

Supporting Information

Evaluation of spin-orbit couplings with linear-response TDDFT, TDA, and TD-DFTB

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SI-1. Block Matrix Transformation for Gaussian 09

In this section, we discuss the block matrix transformation (BMT) for atomic integrals in the interface to Gaussian 09. In Gaussian 09, the output order for d orbitals is XX, YY, ZZ, XY, XZ, YZ; for f orbitals, it is XXX, YYY, ZZZ, XYY, XXY, XXZ, XZZ, YZZ, YYZ, XYZ. In MolSOC, the order for d orbitals is XX, XY, XZ, YY, YZ, ZZ; for f orbitals, it is XXX, XXY, XXZ, XYY, XYZ, XZZ, YYY, YYZ, YZZ, ZZZ.

The transformation matrix for d orbitals is

$$\begin{pmatrix} \phi_{d_{xx}} \\ \phi_{d_{yy}} \\ \phi_{d_{zz}} \\ \phi_{d_{xy}} \\ \phi_{d_{xz}} \\ \phi_{d_{yz}} \end{pmatrix}^T = \begin{pmatrix} \phi_{d_{xx}} \\ \phi_{d_{xy}} \\ \phi_{d_{xz}} \\ \phi_{d_{yy}} \\ \phi_{d_{yz}} \\ \phi_{d_{zz}} \end{pmatrix}^T \mathbf{C}_{d,6 \times 6}^T \mathbf{C}_{d,6 \times 6}^T \equiv \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}^T,$$

while for f orbitals, it is

$$\begin{pmatrix} \phi_{x^3} \\ \phi_{y^3} \\ \phi_{z^3} \\ \phi_{xy^2} \\ \phi_{x^2y} \\ \phi_{x^2z} \\ \phi_{xz^2} \\ \phi_{yz^2} \\ \phi_{y^2z} \\ \phi_{xyz} \end{pmatrix}^T = \begin{pmatrix} \phi_{x^3} \\ \phi_{x^2y} \\ \phi_{x^2z} \\ \phi_{xy^2} \\ \phi_{xyz} \\ \phi_{xz^2} \\ \phi_{y^3} \\ \phi_{y^2z} \\ \phi_{yz^2} \\ \phi_{z^3} \end{pmatrix}^T \mathbf{C}_{f,10 \times 10}^T \mathbf{C}_{f,10 \times 10}^T \equiv \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}^T.$$

For s and p orbitals, these matrices are identity matrices.

Suppose we have a matrix $\mathbf{H}_{10 \times 10}^I$ for atomic integrals obtained from MolSOC, which includes 1 s , 3 p , and 6 d orbitals. This matrix can be blocked as

$$\mathbf{H}_{10 \times 10}^I = \begin{pmatrix} \mathbf{H}_{ss,1 \times 1} & \mathbf{H}_{sp,1 \times 3} & \mathbf{H}_{sd,1 \times 6} \\ \mathbf{H}_{ps,3 \times 1} & \mathbf{H}_{pp,3 \times 3} & \mathbf{H}_{pd,3 \times 6} \\ \mathbf{H}_{ds,6 \times 1} & \mathbf{H}_{dp,6 \times 3} & \mathbf{H}_{dd,6 \times 6} \end{pmatrix}.$$

Applying the transformation matrix defined above, the atomic integral matrix $\mathbf{H}_{10 \times 10}^I$ used for the Gaussian 09 interface can be reconstructed as

$$\mathbf{H}_{10 \times 10}^{II} = \begin{pmatrix} \mathbf{1}_{s,1 \times 1} & & \\ & \mathbf{1}_{p,3 \times 3} & \\ & & \mathbf{C}_{d,6 \times 6} \end{pmatrix} \mathbf{H}_{10 \times 10}^I \begin{pmatrix} \mathbf{1}_{s,1 \times 1} & & \\ & \mathbf{1}_{p,3 \times 3} & \\ & & \mathbf{C}_{d,6 \times 6}^T \end{pmatrix}.$$

SI-2. STO Fitting

Some fits of Slater type orbitals (STOs) with Gaussian type orbitals (GTOs) are shown in Figure 1S. Fitting errors are usually on the order of $10^{-5} \sim 10^{-7}$ depending on the number of nodes in the wave function.

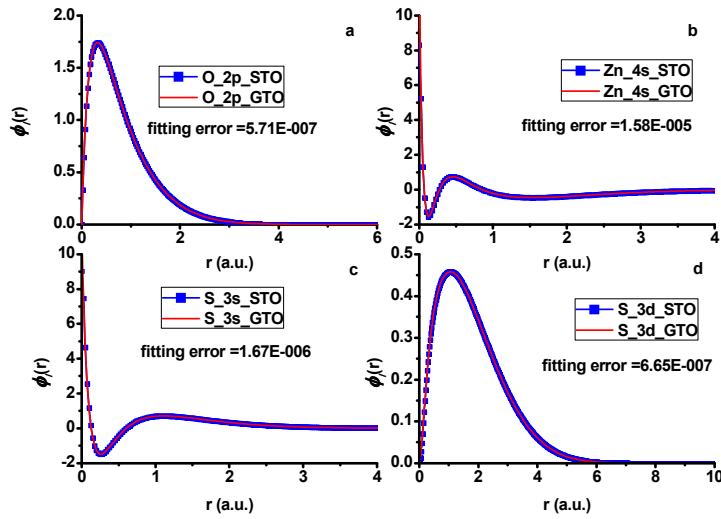


Figure 1S. Radial part of the atomic wave function *versus* distance for orbitals: a. O 2p, b. Zn 4s, c. S 3s, d. S 3d

SI-3. BMT for atomic integrals in the interface to DFTB+

In DFTB+, the angular-dependent part of the atomic orbitals is of tesseral harmonic form^{S1}. Therefore, the transformation matrix between spherical $\phi_{l,m}$ ($l \in \{s=0, p=1, d=2, f=3\}$, $m = \{-l, -l+1, \dots, l-1, l\}$) and Cartesian GTOs $\phi_{n,l}$ ($n = \{1, 2, \dots, 2l+1\}$) can be written as,

$$\phi_{s,0} = \mathbf{C}_{s,1 \times 1} \phi_{1,s}^s,$$

$$\text{where } \mathbf{C}_{s,1 \times 1} \equiv (c_s), \quad c_s = \frac{1}{\sqrt{4\pi}},$$

$$\begin{pmatrix} \phi_{p,-1} \\ \phi_{p,0} \\ \phi_{p,1} \end{pmatrix} = \mathbf{C}_{p,3 \times 3} \begin{pmatrix} \phi_{1,p_x} \\ \phi_{1,p_y} \\ \phi_{1,p_z} \end{pmatrix},$$

$$\text{where } \mathbf{C}_{p,3 \times 3} \equiv \begin{pmatrix} 0 & c_p & 0 \\ 0 & 0 & c_p \\ c_p & 0 & 0 \end{pmatrix}, \quad c_p = \sqrt{\frac{3}{4\pi}},$$

$$\begin{pmatrix} \phi_{d,-2} \\ \phi_{d,-1} \\ \phi_{d,0} \\ \phi_{d,+1} \\ \phi_{d,+2} \end{pmatrix} = \mathbf{C}_{d,5 \times 6} \begin{pmatrix} \phi_{1,d_{xx}} \\ \phi_{2,d_{xy}} \\ \phi_{3,d_{xz}} \\ \phi_{4,d_{yy}} \\ \phi_{5,d_{yz}} \\ \phi_{6,d_{zz}} \end{pmatrix},$$

$$\text{where } \mathbf{C}_{d,5 \times 6} \equiv \begin{pmatrix} 0 & c_d & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & c_d & 0 \\ -c'_d & 0 & 0 & -c'_d & 0 & 2c'_d \\ 0 & 0 & c_d & 0 & 0 & 0 \\ c_d/2 & 0 & 0 & -c_d/2 & 0 & 0 \end{pmatrix}, \quad c_d = \frac{1}{2} \sqrt{\frac{15}{\pi}}, \quad c'_d = \frac{1}{4} \sqrt{\frac{5}{\pi}},$$

$$\begin{pmatrix} \phi_{f,-3} \\ \phi_{f,-2} \\ \phi_{f,-1} \\ \phi_{f,0} \\ \phi_{f,+1} \\ \phi_{f,+2} \\ \phi_{f,+2} \end{pmatrix} = \mathbf{C}_{f,7 \times 10} \begin{pmatrix} \phi_{f,x^3} \\ \phi_{f,x^2y} \\ \phi_{f,x^2z} \\ \phi_{f,xy^2} \\ \phi_{f,xyz} \\ \phi_{f,xz^2} \\ \phi_{f,y^3} \\ \phi_{f,y^2z} \\ \phi_{f,yz^2} \\ \phi_{f,z^3} \end{pmatrix},$$

where,

$$\mathbf{C}_{f,7 \times 10} \equiv \begin{pmatrix} 0 & 3c_{f1} & 0 & 0 & 0 & 0 & -c_{f1} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2c_{f2} & 0 & 0 & 0 & 0 & 0 \\ 0 & -c_{f3} & 0 & 0 & 0 & 0 & -c_{f3} & 0 & 4c_{f3} & 0 \\ 0 & 0 & -3c_{f4} & 0 & 0 & 0 & 0 & -3c_{f4} & 0 & 2c_{f4} \\ -c_{f3} & 0 & 0 & -c_{f3} & 0 & 4c_{f3} & 0 & 0 & 0 & 0 \\ 0 & 0 & c_{f2} & 0 & 0 & 0 & 0 & -c_{f2} & 0 & 0 \\ c_{f1} & 0 & 0 & -3c_{f1} & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$c_{f1} = \sqrt{\frac{35}{32\pi}}, c_{f2} = \sqrt{\frac{105}{16\pi}}, c_{f3} = \sqrt{\frac{21}{32\pi}}, c_{f4} = \sqrt{\frac{7}{16\pi}}.$$

Now, we can apply the MBT following the same strategy as in Section S1,

Suppose we have a matrix $\mathbf{H}_{14 \times 14}^I$ for atomic integrals obtained from MolSOC, which includes 1 s , 3 p and 10 f orbitals. This matrix can be blocked as

$$\mathbf{H}_{14 \times 14}^I = \begin{pmatrix} \mathbf{H}_{ss,1 \times 1} & \mathbf{H}_{sp,1 \times 3} & \mathbf{H}_{sf,1 \times 10} \\ \mathbf{H}_{ps,3 \times 1} & \mathbf{H}_{pp,3 \times 3} & \mathbf{H}_{pf,3 \times 10} \\ \mathbf{H}_{fs,10 \times 1} & \mathbf{H}_{fp,10 \times 3} & \mathbf{H}_{ff,10 \times 10} \end{pmatrix}.$$

Applying the transformation matrix defined above, the atomic integral matrix $\mathbf{H}_{11 \times 11}^II$ used for the DFTB+ interface can be reconstructed as

$$\mathbf{H}_{11 \times 11}^II = \begin{pmatrix} \mathbf{C}_{s,1 \times 1} & & & \\ & \mathbf{C}_{p,3 \times 3} & & \\ & & \mathbf{C}_{f,7 \times 10} & \\ & & & \end{pmatrix} \mathbf{H}_{14 \times 14}^I \begin{pmatrix} \mathbf{C}_{s,1 \times 1} & & & \\ & \mathbf{C}_{p,3 \times 3} & & \\ & & \mathbf{C}_{f,10 \times 7}^T & \\ & & & \end{pmatrix}.$$

SI-4. Energy of Excited States

Table S1. Basis set effects on state energies for 2tThy at TDDFT/B3LYP level.

		ΔE (eV) (TD-B3LYP)		
		cc-pVDZ	aug-cc-pVDZ	cc-pVTZ
\mathbf{S}_0	1gs	0.00	0.00	0.00
\mathbf{T}_1	$^3\pi\pi^*$	1.68	1.70	1.68
\mathbf{T}_2	$^3n\pi^*$	1.89	1.92	1.90
\mathbf{S}_1	$^1n\pi^*$	2.28	2.28	2.28

Table S2. Density functional effects on state energies for 2tThy at TDDFT/TZVP level.

								ΔE (eV) (TZVP)	
B3LYP	B3LYP	PBE0	CAM-B3LYP	ω B97XD	ω B97XD	M062X	PBE	TD-DFTB	
TDDFT	TDA	TDDFT	TDDFT	TDDFT	TDA	TDDFT	TDDFT		

S₀	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
T₁	1.67	1.80	1.62	1.53	1.66	1.87	1.72	1.69	1.96
T₂	1.88	1.96	1.90	1.94	2.00	2.07	2.00	1.86	2.08
S₁	2.26	2.28	2.33	2.36	2.38	2.41	2.29	2.15	1.99

Table S3. Vertical excitation energies and dominant excitations for formaldehyde and acetone at TDDFT/TZVP/(CAM-)B3LYP and TD-DFTB levels.

		B3LYP		CAM-B3LYP		TD-DFTB	
		ΔE (eV)	dominant excitation	ΔE (eV)	dominant excitation	ΔE (eV)	dominant excitation
formaldehyde	S ₁	4.02	n _H →π _L [*] (1.00)	4.00	n _H →π _L [*] (0.99)	4.50	n _H →π _L [*] (1.00)
	T ₁	3.29	n _H →π _L [*] (1.00)	3.26	n _H →π _L [*] (0.99)	4.50	n _H →π _L [*] (1.00)
	T ₂	5.61	π _{H-1} →π _L [*] (1.00)	5.52	π _{H-1} →π _L [*] (1.00)	7.24	π _{H-1} →π _L [*] (1.00)
acetone	S ₁	4.48	n _H →π _L [*] (0.99)	4.52	n _H →π _L [*] (0.98)	4.72	n _H →π _L [*] (1.00)
	T ₁	3.84	n _H →π _L [*] (0.99)	3.88	n _H →π _L [*] (0.98)	4.71	n _H →π _L [*] (1.00)
	T ₂	5.73	π _{H-1} →π _L [*] (0.94)	5.69	π _{H-1} →π _L [*] (0.91)	6.79	π _{H-1} →π _L [*] (1.00)

Table S4. State energies and dominant excitations for thymine (Thy), 4-thiothymine (4tThy), and 2,4-thiothymine (2,4tThy) from TD(A)DFT/TZVP (B3LYP, ωB97XD, and PBE), TD-DFTB, and CASPT2.

		¹ (n→π [*]) S ₁ or S ₂		³ (π→π [*]) T ₁		³ (n→π [*]) T ₂	
		ΔE (eV)	dominant excitation	ΔE (eV)	dominant excitation	ΔE (eV)	dominant excitation
Thy	TD-B3LYP	3.93	n _{H-1} →π _L [*] (0.96)	1.88	π _H →π _L [*] (1.00)	3.60	n _{H-1} →π _L [*] (0.93)
	TD-ωB97XD	4.44	n _{H-1} →π _L [*] (0.90)	1.80	π _H →π _L [*] (1.00)	4.06	n _{H-1} →π _L [*] (0.84)
	TD-PBE	3.21	n _{H-1} →π _L [*] (1.00)	2.07	π _H →π _L [*] (1.00)	2.97	n _{H-1} →π _L [*] (1.00)
	TDA-B3LYP	3.94	n _{H-1} →π _L [*] (0.97)	2.16	π _H →π _L [*] (0.98)	3.63	n _{H-1} →π _L [*] (0.94)
	TD-DFTB	2.93	n _{H-1} →π _L [*] (0.87)	2.64	π _H →π _L [*] (0.94)	2.93	n _{H-1} →π _L [*] (0.94)
	CASPT2	4.20	n _{H-2} →π _L [*] (0.58)	2.56	π _H →π _L [*] (0.76)	4.17	n _{H-2} →π _L [*] (0.41)
4tThy	TD-B3LYP	2.51	n _{H-1} →π _L [*] (0.15)	2.11	π _{H-1} →π _L [*] (0.98)	2.20	n _{H-1} →π _L [*] (0.20)
	TD-ωB97XD	2.79	n _H →π _L [*] (0.99)	2.08	π _{H-1} →π _L [*] (0.95)	2.49	n _H →π _L [*] (1.00)
	TD-PBE	2.24	n _H →π _L [*] (0.96)	1.95	n _H →π _L [*] (1.00)	2.22	n _H →π _L [*] (1.00)
	TDA-B3LYP	2.52	n _H →π _L [*] (1.00)	2.22	n _H →π _L [*] (1.00)	2.29	π _{H-1} →π _L [*] (1.00)
	TD-DFTB	1.91	n _H →π _L [*] (0.99)	2.22	n _H →π _L [*] (0.98)	2.22	π _{H-1} →π _L [*] (0.98)
	CASPT2	2.72	n _H →π _L [*] (1.00)	1.91	n _H →π _L [*] (1.00)	2.22	π _{H-1} →π _L [*] (1.00)
2,4tThy	TD-B3LYP	2.48	n _H →π _L [*] (0.89)	2.67	π _{H-1} →π _L [*] (0.8)	2.70	n _H →π _L [*] (0.81)
	TD-ωB97XD	2.76	n _H →π _L [*] (0.86)	2.09	π _{H-3} →π _L [*] (0.89)	2.17	n _H →π _L [*] (0.78)
	TD-PBE	2.13	n _{H-2} →π _L [*] (0.13)	2.05	π _{H-3} →π _L [*] (0.75)	2.45	n _{H-2} →π _L [*] (0.19)
	TDA-B3LYP	2.49	n _H →π _L [*] (0.72)	2.19	π _{H-1} →π _L [*] (0.25)	2.28	n _H →π _L [*] (0.69)
	TD-DFTB	1.83	n _{H-2} →π _L [*] (0.24)	1.91	n _H →π _L [*] (0.97)	2.20	n _{H-2} →π _L [*] (0.26)
	CASPT2	2.64	n _H →π _L [*] (0.95)	2.19	n _H →π _L [*] (0.78)	2.28	π _{H-3} →π _L [*] (0.84)
	TD-DFTB	1.83	n _H →π _L [*] (0.86)	1.83	n _{H-2} →π _L [*] (0.19)	2.20	π _{H-3} →π _L [*] (0.85)
	CASPT2	2.64	n _{H-2} →π _L [*] (0.13)	1.83	n _H →π _L [*] (1.00)	2.20(T ₃)	π _{H-1} →π _L [*] (0.13)
		n _H →π _L [*] (1.00)	2.60	n _H →π _L [*] (1.00)	2.62	π _{H-3} →π _L [*] (0.89)	
		n _H →π _L [*] (0.49)		π _{H-1} →π _L [*] (0.81)		n _H →π _L [*] (0.46)	
		n _{H-2} →π _L [*] (0.37)				n _{H-2} →π _L [*] (0.36)	

Table S5. Vertical excitation energies and dominant excitations for psoralens from TDDFT/TZVP/B3LYP, ω B97XD, TD-DFTB.

	B3LYP			ω B97XD		TD-DFTB		
		ΔE (eV)	dominant excitations	ΔE (eV)	dominant excitations	ΔE (eV)	dominant excitations	
psoralenOO	S ₁	3.82	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.92)	4.30	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.89)	3.09	$n_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (1.00)	
	S ₂	4.40	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.85)	4.78	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.78) $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.17)	3.41	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.99)	
	S ₃	4.51	$n_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.95)	4.96	$n_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.80)	4.04	$\pi_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.99)	
	T ₁	2.85	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.62) $\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.26)	2.85	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.64) $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.14) $\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.13)	2.96	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (1.00)	
	T ₂	3.04	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.62) $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.17) $\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.13)	3.23	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.61) $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.21)	3.09	$n_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (1.00)	
	T ₃	3.68	$\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.65) $\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.17)	4.03	$\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.44) $\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.19) $\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.14)	3.34	$\pi_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (1.00)	
	T ₄	4.15	$n_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.90)	4.44	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L+1}}^*$ (0.29) $\pi_{\text{H-4}} \rightarrow \pi_{\text{L}}^*$ (0.15) $\pi_{\text{H-1}} \rightarrow \pi_{\text{L+2}}^*$ (0.14)	3.99	$\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (1.00)	
	T ₅	4.31	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L+1}}^*$ (0.61)	4.54	$n_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.75) $n_{\text{H-2}} \rightarrow \pi_{\text{L+2}}^*$ (0.16)	4.19	$n_{\text{H-1}} \rightarrow \pi_{\text{L+1}}^*$ (1.00)	
	psoralenOS	S ₁	3.56	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.95)	4.04	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.90)	2.79	$n_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (1.00)
		S ₂	3.91	$n_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.95)	4.21	$n_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.82)	3.05	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (1.00)
S ₃		4.19	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.75) $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.19)	4.57	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.70) $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.23)	3.63	$\pi_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.88) (S ₄)	
T ₁		2.76	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.48) $\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.42)	2.75	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.65) $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.14) $\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.10)	2.73	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (1.00)	
T ₂		2.90	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.50) $\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.24) $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.18)	3.15	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.62) $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.21)	2.79	$n_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (1.00)	
T ₃		3.38	$\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.65) $\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.19)	3.64	$\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.42) $\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.19) $\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.18)	3.17	$\pi_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (1.00)	
T ₄		3.55	$n_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.91)	3.80	$n_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.78)	3.43	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L+1}}^*$ (1.00)	
T ₅		4.15	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L+1}}^*$ (0.77)	4.34	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L+1}}^*$ (0.43)	3.54	$n_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (1.00)	
psoralenSO	S ₁	3.64	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.96)	4.22	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.66) $\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.20)	2.96	$n_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (1.00)	
	S ₂	4.11	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.82) $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.13)	4.52	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.62) $\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.21)	3.13	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (1.00)	
	S ₃	4.47	$n_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.95)	4.93	$n_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.80)	3.57	$\pi_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.93)	
	T ₁	2.77	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.66) $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.12) $\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.10)	2.76	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.59) $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.15)	2.84	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (1.00)	
	T ₂	2.99	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.66) $\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.20)	3.21	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.38) $\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.27) $\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.22)	2.96	$n_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (1.00)	
	T ₃	3.42	$\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.70) $\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.18)	3.72	$\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.43) $\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.37)	3.05	$\pi_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (1.00)	
	T ₄	4.11	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L+1}}^*$ (0.89)	4.37	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L+1}}^*$ (0.76)	3.41	$\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (1.00)	
	T ₅	4.12	$n_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.90)	4.51 (T ₆)	$n_{\text{H-2}} \rightarrow \pi_{\text{L}}^*$ (0.75) (T ₆)	3.61	$n_{\text{H-1}} \rightarrow \pi_{\text{L+1}}^*$ (1.00)	

Table S6. Vertical excitation energies and dominant excitations for BODIPY at TDDFT/TZVP/(CAM-)B3LYP level.

		B3LYP		CAM-B3LYP	
		ΔE (eV)	dominant excitations	ΔE (eV)	dominant excitations
BODIPY	S ₁	2.58	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.99)	2.69	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (0.98)
	T ₁	1.34	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (1.00)	1.15	$\pi_{\text{H}} \rightarrow \pi_{\text{L}}^*$ (1.00)
	T ₂	2.70	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.87)	2.83	$\pi_{\text{H-1}} \rightarrow \pi_{\text{L}}^*$ (0.54)
					$\pi_{\text{H}} \rightarrow \pi_{\text{L+1}}^*$ (0.17)

SI-5. Cartesian coordinates

Cartesian coordinates in Angstrom, for all molecules investigated in this work.

formaldehyde

C	-0.132229	-0.000002	0.000010
O	1.064400	0.000002	-0.000012
H	-0.717794	0.939142	0.000000
H	-0.717798	-0.939142	0.000039

acetone

C	-0.166195	0.001194	-0.173304
O	0.995476	0.002610	-0.496361
C	-0.968665	1.278406	-0.070441
H	-0.314973	2.141560	-0.175067
H	-1.722697	1.297114	-0.861767
H	-1.501870	1.323562	0.881793
C	-0.902277	-1.278207	0.154427
H	-1.095277	-1.316243	1.230069
H	-1.871297	-1.310577	-0.347823
H	-0.301731	-2.139413	-0.130635

2-thiothymine

N	-1.812458	-0.393339	0.564053
C	-3.193236	-0.497647	0.446440
N	-3.844849	0.727222	0.400820
C	-3.182787	1.890877	0.147251
C	-1.838212	1.960323	0.056073
C	-1.069971	0.745890	0.326133
S	-3.900754	-1.711592	-0.613819
O	0.152551	0.704996	0.383914
C	-1.102378	3.229382	-0.235122
H	-3.812160	2.766764	0.047198
H	-0.389778	3.462163	0.559503

H	-0.533579	3.151194	-1.165183
H	-1.799275	4.062677	-0.331434
H	-4.844612	0.746269	0.519835
H	-1.281199	-1.231706	0.748732

thymine

C	-2.909875	-0.629050	-0.750426
C	-0.969207	0.789501	-0.288958
C	-1.853272	1.844318	0.067623
C	-3.262872	1.547385	0.254145
H	-3.983226	2.239771	0.660440
O	-3.385348	-1.615949	-1.278475
O	0.248383	0.881498	-0.508213
C	-1.400473	3.243296	0.147397
H	-1.641309	3.662743	1.134181
H	-0.331135	3.324808	-0.036402
H	-1.941543	3.870633	-0.574804
N	-1.583501	-0.490619	-0.420219
H	-0.982147	-1.215500	-0.786819
N	-3.713370	0.446397	-0.387742
H	-4.702890	0.311532	-0.560634

4-thiothymine

N	-1.849545	-0.436139	0.362328
C	-3.213053	-0.450129	0.523403
N	-3.827070	0.740518	0.284492
C	-3.150749	1.901485	-0.101755
C	-1.808952	1.903194	-0.257845
C	-1.110224	0.694914	-0.019118
O	-3.814395	-1.461620	0.856259
S	0.589846	0.528584	-0.157243
C	-1.058533	3.135119	-0.669847
H	-3.767423	2.772650	-0.261638
H	-0.316476	3.413561	0.083639
H	-0.530266	2.975915	-1.614157
H	-1.739102	3.976314	-0.801042
H	-4.827252	0.751073	0.393826
H	-1.391740	-1.316080	0.538097

2,4-thiothymine

N	-1.849597	-0.439399	0.257464
C	-3.197739	-0.498714	0.178537
N	-3.814670	0.659732	-0.097117
C	-3.143553	1.873525	-0.293316

C	-1.797095	1.931963	-0.217287
C	-1.095406	0.734827	0.066154
S	-4.031552	-1.942734	0.416010
S	0.607536	0.618256	0.175149
C	-1.043647	3.210682	-0.420485
H	-3.770420	2.725984	-0.502749
H	-0.469950	3.468154	0.474247
H	-0.338645	3.119587	-1.251494
H	-1.724296	4.032763	-0.639190
H	-4.819327	0.632279	-0.157057
H	-1.386158	-1.308939	0.468901

psoralenOO

O	-4.022976	0.983961	0.000000
C	-3.003331	0.354454	0.000000
O	-1.811019	1.055041	0.000000
C	-2.893000	-1.094271	0.000000
C	-1.697697	-1.707320	0.000000
C	-0.477245	-0.953034	0.000000
C	-0.595087	0.454056	0.000000
C	0.511143	1.287736	0.000000
C	0.785333	-1.547040	0.000000
C	1.909768	-0.737538	0.000000
C	1.737466	0.658321	0.000000
O	2.940243	1.278519	0.000000
C	3.333491	-0.942117	0.000000
C	3.882011	0.287390	0.000000
H	-3.829527	-1.635518	0.000000
H	-1.635709	-2.791427	0.000000
H	0.867762	-2.628465	0.000000
H	0.399029	2.363736	0.000000
H	3.867102	-1.879343	0.000000
H	4.904183	0.629340	0.000000

psoralenOS

O	-4.477112	0.621239	0.000000
C	-3.334935	0.233828	0.000000
C	-2.931630	-1.158396	0.000000
C	-1.664873	-1.610948	0.000000
C	-0.463569	-0.820333	0.000000
C	-0.513687	0.595613	0.000000
C	0.650336	1.358530	0.000000
C	0.775055	-1.471417	0.000000
C	1.942257	-0.727952	0.000000

C	1.843685	0.672996	0.000000
O	3.078216	1.230536	0.000000
C	3.352340	-1.008775	0.000000
C	3.964994	0.190491	0.000000
H	-3.762942	-1.855206	0.000000
H	-1.517347	-2.687597	0.000000
H	0.802631	-2.555813	0.000000
H	0.619675	2.441384	0.000000
H	3.835735	-1.972817	0.000000
H	5.004204	0.476804	0.000000
S	-2.031091	1.484315	0.000000

psoralenSO

O	-4.107347	0.881651	0.000000
C	-3.062861	0.294171	0.000001
O	-1.900266	1.040072	0.000000
C	-2.899047	-1.151174	0.000000
C	-1.682977	-1.720953	0.000000
C	-0.493379	-0.918241	0.000000
C	-0.662591	0.481833	0.000000
C	0.415133	1.345669	0.000000
C	0.791493	-1.450680	0.000000
C	1.898093	-0.609589	0.000000
C	1.686170	0.789992	0.000000
C	3.294341	-0.939253	0.000000
C	4.087971	0.150926	0.000000
H	-3.815972	-1.725048	0.000000
H	-1.579979	-2.801848	0.000000
H	0.920954	-2.528125	0.000000
H	0.243810	2.414823	0.000000
H	3.671532	-1.953684	0.000000
H	5.167591	0.183633	0.000000
S	3.199271	1.652304	0.000000

BODIPY

B	0.964140	-1.115596	0.015703
F	0.577677	-1.832741	1.132554
N	-1.954648	-1.949652	-0.493743
H	-1.085747	-2.265180	-0.905943
C	-3.058036	-2.695328	-0.283564
F	0.700261	-1.875492	-1.146729
N	0.135194	0.232394	-0.070960
C	-4.011867	-1.907384	0.327021
H	-4.994277	-2.225143	0.634301

N	2.450963	-0.745701	0.066669
C	-3.453183	-0.630430	0.476775
C	-2.162814	-0.672294	-0.039057
C	-1.188910	0.379731	-0.079218
C	-1.503388	1.792421	-0.136602
C	-2.711540	2.483789	-0.249689
H	-3.654061	1.958497	-0.312641
C	-2.673677	3.860319	-0.310304
H	-3.597118	4.418096	-0.398653
C	-1.452866	4.549794	-0.276214
H	-1.455870	5.631623	-0.328166
C	-0.252506	3.875667	-0.200240
H	0.686148	4.415586	-0.198362
C	-0.282938	2.483443	-0.137433
C	0.756446	1.493740	-0.098250
C	2.104548	1.633654	-0.058721
H	2.529639	2.629020	-0.072794
C	2.971604	0.527951	0.014257
C	4.361125	0.440513	0.075417
C	4.679365	-0.916851	0.164995
H	5.661819	-1.354300	0.232609
C	3.479631	-1.612878	0.157623
H	5.044703	1.274885	0.058720
H	3.299949	-2.674489	0.215219
H	-3.909869	0.215591	0.961629
H	-3.093189	-3.729422	-0.583598

Reference

[S1] Görrler-Walrand, C.; Binnemans, K. *Rationalization of Crystal-Field Parametrization*, In: *Handbook on the Physics and Chemistry of Rare Earths* Vol. 23, eds. Gschneidner, K. A. and Eyring, L. North Holland, 1996.