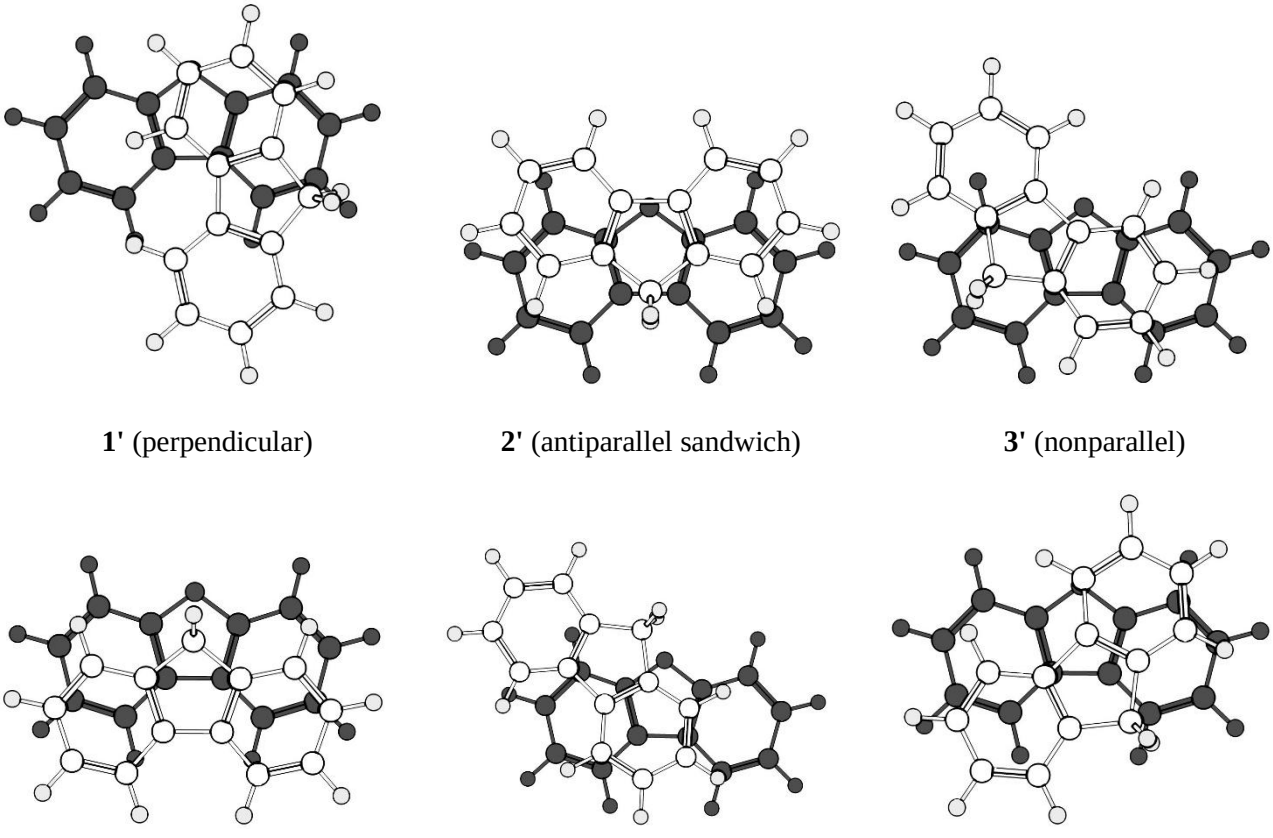


8 (nonparallel)

Figure S1 Structures of dibenzofuran dimer in the ground electronic state.

Table S1 Relative energies E_{rel}, binding energies E_b and angles between C_2 axes of DBF molecules α for the found structures of dibenzofuran dimer in the ground electronic state.

Structure	E_{rel}/kcal mol^{-1}	$-E_b$/kcal mol^{-1}	α/deg
1	0	9.3 (9.3)	87
2	1.3	7.9 (8.1)	180
3	1.2	8.1 (8.2)	180
4	1.1	8.2 (8.2)	179
5	1.2	8.1 (8.2)	1
6	1.0	8.3 (8.2)	12
7	0.7	8.6 (8.4)	150
8	1.5	7.7 (7.5)	135



1' (perpendicular) **2'** (antiparallel sandwich) **3'** (nonparallel)

4' (parallel shifted) **5'** (nonparallel) **6'** (nonparallel)

Figure S2 Structures of DBF–FL complex in the ground electronic state.

(*a*) (*b*)

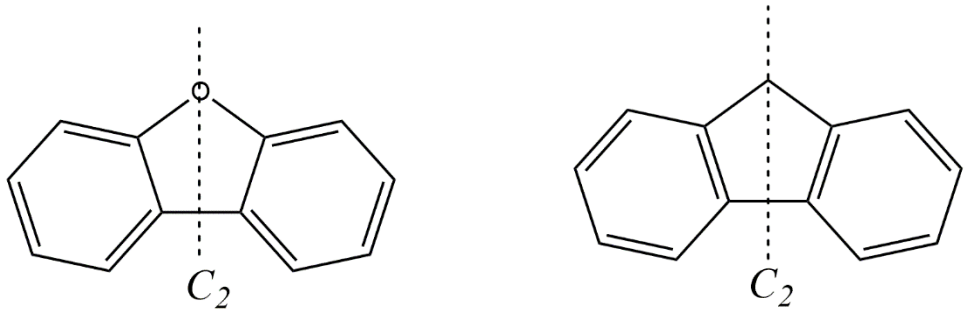


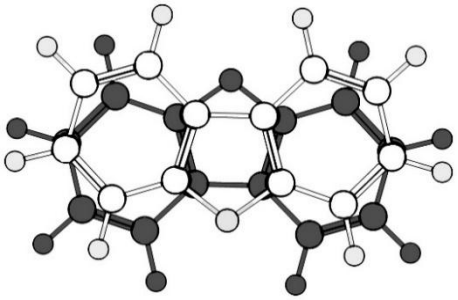
Figure S3 Structures of (*a*) DBF and (*b*) FL molecules with the C_2 symmetry axis.

Table S2 Relative energies E_{rel}, binding energies E_b, and angles between C_2 axes of molecules α for the structures of DBF–FL complex in the ground electronic state.

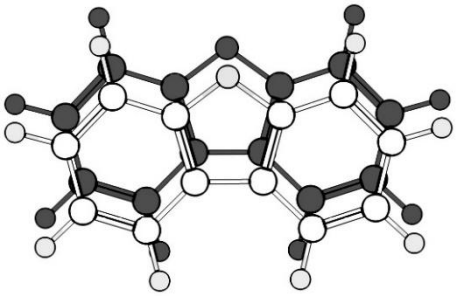
Structure	E_{rel}/kcal mol^{-1}	$-E_b$/kcal mol^{-1}	α/deg
1'	0	9.7 (9.5)	91
2'	1.1	8.6 (8.5)	180
3'	0.6	9.1 (8.9)	136
4'	1.2	9.1 (9.1)	0
5'	0.8	8.5 (8.3)	43
6'	0.7	8.8 (8.7)	135

Table S3 Calculated values of wavelength of electronic transitions λ (nm) and oscillator strengths f in absorption spectra of DBF and FL, as well as $(DBF)_2$ and DBF–FL vdW complexes.

	$S_0 \rightarrow S_1$		$S_0 \rightarrow S_2$		$S_0 \rightarrow S_3$		$S_0 \rightarrow S_4$		$S_0 \rightarrow S_5$	
	λ	f	λ	f	λ	f	λ	f	λ	f
DBF	247	0.03092	245	0.40875	216	0.01288	197	0.13815	188	0.89180
FL	249	0.23702	240	0.27093	231	0.00528	198	0.00261	194	0.02304
$(DBF)_2$ **1**	251	0.04021	251	0.01248	248	0.27243	246	0.27983	229	0.02540
$(DBF)_2$ **2**	269	0.00000	253	0.00000	248	0.03679	247	0.45881	228	0.09640
$(DBF)_2$ **3**	253	0.00001	252	0.00000	251	0.06082	247	0.44971	232	0.00000
$(DBF)_2$ **4**	256	0.00006	255	0.48879	252	0.00003	248	0.08084	227	0.00012
$(DBF)_2$ **5**	254	0.00204	251	0.00519	248	0.04218	246	0.46032	232	0.01892
$(DBF)_2$ **6**	255	0.02449	255	0.46027	251	0.02207	248	0.04119	227	0.00074
$(DBF)_2$ **7**	253	0.10587	251	0.00730	250	0.05547	245	0.36905	232	0.00563
$(DBF)_2$ **8**	253	0.09793	253	0.10976	249	0.01732	247	0.38935	228	0.00088
DBF–FL **1'**	254	0.02376	250	0.17648	248	0.24940	243	0.14126	235	0.01458
DBF–FL **2'**	270	0.00037	251	0.19724	250	0.01684	244	0.28690	234	0.00496
DBF–FL **3'**	254	0.08876	252	0.00362	249	0.31136	244	0.03914	241	0.19961
DBF–FL **4'**	268	0.00026	250	0.01926	249	0.19823	243	0.31328	234	0.00516
DBF–FL **5'**	259	0.05365	251	0.03701	247	0.36193	245	0.14715	237	0.01957
DBF–FL **6'**	254	0.08186	252	0.05182	248	0.24611	243	0.08684	238	0.10539



1* (antiparallel sandwich)



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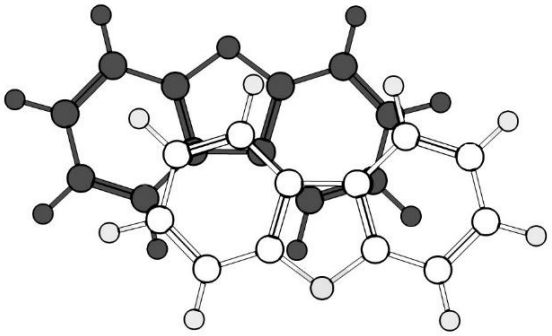

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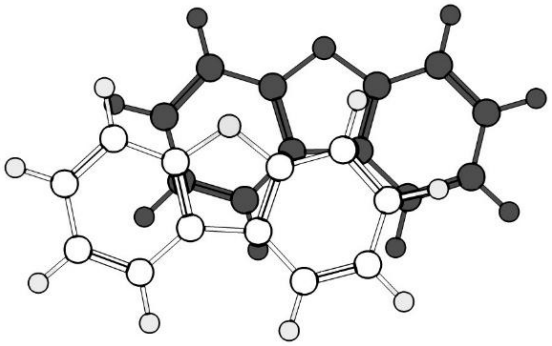

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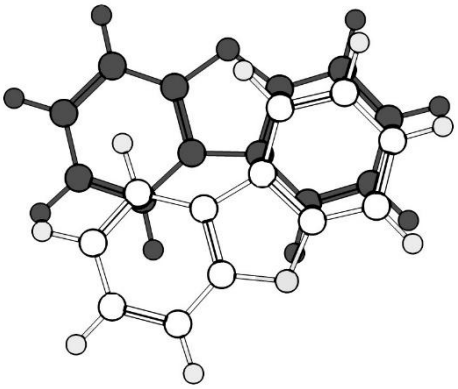

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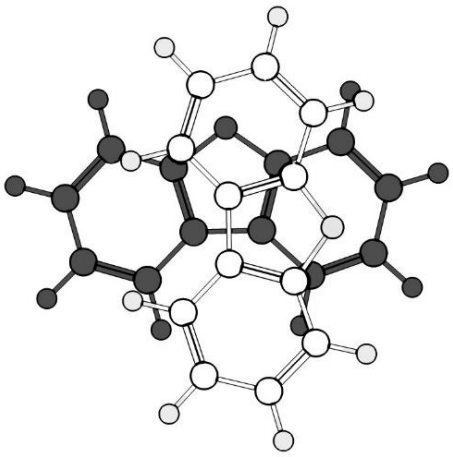

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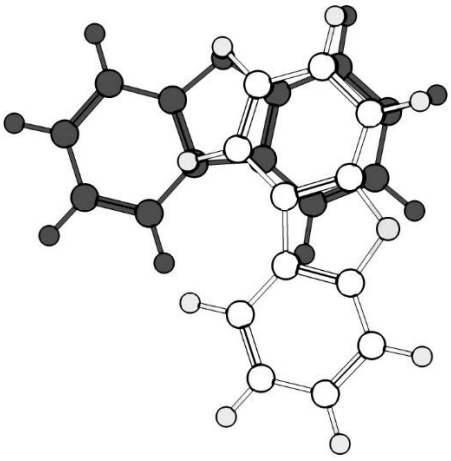
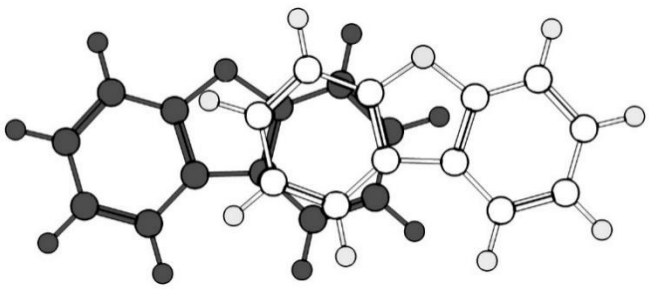


7* (perpendicular shifted)

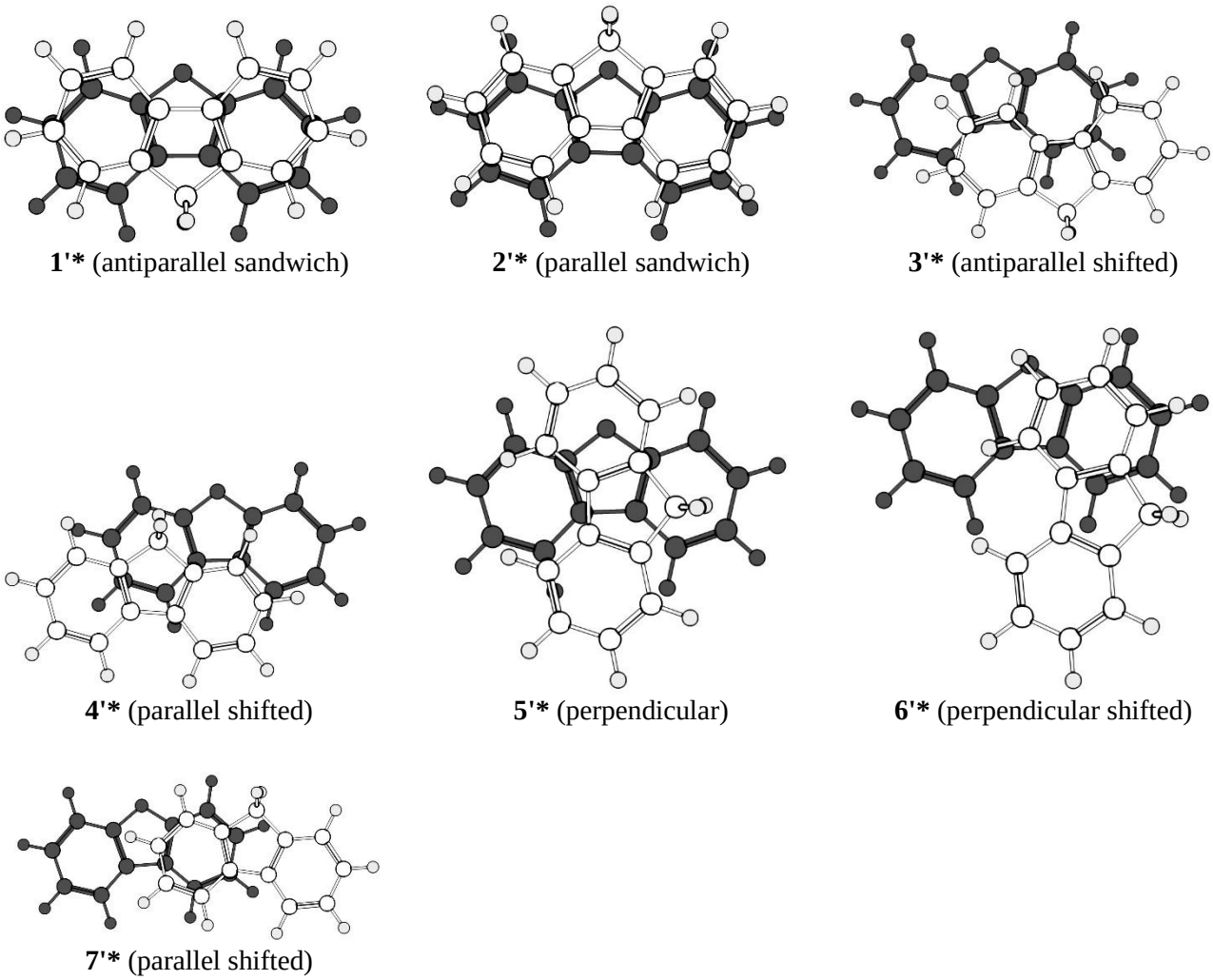


8* (parallel shifted)

Figure S4 Structures dibenzofuran dimer in the excited electronic state S_1.

Table S4 Relative energies E_{rel}, binding energies E_b, and angles between C_2 axes of molecules α for the dibenzofuran dimer structures in the excited electronic state S_1.

Structure	E_{rel}/kcal mol^{-1}	$-E_b$/kcal mol^{-1}	α/deg
1*	0	25.3 (19.3)	180
2*	1.3	24.0 (19.7)	0
3*	4.6	20.7 (17.0)	180
4*	6.2	19.1 (17.6)	4
5*	7.6	17.7 (14.4)	148
6*	8.0	17.3 (14.2)	91
7*	10.1	15.3 (13.6)	93
8*	11.5	13.8 (12.2)	4



1'* (antiparallel sandwich) **2'*** (parallel sandwich) **3'*** (antiparallel shifted)

4'* (parallel shifted) **5'*** (perpendicular) **6'*** (perpendicular shifted)

7'* (parallel shifted)

Figure S5 Structures of the DBF–FL excimer.

Table S5 Relative energies E_{rel}, binding energies E_b, angles between C_2 axes of molecules α and value of charge transfer (CT) for structures of DBF–FL complex in the excited electronic state S_1.

Structure	E_{rel}/kcal mol^{-1}	$-E_b$/kcal mol^{-1}	α/deg	CT
1'*	0	24.0 (15.3)	180	0.13
2'*	0.4	24.4 (15.1)	0	0.12
3'*	5.3	19.6 (12.4)	179	0.12
4'*	5.5	19.4 (12.6)	6	0.15
5'*	6.3	18.6 (12.2)	91	0.29
6'*	11.5	13.3 (11.4)	97	0.29
7'*	11.7	13.2 (10.9)	12	0.18

Table S6 Calculated values of wavelength of electronic transitions λ (nm) and oscillator strengths f of fluorescence bands in the spectra of DBF and FL, as well as $(DBF)_2$ excimer and DBF–FL exciplex.

Molecule	λ/nm	f	λ_{exp}/nm	References
DBF	280	0.30375	303 297 320	S12 S10 S2
FL	274	0.67255	305 296	S12 S10, S11
$(DBF)_2$ **1***	358	0.00000	300 366 370	S10 S8 S9
$(DBF)_2$ **2***	354	0.00006		
$(DBF)_2$ **3***	338	0.00000		
$(DBF)_2$ **4***	331	0.00679		
$(DBF)_2$ **5***	331	0.01120		
$(DBF)_2$ **6***	307	0.02214		
$(DBF)_2$ **7***	311	0.01581		
$(DBF)_2$ **8***	310	0.01063		
(DBF)–FL **1'***	361	0.00008	298	S10
(DBF)–FL **2'***	365	0.00029		
(DBF)–FL **3'***	339	0.00188		
(DBF)–FL **4'***	336	0.01438		
DBF–FL **5'***	317	0.08181		
DBF–FL **6'***	311	0.07026		
DBF–FL **7'***	311	0.02231		

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