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On the Origin of the Inverted Singlet-Triplet Gap of the 5th Generation Light-Emitting Molecules

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Table S1 Vertical excitation energies (in eV) calculated at the TDDFT level of theory. The molecular structures were optimized at the B3LYP/def2-TZVPD level.

Molecule →	**1**		**2**		**3**		**4**		**5**		**6**	
Method	S_1	T_1	S_1	T_1	S_1	T_1	S_1	T_1	S_1	T_1	S_1	T_1
S-VWN	1.178	1.035	2.696	2.470	1.652	1.470	1.930	1.727	2.150	1.959	2.127	1.927
BP86	-	-	2.666	2.478	1.680	1.456	1.961	1.710	2.184	1.950	2.160	1.918
PBE	1.198	1.024	2.660	2.477	1.677	1.460	1.957	1.715	2.180	1.953	2.156	1.921
TPSS	1.226	1.040	2.735	2.540	1.722	1.488	2.011	1.747	2.241	1.996	2.216	1.961
TPSSH	1.247	1.040	2.863	2.644	1.777	1.512	2.087	1.784	2.333	2.052	2.306	2.012
B3LYP	1.234	1.034	2.902	2.684	1.778	1.517	2.098	1.796	2.352	2.071	2.324	2.028
PBE0	1.262	1.026	3.000	2.750	1.829	1.526	2.161	1.811	2.426	2.101	2.397	2.055
BHLYP	1.342	1.053	3.350	3.042	1.994	1.606	2.371	1.902	2.676	2.242	2.646	2.189
MN15	1.221	1.069	2.984	2.812	1.798	1.580	2.142	1.875	2.409	2.165	2.374	2.118
CAM-B3LYP	1.266	1.011	3.118	2.854	1.875	1.542	2.230	1.839	2.510	2.147	2.478	2.096
tuned-CAM-B3LYP	1.196	1.003	2.852	2.644	1.741	1.490	2.061	1.774	2.313	2.046	2.283	2.000
ωB97X-D	1.284	1.051	3.146	2.900	1.897	1.586	2.254	1.887	2.536	2.196	2.503	2.142
LH14t-calPBE	1.241	1.033	2.983	2.760	1.778	1.517	2.145	1.829	2.411	2.117	2.379	2.068

Table S2 Percentage of HOMO-LUMO configuration in the first excited states using different *ab initio* approaches.

Molecule →	**1**		**2**		**3**		**4**		**5**		**6**	
State	S_1	T_1	S_1	T_1	S_1	T_1	S_1	T_1	S_1	T_1	S_1	T_1
XMC-CASPT2	81	93	86	90	86	91	75	85	85	93	85	94
CC2	97.9	98.5	96.5	98.1	94.1	97.7	90.9	96.4	89.3	95.6	91.5	97.6
ADC(2)	97.8	98.4	95.8	97.7	94.1	97.6	91.0	96.3	89.4	95.6	91.5	97.5

Table S3 Vertical, adiabatic, and 0–0 excitation energies calculated at the ADC(2) level of theory (in eV). The molecular structures of ground states were optimized at the MP2/def2-TZVP level of theory, whereas excited state geometries were optimized at the ADC(2)/def2-TZVP level of theory.

	Vertical		Adiabatic		0–0	
Molecule	S_1	T_1	S_1	T_1	S_1	T_1
1	0.993	1.132	0.936	1.080	0.955	1.027
2	2.663	2.913	2.582	2.838	2.437	2.551
3	1.540	1.658	1.471	1.591	1.415	1.491
4	1.915	2.002	1.779	1.906	1.692	1.764
5	2.154	2.296	2.013	2.145	1.901	1.995
6	2.087	2.218	2.008	2.142	1.905	2.002

Table S4 Vertical excitation energies (in eV) calculated at different levels of theory from literature.

Molecule →		**1**			**2**		
Ref.	method	$E(S_1)$	$E(T_1)$	ΔE_{ST}	$E(S_1)$	$E(T_1)$	ΔE_{ST}
1	SA-CASSCF/def2-TZVP	0.826	0.936	-0.110	-	-	-
1	SC-NEVPT2/def2-TZVP	1.107	1.259	-0.152	-	-	-
1	SCS-CC2/def2-TZVP	1.110	1.330	-0.220	-	-	-
2	CIS/def2-TZVP	1.797	1.460	0.337	4.328	3.918	0.410
2	CIS(D)/def2-TZVP	1.042	1.322	-0.280	2.627	3.150	-0.523
2	SCS-CC2/def2-TZVP	1.110	1.334	-0.224	2.847	3.226	-0.379
2	SCS-ADC(2)/def2-TZVP	1.080	1.308	-0.228	2.790	3.174	-0.384
3	CIS/cc-pVDZ	1.83	1.50	0.33	-	-	-
3	CIS(D)/cc-pVDZ	1.07	1.37	-0.30	-	-	-
3	ADC(2)/cc-pVDZ	1.04	1.20	-0.16	-	-	-
3	EOM-CCSD/cc-pVDZ	1.09	1.19	-0.10	-	-	-
4	RASSCF/def2-TZVP	0.65	0.93	-0.28	2.56	2.95	-0.39
4	RASPT2/def2-TZVP	0.86	0.89	-0.03	2.54	2.67	-0.13
4	CIS/def2-TZVP	1.64	1.00	0.64	4.35	3.78	0.57
4	CIS(D)/def2-TZVP	0.91	1.12	-0.21	2.49	3.10	-0.61
4	B2PLYP/def2-TZVP	1.12	1.10	0.02	2.75	2.79	-0.04
4	DLPNO-STEOM-CCSD/def2-TZVP	0.61	1.04	-0.43	2.35	3.01	-0.66
5	ADC(3)/cc-pVDZ	0.777	0.869	-0.092	2.665	2.774	-0.109
5	ADC(2)/cc-pVDZ	1.038	1.198	-0.160	2.578	2.856	-0.278
5	EOM-CCSD/cc-pVDZ	1.092	1.191	-0.099	2.791	2.971	-0.180
5	FNO-EOM-CCSD/cc-pVDZ	1.126	1.230	-0.104	3.418	3.632	-0.214
5	DLPNO-NEVPT2(6,6)/def2-SV(P)	1.112	1.301	-0.189	2.552	2.896	-0.344
5	ωB2PLYP/def2-SVP	1.316	1.274	0.042	3.028	3.246	-0.218
5	SA-SF-PBE50/def2-SVP	1.095	1.204	-0.109	2.909	3.090	-0.181
6	ADC(2)/cc-pVDZ	-	-	-	2.569	2.851	-0.282
6	CC2/cc-pVDZ	-	-	-	2.676	2.947	-0.271
6	EOM-CCSD/cc-pVDZ	-	-	-	2.781	2.963	-0.182
6	CASPT2/cc-pVDZ	-	-	-	2.326	2.551	-0.225
7	DFT/MRCI/TZVP	-	-	-	2.59	2.60	-0.01

Table S5 Vertical excitation energies calculated at various levels of theory (in eV). The molecular structures of ground states were optimized at the CASPT2(12,9)/def2-TZVP level of theory.

	CASSCF (12,9)		CASSCF (14,14)		CASPT2 (12,9)		CASPT2 (14,14)	
Molecule	S_1	T_1	S_1	T_1	S_1	T_1	S_1	T_1
1	1.154	1.317	0.632	1.005	1.165	1.313	0.958	1.064
2	3.199	3.425	1.560	2.202	2.265	2.283		
3	1.846	1.920	0.917	1.353	1.293	1.349		
4	2.487	2.321	1.694	1.777	1.680	1.898		
5	2.775	2.515	1.421	1.834	1.872	2.526		
6	2.675	2.511	1.104	1.674	1.814	1.974		

Table S6 The triplet excitation energies (in eV) obtained using the SFDFT approach.

Molecule →	**1**	**2**	**3**	**4**	**5**	**6**
T_1	1.217	3.045	1.659	1.911	2.146	2.199

Table S7 Spin contamination of the ΔSCF calculations using two DFT functionals and the Hartree-Fock level. The molecular structures were optimized at the B3LYP/def2-TZVPD level.

	B3LYP		ωB97X-D		HF	
Molecule	S_1	T_1	S_1	T_1	S_1	T_1
1	1.09	2.01	1.17	2.02	2.01	2.24
2	1.10	2.01	1.17	2.02		
3	1.09	2.01	1.16	2.02		
5	1.09	2.01	1.16	2.02		
6	1.09	2.01	1.16	2.02		

Table S8 Vertical excitation energies (in eV) calculated with the ΔSCF approach employing two DFT functionals. The molecular structures were optimized at the B3LYP/def2-TZVPD level.

	B3LYP		ωB97X-D	
Molecule	S_1	T_1	S_1	T_1
1	0.958	1.074	0.896	1.175
2	2.578	2.732	2.746	3.077
3	1.472	1.565	1.493	1.713
5	2.028	2.126	2.127	2.342
6	1.993	2.081	2.091	2.277

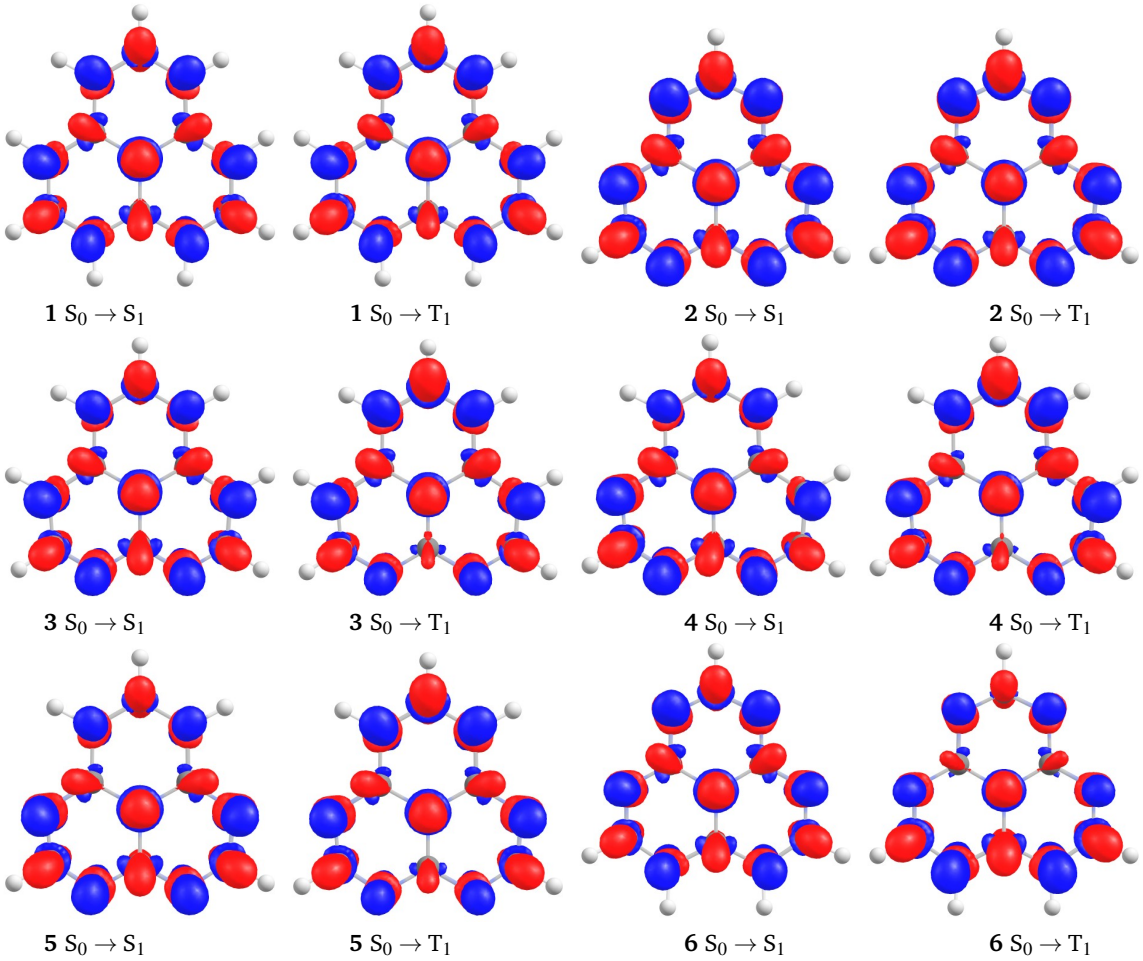

Fig. S1 Density differences for $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ excitations calculated at the DFT B3LYP/def2-TZVPD level of theory. Regions of decreasing density are in blue, red color denotes regions of increasing density (isosurface 0.004).

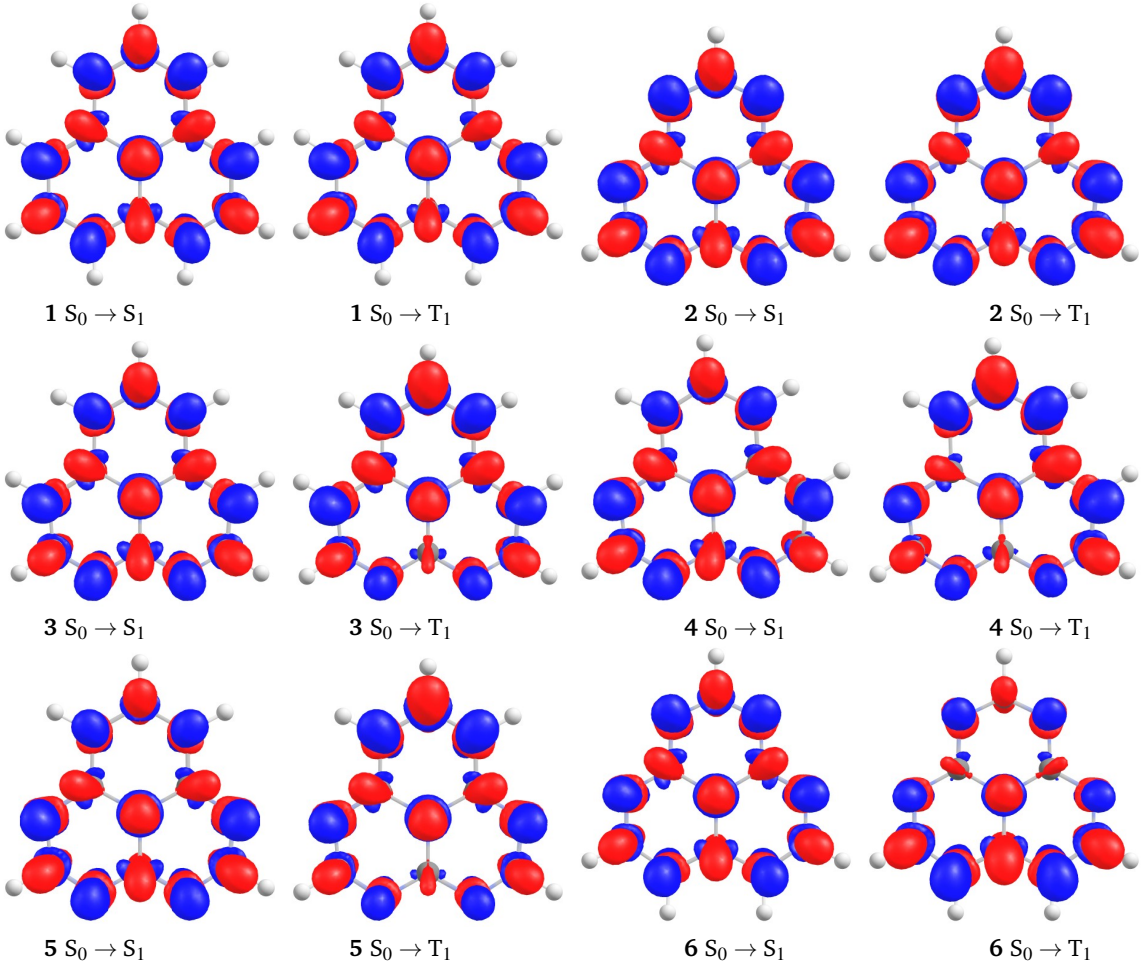

Fig. S2 Density differences for $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ excitations calculated at the DFT ωB97X-D/def2-TZVPD level of theory. Regions of decreasing density are in blue, red color denotes regions of increasing density (isosurface 0.004).

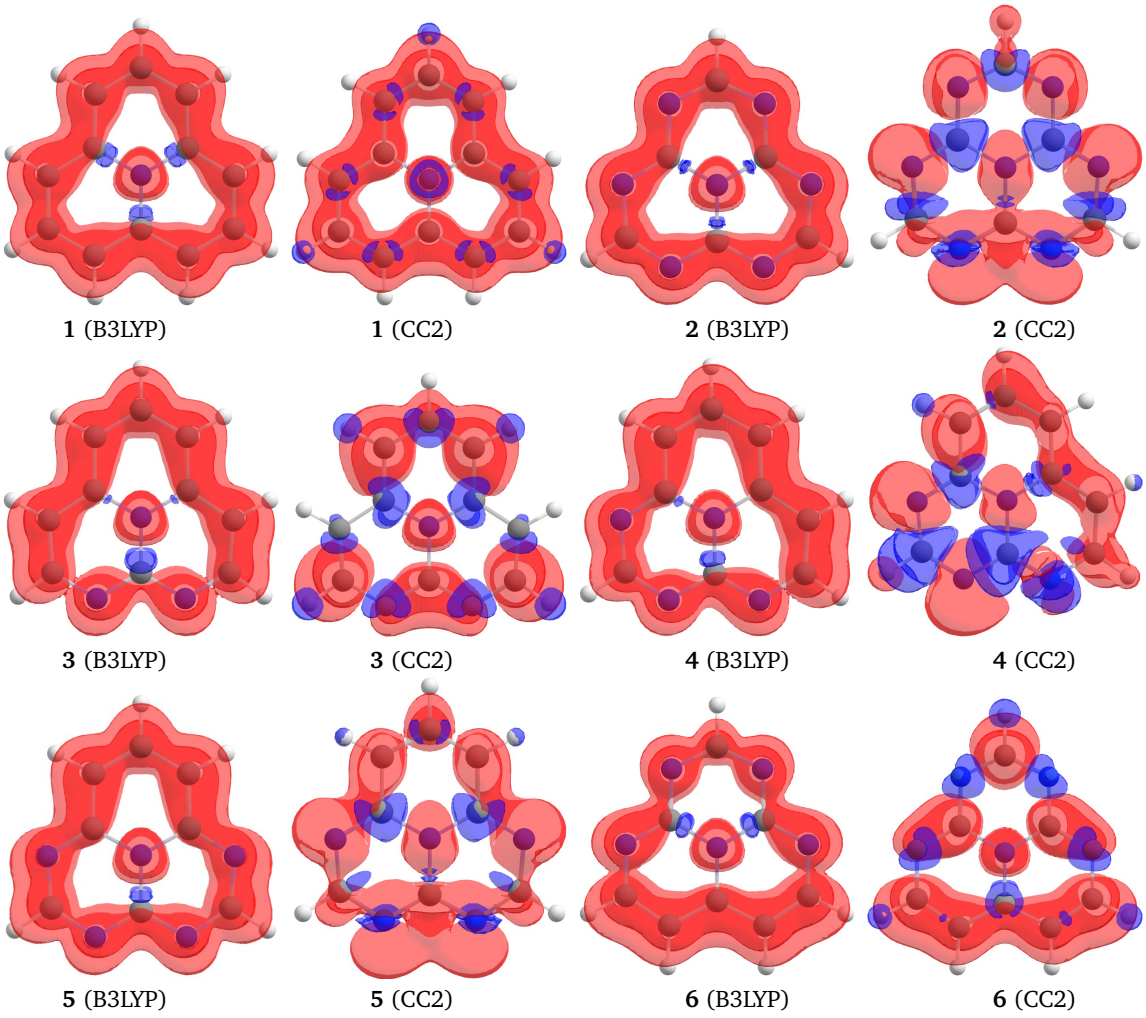

Fig. S3 Spin densities of the lowest T_1 state calculated at the B3LYP/def2-TZVPD and CC2/def2-TZVP levels for molecules **1** to **6**.

Notes and references

1 J. Sanz-Rodrigo, G. Ricci, Y. Olivier and J. C. Sancho-García, *J. Phys. Chem. A*, 2021, **125**, 513–522.

2 G. Ricci, E. San-Fabián, Y. Olivier and J. C. Sancho-García, *ChemPhysChem*, 2021, **22**, 553–560.

3 P. de Silva, *J. Phys. Chem. Lett.*, 2019, **10**, 5674–5679.

4 S. Ghosh and K. Bhattacharyya, *J. Phys. Chem. A*, 2022, **126**, 1378–1385.

5 R. Pollice, P. Friederich, C. Lavigne, G. dos Passos Gomes and A. Aspuru-Guzik, *Matter*, 2021, **4**, 1654–1682.

6 J. Ehrmaier, E. J. Rabe, S. R. Pristash, K. L. Corp, C. W. Schlenker, A. L. Sobolewski and W. Domcke, *J. Phys. Chem. A*, 2019, **123**, 8099–8108.

7 F. Dinkelbach, M. Bracker, M. Kleinschmidt and C. M. Marian, *J. Phys. Chem. A*, 2021, **125**, 10044–10051.