

Charge-Transfer Excited States in Phosphorescent Organo-Transition Metal Compounds: A Difficult Case for Time Dependent Density Functional Theory?

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1. VERTICAL ABSORPTION ENERGIES AND 0-0 CORRECTION

#	ZPE _{T₁}	ZPE _{S₀}	ΔE_{relax}
1	7.04	7.13	0.26
2	16.86	16.95	0.13
3	8.67	8.76	0.31
4	6.82	6.91	0.03
5	6.47	6.57	0.28
6	12.50	12.58	0.32
7	6.38	6.49	0.18
8	12.64	12.74	0.27
9	9.65	9.74	0.32
10	8.65	8.75	0.29
11	12.33	12.46	0.27
12	13.01	13.11	0.27
13	9.38	9.45	0.15
14	7.75	7.86	0.19
15	7.38	7.48	0.28
16	14.10	14.21	0.32
17	7.68	7.77	0.46

Table S1: Energy contributions (B3LYP/6-31G*) to the correction of vertical excitation energies according to main article Eq. 7. We also report the relaxation energy on the T₁ B3LYP/6-31G* potential energy surface (ΔE_{relax}). The latter was obtained by T₁ geometry optimization at the unrestricted Kohn-Sham level with the S₀ minimum as initial geometry. For several cases the SCF cycle for the UKS calculations at the S₀ minimum geometry converged to an excited triplet state. Initialization with the density matrix at the T₁ minimum geometry solved this issue. Relaxation of structure **13** lead to a severe overtwisting of the geometry.¹ ΔE_{relax} has been obtained from a LC-PBE (tuned) optimization in this case. All energies in eV.

#	PBE	B3LYP	LC-PBE		
			tuned	TDA	$\gamma = 0.3 \text{ a}_0^{-1}$
1	1.58	1.95	2.08	2.22	2.13
2	1.56	2.02	2.05	2.07	2.54
3	2.00	2.17	2.28	2.41	2.23
4	1.97	2.20	2.30	2.52	2.29
5	2.22	2.29	2.16	2.60	2.32
6	2.01	2.38	2.36	2.41	2.58
7	2.17	2.44	2.58	2.65	2.67
8	2.15	2.52	2.55	2.62	2.70
9	2.14	2.56	2.75	2.92	2.75
10	2.15	2.58	2.77	2.99	2.76
11	2.16	2.53	2.42	3.06	2.59
12	2.15	2.63	2.57	2.60	2.83
13	2.06	2.53	2.62	2.97	2.57
14	2.31	2.68	2.83	3.01	2.81
15	2.39	2.68	2.53	3.11	2.78
16	2.59	2.81	2.92	3.05	2.88
17	2.74	3.03	3.20	3.45	3.18

Table S2: Vertical T_1 absorption energies [eV].

#	PBE	B3LYP	LC-PBE		
			tuned	TDA	$\gamma = 0.3 \text{ a}_0^{-1}$
1	1.83 (0.076)	2.48 (0.126)	2.76 (0.155)	2.83 (0.187)	3.18 (0.224)
2	1.75 (0.031)	2.28 (0.033)	2.31 (0.016)	2.35 (0.020)	2.99 (0.011)
4	2.17 (0.002)	2.73 (0.017)	3.22 (0.052)	3.29 (0.054)	3.25 (0.056)
5	2.70 (0.020)	3.09 (0.054)	3.63 (0.124)	3.77 (0.148)	3.44 (0.095)
7	2.33 (0.000)	2.75 (0.001)	2.94 (0.001)	2.97 (0.001)	3.25 (0.004)
14	2.45 (0.000)	3.08 (0.004)	3.47 (0.011)	3.51 (0.016)	3.66 (0.021)

Table S3: Vertical S_1 absorption energies [eV], oscillator strengths in parentheses.

1.1 Influence of basis set size

#	6-311G* & LANL2DZ	6-311++G** & LANL2TZF
5	2.29	2.25
7	2.44	2.37
15	2.68	2.63

Table S4: Vertical T_1 absorption energies [eV] at the B3LYP level using basis sets of different size.

1.2 Influence of solvent model

#	COSMO	SMD
5	2.287	2.290
7	2.438	2.444
15	2.677	2.683

Table S5: Vertical T_1 absorption energies [eV] at the B3LYP/6-311G* & LANL2DZ level using the COSMO and SMD model for solvation (see main text).

2. FRONTIER MOLECULAR ORBITALS

In the following figures, initial (top) and final (bottom) molecular orbitals corresponding to the dominant single-particle transition for the T_1 state are plotted for the PBE (left) and B3LYP (right) functionals. These are mostly HOMO to LUMO transitions with the exception of **9**, **13**, **16** at the B3LYP level, which are HOMO-1 to LUMO.

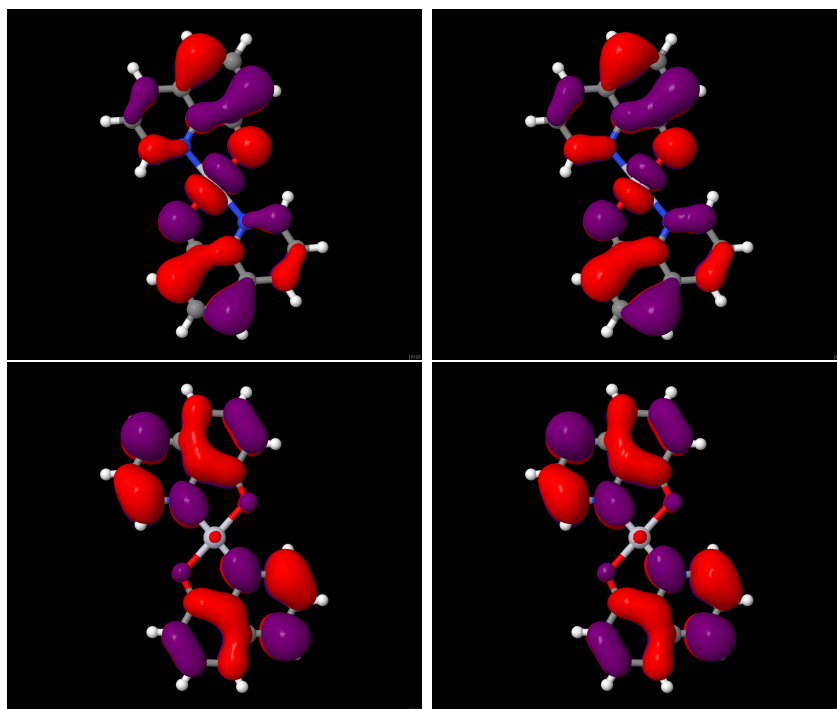


Figure S1: **Structure 1**

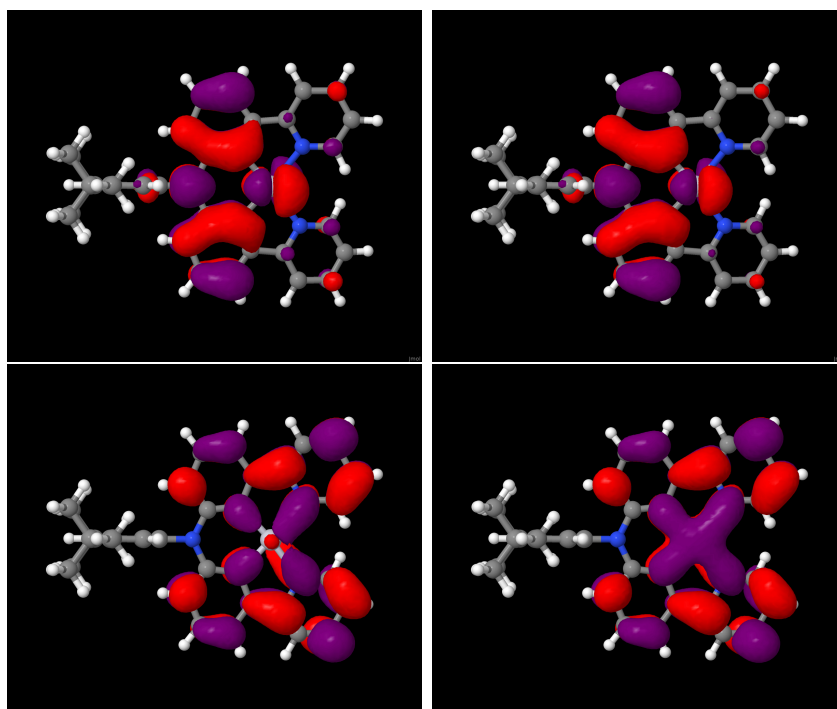


Figure S2: **Structure 2**

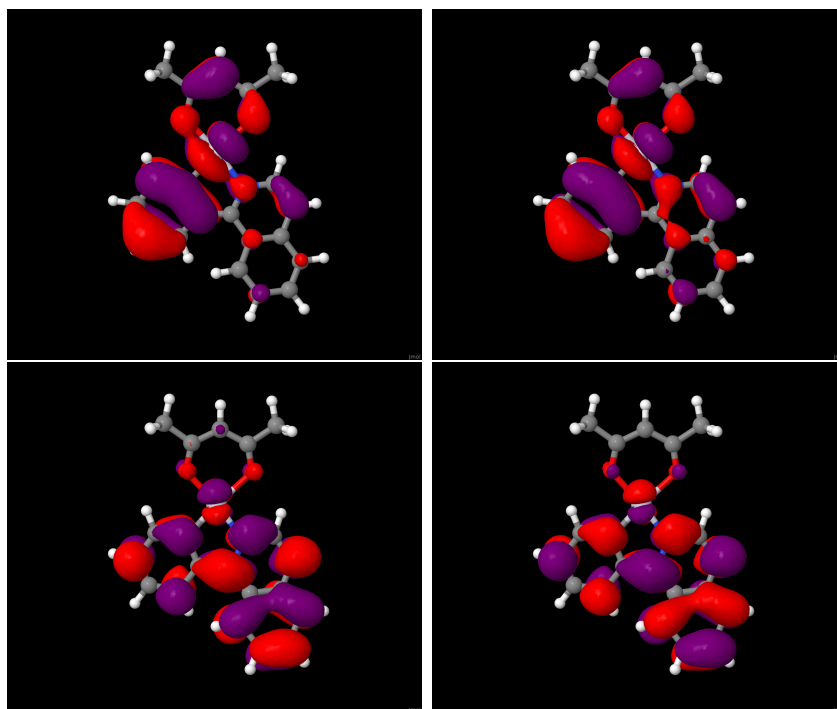


Figure S3: **Structure 3**

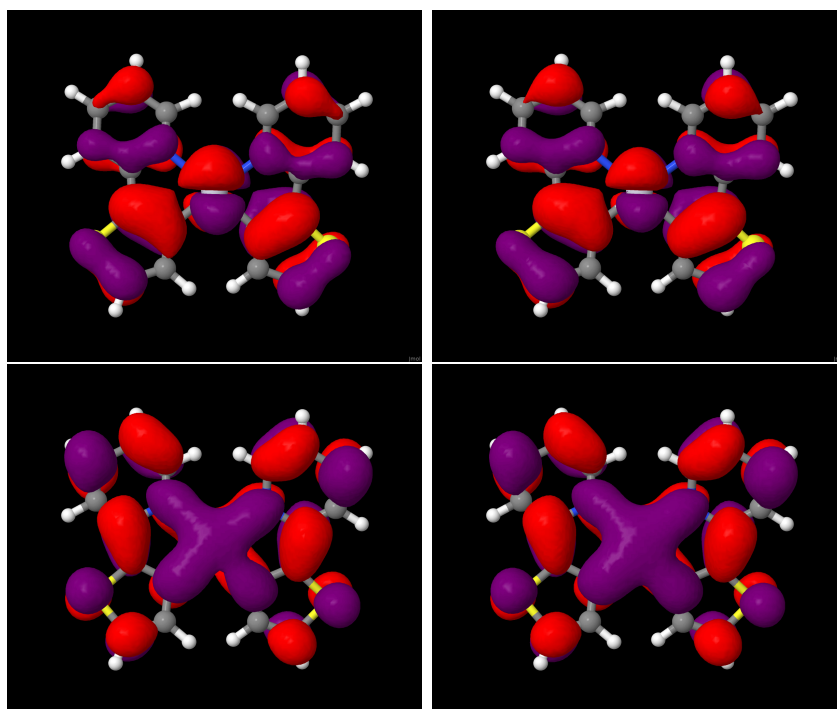


Figure S4: **Structure 4**

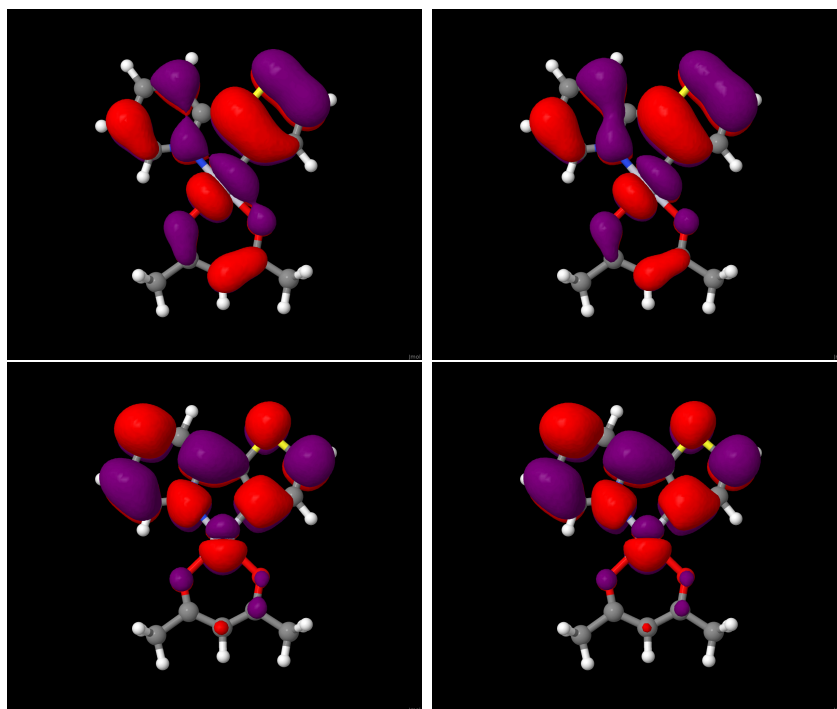


Figure S5: **Structure 5**

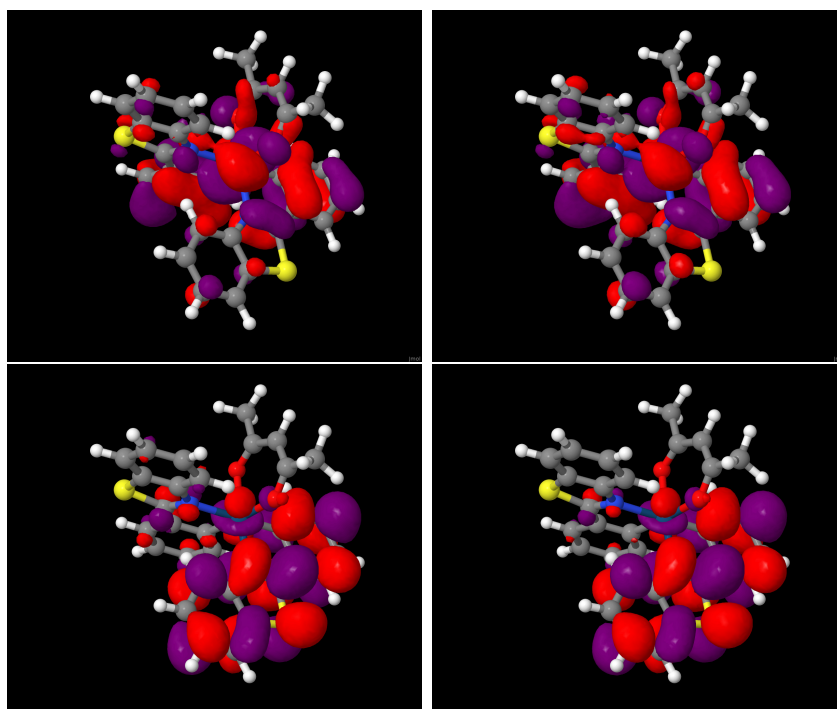


Figure S6: **Structure 6**

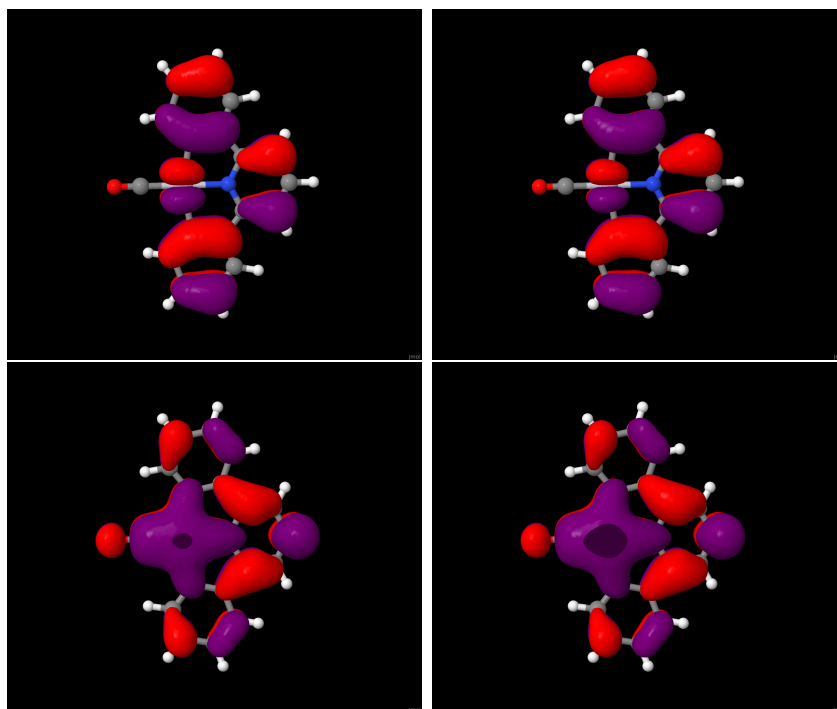


Figure S7: **Structure 7**

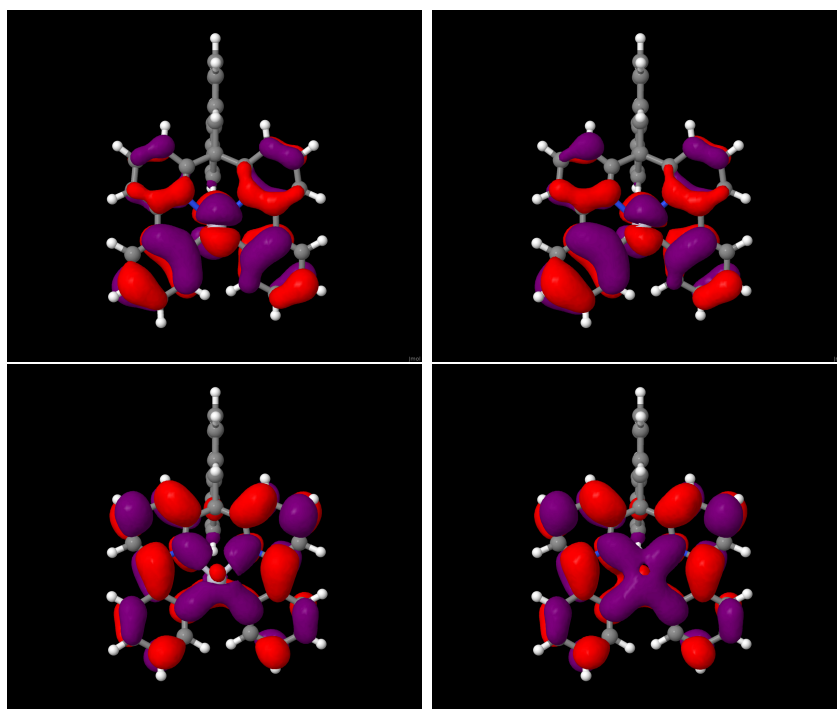


Figure S8: **Structure 8**

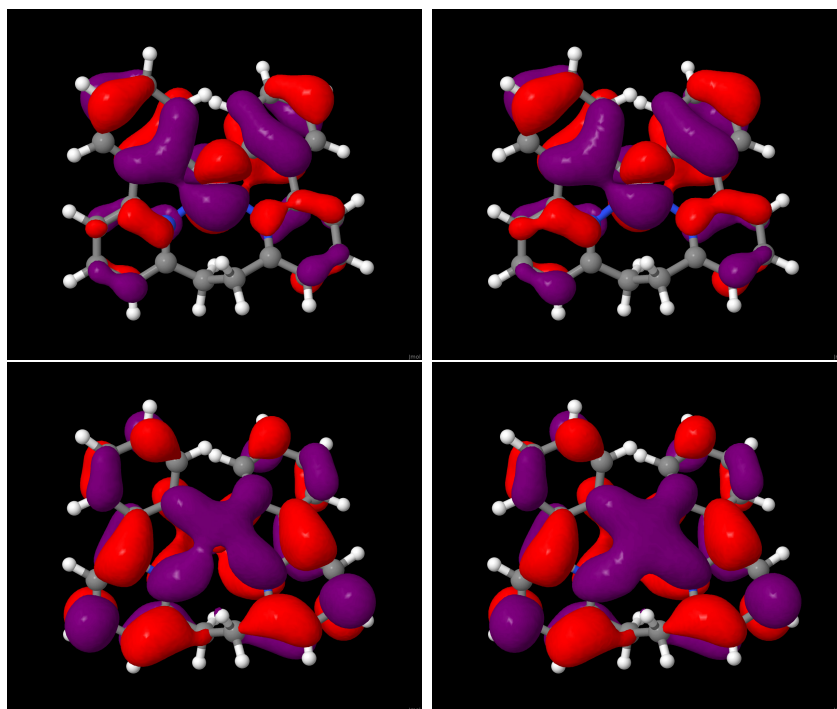


Figure S9: **Structure 9**

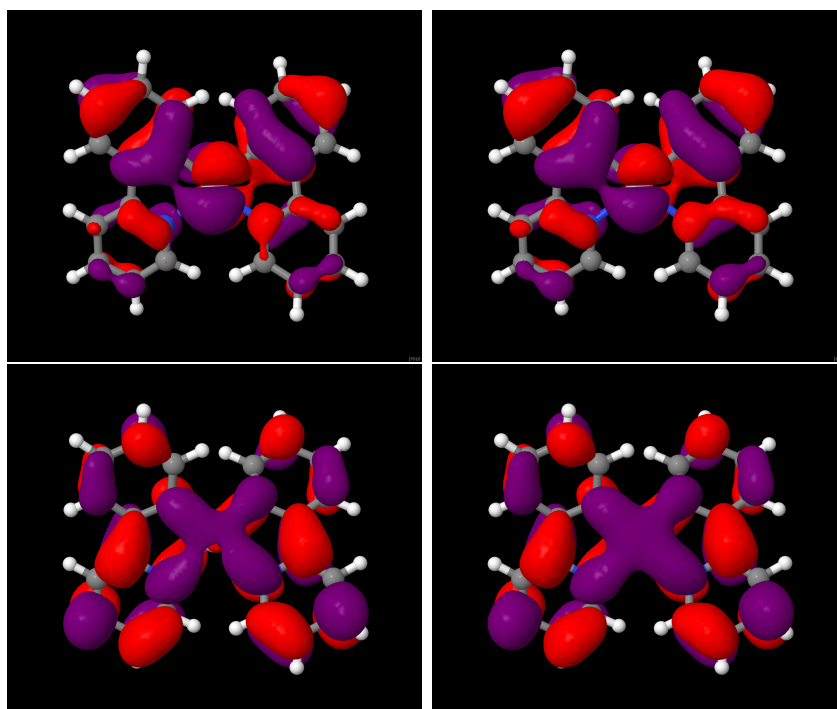


Figure S10: **Structure 10**

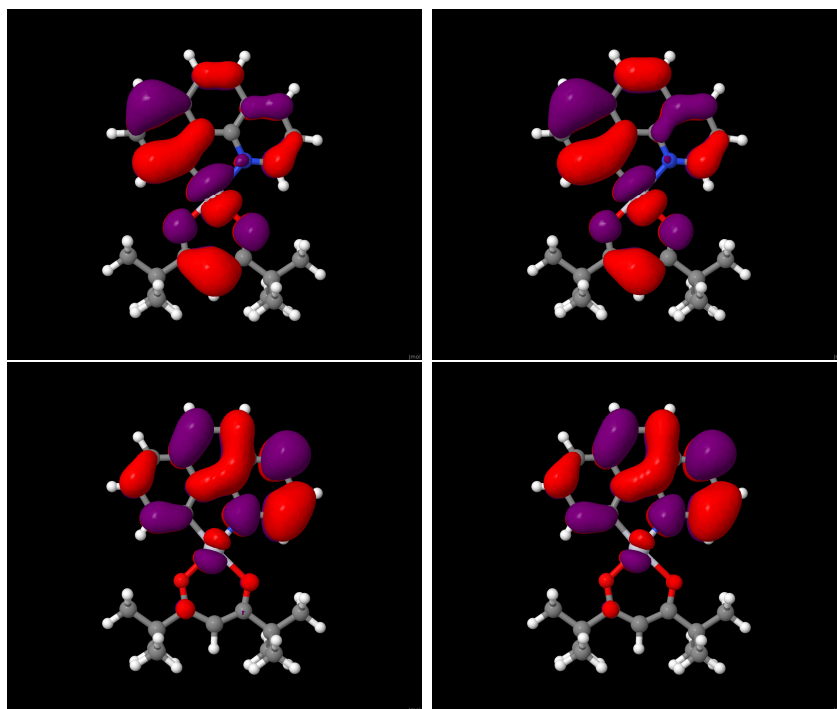


Figure S11: **Structure 11**

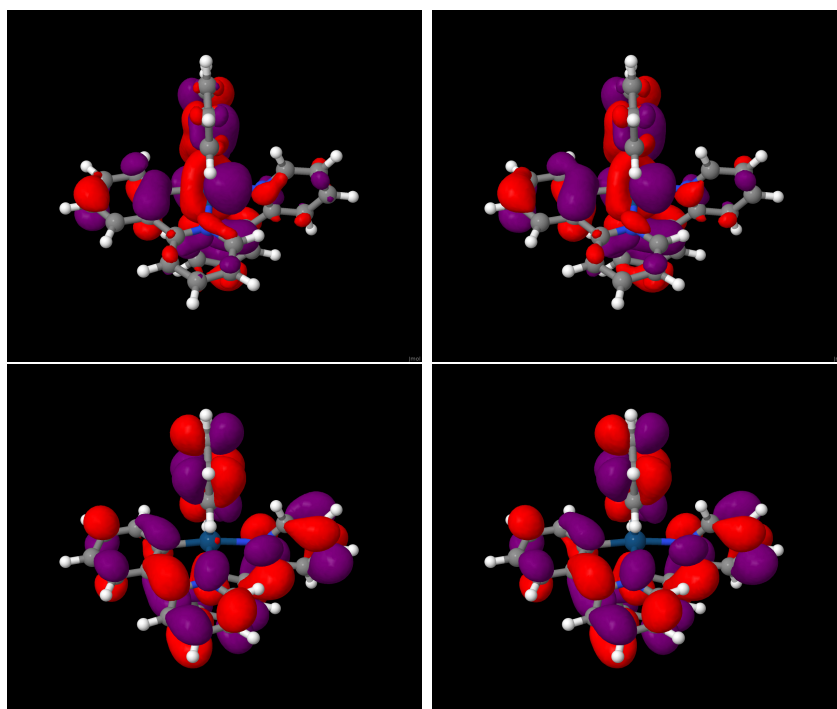


Figure S12: **Structure 12**

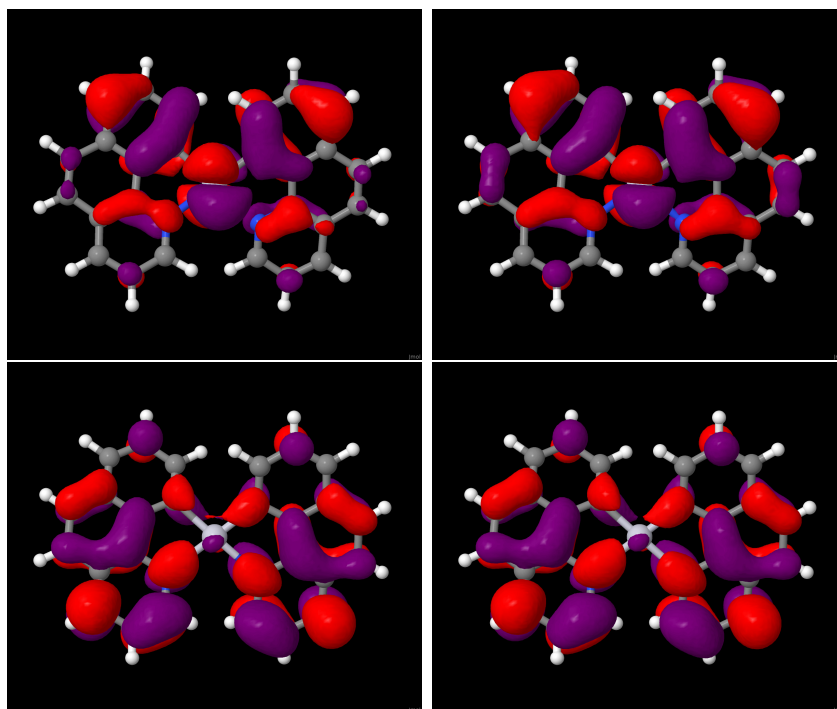


Figure S13: **Structure 13**

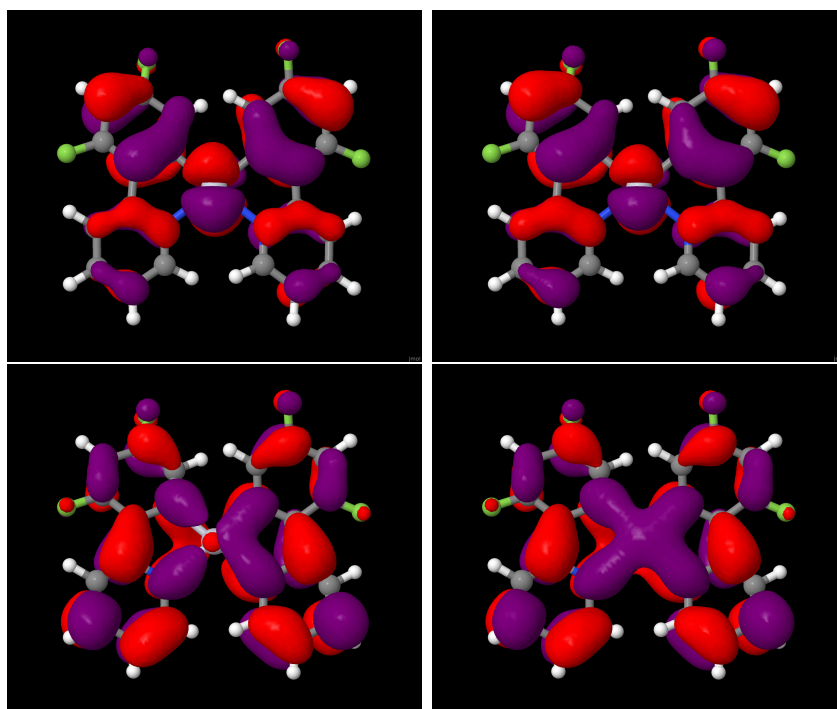


Figure S14: **Structure 14**

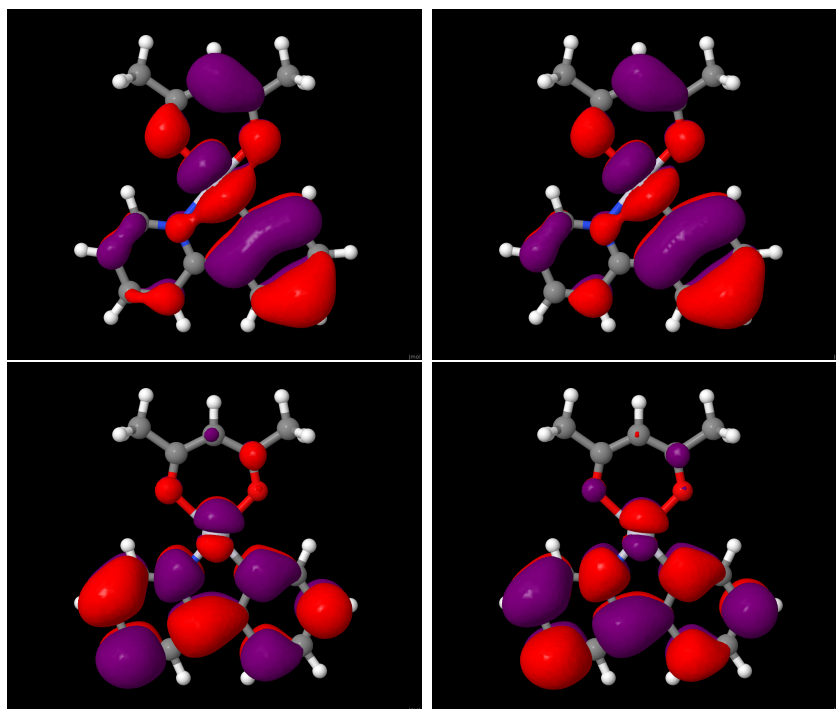


Figure S15: **Structure 15**

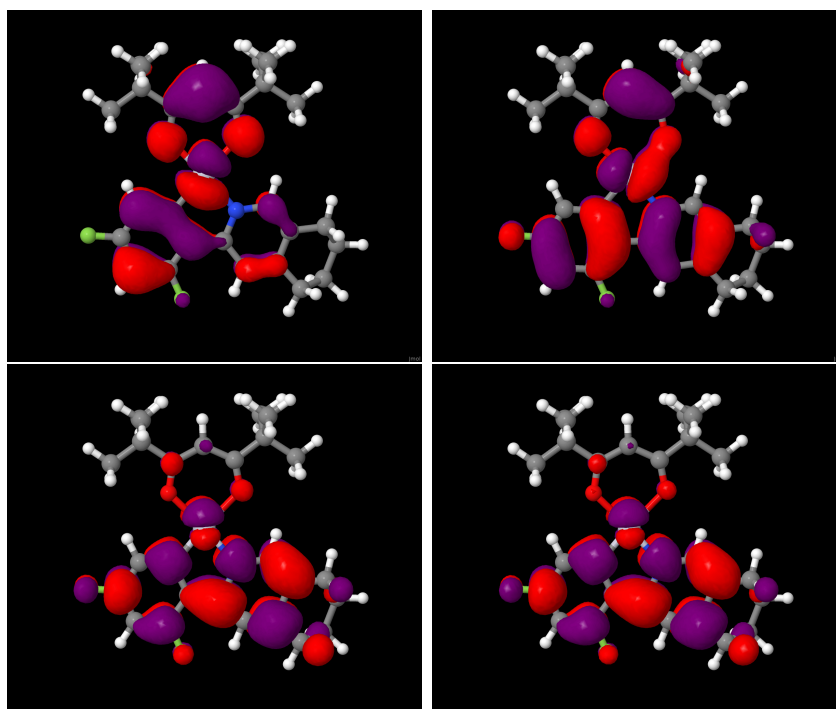


Figure S16: **Structure 16**

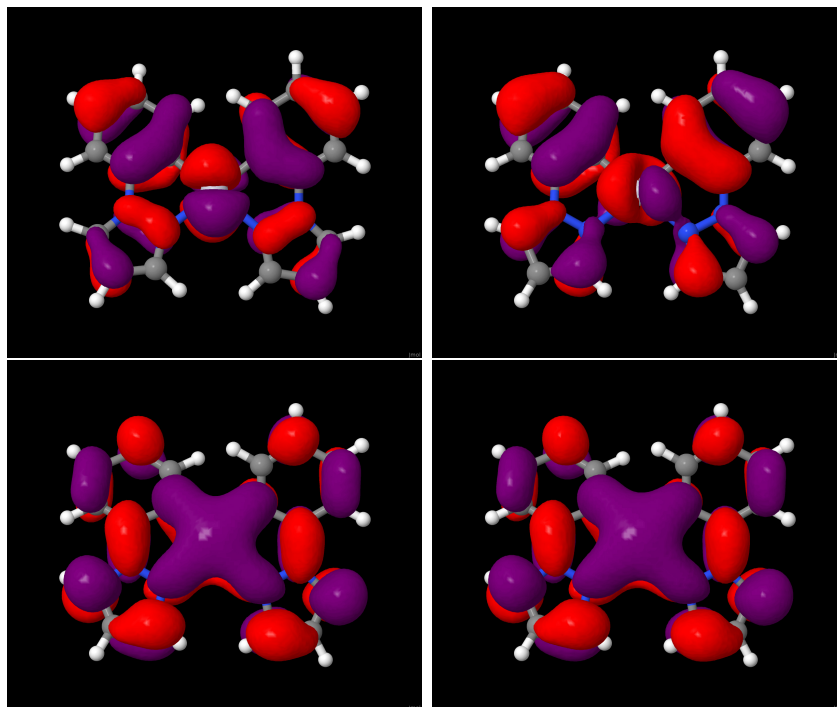


Figure S17: **Structure 17**

REFERENCES

1. P. Wiggins, J. G. Williams, and D. J. Tozer, "Excited state surfaces in density functional theory: a new twist on an old problem," *J. Chem. Phys.*, vol. 131, no. 9, p. 091101, 2009.