

Info Mol4

OPT FOR $S_0/S_1/T_1$:cam-b3lyp/6-31+g

TD-DFT: cam-b3lyp/6-31+g

SCF: cam-b3lyp/6-31+g*

CASSCF/NEVPT2: cam-b3lyp/6-31+g* ActiveSpace=(6 α 6 β ,12orb)

SOC: cam-b3lyp/6-31+g*

 $\Delta\text{SCF:cam-b3lyp/6-311+g}^*$

TD-DFT

S0-S1: Singlet-A 3.6039 eV 344.02 nm f=0.7192 <S**2>=0.000

56 -> 57 0.68812

NTO Alys:

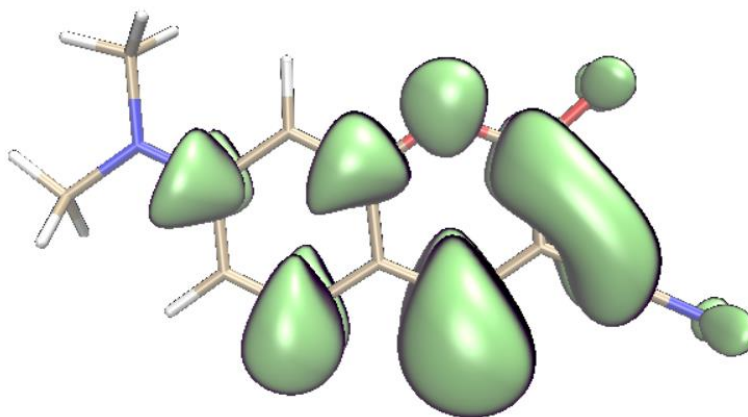


Fig1.CDD

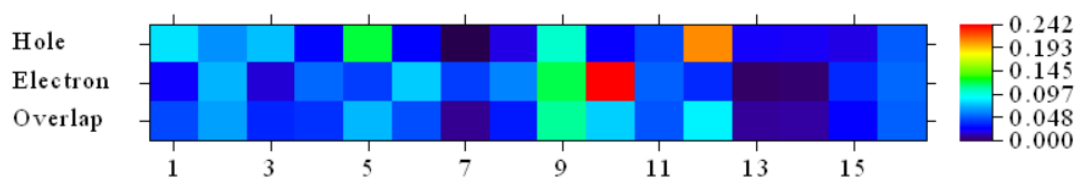


Fig2.Atoms Ele-Hole Martix(Heatmap)

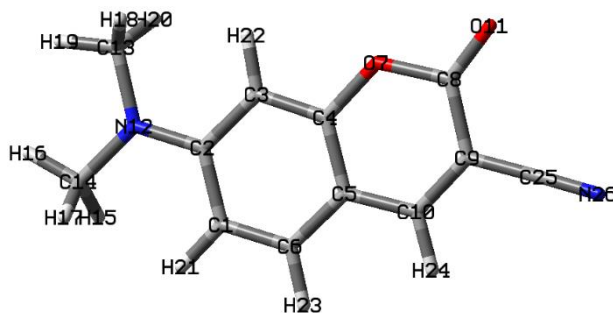


Fig3.Atoms Number

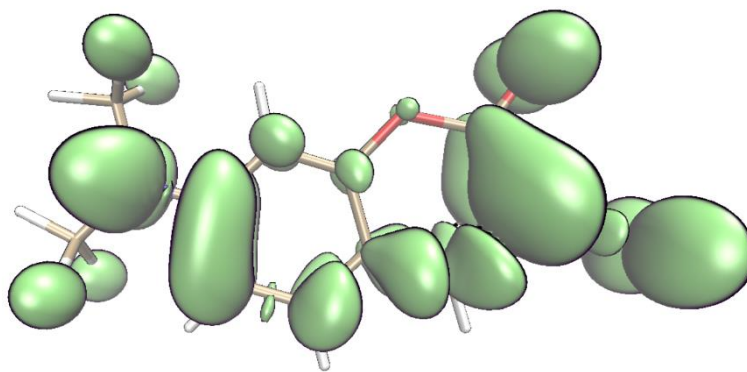


Fig4. Transition Dipole Density

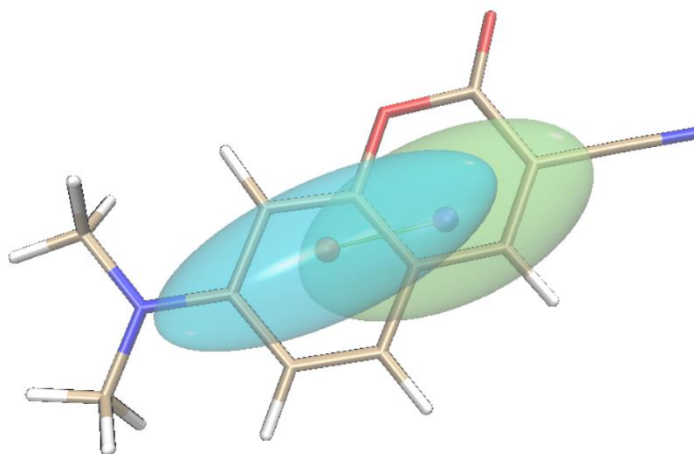


Fig5.Cele/Chole and Dipole Centroid

Whats More:

Molecule ID	M4	
Method	cam-b3lyp/6-31g*opted,exc	
Converged	YES	
Total Energy	-24834.25865	eV
Total Energy	-912.6417107	a.u.
HOMO Energy	-7.123285427	eV
LUMO Energy	-2.334623010	eV
HOMO-LUMO Gap	4.788662417	eV
Approx. IP	7.123285427	eV
Approx. EA	2.334623010	eV
Electronegativity	4.728954218	eV
Chemical Hardness	2.394331209	eV
Chemical Softness	11.36492725	eV ^{-1/2}
Global Electrophilicity Index		

	0.171618899	eV
Dipole X	-12.05311628	Debye
Dipole Y	-4.597158797	Debye
Dipole Z	0.022782961	Debye
Dipole Moment	12.90007752	Debye
Transition Dipole Moment (X, Y, Z):		
	3.923328, 0.318618, 0.000162	Debye
Centroid Distance	1.897	Angstrom
Hole Centroid (X, Y, Z):		
	-0.671532, -0.156430, -0.000097	Angstrom
Electron Centroid (X, Y, Z):		
	1.195222, -0.496024, -0.000062	Angstrom
Coulomb Attraction Energy		
	0.168991	eV
Number of Electrons 138		

 Δ SCF:

T1-S0:

S0 Energy: -722.669703 E_h (T1 Opt,spin=1)T1 Energy: -722.593545 E_h (T1 Opt,spin=3) Δ E (Hartree): +0.076158 E_h Δ E (eV): +2.07 eV, 598 nm[This Value is Similar to CASPT2\(12,12\) down site page\(591.1 nm\)](#)

T1 opt at 6-31+g*/cam-b3lyp

CASSCF/PT2

S1-S0(NEVPT2 Corrected):

S0: -2.10008332 Hartree

S1: -2.09960712 Hartree

(CASSCF): 2.697 eV (459.7 nm), CASSCF energy = -718.927659823864

CASCI E = -718.927659823864 E(CI) = -20.9665094263817 $S^2 = 0.0000000$

CASCI state-averaged energy = -718.927659823864

CASCI energy for each state

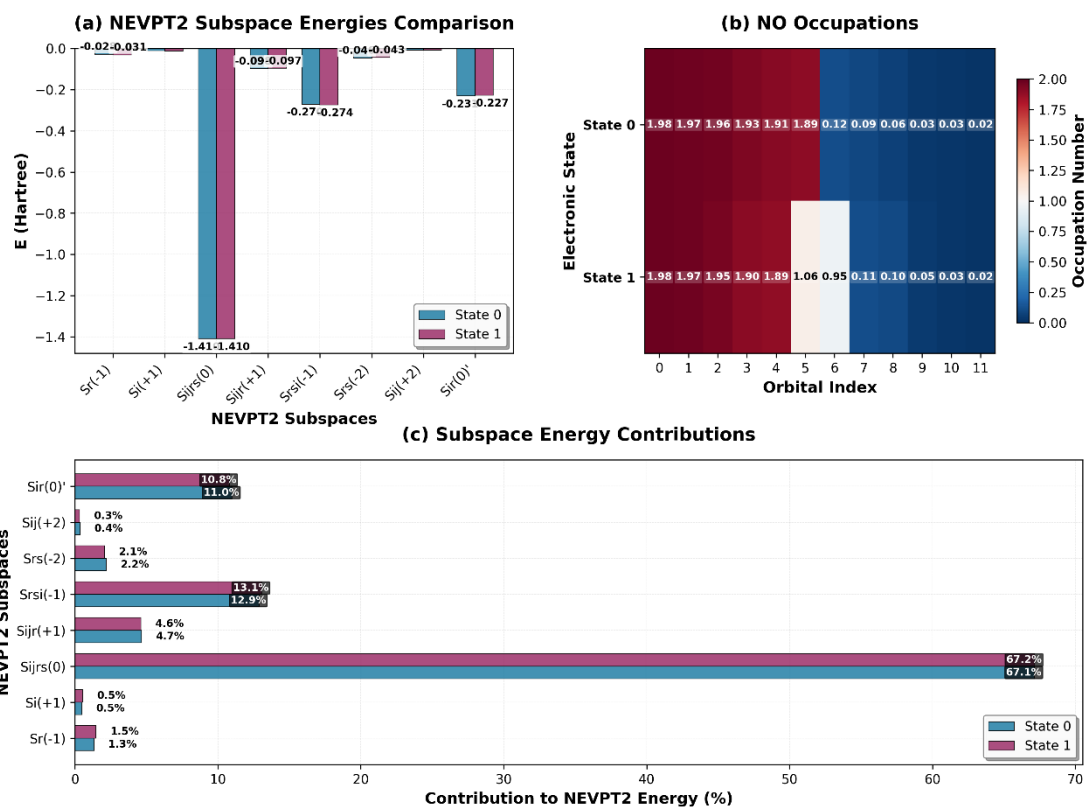
State 0 weight 0.5 E = -718.977218755343 $S^2 = 0.0000000$ State 2 weight 0.5 E = -718.878100892386 $S^2 = 0.0000000$ 

Fig.6-1 NEVPT2 Analysis of S1-S0

S0-T1(NEVPT2 Corrected):

T1: -1.41900373 Hartree

S0: -1.42132323 Hartree

(CASSCF): 2.0978 eV(591.1 nm),CASSCF energy = -720.512009885061

CASCI E = -720.512009885061 E(CI) = -18.1705439928862 $S^2 = 1.0000000$

CASCI state-averaged energy = -718.512009885061

CASCI energy for each state

State 0 weight 0.5 $E = -718.566335419872$ $S^2 = 0.0000000$

State 1 weight 0.5 $E = -718.48923541987$ $S^2 = 2.0000000$

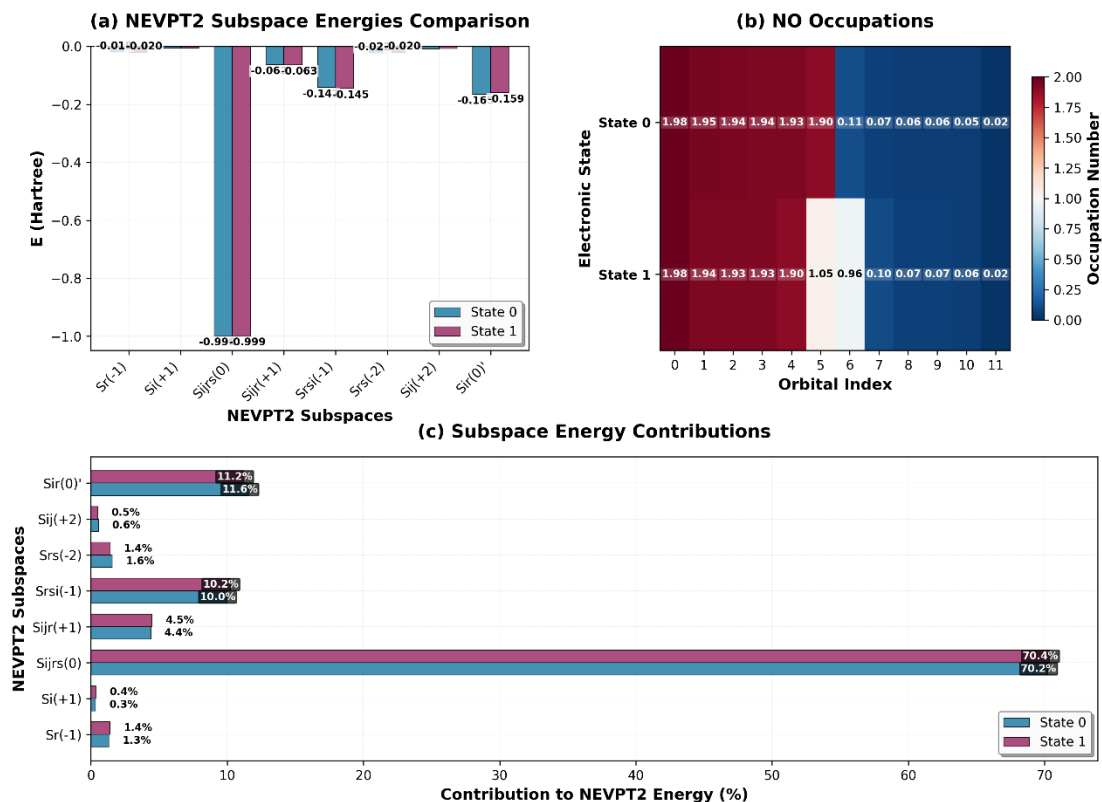


Fig.6-2 NEVPT2 Analysis of T1-S0

SOC

How:

Using Custom Script. This Spt was starting from the theoretical foundation, the essence of spin-orbit coupling is a relativistic effect. Within the non-relativistic quantum mechanics framework, we use perturbation theory to handle it. The complete SOC Hamiltonian includes one-electron and two-electron terms:

$$H_S O = H_S O^{1e} + H_S O^{2e}$$

where the one-electron term dominates:

$$H_S O^{1e} = \frac{\alpha^2}{2} \sum_i \sum_A Z_A \frac{\mathbf{r}_{iA} \times \mathbf{p}_i}{|\mathbf{r}_{iA}|^3} \cdot \mathbf{s}_i$$

In our implementation, through the `compute_soc` function, we first obtain the one-electron SOC integrals [int1e_prinvxp](#) from PySCF. These integrals already contain the form of $\frac{\mathbf{r} \times \mathbf{p}}{r^3}$. Then, these integrals are transformed from the atomic orbital basis to the molecular orbital basis, and we focus on the active space part, because in the CASSCF method, electron correlation is primarily described within the active space.

The core challenge lies in calculating the SOC matrix elements between two multi-electron states:

$$\langle \Psi_I | \widehat{H}_{SO} | \Psi_J \rangle$$

Here, $|\Psi_I\rangle$ and $|\Psi_J\rangle$ are CASCI wavefunctions. We have adopted several progressive calculation strategies: the preferred method utilizes the [contract_1e](#) functionality of the FCI module to directly apply the SOC operator to the CI vectors; when this method encounters numerical difficulties, we fall back to an approximate method based on the Singular Value Decomposition (SVD) of the SOC matrix, estimating the coupling strength through the maximum singular value and the wavefunction overlap; the last resort is the eigenvalue method, which uses the maximum eigenvalue of the SOC matrix as a measure of coupling strength.

In the [analyze_soc_origin](#) function, we delve into the physical origins of SOC. By examining the distribution of the SOC operator's norm in different directions, we can understand the anisotropic characteristics. When analyzing orbital contributions, we not only look at the diagonal elements but also consider off-diagonal couplings, which can reveal which molecular orbitals play a key role in promoting spin-orbit mixing. The matrix density analysis then reveals the network structure characteristics of the SOC coupling.

For heavy-atom-free systems, SOC mainly originates from the orbital angular momentum coupling of light atoms (C, N, O, etc.). The SOC strength in these systems is typically weak, on the order of $0.01 - 1 \text{ cm}^{-1}$, much smaller than the hundreds of cm^{-1} in systems containing heavy atoms. Our calculation result of 0.02 cm^{-1} falls precisely within this typical range, validating the reasonableness of the method.

After obtaining the SOC matrix elements, the calculation of phosphorescence properties is based on Fermi's Golden Rule. The radiative transition rate is proportional to the square of the SOC matrix

element and the cube of the energy gap:

$$k_{phos} \propto |\langle S_0 | \widehat{H}_{SO} | T_1 \rangle|^2 \cdot \Delta E^3$$

This first-principles approach completely avoids empirical parameters and is particularly suitable for exploring new heavy-atom-free phosphorescent systems, providing a theoretical basis for understanding the relationship between molecular structure, electronic states, and luminescent properties.

Result:

S1-S0 SOC:

SOC vector (x,y,z): [2.56e-08, 3.51e-08, 4.16e-08] a.u.

SOC norm: 6.01e-09 a.u. (0.001 cm^{-1})

Phosphorescence energy: 2.861 eV (433 nm)

Transition rate: 1.092 s^{-1}

Phosphorescence lifetime: 0.916 s

SOC btwn S1-S0 is very weak,its physically reasonable.

T1-S0 SOC:

SOC vector (x,y,z): [1.41e-06, 1.80e-06, 0.00e+00] a.u.

SOC norm: 2.29e-06 a.u. (0.50 cm^{-1})

Phosphorescence energy: 2.3 eV (539 nm)

Transition rate: 3.098 s^{-1}

Phosphorescence lifetime: 0.323 s

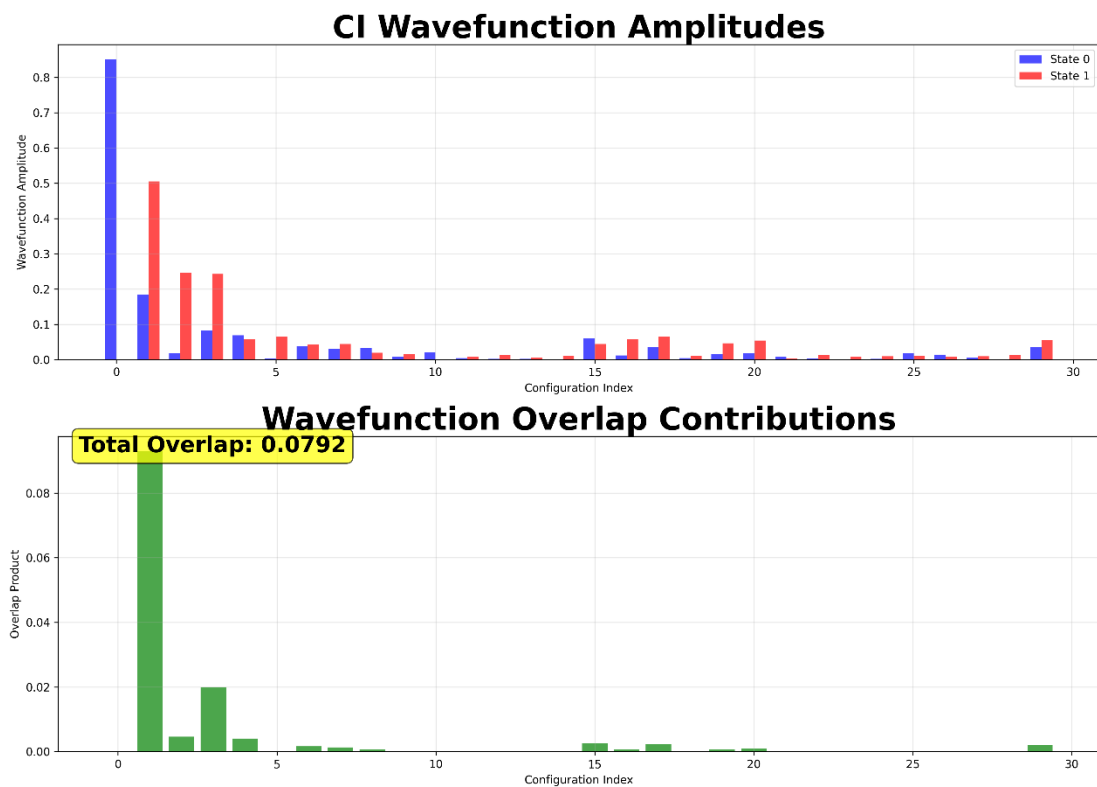


Fig7.CI Wavefunction

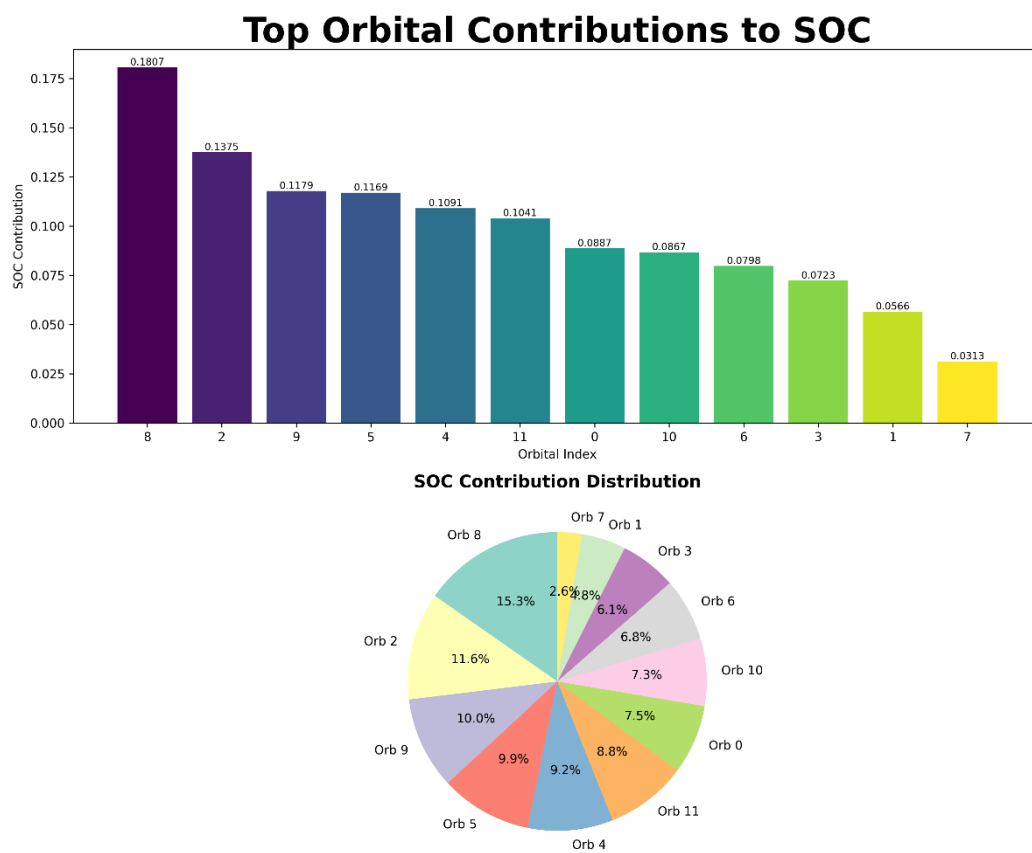


Fig8.Orbital Contribution to SOC

Spin-Orbit Coupling Matrix Elements

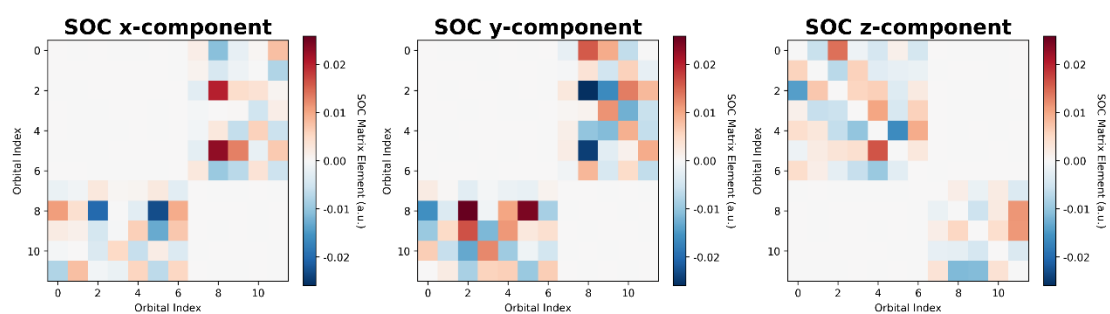


Fig9.SOC Martix Heatmap

UV-Vis Absorption Spectra

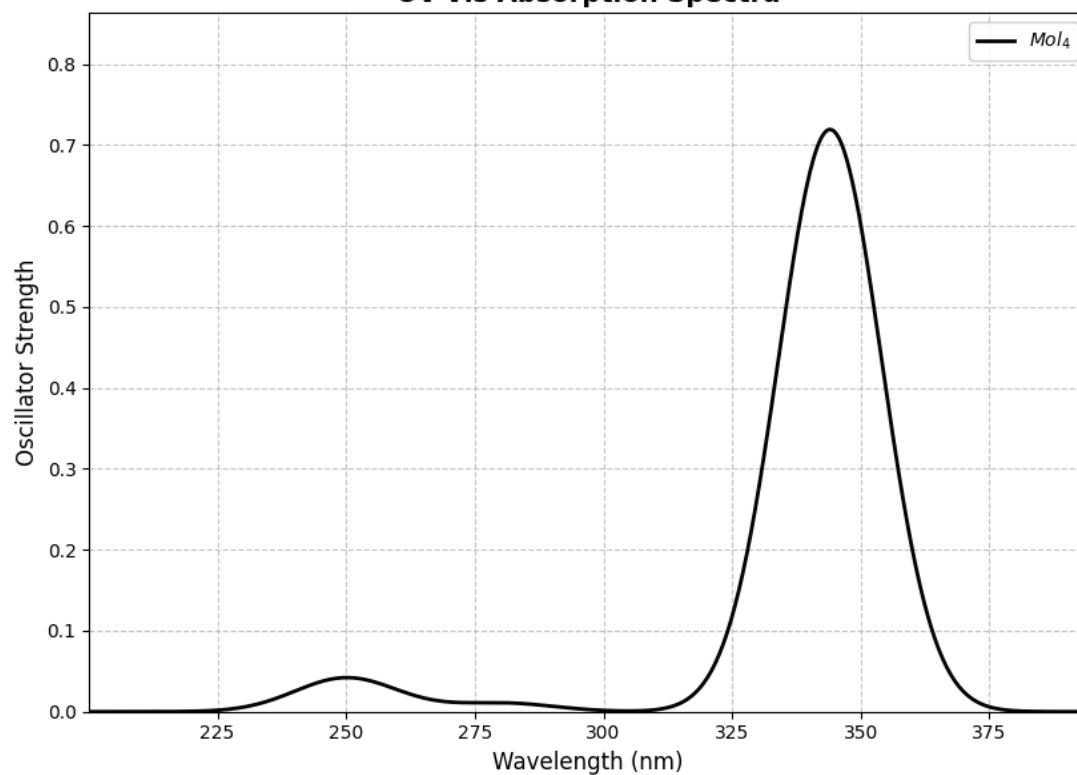


Fig10. UV-Vis of Mol4

Total

$S_0 \rightarrow S_1$ (TD-DFT): 3.6039 eV | 344.02 nm

EMISSION (S_1 geometry):

$S_1 \rightarrow S_0$ (CASSCF/NEVPT2): 2.697 eV | 459.7 nm

PHOSPHORESCENCE (T_1 geometry):

$T_1 \rightarrow S_0$ (Δ SCF): 2.07 eV | 598 nm

$T_1 \rightarrow S_0$ (CASSCF/NEVPT2): 2.0978 eV | 591.1 nm

$T_1 \rightarrow S_0$ (SOC): 2.3 eV | 539 nm

STOKES SHIFT (S_1 emission vs S_0 absorption):

Energy Shift: 0.9069 eV

Wavelength Shift: 115.68 nm

$S_1 - T_1$ ENERGY GAP (at T_1 geometry):

$\Delta E(S_1 - T_1): \approx 0.40 - 0.63$ eV

Jablonski Diagram for Mol4

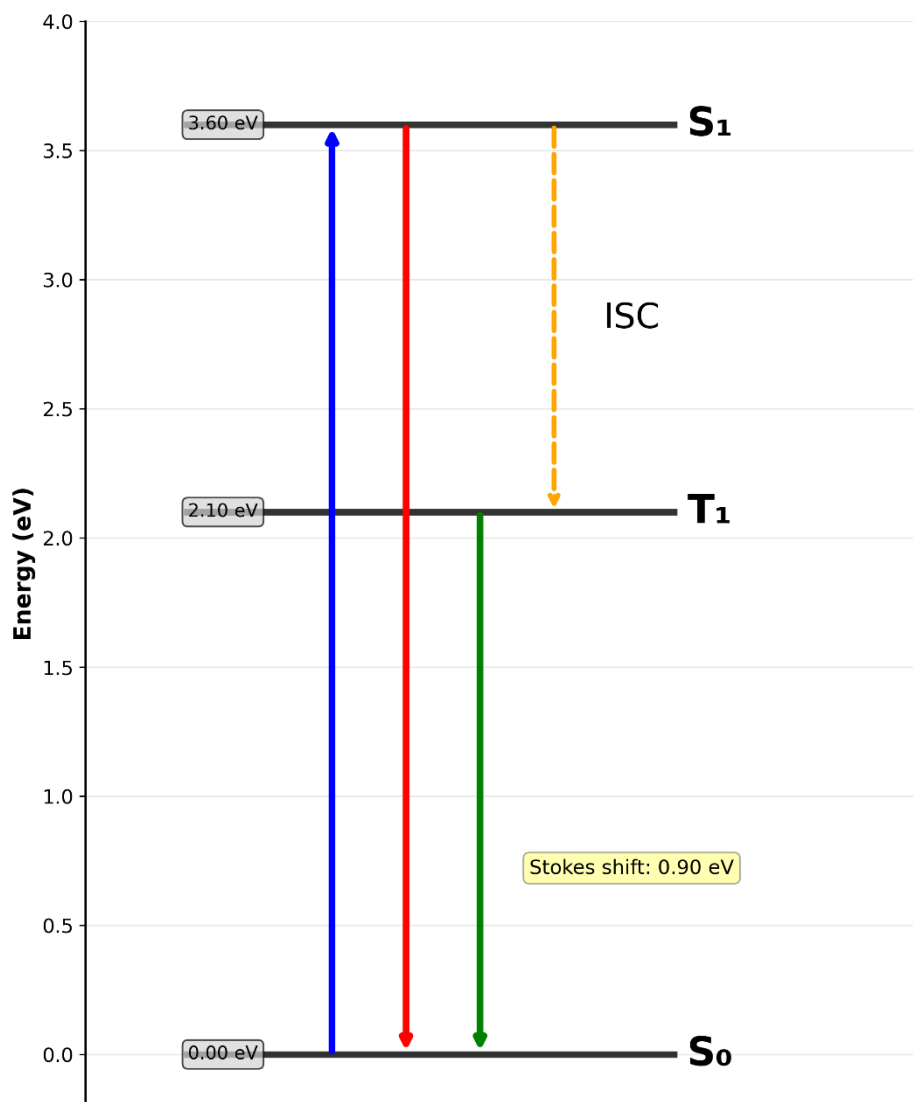


Fig11. Energy level diagram of S_0 - T_1 - S_1

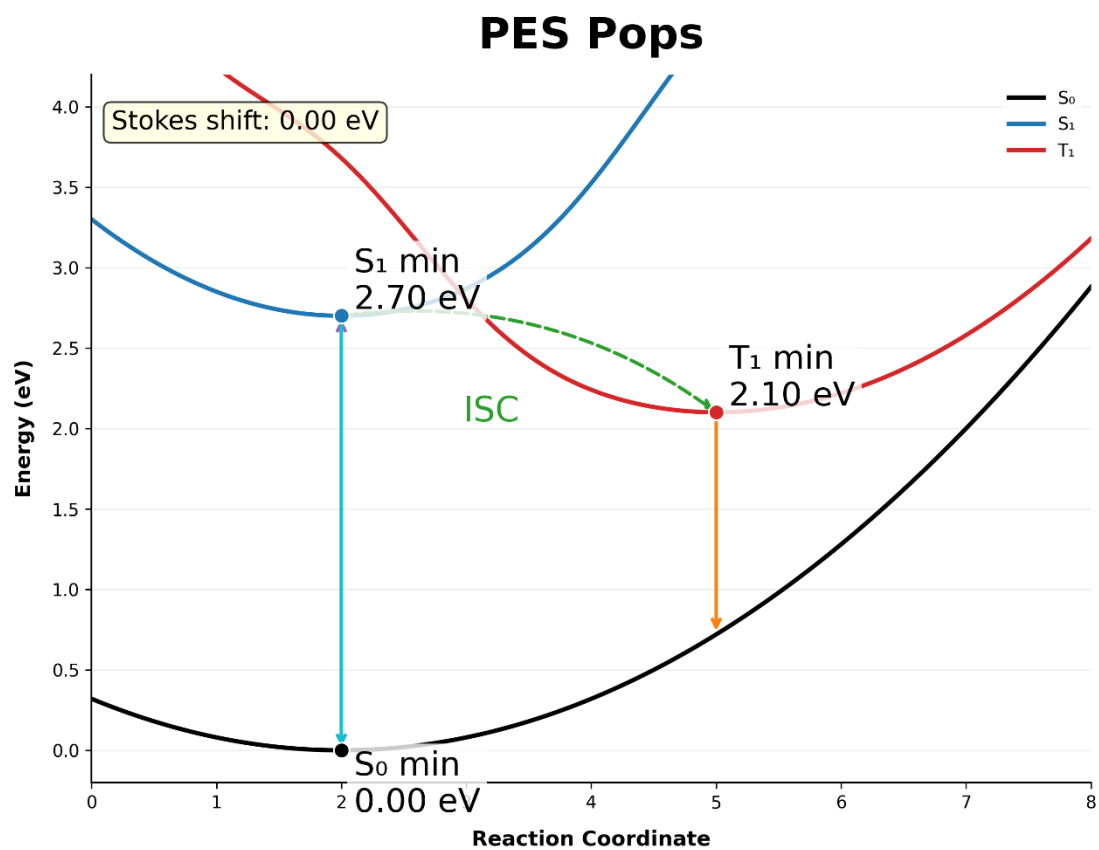


Fig12. Potential Energy Surface Diagram for Photophysical Processes of Mol4

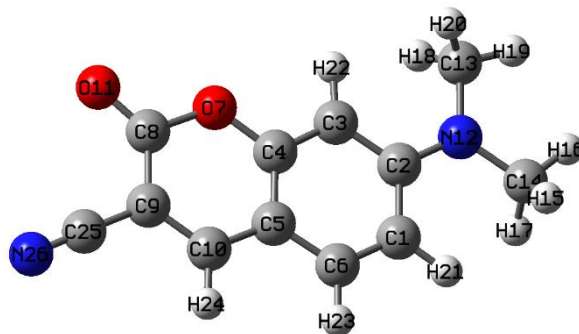
Reaction Coordinate:

Fig13. Atoms Number

T1-S0:

BL:

C9-C10: 0.0712 Å (1.3901 → 1.4612 Å) (5.1%)
O7-C8: 0.0519 Å (1.4519 → 1.3999 Å) (3.6%)
C5-C10: 0.0406 Å (1.4223 → 1.3817 Å) (2.9%)
C3-C4: 0.0292 Å (1.3926 → 1.3634 Å) (2.1%)
C9-C25: 0.0250 Å (1.4247 → 1.3997 Å) (1.8%)
C8-C9: 0.0196 Å (1.4651 → 1.4456 Å) (1.3%)
C1-C6: 0.0157 Å (1.3869 → 1.3712 Å) (1.1%)
C5-C6: 0.0152 Å (1.4229 → 1.4381 Å) (1.1%)
C25-N26: 0.0140 Å (1.1883 → 1.1743 Å) (1.2%)
C4-C5: 0.0138 Å (1.4257 → 1.4395 Å) (1.0%)

BA:

C5-C10-C9: 2.94° (121.81 → 118.87°) (2.4%)
C5-C10-H24: 2.77° (119.14 → 121.90°) (2.3%)
C9-C8-O11: 2.05° (127.96 → 125.91°) (1.6%)
C4-C5-C6: 1.91° (117.05 → 115.15°) (1.6%)
C4-C5-C10: 1.72° (118.53 → 120.24°) (1.4%)
O7-C8-C9: 1.65° (115.25 → 116.90°) (1.4%)
C9-C25-N26: 1.32° (178.86 → 177.55°) (0.7%)
C3-C4-C5: 0.80° (122.59 → 123.40°) (0.7%)
C5-C6-H23: 0.73° (118.75 → 118.02°) (0.6%)
C8-C9-C25: 0.70° (117.55 → 118.25°) (0.6%)

DPA:

C14-N12-C13-H20: 0.13° (-119.54 → -119.42°) (0.1%)
H20-C13-N12-C14: 0.13° (-119.54 → -119.42°) (0.1%)
C2-N12-C13-H20: 0.10° (60.50 → 60.59°) (0.1%)
H20-C13-N12-C2: 0.10° (60.50 → 60.59°) (0.1%)

S1-S0:

BL:

C9-C10: 0.0317 Å (1.3901 → 1.4218 Å) (2.3%)
C8-C9: 0.0295 Å (1.4651 → 1.4357 Å) (2.0%)
C3-C4: 0.0186 Å (1.3926 → 1.3740 Å) (1.3%)
O7-C8: 0.0174 Å (1.4519 → 1.4344 Å) (1.2%)
C25-N26: 0.0164 Å (1.1883 → 1.1719 Å) (1.4%)
C9-C25: 0.0134 Å (1.4247 → 1.4113 Å) (0.9%)
C4-O7: 0.0129 Å (1.3929 → 1.3800 Å) (0.9%)
C10-H24: 0.0124 Å (1.0943 → 1.0818 Å) (1.1%)
C1-C6: 0.0114 Å (1.3869 → 1.3755 Å) (0.8%)
C14-H16: 0.0099 Å (1.0981 → 1.0883 Å) (0.9%)

BA:

C5-C10-C9: 2.57° (121.81 → 119.24°) (2.1%)
C5-C10-H24: 1.75° (119.14 → 120.89°) (1.5%)
C9-C25-N26: 1.63° (178.86 → 177.23°) (0.9%)
O7-C8-O11: 1.28° (116.78 → 115.51°) (1.1%)
C10-C9-C25: 1.27° (121.21 → 119.94°) (1.0%)
C8-C9-C10: 1.04° (121.24 → 122.28°) (0.9%)
O7-C8-C9: 0.96° (115.25 → 116.21°) (0.8%)
C9-C10-H24: 0.82° (119.05 → 119.87°) (0.7%)
C4-C5-C6: 0.79° (117.05 → 116.26°) (0.7%)
C4-C5-C10: 0.75° (118.53 → 119.27°) (0.6%)

DPA:

C13-N12-C14-H17: 0.15° (-119.24 → -119.39°) (0.1%)
H17-C14-N12-C13: 0.15° (-119.24 → -119.39°) (0.1%)
C14-N12-C13-H18: 0.14° (119.44 → 119.58°) (0.1%)
H18-C13-N12-C14: 0.14° (119.44 → 119.58°) (0.1%)
C2-N12-C14-H15: 0.12° (-60.72 → -60.60°) (0.1%)
H15-C14-N12-C2: 0.12° (-60.72 → -60.60°) (0.1%)
C2-N12-C14-H17: 0.12° (60.72 → 60.60°) (0.1%)
H17-C14-N12-C2: 0.12° (60.72 → 60.60°) (0.1%)
C2-N12-C13-H18: 0.11° (-60.52 → -60.41°) (0.1%)
H18-C13-N12-C2: 0.11° (-60.52 → -60.41°) (0.1%)

