Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Extension of Molecules with Inverted Singlet-Triplet Gap with Conjugated Branches to Alter the Oscillator Strength

Hwon Kim[a], *Gregory D. Scholes*[b], *Seung Kyu Min*[a]

a. *Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), South Korea*

b. *Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA*

Active space used for CASSCF

Molecule 1

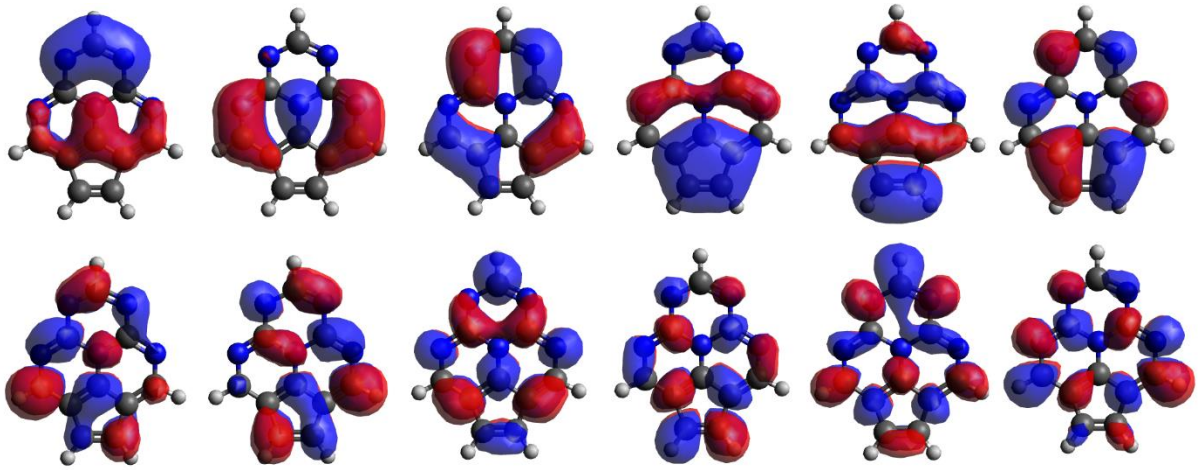

Figure S1. Active space used for Molecule **1**

Molecule 2

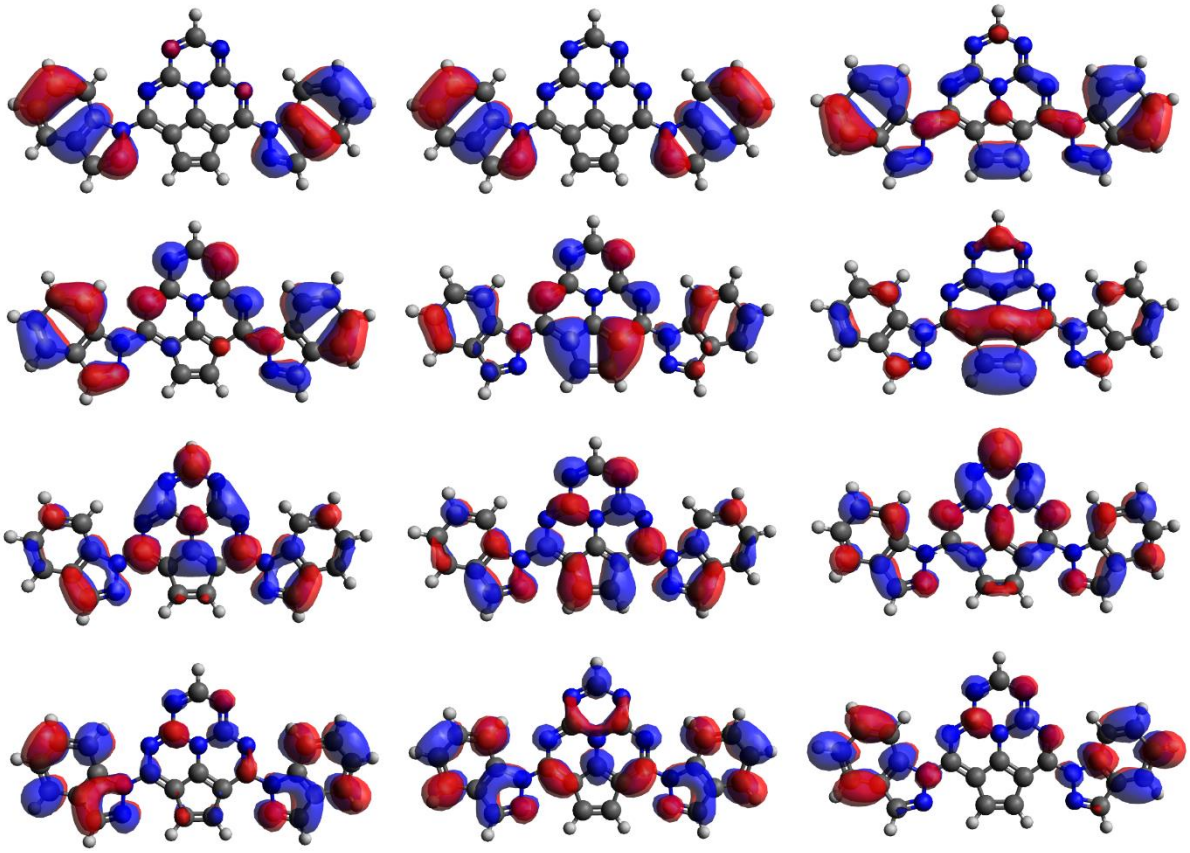

Figure S2. Active space used for Molecule **2**

Molecule 3t

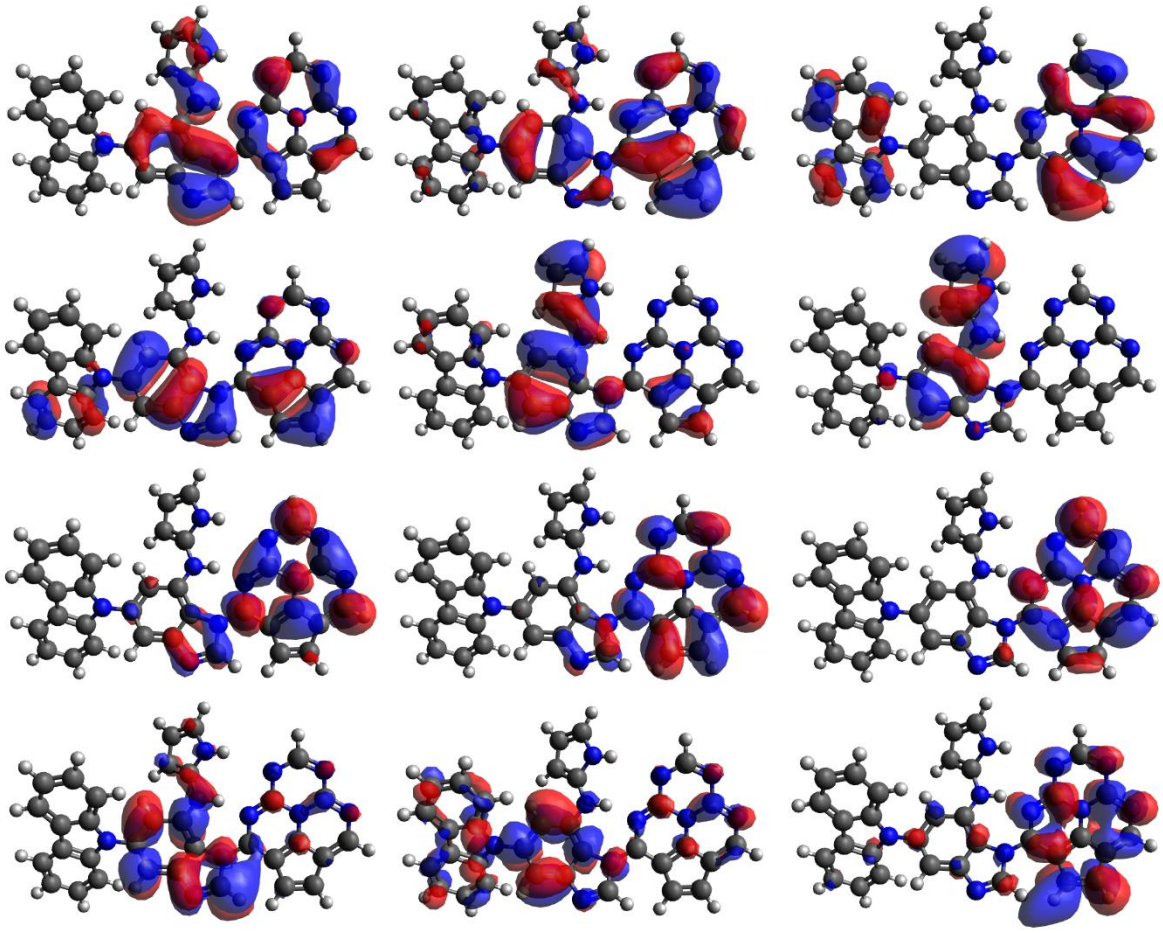

Figure S3. Active space used for Molecule **3t**

Molecule 4

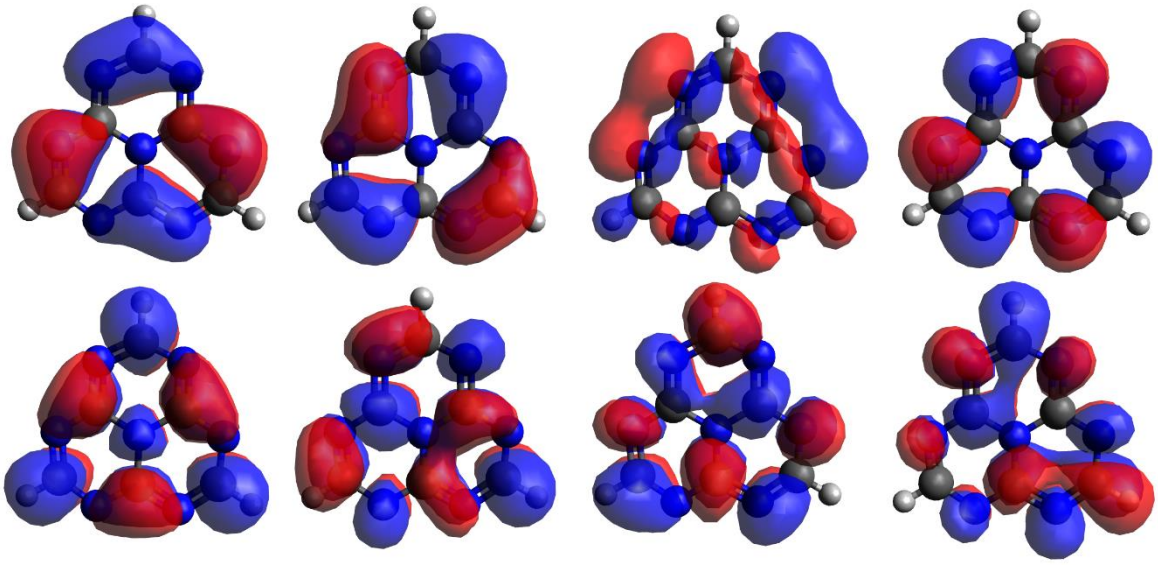

Figure S4. Active space used for the CASSCF (8,8) step of Molecule **4**

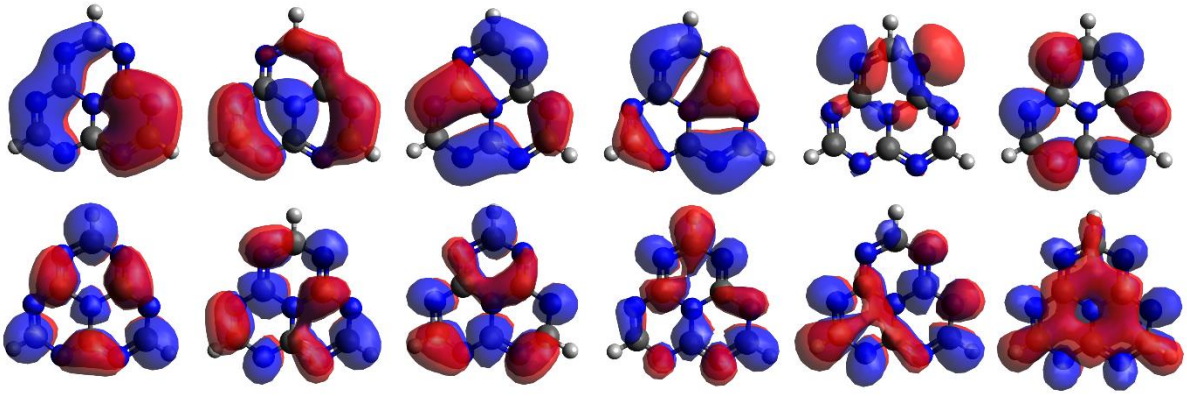

Figure S5. Active space used for the CASSCF (12,12) step of Molecule **4**

Molecule 5t

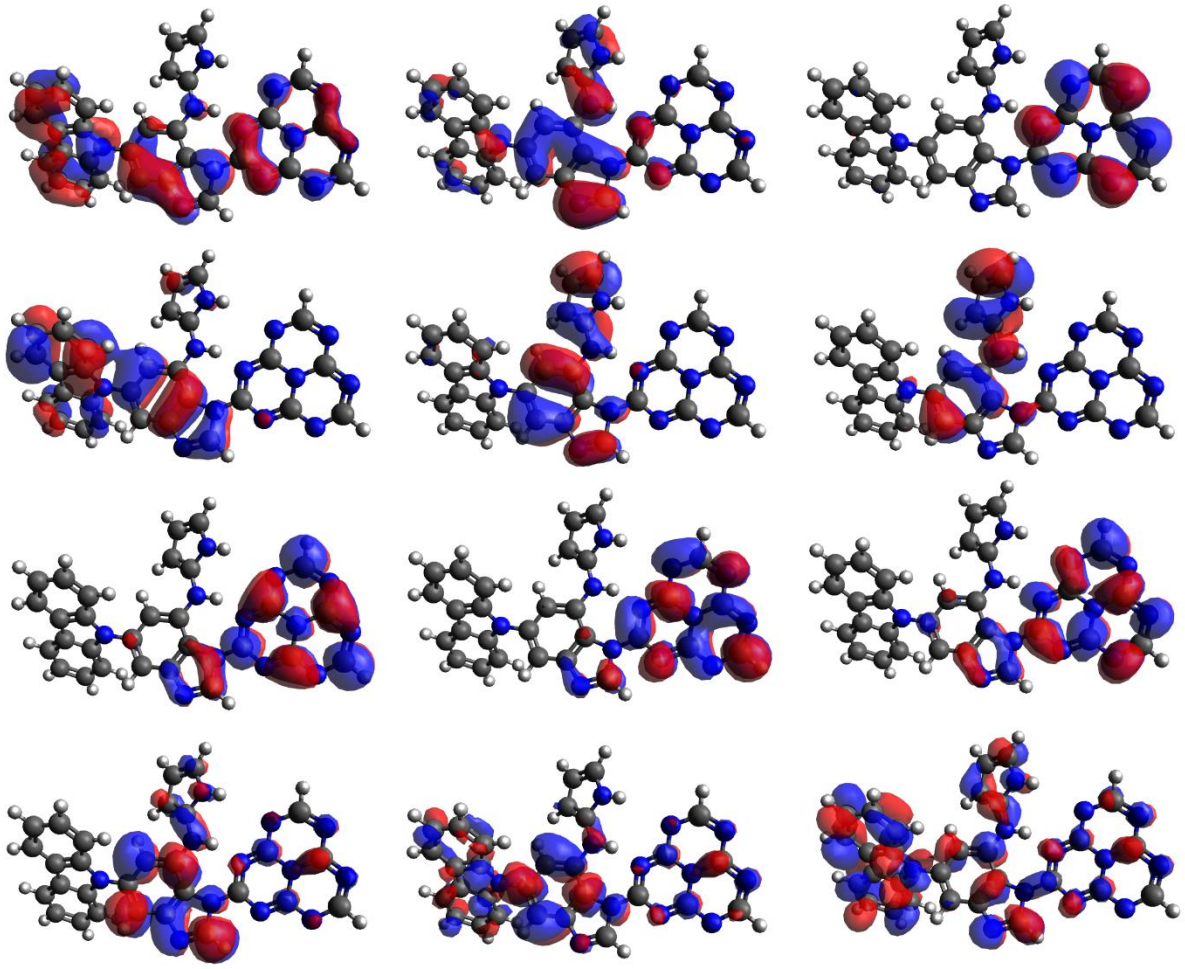

Figure S6. Active space used for Molecule **5t**

Molecule 6

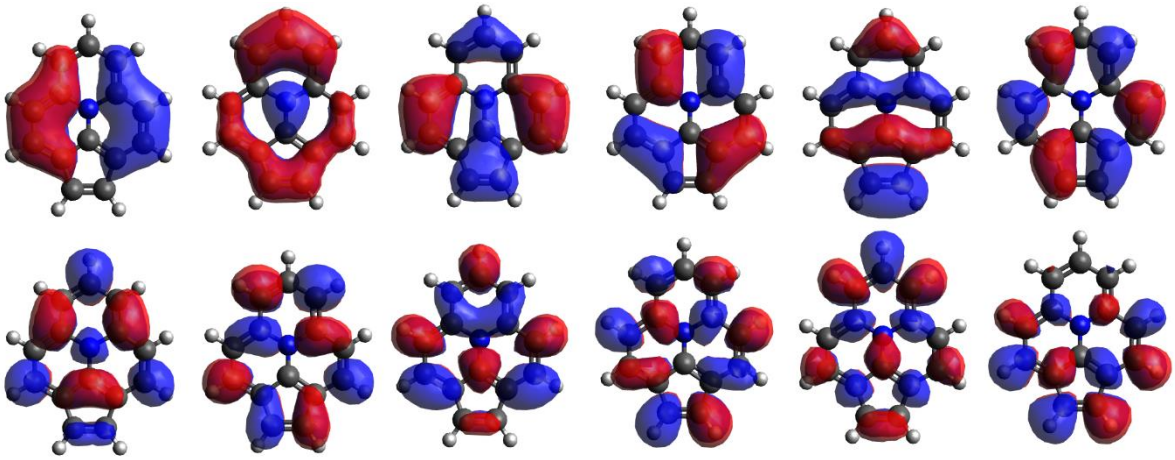

Figure S7. Active space used for Molecule **6**

Molecule 7t

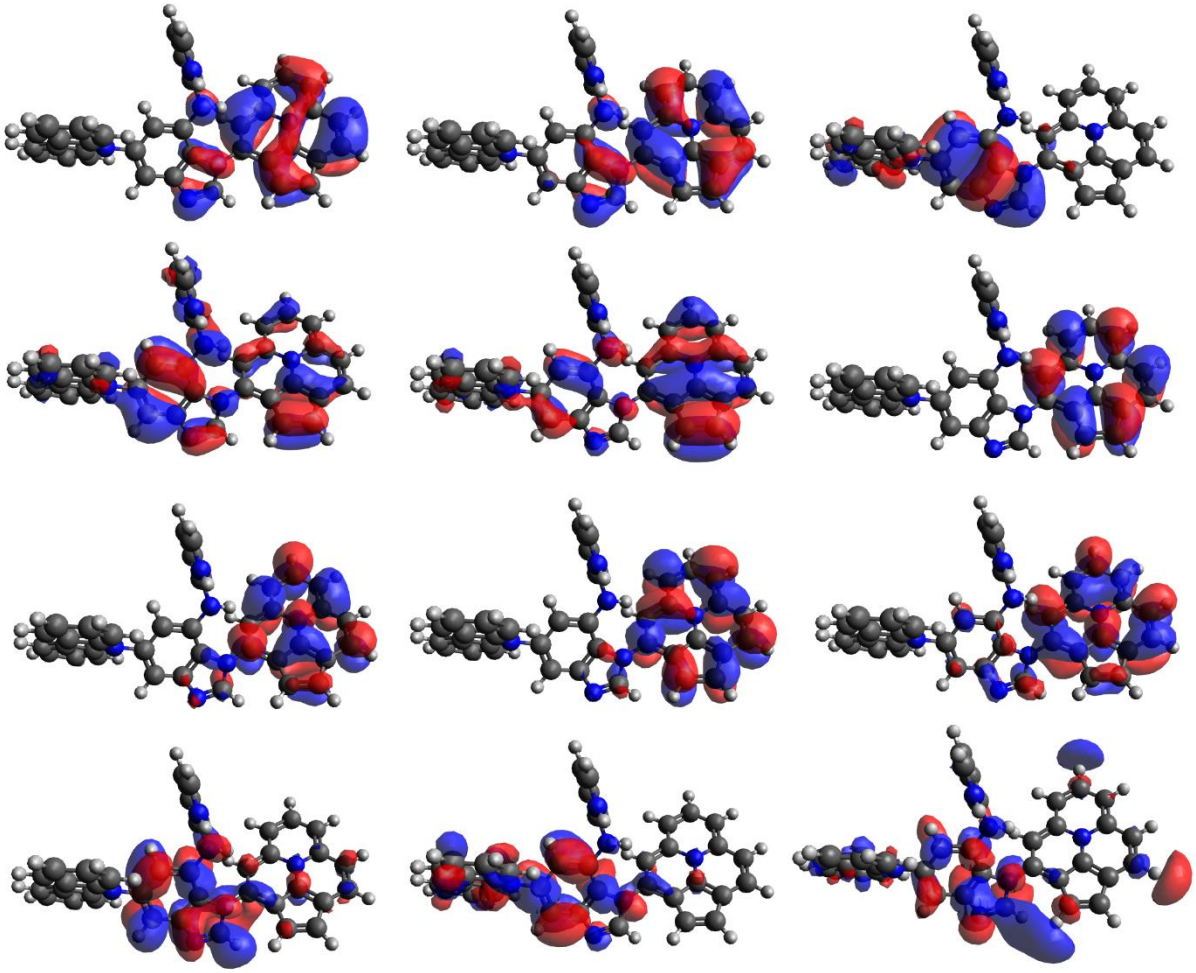

Figure S8. Active space used for Molecule **7t**

Interaction with 2UE DEC

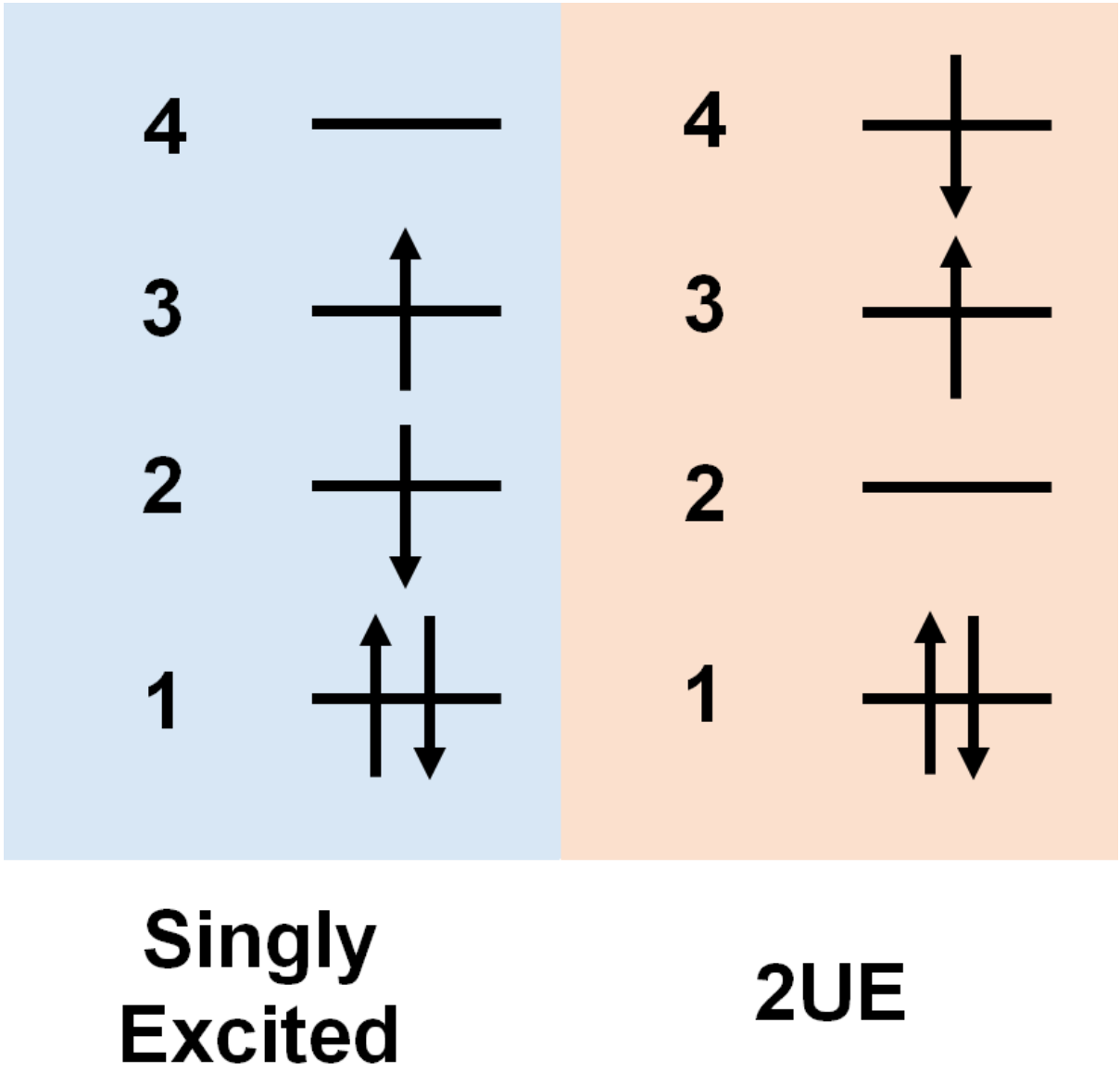

Figure S9. The electron configuration for the zeroth-order singly excited state with HOMO-LUMO excitation and the 2UE doubly excited state

The configuration state function (CSF) made with the configurations shown in Figure S10 is

$$\left|\psi^{Singlet}_{Singly\ Excited}\right\rangle = \frac{1}{\sqrt{2}}\left|\varphi_1^{\alpha}\varphi_1^{\beta}\varphi_2^{\alpha}\varphi_3^{\beta}\right\rangle - \frac{1}{\sqrt{2}}\left|\varphi_1^{\alpha}\varphi_1^{\beta}\varphi_2^{\beta}\varphi_3^{\alpha}\right\rangle$$

$$\left|\psi^{Triplet}_{Singly\ Excited}\right\rangle = \frac{1}{\sqrt{2}}\left|\varphi_1^{\alpha}\varphi_1^{\beta}\varphi_2^{\alpha}\varphi_3^{\beta}\right\rangle + \frac{1}{\sqrt{2}}\left|\varphi_1^{\alpha}\varphi_1^{\beta}\varphi_2^{\beta}\varphi_3^{\alpha}\right\rangle$$

$$\left|\psi^{Singlet}_{2UE}\right\rangle = \frac{1}{\sqrt{2}}\left|\varphi_1^{\alpha}\varphi_1^{\beta}\varphi_3^{\alpha}\varphi_4^{\beta}\right\rangle - \frac{1}{\sqrt{2}}\left|\varphi_1^{\alpha}\varphi_1^{\beta}\varphi_3^{\beta}\varphi_4^{\alpha}\right\rangle$$

$$\left|\psi_{2UE}^{Triplet}\right\rangle = \frac{1}{\sqrt{2}}\left|\varphi_1^{\alpha}\varphi_1^{\beta}\varphi_3^{\alpha}\varphi_4^{\beta}\right\rangle + \frac{1}{\sqrt{2}}\left|\varphi_1^{\alpha}\varphi_1^{\beta}\varphi_3^{\beta}\varphi_4^{\alpha}\right\rangle$$

The coupling term between each spin multiplicity is

$$\left\langle\psi_{Singly\ Excited}^{Singlet}\middle|\hat{H}\middle|\psi_{2UE}^{Singlet}\right\rangle = \langle\varphi_2|\hat{h}|\varphi_4\rangle + 2\langle\varphi_1\varphi_2|\varphi_1\varphi_4\rangle - \langle\varphi_1\varphi_2|\varphi_4\varphi_1\rangle + \langle\varphi_3\varphi_2|\varphi_3\varphi_4\rangle + \langle\varphi_2\varphi_3|\varphi_3\varphi_4\rangle$$

$$\left\langle\psi_{Singly\ Excited}^{Triplet}\middle|\hat{H}\middle|\psi_{2UE}^{Triplet}\right\rangle = -\langle\varphi_2|\hat{h}|\varphi_4\rangle - 2\langle\varphi_1\varphi_2|\varphi_1\varphi_4\rangle + \langle\varphi_1\varphi_2|\varphi_4\varphi_1\rangle - \langle\varphi_3\varphi_2|\varphi_3\varphi_4\rangle + \langle\varphi_2\varphi_3|\varphi_3\varphi_4\rangle$$

from which cannot be determined which coupling is stronger as two are not multiples of each other.

Characters of S_1 and T_1 states from SOS-B2GP-PLYP21 functional

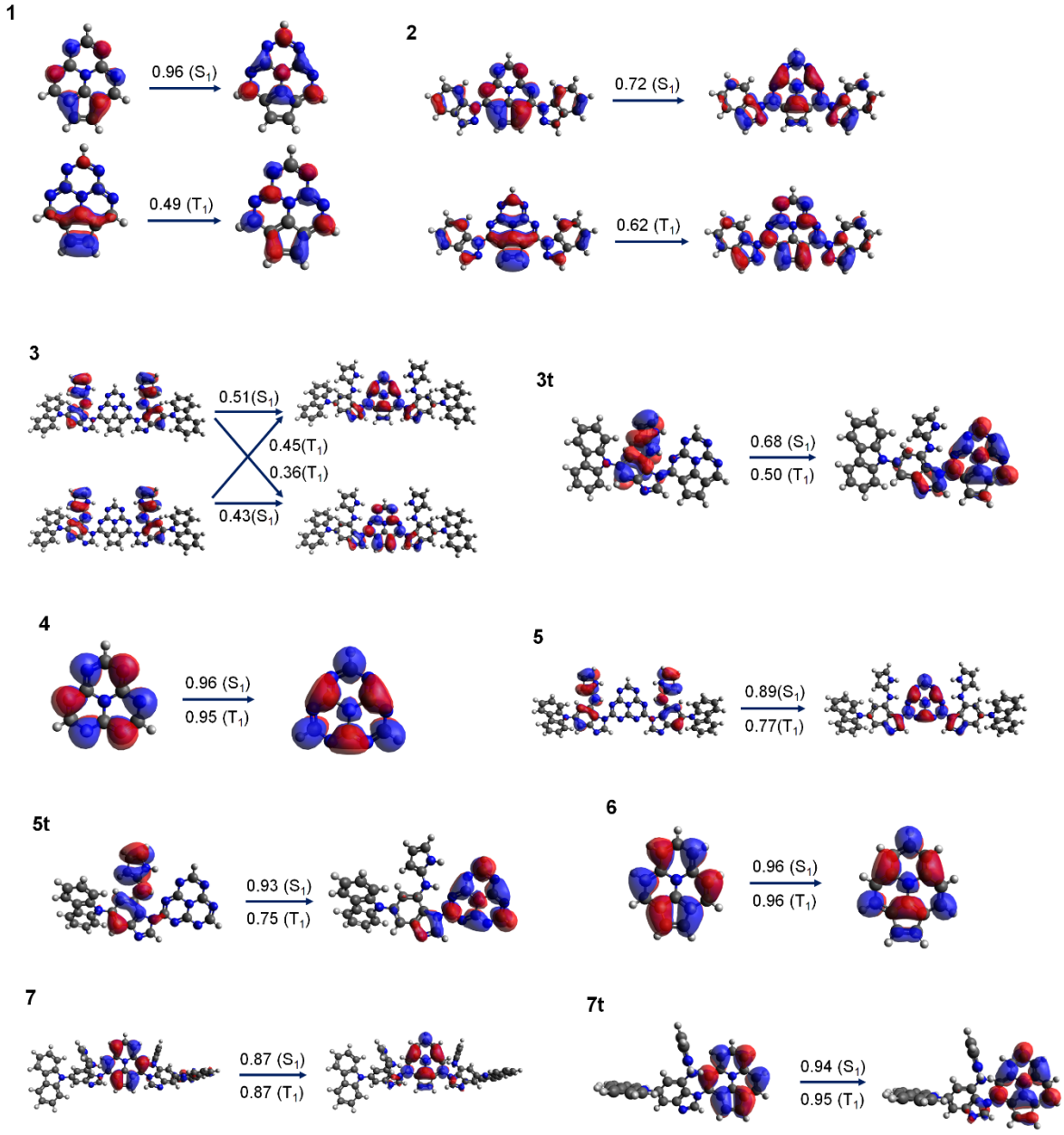

Figure S10. The characters of the molecules with the amplitudes of each transition, calculated with SOS-B2GP-PLYP21 functional

Characters of S_1 and T_1 states from SCS-PBE-QIDH functional

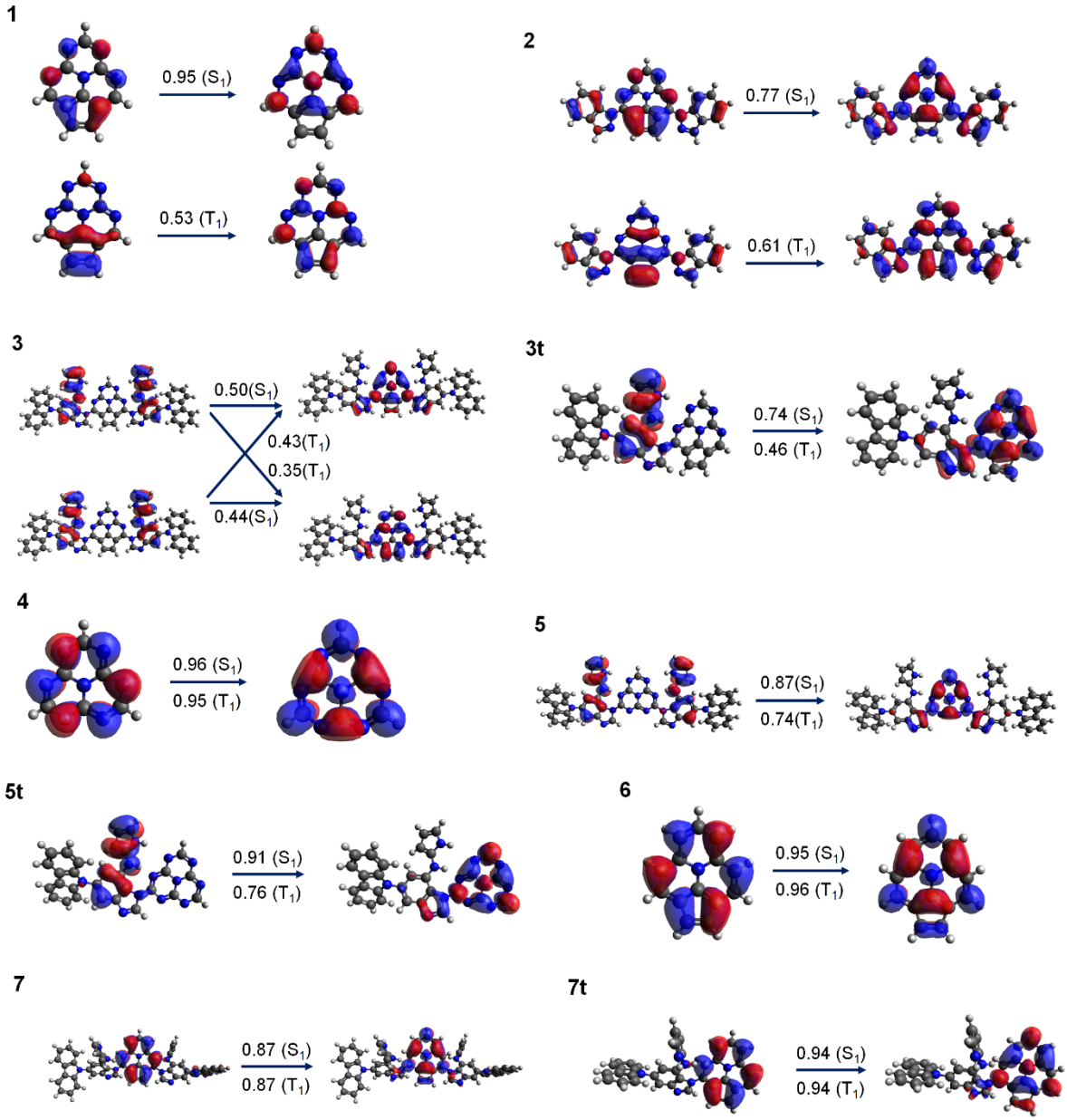

Figure S11. The characters of the molecules with the amplitudes of each transition, calculated with SCS-PBE-QIDH functional

CT Distance (D_{CT})

	SOS-B2GP-PLYP21	SCS-PBE-QIDH	SOS-RSX-QIDH	CASSCF
1	0.276	0.268	0.257	2.55×10^{-2}
2	0.179	0.182	0.182	0.623
3	0.591	0.574	0.422	N/A
3t	1.26	1.23	0.678	1.53
4	6.89×10^{-3}	6.67×10^{-3}	6.62×10^{-3}	6.90×10^{-2}
5	0.388	0.381	0.293	N/A
5t	1.69	1.66	1.37	2.09
6	0.434	0.434	0.430	2.55×10^{-2}
7	3.01×10^{-2}	3.10×10^{-2}	3.50×10^{-2}	N/A
7t	0.123	0.123	0.124	0.105

Table S1. The distance between the S_0 and S_1 state's barycenter of electron density. The unit of the distance is in picometers.

Transition Dipole

	SOS-B2GP-PLYP21	SCS-PBE-QIDH	SOS-RSX-QIDH	CASSCF
1	0.786	0.841	0.956	1.02
2	2.69	2.87	3.07	2.97
3	6.85	6.99	8.19	N/A
3t	4.32	4.45	5.21	3.36
4	0.00	0.00	0.00	0.200
5	6.73	6.85	7.94	N/A
5t	3.93	4.02	4.78	3.88
6	0.474	0.489	0.505	0.504
7	1.14	1.16	1.16	N/A
7t	0.665	0.684	0.690	0.232

Table S2. The transition dipole of the S_0-S_1 transitions. The unit is in Debye.

Scatter plot of V_{DL} and Transition Dipole

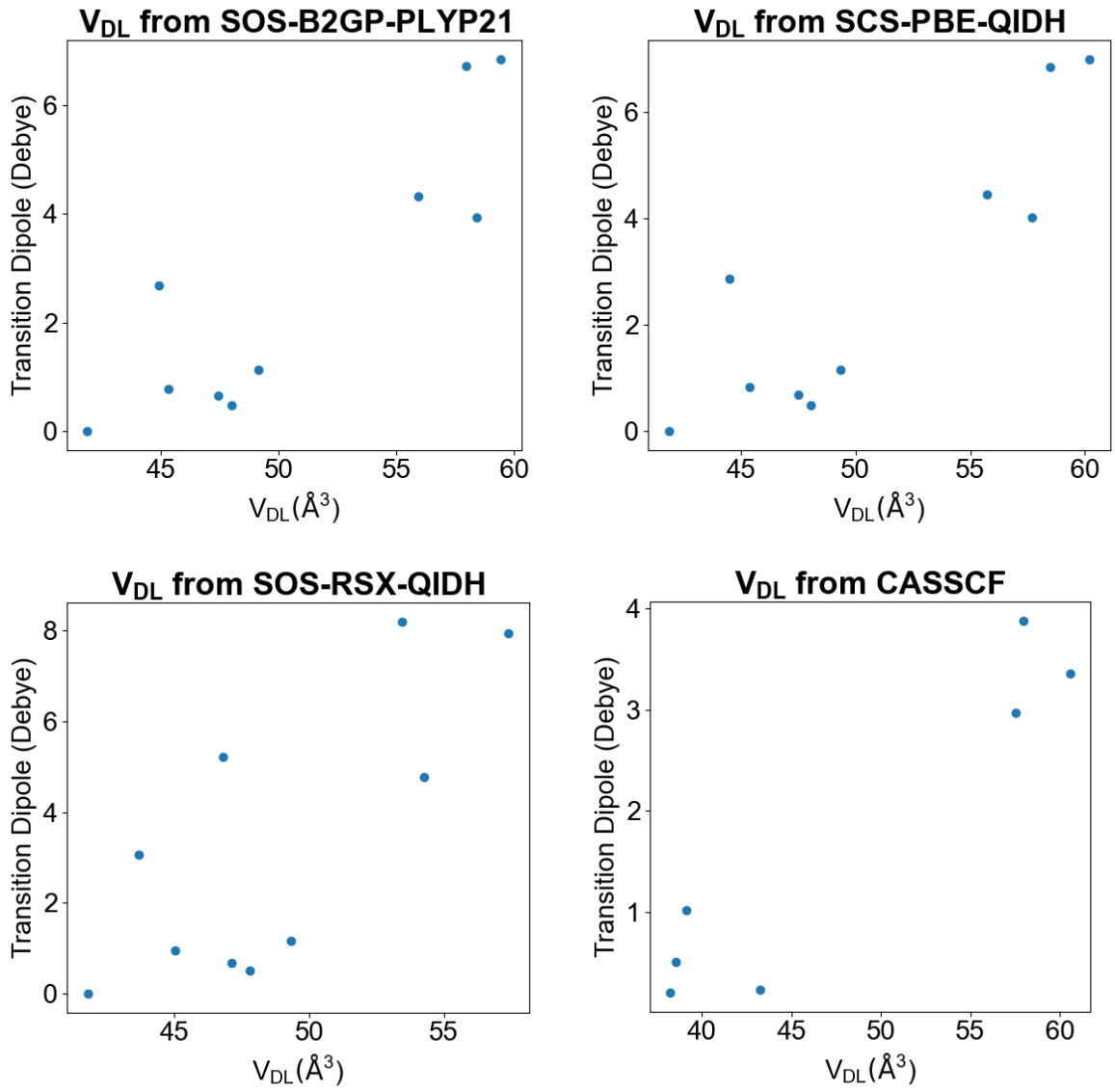

Figure S12. Scatter plot of V_{DL} and transition dipole from each functionals and the CASSCF calculation. CASSCF shows especially strong correlation with the four molecules with localized excitations (**1**, **4**, **6**, **7t**) having V_{DL} under 45 Å^3 and transition dipole of 1D or less and the three molecules with delocalized excitations (**2**, **3t**, **5t**) having V_{DL} above 55 Å^3 and transition dipole of 3D or more.

Transition Density Matrix

The one-particle reduced transition density matrices (TDM) are provided in the basis of 12 optimized active orbitals from the CASSCF(12,12) calculations. The matrix elements are defined as $T_{ij} = \left\langle S_1 \middle| \hat{a}_i{}^{\dagger} \hat{a}_j \middle| S_0 \right\rangle$. Each block represents one row of TDM. The optimized orbitals are provided in the Supplementary_Information.zip file in molden file format.

Molecule **1**

-2.64e-06 -1.26e-06 -1.85e-03 -3.67e-06 -4.00e-06 -1.17e-02 1.83e-06 5.75e-04 -3.14e-05 1.06e-02 4.81e-06 8.11e-04

2.65e-06 -7.37e-06 8.16e-03 1.99e-05 -3.74e-06 4.37e-04 -8.73e-06 -2.00e-03 2.53e-05 3.38e-03 -2.11e-05 6.72e-03

3.47e-03 9.10e-04 -2.04e-05 1.17e-02 2.69e-03 -8.19e-05 2.10e-02 -2.01e-04 -6.30e-02 -6.82e-05 -2.69e-03 -1.45e-05

2.55e-07 6.27e-06 -3.56e-03 2.09e-07 3.19e-05 3.39e-02 3.14e-04 5.14e-02 -1.39e-04 3.97e-02 4.44e-06 1.09e-02

-1.07e-06 -1.63e-05 1.08e-02 4.51e-05 -2.00e-05 -6.54e-02 -3.60e-04 -7.44e-02 -6.36e-05 -1.96e-02 2.24e-05 8.95e-03

-6.71e-03 -1.79e-03 -2.55e-05 8.25e-03 -2.58e-02 2.53e-06 5.63e-02 -2.85e-04 -1.60e-02 1.44e-05 1.16e-02 -4.18e-06

-1.03e-04 -9.14e-05 -6.05e-03 6.49e-04 -6.38e-04 1.19e+00 -4.64e-04 -7.70e-02 -1.76e-06 8.21e-02 -4.44e-05 -3.25e-02

-8.47e-03 -2.33e-02 -1.84e-04 1.22e-01 -1.91e-01 -6.10e-03 -1.74e-02 4.93e-04 -5.04e-03 -4.19e-04 -5.73e-03 1.58e-04

-4.16e-05 2.08e-05 -1.14e-01 -2.25e-04 -1.17e-04 1.95e-01 -2.84e-05 -3.78e-03 5.60e-06 1.67e-02 -1.93e-06 -1.24e-02

1.05e-02 3.25e-03 -8.46e-05 5.43e-02 -5.82e-02 8.93e-05 1.75e-03 -1.31e-05 1.09e-03 2.04e-06 -1.17e-03 -5.05e-06

7.75e-06 -2.49e-05 -1.92e-02 -2.05e-05 5.59e-05 6.99e-02 -6.79e-06 -1.98e-03 3.62e-06 7.56e-03 -6.48e-07 -8.62e-04

4.18e-03 1.77e-02 1.20e-05 1.79e-04 2.37e-02 -3.76e-05 -6.86e-04 -4.80e-07 3.51e-03 -6.31e-06 -1.19e-03 1.09e-05

Molecule **2**

-1.66e-05 1.41e-03 -2.15e-06 6.46e-04 7.81e-03 -1.45e-05 -2.13e-03 -1.17e-05 2.33e-03 -5.68e-05 -5.31e-07 4.35e-04

1.06e-03 1.44e-05 4.77e-04 1.88e-06 4.28e-05 1.47e-03 -2.42e-06 2.08e-03 5.62e-05 2.40e-03 -4.58e-04 3.21e-06

-8.36e-08 3.38e-05 -8.60e-07 -1.20e-03 -7.69e-03 -9.70e-06 4.19e-03 -9.63e-06 2.47e-04 -3.77e-06 -9.23e-06 4.13e-03

-3.95e-04 -1.84e-06 -1.50e-05 4.27e-06 1.90e-05 3.01e-03 2.52e-05 6.93e-03 -1.17e-05 -6.01e-04 3.33e-03 5.61e-06

-5.19e-03 -2.79e-05 7.96e-03 -4.97e-06 5.29e-05 6.61e-02 5.43e-05 8.37e-03 -1.22e-05 -1.02e-03 -6.73e-03 -3.26e-05

2.18e-05 -2.67e-03 -1.22e-05 -7.94e-03 -6.08e-02 -4.73e-05 1.37e-02 -4.35e-05 1.95e-03 -3.82e-05 6.84e-06 -1.71e-03

6.73e-02 5.57e-04 -1.15e-01 5.04e-04 1.96e-03 -1.16e+00 -2.67e-04 -8.36e-02 1.57e-04 8.84e-03 2.45e-02 7.21e-05

-6.02e-04 4.29e-02 6.08e-04 9.87e-02 6.30e-01 5.11e-03 2.10e-02 2.63e-04 8.78e-04 -5.14e-05 -8.37e-05 -4.88e-03

1.15e-02 5.79e-05 -2.17e-02 1.74e-05 -1.09e-03 -8.77e-02 -5.01e-05 -6.47e-03 2.41e-05 1.08e-03 1.66e-03 1.62e-05

-2.12e-04 -4.06e-04 4.19e-04 3.09e-04 -6.29e-02 1.62e-03 -1.38e-03 1.27e-04 3.48e-04 -2.67e-05 -3.32e-05 6.06e-04

3.61e-05 1.07e-02 -1.72e-04 1.17e-02 -9.74e-02 -6.18e-04 -2.17e-03 -3.18e-05 -2.24e-04 6.15e-06 3.23e-06 1.62e-03

-3.13e-02 -1.33e-04 4.71e-02 -2.67e-05 -2.66e-04 1.54e-01 3.73e-05 1.09e-02 -1.63e-05 -9.88e-04 -2.29e-03 -2.82e-06

Molecule **3t**

1.58e-04 2.15e-03 6.77e-04 -1.99e-03 2.13e-04 3.39e-03 -4.16e-03 -2.21e-03 -5.02e-03 4.58e-03 -7.62e-03 4.82e-03

-4.32e-04 2.98e-03 1.64e-03 -8.83e-04 2.00e-03 7.61e-03 1.96e-03 1.09e-03 -7.08e-03 -1.35e-02 2.87e-03 -2.52e-03

2.20e-04 4.89e-04 -3.51e-04 7.78e-04 -9.49e-04 -2.01e-03 1.35e-03 9.70e-04 -8.84e-03 -2.34e-02 4.02e-03 -2.80e-03

-1.17e-03 1.68e-04 2.65e-04 -5.38e-03 1.02e-03 4.40e-03 -2.74e-03 3.88e-03 4.03e-03 5.02e-04 -4.61e-03 -8.76e-04

-1.83e-03 -3.64e-03 2.50e-04 -3.55e-03 -2.21e-03 -1.67e-02 -1.60e-03 1.70e-03 -6.35e-03 1.81e-03 -1.17e-03 -2.67e-03

1.88e-03 -3.97e-03 -3.35e-04 1.39e-03 -5.77e-03 -1.74e-02 -5.72e-03 -1.89e-03 4.15e-03 2.05e-03 -3.56e-03 2.80e-03

-3.08e-02 1.47e-01 -7.06e-02 -5.33e-02 2.94e-01 1.11e+00 6.38e-03 1.73e-02 -4.01e-03 3.18e-03 2.09e-02 3.76e-03

-2.00e-02 1.02e-01 -3.76e-02 9.69e-02 1.44e-01 6.34e-01 -1.79e-03 2.08e-02 -4.44e-03 2.48e-03 1.33e-02 7.19e-03

-1.85e-02 1.23e-02 -1.61e-02 3.40e-03 -8.70e-03 3.00e-02 -5.85e-04 -1.62e-06 -1.53e-03 -1.15e-04 6.00e-04 7.53e-04

1.03e-02 -3.45e-02 -2.62e-02 6.21e-03 -6.86e-03 -2.88e-02 5.25e-04 1.42e-04 -1.09e-03 -3.27e-03 1.44e-03 -1.47e-03

-8.63e-03 -1.21e-02 9.74e-03 -3.19e-02 2.00e-02 6.91e-02 1.83e-03 -1.22e-03 4.65e-04 6.05e-05 8.90e-05 3.91e-04

6.21e-03 1.70e-02 -1.50e-02 -6.25e-03 1.31e-03 3.77e-02 4.62e-04 1.72e-04 5.35e-04 3.60e-04 2.77e-03 -2.55e-04

Molecule **4**

-1.92e-04 -1.38e-04 3.31e-03 -1.59e-03 -3.35e-08 2.96e-02 2.23e-03 2.07e-02 5.12e-03 -5.17e-03 4.16e-03 -4.70e-04

7.39e-04 4.54e-04 1.86e-03 6.97e-03 2.74e-07 8.00e-03 -1.18e-03 3.42e-03 -4.71e-03 4.82e-04 -2.49e-02 -3.65e-04

-2.35e-03 3.67e-04 2.14e-03 -6.54e-03 -3.19e-07 -1.65e-03 4.67e-03 1.34e-02 -1.04e-01 -3.30e-04 -1.28e-02 -2.89e-03

-1.13e-03 3.45e-03 1.29e-02 -1.99e-05 8.74e-08 -1.48e-02 -5.79e-04 9.81e-02 1.41e-02 5.69e-03 1.31e-03 6.83e-04

-2.64e-08 8.87e-08 2.12e-07 2.91e-09 -7.51e-09 -1.82e-07 2.10e-08 3.14e-06 -1.19e-07 7.11e-07 1.36e-09 1.53e-08

-1.06e-03 -4.54e-04 -2.23e-03 -9.29e-03 -3.28e-07 3.59e-03 -8.15e-02 7.17e-04 -7.16e-03 3.63e-05 3.77e-03 -1.66e-02

1.15e-02 -1.40e-02 2.16e-02 1.84e-03 2.89e-07 -1.22e+00 -5.92e-03 -7.12e-02 8.08e-03 1.69e-02 1.07e-02 6.60e-03

2.77e-02 5.12e-03 2.31e-02 1.54e-01 4.99e-06 -2.47e-03 -6.45e-03 -1.30e-03 6.13e-03 8.53e-04 -6.10e-04 2.50e-03

6.81e-03 -3.31e-03 -1.50e-01 2.03e-02 -1.56e-07 -8.42e-02 1.24e-04 -1.53e-02 1.51e-03 5.38e-03 2.54e-03 1.58e-03

-7.83e-03 1.52e-04 -4.25e-03 -7.60e-03 5.65e-07 4.65e-03 1.84e-03 1.75e-04 -3.99e-03 -1.16e-04 -5.06e-03 -9.03e-04

5.17e-03 -3.25e-02 -8.77e-03 -1.99e-03 -4.73e-08 8.18e-03 6.45e-04 8.27e-03 8.89e-04 -5.80e-04 -5.83e-04 -7.09e-05

-6.30e-05 -5.06e-04 -7.22e-03 1.19e-04 -2.38e-09 -8.16e-02 1.09e-04 -4.63e-03 1.09e-03 9.50e-04 7.13e-04 4.37e-04

Molecule **5t**

2.16e-04 -1.64e-05 1.87e-05 6.00e-03 5.72e-03 -5.47e-02 1.54e-02 1.32e-02 -5.61e-03 1.14e-03 -5.65e-03 -6.06e-03

1.21e-03 -5.87e-04 -5.80e-04 -5.24e-03 -8.08e-05 9.41e-03 -3.40e-03 -1.28e-03 9.43e-03 -1.10e-03 1.82e-03 1.72e-03

-8.37e-05 -4.55e-04 -1.92e-03 4.81e-04 6.96e-05 1.66e-03 1.90e-04 -3.05e-03 -6.62e-03 -2.84e-03 5.64e-04 -1.48e-03

-4.91e-04 -1.57e-03 9.47e-04 6.43e-03 -1.48e-04 -3.52e-02 7.63e-03 5.32e-04 -1.85e-02 5.01e-03 2.95e-03 -8.18e-03

1.47e-03 2.14e-03 -3.17e-04 -5.13e-03 -3.96e-03 1.14e-02 -4.49e-03 1.04e-02 4.70e-02 -1.29e-02 5.07e-03 4.36e-03

-1.59e-03 -2.37e-03 1.86e-03 1.95e-02 3.11e-03 -8.97e-02 1.71e-02 4.81e-03 -1.56e-03 2.33e-03 6.48e-03 1.10e-04

-1.88e-02 -2.44e-02 2.53e-02 2.77e-01 8.14e-02 -1.26e+00 9.66e-02 5.45e-02 3.42e-02 -9.92e-03 4.77e-03 1.09e-02

2.15e-02 1.82e-02 -1.27e-02 -6.37e-02 6.35e-03 2.43e-02 6.93e-04 1.82e-03 -4.65e-03 9.45e-04 -1.32e-03 -9.46e-04

-1.46e-03 8.04e-03 -1.62e-02 -2.29e-02 7.72e-02 3.16e-02 -2.37e-04 -3.14e-03 -8.62e-03 2.86e-03 -1.51e-03 -1.21e-03

-3.23e-03 -4.49e-03 -2.16e-02 4.26e-02 -1.28e-02 -7.45e-02 4.13e-03 3.34e-03 6.12e-03 4.33e-04 8.40e-04 1.39e-03

-1.87e-02 1.03e-03 2.89e-03 2.37e-02 2.05e-02 -5.54e-02 7.55e-03 5.26e-03 6.69e-04 -5.01e-04 2.44e-04 -2.20e-04

-1.07e-02 -1.68e-03 -1.46e-03 8.23e-03 1.08e-02 -3.86e-02 4.25e-03 2.39e-03 -3.86e-04 2.25e-04 4.52e-04 -9.58e-04

Molecule **6**

-7.36e-08 4.82e-04 3.55e-08 -1.03e-03 -1.05e-06 4.41e-02 -2.70e-06 2.26e-02 2.63e-06 3.93e-03 2.69e-03 -6.15e-07

4.38e-04 5.31e-07 9.19e-03 1.42e-06 -7.59e-03 -9.57e-07 -4.07e-04 5.06e-07 1.43e-02 7.99e-07 -2.38e-06 1.43e-02

1.56e-07 4.75e-03 6.75e-07 1.07e-02 -3.04e-07 3.42e-03 -1.42e-06 -4.81e-02 -5.19e-06 -3.19e-02 -5.81e-03 -2.93e-06

3.40e-03 6.32e-07 -6.98e-03 6.12e-07 -9.22e-03 -1.24e-06 -5.14e-03 -5.41e-06 8.30e-02 -

2.27e-06 -4.34e-06 1.92e-02

-1.94e-06 -1.07e-02 2.20e-06 -3.06e-02 -6.38e-07 1.26e-01 -4.45e-06 8.89e-02 -2.51e-06 1.18e-02 -2.07e-02 -3.24e-06

4.86e-03 -4.04e-07 -9.26e-03 -2.17e-06 1.38e-02 1.75e-05 4.77e-02 -3.11e-07 -2.26e-03 -1.89e-06 -1.84e-07 -6.97e-04

-6.88e-06 -1.56e-02 8.17e-06 -8.51e-02 -1.67e-05 1.20e+00 -1.74e-05 -9.78e-02 -8.77e-06 5.31e-02 -3.88e-02 -1.24e-05

3.30e-02 -8.17e-07 -8.39e-02 -5.88e-06 7.56e-02 -3.13e-05 -1.22e-02 5.63e-07 6.10e-03 -1.50e-06 1.68e-06 -2.81e-03

4.05e-06 1.15e-02 -9.06e-06 1.13e-01 -6.76e-07 -4.01e-02 2.91e-07 -7.21e-03 -5.17e-07 -4.67e-03 5.68e-03 7.01e-07

6.12e-05 1.46e-06 -2.66e-02 4.00e-07 3.45e-02 -7.75e-06 4.05e-03 9.72e-07 -3.21e-03 -9.72e-07 6.24e-07 -2.97e-03

-4.28e-05 -2.18e-06 8.21e-03 -1.62e-06 -2.03e-02 3.54e-06 -4.37e-03 -1.11e-06 -1.03e-03 1.29e-07 -1.60e-07 -3.86e-03

-5.40e-07 1.84e-02 -1.38e-06 9.31e-03 -3.05e-06 -1.96e-02 2.16e-07 1.28e-02 7.14e-07 1.83e-03 2.21e-05 -1.14e-07

Molecule **7t**

-1.95e-04 1.45e-04 6.21e-04 5.80e-05 -1.90e-03 8.32e-03 8.28e-04 1.62e-03 1.15e-02 -5.83e-04 9.18e-04 1.05e-04

9.34e-04 -2.06e-03 -2.66e-03 -3.04e-04 1.31e-02 4.62e-03 -5.61e-03 -1.83e-03 -6.56e-02 4.30e-03 2.42e-03 1.13e-03

-1.33e-03 8.50e-03 1.23e-03 8.48e-04 1.95e-03 -4.55e-02 1.62e-03 1.51e-02 -1.15e-02 -2.15e-05 4.03e-04 -8.14e-04

-1.73e-05 7.60e-04 -4.57e-05 -5.21e-05 9.12e-04 -4.18e-03 7.69e-05 2.07e-03 -5.06e-03 6.65e-04 1.95e-04 1.88e-04

-5.80e-03 4.31e-02 6.46e-03 2.97e-03 3.28e-04 1.40e-01 7.06e-04 8.74e-02 1.44e-03 -4.96e-03 -3.75e-03 -1.68e-04

6.76e-04 -1.34e-03 2.83e-03 4.52e-04 1.80e-02 -7.62e-03 -2.88e-02 2.34e-03 2.72e-03 1.09e-03 1.06e-03 4.01e-04

1.49e-02 -1.17e-01 -1.31e-02 -4.40e-03 3.79e-03 -1.27e+00 7.57e-03 6.30e-02 3.36e-03 -3.37e-03 -1.72e-03 -1.44e-03

-1.11e-03 -9.66e-03 5.76e-02 6.05e-03 1.19e-01 7.10e-03 1.35e-02 -3.58e-05 1.52e-03 -4.36e-04 -1.89e-04 -1.41e-04

1.02e-02 -7.34e-02 -1.48e-02 -6.29e-03 5.30e-03 3.96e-02 6.55e-04 -1.36e-02 6.07e-04 6.59e-04 3.90e-04 2.00e-04

-3.04e-05 7.81e-03 -1.44e-03 7.71e-04 -6.52e-03 2.30e-02 -9.79e-04 -6.67e-04 -1.71e-04 1.29e-04 1.03e-04 5.58e-05

1.88e-03 4.87e-03 -6.94e-05 -4.81e-04 -4.10e-03 8.72e-03 -6.08e-04 -2.24e-04 -9.20e-05 1.11e-04 1.12e-04 6.78e-05

3.27e-05 9.19e-04 -6.42e-04 3.47e-04 -6.61e-04 1.92e-03 -3.34e-04 -2.64e-04 2.54e-04 3.37e-05 7.56e-05 -1.36e-05

Natural Transition Orbital

The natural transition orbitals (NTO) are obtained diagonalization the TDM(T) provided above. The electron NTOs are eigenvectors of the matrix $TT^{\dagger}$, while the hole NTOs are eigenvectors of the matrix $T^{\dagger}T$. Integrals from the PySCF[1-3] program were used to obtain the transition dipole and the exchange integral between the hole and electron NTO pair with the largest eigenvalue.

ΔE_{ST} of 1, 2, and 3t

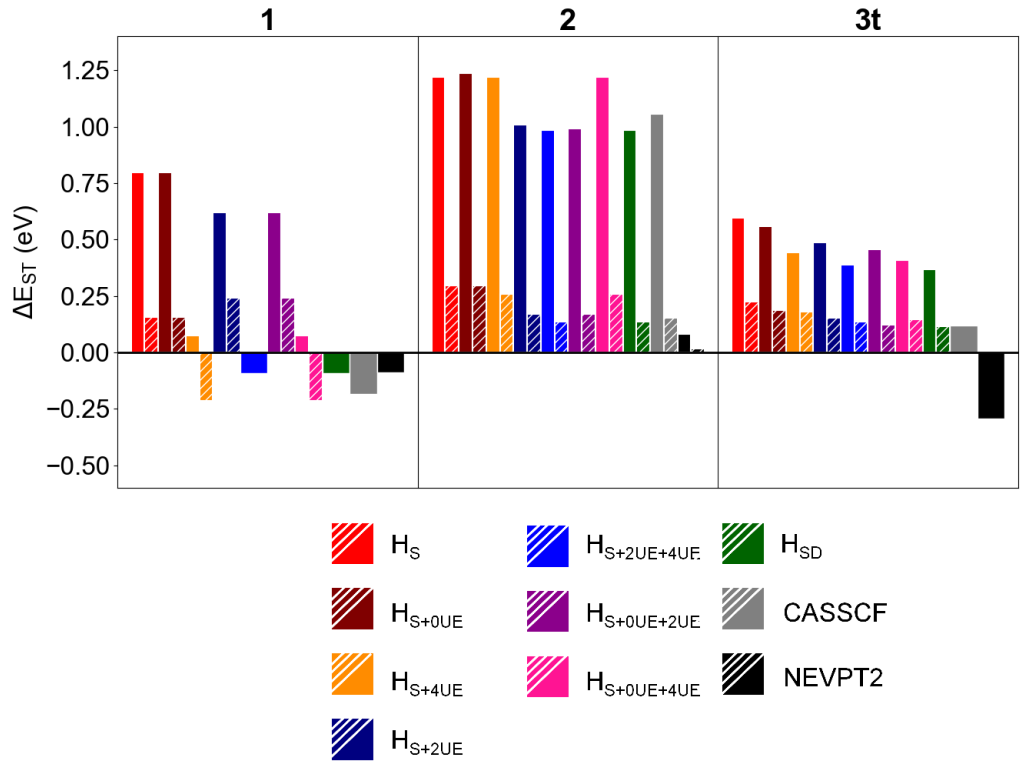

Figure S13. ΔE_{ST} of molecules that have T_1 states with differing characters from those of the S_1 states. The hatched bars show the difference of energy between the S_1 state and the triplet state that has the same configuration as its configuration with the largest coefficient.

Reference

1) Recent developments in the PySCF program package, Q. Sun, X. Zhang, S. Banerjee, P. Bao, M. Barbry, N. S. Blunt, N. A. Bogdanov, G. H. Booth, J. Chen, Z.-H. Cui, J. J. Eriksen, Y. Gao, S. Guo, J. Hermann, M. R. Hermes, K. Koh, P. Koval, S. Lehtola, Z. Li, J. Liu, N. Mardirossian, J. D. McClain, M. Motta, B. Mussard, H. Q. Pham, A. Pulkin, W. Purwanto, P. J. Robinson, E. Ronca, E. R. Sayfutyarova, M. Scheurer, H. F. Schurkus, J. E. T. Smith, C. Sun, S.-N. Sun, S. Upadhyay, L. K. Wagner, X. Wang, A. White, J. Daniel Whitfield, M. J. Williamson, S. Wouters, J. Yang, J. M. Yu, T. Zhu, T. C. Berkelbach, S. Sharma, A. Yu. Sokolov, and G. K.-L. Chan, J. Chem. Phys. **153**, 024109 (2020)
2) PySCF: the Python-based simulations of chemistry framework, Q. Sun, T. C. Berkelbach, N. S. Blunt, G. H. Booth, S. Guo, Z. Li, J. Liu, J. McClain, S. Sharma, S. Wouters, and G. K.-L. Chan, WIREs Comput. Mol. Sci. **8**, e1340 (2018)
3) Libcint: An efficient general integral library for Gaussian basis functions, Q. Sun, J. Comp. Chem. 36, 1664 (2015)