# Supporting Information

# 1. Generation of SALCs and SAMOs

The Reducible Representation (RR),  $\Gamma_{red}$ , is obtained by applying the symmetry operations of the point group on the p atomic orbitals localized on every atomic sites. The atomic orbitals that remain on their atomic sites upon a symmetry operation contribute with +1 on the diagonal of the  $\Gamma_{red}$  matrix while the atomic orbitals which retain their position but change their phase upon the symmetry operation contribute with -1. The atomic orbitals which exchange their position with another upon a symmetry operation contributes with 0 on the diagonal of the  $\Gamma_{red}$  matrix.

The following reduction of  $\Gamma_{red}$  in terms of the irreducible representations (iRRs) of the group is obtained employing the following formula:

$$n_{\alpha} = \frac{1}{g} \sum_{\hat{R}} \Theta^{\alpha}(\hat{R}) \Theta_{red}^{*}(\hat{R})$$
(S1.1)

in which g is the order of the group,  $\alpha$  is the iRR,  $\Theta^{\alpha}$  is the character of the  $\alpha$  iRR,  $\Theta_{red}$  is the character of the RR ( $\Gamma_{red}$ ). The sum runs over the symmetry operators,  $\hat{R}$ , of the group.

The Symmetry Adapted Linear Combinations (SALCs) are constructed by applying the projection operator ( $\hat{P}^{\alpha}$ ) on the atomic orbitals  $\chi_i$ .  $\hat{P}^{\alpha}$  is defined by the following expression:

$$\hat{P}^{\alpha} = \sum_{\hat{R}} \Theta^{\alpha}(\hat{R}) \hat{O}_{\hat{R}}$$
(S1.2)

In which  $\partial_R$  is the symmetry operator, associated with the iRR  $\alpha$ .  $\hat{P}^{\alpha}$  operates on all the non-symmetry equivalent atomic orbitals.

The generation of the Symmetry Adapted Molecular Orbitals (SAMOs) is carried out within the Hückel approximation[1-4]. If the  $\alpha$  iRR appears only once in the  $\Gamma_{red}$  the  $\alpha$ -SAMO coincides with the resulting  $\alpha$ -SALC, whereas if the  $\alpha$  iRR appears *n* times in  $\Gamma_{red}$  (with n > 1) the set of  $\alpha$ -SAMOs is obtained through the linear combinations of the *n*  $\alpha$ -SALCs. In this latter case, the proper linear combinations can be found by building and diagonalizing a SALC based Hückel Hamiltonian, which is symmetry factorized considering that only the SALCs belonging to the same iRR can interact. Each matrix element is evaluated within the Hückel approximation, i.e.  $\langle \chi_i | \hat{H} | \chi_i \rangle = \alpha$  the site energy,  $\langle \chi_i | \hat{H} | \chi_j \rangle = \beta$  the resonance integral (different from zero only with  $\chi_i$  and  $\chi_j$  connected atomic site) and  $\langle \chi_i | \chi_j \rangle = \delta_{ij}$ , with  $\delta_{ij}$  the Kronecker's delta.

The diagonal elements of the Hückel secular determinant are  $\alpha$ -*E* and the off-diagonal are  $\beta$ . By dividing all the elements of the determinant by  $\beta$  and calling  $x = (\alpha - E)/\beta$ , the Hückel determinant (not considering the heteroatoms) can be written as follows:

$$\begin{vmatrix} \alpha - E & \beta & 0 & \cdots \\ \beta & \alpha - E & \beta & \cdots \\ 0 & \beta & \alpha - E & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} \rightarrow \begin{vmatrix} x & 1 & 0 & \cdots \\ 1 & x & 1 & \cdots \\ 0 & 1 & x & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix}$$
(S1.3)

Note that the site energy and the resonance integral involving a N atom will acquire the form  $\alpha_N = \alpha_C + h\beta_{\text{and}} \beta_N = k\beta_C$ , respectively, in which *h* and *k* are coefficients empirically determined. It follows that the *x* term associated with the N atom will be written as:

$$x_N = \frac{\alpha_N - E}{\beta} = \frac{\alpha + h\beta - E}{\beta} = \frac{\alpha - E}{\beta} + \frac{h\beta}{\beta} = x + h$$
(S1.4)

In our case, following the literature [5], the h and k will be set to 1.5 and 0.8, respectively, corresponding to the values used for the N atom of the pyrrole.

### 1.1D<sub>3h</sub> point group

#### 1.1.1: The cyclazine case

The following section is related to the symmetry analysis and the generation of the SALCs and SAMOs of the  $a_1^{''}$  and  $a_2^{''}$  iRR of the D<sub>3h</sub> point group, by considering the sole *p*-type orbitals of the C atoms and N central atom of the cyclazine-like structure.



*Figure S1*: *a*) cyclazine structure; *b*) definition of the *p* atomic orbitals of the triangulene systems considered in the analysis.

D <sub>3h</sub>	Е	2C <sub>3</sub> (z)	3C' <sub>2</sub>	$\sigma_h(xy)$	2S <sub>3</sub>	$3\sigma_{\rm v}$	linear functions, rotations
$A'_1$	+1	+1	+1	+1	+1	+1	-
A'2	+1	+1	-1	+1	+1	-1	R <sub>z</sub>
E'	+2	-1	0	+2	-1	0	(x, y)
$A''_1$	+1	+1	+1	-1	-1	-1	-
A"2	+1	+1	-1	-1	-1	+1	Z
E"	+2	-1	0	-2	+1	0	$(R_x, R_y)$

*Table S1*: character table of  $D_{3h}$  point group

The application of the symmetry operations to the cyclazine core (see Figure S1) results in the following RR:

$$\Gamma_{red}^{D_{3h}} = (13,1,1-1,-1,-1,-1,-13,-1,-1,1,1,1)$$

which then is reduced by means of eq.S1.1 resulting in the following direct sum of the iRRs:

$$\Gamma_{red}^{D_{3h}} = a_1' \oplus 4a_2' \oplus 4e''$$

Because of the high symmetry point group of the cyclazine molecule, the projection operator of the different IRRs has to be applied onto a limited number of atomic orbitals, namely  $\chi_1$ ,  $\chi_2$ ,  $\chi_3$  and  $\chi_{13}$ .

The application of the  $a_1''$  projection operator generates one sole SALC, identified with the label  $\psi_1^{a_1}$ , bearing a non-bonding character.

$$P^{a_{1}}\chi_{1} = \chi_{1} + \chi_{9} + \chi_{5} - \chi_{1} - \chi_{9} - \chi_{5} + \chi_{1} + \chi_{9} + \chi_{5} - \chi_{1} - \chi_{9} - \chi_{5} = 0$$

$$P^{a_{1}}\chi_{2} = \chi_{2} + \chi_{10} + \chi_{6} - \chi_{12} - \chi_{8} - \chi_{4} + \chi_{2} + \chi_{10} + \chi_{6} - \chi_{12} - \chi_{8} - \chi_{4} \rightarrow$$

$$\rightarrow P^{a_{1}}\chi_{2} = \psi_{1}^{a_{1}} = 1/\sqrt{6}(\chi_{2} + \chi_{10} + \chi_{6} - \chi_{12} - \chi_{8} - \chi_{4})$$

$$P^{a_{1}}\chi_{3} = \chi_{3} + \chi_{11} + \chi_{7} - \chi_{3} - \chi_{11} - \chi_{7} + \chi_{3} + \chi_{11} + \chi_{7} - \chi_{3} - \chi_{11} - \chi_{7} = 0$$

$$P^{a_{1}}\chi_{13} = \chi_{13} + \chi_{13} + \chi_{13} - \chi_{13} - \chi_{13} - \chi_{3} + \chi_{13} + \chi_{13} - \chi_{13} - \chi_{13} - \chi_{13} = 0$$

The application of the  $a_2''$  projection operator generates the following four SALCs:

$$\hat{p}^{a_{2}}\chi_{1} = \chi_{1} + \chi_{9} + \chi_{5} + \chi_{1} + \chi_{9} + \chi_{5} + \chi_{1} + \chi_{9} + \chi_{5} + \chi_{1} + \chi_{9} + \chi_{5} \rightarrow \phi_{1} = 1/\sqrt{3}(\chi_{1} + \chi_{9} + \chi_{5})$$

$$p^{a_{2}'}\chi_{2} = \chi_{2} + \chi_{10} + \chi_{6} + \chi_{12} + \chi_{8} + \chi_{4} + \chi_{2} + \chi_{10} + \chi_{6} + \chi_{12} + \chi_{8} + \chi_{4} \rightarrow \phi_{2} = 1/\sqrt{6}(\chi_{2} + \chi_{10} + \chi_{6} + \chi_{12} + \chi_{8} + \chi_{4})$$

$$p^{a_{2}'}\chi_{3} = \chi_{3} + \chi_{11} + \chi_{7} + \chi_{3} + \chi_{11} + \chi_{7} + \chi_{3} + \chi_{11} + \chi_{7} + \chi_{3} + \chi_{11} + \chi_{7} \rightarrow \phi_{3} = 1/\sqrt{3}(\chi_{3} + \chi_{11} + \chi_{7})$$

$$\hat{p}^{a_{2}'}\chi_{13} = \chi_{13} + \chi_{13} + \chi_{13} + \chi_{13} + \chi_{13} + \chi_{13} + \chi_{13} \rightarrow \phi_{4} = \chi_{13}$$

The  $a_2^{"}$  Hückel Hamiltonian is constructed by evaluating the matrix terms between each pair of the  $a_2^{"}$  SALCs as explained at the beginning of this section. The resulting determinant is written in term of x (see eq.S1.3)

$$\det\left(a_{2}^{''}\right) = \begin{vmatrix} x & \sqrt{2} & 0 & 0\\ \sqrt{2} & x & \sqrt{2} & 0\\ 0 & \sqrt{2} & x & 0.36\\ 0 & 0 & 0.36 & x + 1.5 \end{vmatrix}$$

The diagonalization of the Hamiltonian leads to the following four linear combinations of SALCs, i.e. the  $a_2$ -SAMOs:

$$\begin{split} \psi_{1}^{a_{2}'} &= 0.448\phi_{1} + 0.654\phi_{2} + 0.507\phi_{3} + 0.336\phi_{4} \\ \psi_{2}^{a_{2}'} &= -0.257\phi_{1} - 0.273\phi_{2} + 0.033\phi_{3} + 0.926\phi_{4} \\ \psi_{3}^{a_{2}'} &= -0.698\phi_{1} + 0.021\phi_{2} + 0.697\phi_{3} - 0.163\phi_{4} \\ \psi_{4}^{a_{2}'} &= -0.496\phi_{1} + 0.704\phi_{2} - 0.505\phi_{3} + 0.052\phi_{4} \end{split}$$

As explained in the main text, the highest occupied SAMO and lowest unoccupied SAMO, to be compared with the HOMO and LUMO of the triangulene compounds, are identified by ordering the SAMOs according to their energy and filling them with the electrons considered in the analysis (14 electrons in our case). Consequently, we need to compute the energy associated with the  $e^{''}$ -SAMOs as well.

To find the SALCs and SAMOs associated with the 2D-iRR (e'') we can resort to the character table of the C<sub>3</sub> point group, noting that rotational symmetry of the SALCs is inherently dictated by the C<sub>3</sub> axis. Each resulting SALC pair ( $\varphi_a$  and  $\varphi_b$ ), bearing imaginary coefficients, will be linearly combined to obtain real SALCs:  $\phi_{1,1}^e = (\varphi_a + \varphi_b)_{and} \phi_{1,2}^e = (\varphi_a - \varphi_b)/i$ .

	Table S2: chara	cter table of $C_3$ group.	$\varepsilon = exp^{[i0]}(\frac{2\pi i}{3})$	
C <sub>3</sub>	E	C <sub>3</sub> (z)	$C_{3}^{-1}$	linear functions, rotations
А	+1	+1	+1	z, R <sub>z</sub>
E	+1 +1	<b>3</b> + <b>3</b> +	* <b>3</b> + 3+	$x+iy; R_x+iR_y$ x-iy; R_x-iR_y

The application of the e projection operator produces the following five pairs of complex SALCs (left), which then are linearly combined to give the real SALCs (right):

$$\begin{cases} p^{e}\chi_{1} = \chi_{1} + \varepsilon\chi_{9} + \varepsilon^{*}\chi_{5} \\ p^{e}\chi_{1} = \chi_{1} + \varepsilon^{*}\chi_{9} + \varepsilon\chi_{5} \\ p^{e}\chi_{2} = \chi_{2} + \varepsilon\chi_{10} + \varepsilon^{*}\chi_{6} \\ p^{e}\chi_{2} = \chi_{2} + \varepsilon^{*}\chi_{10} + \varepsilon\chi_{6} \\ p^{e}\chi_{2} = \chi_{2} + \varepsilon^{*}\chi_{10} + \varepsilon\chi_{6} \\ p^{e}\chi_{3} = \chi_{3} + \varepsilon\chi_{11} + \varepsilon^{*}\chi_{7} \\ p^{e}\chi_{3} = \chi_{3} + \varepsilon\chi_{11} + \varepsilon^{*}\chi_{7} \\ p^{e}\chi_{4} = \chi_{4} + \varepsilon\chi_{12} + \varepsilon^{*}\chi_{8} \\ p^{e}\chi_{4} = \chi_{4} + \varepsilon^{*}\chi_{12} + \varepsilon^{*}\chi_{8} \\ p^{e}\chi_{4} = \chi_{4} + \varepsilon^{*}\chi_{12} + \varepsilon\chi_{8} \\ p^{e}\chi_{13} = \chi_{13} + \varepsilon^{*}\chi_{13} + \varepsilon^{*}\chi_{13} \\ p^{e}\chi_{13} = \chi_{13} + \varepsilon^{*}\chi_{13} + \varepsilon^{*}\chi_{13} \\ p^{e}\chi_{13} = \chi_{13} + \varepsilon^{*}\chi_{13} + \varepsilon\chi_{13} \\ p^{e}\chi_{13} = \chi_{13} - \chi_{13} - \chi_{13} = 0 \\ \end{cases}$$

We obtain two determinants, one in terms of  $\phi_{i,1}$  and the other in terms of  $\phi_{i,2}$  SALCs:

$$\det(e)_{i,1} = \begin{vmatrix} x & 1 & 0 & 1/6 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1/6 & 0 & 1 & x \end{vmatrix} \qquad \qquad \det(e)_{i,2} = \begin{vmatrix} x & 1 & 0 & -1/2 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ -1/2 & 0 & 1 & x \end{vmatrix}$$

We need to solve just one of them to find the eigenvalues and order all the SAMOs according to their energy. At the end, we obtain the following order:

*Table S3:*  $D_{3h}$  eigenvalues; HOMO and LUMO define the highest occupied and lowest unoccupied SAMOs, respectively.

Eigenvalue	Eigenvector (SAMO)	
2.044	$\psi^{a_1}_{\ 1}$	
1.666	$\psi_1^e$	
1.487	$\psi^{a_1}_2$	
0.500	$\psi^e_2$	
0.000	$\psi^{a_2}_{\ 1}$	НОМО
-0.042	$\psi^{a_1}_{\ 3}$	LUMO
-0.500	$\psi^e_3$	
-1.666	$\psi^e_4$	
-1.989	$\psi^{a_2}_{\ 4}$	

### 1.1.2 D<sub>3h</sub> symmetry compounds

**Table S4**:  $S_1$  and  $T_1$  excitation energies computed at SCS-CC2/def2-TZVP and NEVPT2/def2-TZVP for the  $D_{3h}$  symmetry compounds.

	S	CS-CC2		NEVPT2 (8,8)			
	[eV]	T <sub>1</sub> [eV]	ΔE <sub>ST</sub> [eV]	$\begin{bmatrix} S_1 (f_{OSC}) \\ [eV] \end{bmatrix}$	T <sub>1</sub> [eV]	ΔE <sub>ST</sub> [eV]	
Cyclazine	1.11 (0.000)	1.33	-0.22	1.07 (0.000)	1.19	-0.12	
2T-B	0.89 (0.000)	1.17	-0.28	0.82 (0.000)	1.02	-0.20	
2T-B-3N	1.64 (0.000)	2.09	-0.45	1.84 (0.000)	2.02	-0.18	
<sup>a</sup> 4T-a	1.23 (0.000)	1.51	-0.28	0.83 (0.000)	1.09	-0.26	
<sup>a</sup> 4T-b	1.44 (0.144)	1.14	0.30	1.24 (0.202)	0.95	0.29	

 $\overline{a}$  From ref.16 in the main text (NEVPT2 with a 10,10 CAS).







*Figure S2*: HOMO and LUMO computed at HF/def2-TZVP for the B centred triangulene (isocontour  $\sigma$ =0.02 e·Bohr-3).



*Figure S3*: HOMO and LUMO computed at HF/def2-TZVP for the B-3N triangulene (isocontour  $\sigma$ =0.02 e·Bohr-3).



**Figure S4:** HOMO and LUMO computed at HF/def2-TZVP level, exchange interaction,  $\Delta E_{ST}$  computed at SCS-CC2/def2-TZVP level for 1,5,9-B-cyclazine (isocontour  $\sigma$ =0.02 e·Bohr-3).



*Figure S5: inversion of the unoccupied orbitals energy order for the triangulene doped with nitrogen atoms.* 



 $D_{3h}$   $C_{2v}$ *Figure S6*: optimized geometry of the ground state (left) at B97-3c and S<sub>1</sub> (right) at TD-PBE0/def2-*TZVP of the triangulene (b) in the main text.* 



*Figure S7:* HOMO and LUMO computed at HF/def2-TZVP, exchange interaction,  $\Delta$ EST and oscillator strength computed at SCS-CC2/def2-TZVP for TABNA-1 (isocontour  $\sigma$ =0.02 e·Bohr-3).

The degeneracy of the HOMO orbitals leads to a larger overlap with the non-degenerate LUMO ( $\Lambda_{HL} = 0.628$ ), with the following positive  $\Delta E_{ST} = 0.167$  eV at SCS-CC2 level ( $f_{osc} = 0.189$ ). The optimization of the S<sub>1</sub> and S<sub>2</sub> removes the degeneracy between the two excited states, with an increase of (adiabatic)  $\Delta E_{ST}$  to 0.248 eV and a decrease of  $f_{osc}$  to 0.164 for S<sub>1</sub>.

## 1.2 Point group C<sub>2v</sub>

The following section is related to the symmetry analysis and the generation of the SALCs and SAMOs of the  $a_2$  and  $a_2$  iRR of the  $C_{2v}$  point group, by considering the sole *p*-type orbitals of the C atoms and N central atom of the cyclazine-like structure.

$C_{2v}$	Е	$C_{2}(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	linear functions, rotations
A <sub>1</sub>	+1	+1	+1	+1	Z
$A_2$	+1	+1	-1	-1	R <sub>z</sub>
$B_1$	+1	-1	+1	-1	x, R <sub>y</sub>
B_2	+1	-1	-1	+1	y, R <sub>x</sub>

*Table S5*: character table of  $C_{2v}$  point group

The application of the symmetry operations to the molecular structure results in the following RR

$$\Gamma_{red}^{c_{2v}} = (13, -3, -13, 3)$$

which then is reduced by means of eq.S1.1 resulting in the following direct sum of the iRRs:

$$\Gamma_{red}^{C_{2v}} = 8b_2 \oplus 5a_2$$

The application of the  $a_2$  projection operator generates the following five SALCs:

$$P^{a_2}\chi_1 = \chi_1 - \chi_1 + \chi_1 - \chi_1 = 0$$

$$P^{a_2}\chi_2 = \chi_2 - \chi_{12} + \chi_2 - \chi_{12} = 2(\chi_2 - \chi_{12}) \rightarrow \phi_2 = 1/\sqrt{2}(\chi_2 - \chi_{12})$$

$$P^{a_2}\chi_3 = \chi_3 - \chi_{11} + \chi_3 - \chi_{11} = 2(\chi_3 - \chi_{11}) \rightarrow \phi_3 = 1/\sqrt{2}(\chi_3 - \chi_{11})$$

$$P^{a_2}\chi_4 = \chi_4 - \chi_{10} + \chi_4 - \chi_{10} = 2(\chi_4 - \chi_{10}) \rightarrow \phi_4 = 1/\sqrt{2}(\chi_4 - \chi_{10})$$

$$P^{a_2}\chi_5 = \chi_5 - \chi_9 + \chi_5 - \chi_9 = 2(\chi_5 - \chi_9) \rightarrow \phi_5 = 1/\sqrt{2}(\chi_5 - \chi_9)$$

$$P^{a_2}\chi_6 = \chi_6 - \chi_8 + \chi_6 - \chi_8 = 2(\chi_6 - \chi_8) \rightarrow \phi_6 = 1/\sqrt{2}(\chi_6 - \chi_8)$$

$$P^{a_2}\chi_1 = \chi_{13} - \chi_1 + \chi_{13} - \chi_{13} = 0$$

The resulting Hückel determinant, written in terms of x, is the following:

$$\det (a_2) = \begin{vmatrix} x & 1 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 1 & x \end{vmatrix}$$

The diagonalization of the Hückel Hamiltonian results in the following linear combinations of  $a_2$ -SALCs, i.e. the  $a_2$ -SAMOs:

$$\psi_1^{a_2} = 0.289\phi_2 + 0.5\phi_3 + 0.577\phi_4 + 0.5\phi_5 + 0.289\phi_6$$

$$\psi_{2}^{a_{2}} = -0.5\phi_{2} - 0.5\phi_{3} + 0.5\phi_{5} + 0.5\phi_{6}$$
  

$$\psi_{3}^{a_{2}} = 0.577\phi_{2} - 0.577\phi_{4} + 0.577\phi_{6}$$
  

$$\psi_{4}^{a_{2}} = 0.5\phi_{2} - 0.5\phi_{3} + 0.5\phi_{5} - 0.5\phi_{6}$$
  

$$\psi_{5}^{a_{2}} = -0.289\phi_{2} + 0.5\phi_{3} - 0.577\phi_{4} + 0.5\phi_{5} - 0.289\phi_{6}$$

The application of the  $b_2$  projection operator generates the following eight SALCs

$$p^{b_2}\chi_1 = \chi_1 + \chi_1 + \chi_1 + \chi_1 = 4\chi_1 \rightarrow \phi_1 = \chi_1$$

$$p^{b_2}\chi_2 = \chi_2 + \chi_{12} + \chi_2 + \chi_{12} = 2(\chi_2 + \chi_{12}) \rightarrow \phi_2 = 1/\sqrt{2}(\chi_2 + \chi_{12})$$

$$p^{b_2}\chi_3 = \chi_3 + \chi_{11} + \chi_3 + \chi_{11} = 2(\chi_3 + \chi_{11}) \rightarrow \phi_3 = 1/\sqrt{2}(\chi_3 + \chi_{11})$$

$$p^{b_2}\chi_4 = \chi_4 + \chi_{10} + \chi_4 + \chi_{10} = 2(\chi_4 + \chi_{10}) \rightarrow \phi_4 = 1/\sqrt{2}(\chi_4 + \chi_{10})$$

$$p^{b_2}\chi_5 = \chi_5 + \chi_9 + \chi_5 + \chi_9 = 2(\chi_5 + \chi_9) \rightarrow \phi_5 = 1/\sqrt{2}(\chi_5 + \chi_9)$$

$$p^{b_2}\chi_6 = \chi_6 + \chi_8 + \chi_6 + \chi_8 = 2(\chi_6 + \chi_8) \rightarrow \phi_6 = 1/\sqrt{2}(\chi_6 + \chi_8)$$

$$p^{b_2}\chi_7 = \chi_7 + \chi_7 + \chi_7 + \chi_7 = 4\chi_7 \rightarrow \phi_7 = \chi_7$$

$$p^{b_2}\chi_{13} = \chi_{13} + \chi_{13} + \chi_{13} + \chi_{13} = 4\chi_{13} \rightarrow \phi_5 = \chi_{13}$$

The corresponding Hückel determinant is:

$$\det\left(b_{2}\right) = \begin{vmatrix} x & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ \sqrt{2} & x & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 & 0 & 1.12 \\ 0 & 0 & 1 & x & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & x & \sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{2} & x & 0.8 \\ 0 & 0 & 1.12 & 0 & 0 & 0 & 0.8 & x+1.5 \end{vmatrix}$$

The diagonalization of the Hückel Hamiltonian results in the following linear combinations of  $b_{2}$ -SALCs, i.e. the eight  $B_{2}$ -SAMOs

$$\begin{split} \psi_{1}^{b_{2}} &= 0.126\phi_{1} + 0.241\phi_{2} + 0.464\phi_{3} + 0.242\phi_{4} + 0.181\phi_{5} + 0.241\phi_{6} + 0.329\phi_{7} + 0.673\phi_{13} \\ \psi_{2}^{b_{2}} &= -0.407\phi_{1} - 0.5\phi_{2} - 0.291\phi_{3} + 0.291\phi_{5} + 0.5\phi_{6} + 0.407\phi_{7} \\ \psi_{3}^{b_{2}} &= 0.324\phi_{1} + 0.334\phi_{2} + 0.026\phi_{3} + 0.346\phi_{4} + 0.472\phi_{5} + 0.334\phi_{6} + 0.006\phi_{7} - 0.573\phi_{13} \\ \psi_{4}^{b_{2}} &= -0.414\phi_{1} - 0.294\phi_{2} + 0.288\phi_{3} + 0.571\phi_{4} + 0.280\phi_{5} - 0.294\phi_{6} - 0.408\phi_{7} + 0.008\phi_{13} \\ \psi_{5}^{b_{2}} &= -0.384\phi_{1} + 0.125\phi_{2} + 0.481\phi_{3} + 0.119\phi_{4} - 0.535\phi_{5} + 0.125\phi_{6} + 0.341\phi_{7} - 0.415\phi_{13} \\ \psi_{6}^{b_{2}} &= 0.408\phi_{1} - 0.289\phi_{2} - 0.283\phi_{3} + 0.576\phi_{4} - 0.288\phi_{5} - 0.289\phi_{6} + 0.412\phi_{7} - 0.005\phi_{13} \\ \psi_{7}^{b_{2}} &= 0.407\phi_{1} - 0.5\phi_{2} + 0.291\phi_{3} - 0.291\phi_{5} + 0.5\phi_{6} - 0.407\phi_{7} \\ \psi_{8}^{b_{2}} &= -0.248\phi_{1} + 0.380\phi_{2} - 0.469\phi_{3} + 0.384\phi_{4} - 0.356\phi_{5} + 0.380\phi_{6} - 0.328\phi_{7} + 0.216\phi_{13} \\ \end{split}$$

The identification of the highest occupied SAMO and lowest unoccupied SAMO is done by ordering the  $a_2$  and  $b_2$  SAMOs by their energy and filling them with the 14 electrons.

Eigenvalue	Eigenvector (SAMO)	
2.663	$\psi_{1}^{b_{2}}$	
1.732	$\psi_{1}^{a_{2}}$	
1.720	$\psi^{b_2}_{\ 2}$	
1.440	$\psi^{b_2}_{\ 3}$	
1.000	$\psi^{a_2}_{\ 2}$	
0.993	$\psi^{b_2}_{\ 4}$	
0.000	$\psi^{a_2}_{\ 3}$	НОМО
-0.457	$\psi^{b_2}_{5}$	LUMO
-0.993	$\psi^{b_2}_{\ 6}$	
-1.000	$\psi^{a_2}_{\ 4}$	
-1.720	$\psi^{b_2}_{\ 7}$	
-1.732	$\psi_{5}^{a_{2}}$	
-2.416	$\psi^{b_2}_{\ 8}$	

**Table S6:**  $C_{2v}$  eigenvalues; HOMO and LUMO define the highest occupied and lowest unoccupied SAMOs, respectively.

# $1.2.1 \ C_{2v} \ symmetry \ compounds$

**Table S7**:  $S_1$  and  $T_1$  excitation energies computed at SCS-CC2/def2-TZVP and NEVPT2/def2-TZVP for the  $C_{2v}$  symmetry compounds.

	SCS-		NEVPT2 (8,8)			
	S <sub>1</sub> (fosc) [eV]	T <sub>1</sub> [eV]	ΔE <sub>st</sub> [eV]	S <sub>1</sub> ( <i>f</i> osc) [eV]	T <sub>1</sub> [eV]	ΔE <sub>ST</sub> [eV]
2T-2N	$0.95(7.89 \cdot 10^{-4})$	1.13	-0.18	$0.96(7.15 \cdot 10^{-4})$	1.08	-0.12
2Т-В-N	$1.13(1.67 \cdot 10^{-3})$	1.42	-0.29	$1.07 (1.44 \cdot 10^{-3})$	1.25	-0.18
5AP	$2.30(3.11 \cdot 10^{-3})$	2.54	-0.24	2.26 (0.026)	2.35	-0.09



**Figure S8**: symmetry adapted HOMO  $(\psi_{3}^{a_{2}})$  and LUMO  $(\psi_{5}^{b_{2}})$  of  $C_{2v}$  point group.





#### HOMO

#### LUMO

Figure S9: HOMO and LUMO orbital of 5AP obtained within the Hückel approximation.



**Figure S10**: HOMO and LUMO computed at HF/def2-TZVP, exchange interaction,  $\Delta E_{ST}$  and oscillator strength computed at SCS-CC2/def2-TZVP for DABNA-1 (isocontour  $\sigma$ =0.02 e·Bohr-3).

The extension of the HOMO and LUMO over the bonds leads to a larger HOMO-LUMO overlap ( $S_{HL} = 0.609$ ) with the consequent high exchange interaction and positive  $\Delta E_{ST}$ 

# 1.3 Point group C<sub>3h</sub>

The following section is related to the symmetry analysis and the generation of the SALCs and SAMOs of the a'' iRR of the C<sub>3h</sub> point group, by considering the sole *p*-type orbitals of the C atoms and N central atom of the cyclazine-like structure.

	Ta	ıble S8: cha	racter table	$e of C_{3h} points$	ε nt group.	$=exp^{[10]}(\frac{2\pi}{3})$	$\left(\frac{\pi i}{3}\right)$
C <sub>3h</sub>	Е	C <sub>3</sub> (z)	$(C_3)^2$	$\sigma_{h}$	$S_3$	(S <sub>3</sub> ) <sup>5</sup>	linear functions, rotations
A'	+1	+1	+1	+1	+1	+1	Rz
E'	+1	$3^+$	$+\mathbf{e}^*$	+1	$3^+$	+ <b>8</b>	x+iy
Ľ	+1	$+\mathbf{\epsilon}_{*}$	$3^+$	+1	$+\mathbf{e}^*$	$3^+$	x-iy
A''	+1	+1	+1	-1	-1	-1	Z
Е"	+1	$3^+$	$+\mathbf{s}_{*}$	-1	-8	<b>-</b> *	R <sub>x</sub> +iR <sub>y</sub>
Ľ	+1	$+\mathbf{a}^*$	$3^+$	-1	<b>-</b> *	3-	$R_x - iR_y$

The application of the symmetry operations to the molecular structure results in the following RR

$$\Gamma_{red}^{C_{3h}} = (13, 1, -1, -13, -1, -1)$$

which then is reduced by means of eq.S1.1 resulting in the following direct sum of the iRRs:

$$\Gamma_{red}^{C_{3h}} = 5a^{''} \oplus 4e^{''}$$

The application of the  $A^{''}$  projection operator generates the following five SALCs:

$$\begin{split} \mathcal{P}^{a} \chi_{1} &= \chi_{1} + \chi_{9} + \chi_{5} + \chi_{1} + \chi_{9} + \chi_{5} \rightarrow \phi_{1} = 1/\sqrt{3}(\chi_{1} + \chi_{5} + \chi_{9}) \\ \mathcal{P}^{a''} \chi_{2} &= \chi_{2} + \chi_{10} + \chi_{6} + \chi_{2} + \chi_{10} + \chi_{6} \rightarrow \phi_{2} = 1/\sqrt{3}(\chi_{2} + \chi_{6} + \chi_{10}) \\ \mathcal{P}^{a''} \chi_{3} &= \chi_{3} + \chi_{11} + \chi_{7} + \chi_{3} + \chi_{11} + \chi_{7} \rightarrow \phi_{3} = 1/\sqrt{3}(\chi_{3} + \chi_{7} + \chi_{11}) \\ \mathcal{P}^{a''} \chi_{4} &= \chi_{4} + \chi_{12} + \chi_{8} + \chi_{4} + \chi_{12} + \chi_{8} \rightarrow \phi_{4} = 1/\sqrt{3}(\chi_{4} + \chi_{8} + \chi_{12}) \\ \mathcal{P}^{a''} \chi_{13} &= 6\chi_{13} \rightarrow \phi_{13} = \chi_{13} \end{split}$$

with the resulting Hückel determinant, written in terms of *x*:

$$\det\left(a^{''}\right) = \begin{vmatrix} x & 1 & 0 & 0 & 0\\ 1 & x & 1 & 0 & 0\\ 0 & 1 & x & 1 & 1.36\\ 0 & 0 & 1 & x & 0\\ 0 & 0 & 1.36 & 0 & x + 1.5 \end{vmatrix}$$

The diagonalization of the Hückel Hamiltonian produces the following linear combinations of a''-SALCs, i.e. the file a''-SAMOs:

$$\begin{split} \psi^a_1 &= 0.103\phi_1 + 0.264\phi_2 + 0.577\phi_3 + 0.224\phi_4 + 0.732\phi_{13} \\ \psi^a_2 &= 0.584\phi_1 + 0.647\phi_2 + 0.132\phi_3 + 0.119\phi_4 - 0.456\phi_{13} \\ \psi^a_3 &= -0.364\phi_1 - 0.144\phi_2 + 0.308\phi_3 + 0.780\phi_4 - 0.378\phi_{13} \\ \psi^a_4 &= 0.662\phi_1 - 0.477\phi_2 - 0.318\phi_3 + 0.441\phi_4 + 0.195\phi_{13} \\ \psi^a_5 &= -0.277\phi_1 + 0.512\phi_2 - 0.673\phi_3 + 0.363\phi_4 + 0.273\phi_{13} \end{split}$$

Note that in this case, the identification of the highest occupied and lowest unoccupied SAMO is not necessary because none of the five SAMOs is reminiscent of the orbital localization obtained at  $D_{3h}$  and  $C_{2v}$  level, thus none of them is compatible with the orbital pattern minimizing the exchange interaction.

## 1.3.1 C<sub>3h</sub> symmetry compounds

**Table S9**:  $S_1$  and  $T_1$  excitation energies computed at SCS-CC2/def2-TZVP and NEVPT2/def2-TZVP for the  $C_{3h}$  symmetry compounds.

	SC	CS-CC2		NEVPT2 (8,8)			
	$S_1(f_{OSC})$	T <sub>1</sub> [eV]	ΔE <sub>ST</sub> [eV]	$S_1(f_{OSC})$	T <sub>1</sub> [eV]	ΔE <sub>ST</sub> [eV]	
2T-N-3NH2	1.86 (0.000)	1.39	0.47	1.49 (0.001)	1.22	0.27	
<sup>a</sup> Triazacyclazine	2.26 (0.000)	2.34	-0.08	2.14 (0.000)	2.19	-0.05	

<sup>*a*</sup> From Ref.13 in the main text (NEVPT2 with a 6,6 CAS).



*Figure S11:* HOMO and LUMO of the  $C_{3h}$  cyclazine computed at HF/def2-TZVP level (isocontour  $\sigma$ =0.02 e·Bohr-3).



**Figure S12**: HOMO and LUMO computed at HF/def2-TZVP level (isocontour  $\sigma$ =0.02 e·Bohr-3), exchange interaction,  $\Delta E_{ST}$  and oscillator strength computed at SCS-CC2/def2-TZVP level for triazacyclazine.

### 1.4 Point group C<sub>3v</sub>

The following section is related to the symmetry analysis and the generation of the SALCs and SAMOs of the  $a_1$  and  $a_2$  iRR of the C<sub>3h</sub> point group, by considering the sole *p*-type orbitals of the C atoms and N central atom of the cyclazine-like structure.

$C_{3v}$	Е	2C <sub>3</sub> (z)	$3\sigma_{\rm v}$	linear functions, rotations
A <sub>1</sub>	+1	+1	+1	Z
$A_2$	+1	+1	-1	R <sub>z</sub>
E	+2	-1	0	$(\mathbf{x}, \mathbf{y}) (\mathbf{R}_{\mathbf{x}}, \mathbf{R}_{\mathbf{y}})$

*Table S10:* character table of  $C_{3v}$  point group.

The application of the symmetry operations to the molecular structure results in the following RR

 $\Gamma_{red}^{C_{3v}}(13,1,1,3,3,3)$ 

which then is reduced by means of eq.S1.1 resulting in the following direct sum of the iRRs:

$$\Gamma_{red}^{C_{3v}} = 4a_1 \oplus a_2 \oplus 4e$$

The application of the  $a_2$  projection operator generates the sole  $\psi_2^{a_2}$  SALC:

$$P^{a_2}\chi_1 = \chi_1 + \chi_9 + \chi_5 - \chi_1 - \chi_9 - \chi_5 = 0$$

$$P^{a_2}\chi_2 = \chi_2 + \chi_{10} + \chi_6 - \chi_{12} - \chi_4 - \chi_8 \rightarrow \psi_1^{a_2} = 1/\sqrt{6}(\chi_2 + \chi_{10} + \chi_6 - \chi_{12} - \chi_4 - \chi_8)$$

$$P^{a_2}\chi_3 = \chi_3 + \chi_{11} + \chi_7 - \chi_3 - \chi_{11} - \chi_7 = 0$$

$$\hat{p}^{a_2}\chi_{13} = \chi_{13} + \chi_{13} + \chi_{13} - \chi_{13} - \chi_{13} - \chi_{13} = 0$$

On the contrary, the application of the  $a_1$  projection operator generates four SALCs:

$$\hat{P}^{a_1}\chi_1 = \chi_1 + \chi_9 + \chi_5 + \chi_1 + \chi_9 + \chi_5 \rightarrow \phi_1 = 1/\sqrt{3}(\chi_1 + \chi_5 + \chi_9)$$

$$\hat{P}^{a_1}\chi_2 = \chi_2 + \chi_{10} + \chi_6 + \chi_{12} + \chi_4 + \chi_8 \rightarrow \phi_2 = 1/\sqrt{6}(\chi_2 + \chi_{10} + \chi_6 + \chi_{12} + \chi_4 + \chi_8)$$

$$\hat{P}^{a_1}\chi_3 = \chi_3 + \chi_{11} + \chi_7 + \chi_3 + \chi_{11} + \chi_7 \rightarrow \phi_3 = 1/\sqrt{3}(\chi_3 + \chi_{11} + \chi_7)$$

$$\hat{P}^{a_1}\chi_{13} = \chi_{13} + \chi_{13} + \chi_{13} + \chi_{13} + \chi_{13} + \chi_{13} \rightarrow \phi_4 = \chi_{13}$$

with the resulting Hückel determinant, written in terms of *x*:

$$\det (a_1) = \begin{vmatrix} x & \sqrt{2} & 0 & 0 \\ \sqrt{2} & x & \sqrt{2} & 0 \\ 0 & \sqrt{2} & x & 0.36 \\ 0 & 0 & 0.36 & x + 1.5 \end{vmatrix}$$

The diagonalization of the Hückel Hamiltonian produces the following linear combinations of  $a_{1-}$  SALCs, i.e. the file  $a_{1-}$ SAMOs:

$$\psi_{1}^{a_{1}} = 0.448\phi_{1} + 0.654\phi_{2} + 0.507\phi_{3} + 0.336\phi_{4}$$
  

$$\psi_{2}^{a_{1}} = -0.257\phi_{1} - 0.273\phi_{2} + 0.033\phi_{3} + 0.926\phi_{4}$$
  

$$\psi_{3}^{a_{1}} = -0.698\phi_{1} + 0.021\phi_{2} + 0.697\phi_{3} - 0.163\phi_{4}$$
  

$$\psi_{4}^{a_{1}} = -0.496\phi_{1} + 0.704\phi_{2} - 0.505\phi_{3} + 0.052\phi_{4}$$

As we did for the D<sub>3h</sub> point group, we need to find the eigenvalues related to the 2D iRR SAMOs to identify the highest occupied SAMO and lowest unoccupied SAMO. To find the SALCs and SAMOs associated with the 2D-iRR (e'') we can resort to the character table of the C<sub>3</sub> point group, noting that rotational symmetry of the SALCs is inherently dictated by the C<sub>3</sub> axis Each resulting SALC pair ( $\varphi_a$  and  $\varphi_b$ ), bearing imaginary coefficients, will be linearly combined to obtain real SALCs:  $\phi_{1,1}^e = (\varphi_a + \varphi_b)_{and} \phi_{1,2}^e = (\varphi_a - \varphi_b)/i_{.}$ 

*Table S11*: character table of  $C_3$  group.  $\varepsilon = exp[in](\frac{2\pi i}{3})$ 

C <sub>3</sub>	Е	C <sub>3</sub> (z)	$C_{3}^{-1}$	linear functions, rotations
А	+1	+1	+1	z, R <sub>z</sub>
E	+1 +1	<b>3</b> + * <b>3</b> +	* <b>3</b> + 3+	$x+iy; R_x+iR_y$ x-iy; R_x-iR_y

The application of the e projection operator produces the following five pairs of complex SALCs (left), which then are linearly combined to give the real SALCs (right):

$$\begin{cases} P^{e}\chi_{1} = \chi_{1} + \varepsilon\chi_{9} + \varepsilon^{*}\chi_{5} \\ P^{e}\chi_{1} = \chi_{1} + \varepsilon^{*}\chi_{9} + \varepsilon\chi_{5} \\ P^{e}\chi_{2} = \chi_{2} + \varepsilon\chi_{10} + \varepsilon^{*}\chi_{6} \\ P^{e}\chi_{2} = \chi_{2} + \varepsilon^{*}\chi_{10} + \varepsilon\chi_{6} \\ P^{e}\chi_{3} = \chi_{3} + \varepsilon\chi_{11} + \varepsilon^{*}\chi_{7} \\ P^{e}\chi_{3} = \chi_{3} + \varepsilon^{*}\chi_{11} + \varepsilon^{*}\chi_{7} \\ P^{e}\chi_{4} = \chi_{4} + \varepsilon\chi_{12} + \varepsilon^{*}\chi_{8} \\ P^{e}\chi_{4} = \chi_{4} + \varepsilon^{*}\chi_{12} + \varepsilon\chi_{8} \\ P^{e}\chi_{13} = \chi_{13} + \varepsilon\chi_{13} + \varepsilon^{*}\chi_{13} \\ P^{e}\chi_{13} = \chi_{13} + \varepsilon^{*}\chi_{13} + \varepsilon^{*}\chi_{13} \\ P^{e}\chi_{13} = \chi_{13} + \varepsilon^{*}\chi_{13} + \varepsilon^{*}\chi_{13} \\ P^{e}\chi_{13} = \chi_{13} + \varepsilon^{*}\chi_{13} + \varepsilon\chi_{13} \\ P^{e}\chi_{13} = \chi_{13} - \chi_{13} - \chi_{13} = 0 \end{cases} \Rightarrow \qquad \begin{cases} \phi_{1,1} = 1/\sqrt{6}(2\chi_{1} - \chi_{9} - \chi_{5}) \\ \phi_{2,2} = 1/\sqrt{2}(\chi_{10} - \chi_{6}) \\ \phi_{2,2} = 1/\sqrt{2}(\chi_{10} - \chi_{6}) \\ \phi_{2,2} = 1/\sqrt{2}(\chi_{10} - \chi_{6}) \\ \phi_{3,2} = 1/\sqrt{2}(\chi_{10} - \chi_{6}) \\ \phi_{3,2} = 1/\sqrt{2}(\chi_{11} - \chi_{7}) \\ \phi_{4,2} = 1/\sqrt{2}(\chi_{11} - \chi_{7}) \\ \phi_{4,2} = 1/\sqrt{2}(\chi_{12} - \chi_{8}) \\ \phi_{4,2} = 1/\sqrt{2}(\chi_{12} - \chi_{8}) \\ \phi_{4,2} = 1/\sqrt{2}(\chi_{12} - \chi_{13} - \chi_{13} - \chi_{13} = 0 \\ \phi_{13,2} = \chi_{13} - \chi_{13} - \chi_{13} = 0 \end{cases}$$

We obtain two determinants, one in terms of  $\phi_{i,1}$  and the other in terms of  $\phi_{i,2}$  SALCs:

		1	0	$1/6_{ }$	1	x	1	0	-1/2
$\det\left(e\right)_{i,1} =$	1	x	1	0	dot(a) -	1	x	1	0
	0	1	x	1	$\det(e)_{i,2} = \begin{bmatrix} 0 \end{bmatrix}$	1	x	1	
	1/6	0	1	<i>x</i>	-	1/2	0	1	x

We need to solve just one of them to find the eigenvalues and order all the SAMOs according to their energy. At the end, we obtain the following order:

Eigenvalue	Eigenvector (SAMO)	
2.044	$\psi_{\ 1}^{a_{1}}$	
1.666	$\psi_1^e$	
1.487	$\psi^{a_1}_{\ 2}$	
0.500	$\psi^e_2$	
0.000	$\psi_{1}^{a_{2}}$	НОМО
-0.042	$\psi^{a_1}_{\ 3}$	LUMO
-0.500	$\psi^e_3$	
-1.666	$\psi_4^e$	
-1.989	$\psi^{a_2}_{\ 4}$	

*Table S12:* C<sub>3v</sub> eigenvalues.

1.4.1  $C_{3v}$  symmetry compound

	SCS-CC2			NEVPT2 (8,8)		
	$\frac{S_1(f_{OSC})}{[eV]}$	T <sub>1</sub> [eV]	ΔE <sub>ST</sub> [eV]	$\begin{bmatrix} S_1 (f_{OSC}) \\ [eV] \end{bmatrix}$	T <sub>1</sub> [eV]	ΔE <sub>ST</sub> [eV]
2T-P	1.14 (0.000)	1.32	-0.18	1.16 (0.000)	1.25	-0.09

**Table S13**:  $S_1$  and  $T_1$  excitation energies computed at SCS-CC2/def2-TZVP and NEVPT2/def2-TZVP for the  $C_{3v}$  symmetry compound based on the B97-3c geometry.









**Figure S13**: difference density plots computed at SCS-CC2/def2-TZVP level for the cyclazine derivatives (isocontour  $\sigma$ =0.002 e·Bohr-3).

# 2. Design INVEST compounds with a non-zero oscillator strength



**Figure S14**:  $\Delta E_{ST}$  and oscillator strength computed at SCS-CC2/def2-TZVP level for the two cyclazine derivatives having the EDGs/EWGs on sites with a high HOMO/LUMO weight (left) and high LUMO/HOMO weight (right).

	CT-del. V [Å <sup>3</sup> ]
$R_1 = H, R_2 = H$	44.77
$R_1 = NH_2, R_2 = H$	45.18
$R_1 = H, R_2 = NH_2$	47.21
$R_1 = H, R_2 = CN$	44.48

Table S14: CT delocalization volume computed at SCS-CC2/def2-TZVP level.

$R_1 = CN, R_2 = H$	46.36
$R_1 = NH_2, R_2 = CN$	42.90
$R_1 = CN, R_2 = NH_2$	48.46

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*Figure S15*: *MOs diagram of 2N-uthrene (left) and 2B-uthrene (right) starting from the HOMO and LUMO of the isolated triangulenes.* 



**Figure S16**: mono-electron difference density plot of  $S_2$  state of 2N-uthrene (left) and 2B-uthrene (right).

**Table S15**: percentage of doubles and higher order excitations computed at CASSCF(8,8)/def2-TZVP and  $\tau_2$  diagnostic computed at SCS-CC2/def2-TZVP level for  $S_1$  and  $T_1$  of 2N-Uthrene and 2N-Zethrene.

	S <sub>1</sub> %D,T	T <sub>1</sub> %D,T
2N-Uthrene	13.87	11.52
2N-Zethrene	5.33	3.36
2B-Uthrene	17.40	16.00
2B-Zethrene	7.06	6.60

# 3. Simulation of the emission spectra

Within the Born-Oppenheimer approximation, the transition dipole moment associated with the vibronic transition between the vibrational states  $\Theta_{i,v_i}$  and  $\Theta_{f,v_f}$  belonging to the electronic states  $\psi_i$  and  $\psi_f$ , respectively, can be written as follows:

$$M_{i,v_i \to f,v_f} = \left\langle \psi_{i}, \Theta_{i,v_i} \right| \hat{\mu} \left| \psi_f, \Theta_{f,v_f} \right\rangle = \left\langle v_i \right| \hat{\mu}_{if} \left| v_f \right\rangle$$
(S2.1)

in which  $\vec{\mu}_{if}$  is the electric transition dipole moment  $(\langle \psi_i | \hat{\mu} | \psi_f \rangle)$ , operating on the electronic wavefunction  $\psi_i$  and  $\psi_f$ . Within the harmonic approximation, the ground and excited state hamiltonian can be written in terms of 3N-6 (or 3N-5 for a linear molecule) harmonic oscillator hamiltonian:

$$H_g = \sum_{k}^{3N-6} \frac{1}{2} (\hat{p}_{gk}^2 + \omega_{gk}^2 Q_{gk}^2)$$
(S2.2)

$$H_e = \sum_{k}^{3N-6} \frac{1}{2} (\hat{p}_{ek}^2 + \omega_{ek}^2 Q_{ek}^2)$$
(S2.3)

In which  $\hat{p}_{\alpha k}$  is the momentum  $\omega_{\alpha k}$  is the harmonic frequency associated with the normal mode  $Q_{\alpha k}$ . The normal modes of the ground state and excited state are related by the so-called Duschinsky rotation matrix  $S_{ij}$  as follows:

$$Q_{ei} = \sum_{j}^{3N-6} S_{ij} Q_{gj} + D_i$$
 (S2.4)

with  $D_i$  the displacement of the excited state geometry with respect the ground state geometry.

Expanding the electric transition dipole moment operator as a Taylor series in the nuclear coordinates (Q) about the equilibrium geometry, we obtain:

$$\vec{\mu}_{if} = \vec{\mu}_{if}^{0} + \sum_{k}^{3N-6} \left( \frac{\partial \vec{\mu}_{if}}{\partial Q_{fk}} \right)_{f0} Q_{fk} = \vec{\mu}_{if}^{0} + \sum_{k}^{3N-6} \vec{\mu}_{fk} Q_{fk}$$
(S2.3)

in which  $\vec{\mu}_{if}^{0}$  is the unperturbed electronic transition dipole moment. The first term in eq.S2.3 represents the Franck-Condon contribution, for which the electric transition dipole moment is considered independent on the nuclear motions, generally a valid approximation for the strongly dipole allowed electronic transition. The second term defines the so-called Herzberg-Teller contribution, which takes into account the variation of the electric transition dipole moment along the 3N-6 nuclear motions, becoming important in the presence of weakly allowed electronic transition. The emission cross-section expression is given by the following formula:

$$\sigma(\omega)_{i \to f} = \frac{4\omega^3}{3\hbar c^3} \sum_{v_i, v_f} P_{i, v_i}(T) \delta(E_{if} + E_{i, v_i} - E_{f, v_f}) |\langle v_f | \vec{\mu}_{if} | v_i \rangle|^2$$
(S2.4)

in which  $P_{i,v_i}(T)$  is the Boltzmann population of the initial state,  $E_{if}$  is the adiabatic energy difference between the initial  $(\Psi_i)$  and final  $(\Psi_f)$  electronic state,  $E_{j,v_j}$  is the vibrational energy associated with the *j*-th electronic state, i.e.  $\hat{H}_{vib} |\Theta_{j,v_j}\rangle = E_{j,v_j} |\Theta_{j,v_j}\rangle$ . By inserting eq.S2.3 in eq.S2.4 we obtain the following expression:

$$\sigma(\omega)_{i \to f} = \frac{4\omega^{3}}{3\hbar c^{3}} \sum_{v_{i},v_{f}} P_{i,v_{i}} \delta(E_{if} + E_{i,v_{i}} - E_{f,v_{f}}) \times$$

$$\times \left\langle v_{f} \left| \vec{\mu}_{if}^{0} + \sum_{k} \vec{\mu}_{fk} Q_{fk} \right| v_{i} \right\rangle \left\langle v_{i} \left| \vec{\mu}_{if}^{0} + \sum_{k'} \vec{\mu}_{fk'} Q_{fk'} \right| v_{f} \right\rangle$$
(S2.5)

Focusing on the last term and developing the product we obtain three terms: a term involving only the unperturbed transition dipole moment, thus recovering the so-called Franck-Condon approximation  $(\sigma(\omega)_{i\to f}^{FC} \propto \langle v_f | \vec{\mu}_{if}^0 | v_i \rangle \langle v_i | \vec{\mu}_{if}^0 | v_f \rangle)$ ; a term containing the integrals involving both the unperturbed transition dipole moment and its derivative with respect to the normal modes, i.e. accounting for both the Franck-Condon and the Herzberg-Teller approximation ( $\sigma(\omega)_{i\to f}^{FC/HT} \propto \langle v_f | \vec{\mu}_{if}^0 | v_i \rangle \langle v_i | \sum_{k} \vec{\mu}_{fk} Q_{fk} | v_f \rangle$ ); a term which does not contain the unperturbed transition ( $\sigma(\omega)_{i\to f}^{FC/HT} \propto \langle v_f | \vec{\mu}_{if}^0 | v_i \rangle \langle v_i | \sum_{k} \vec{\mu}_{fk} Q_{fk} | v_f \rangle$ ); a term which does not contain the unperturbed

transition dipole moment, thus accounting only for the Herzberg-Teller approximation (  $\sigma(\omega)_{i \to f}^{HT} \propto \left\langle v_i \left| \sum_{k} \vec{\mu}_{fk} Q_{fk} \right| v_f \right\rangle \left\langle v_f \left| \sum_{k'} \vec{\mu}_{fk'} Q_{fk'} \right| v_i \right\rangle$ ). Thus, the emission cross-section receives

contribution from three effects, whose expressions are the following:

$$\sigma(\omega)_{i \to f} = \sigma(\omega)_{i \to f}^{FC} + \sigma(\omega)_{i \to f}^{FC/HT} + \sigma(\omega)_{i \to f}^{HT}$$
(S2.6)

$$\sigma(\omega)_{i \to f}^{FC} = \frac{4\omega^{-1}}{3\hbar c^{3}} |\vec{\mu}_{if}^{0}|^{2} \sum_{v_{i}, v_{f}} P_{i, v_{i}} |\langle v_{f} | v_{f} \rangle|^{2} \delta(E_{if} + E_{i, v_{i}} - E_{f, v_{f}})$$
(S2.7)

$$\sigma(\omega)_{i \to f}^{FC/HT} = \frac{4\omega^3}{3\hbar c^3} \sum_{v_i, v_f} P_{i, v_i} \delta(E_{if} + E_{i, v_i} - E_{f, v_f}) \sum_k \vec{\mu}_{if}^0 \vec{\mu}_{fk} \langle v_f | v_i \rangle \langle \Theta_{i, v_i} | Q_{fk} | v_i \rangle$$
(S2.8)

$$\sigma(\omega)_{i \to f}^{HT} = \frac{4\omega^{3}}{3\hbar c^{3}} \sum_{v_{i}, v_{f}} P_{i, v_{i}} \delta(E_{if} + E_{i, v_{i}} - E_{f, v_{f}}) \sum_{k, k'} \vec{\mu}_{fk} \vec{\mu}_{fk'} \langle v_{i} | Q_{fk} | v_{f} \rangle \langle v_{f} | Q_{fk'} | v_{i} \rangle$$
(S2.9)

In eqS2.7 the  $\vec{\mu}_{if}^0$  has been put outside the vibrational wavefunctions integral since it does not depends on the nuclear coordinates. In eqS2.8 and eqS2.9 the derivatives of  $\vec{\mu}_{if}$  with respect the normal modes,  $\vec{\mu}_{fk}$  and  $\vec{\mu}_{fk'}$ , have been put outside the integrals since they are constants. The resolution of the three equation is carried out employing a time-dependent approach, thus moving from the frequency domain to the time domain through the Fourier transform of the delta function. Being:

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega t} dt \qquad (S2.10)$$

It follows that the contributions to the emission cross-section in the time domain can be written as:

$$\sigma(\omega)_{i \to f}^{FC} = \frac{2\omega^3}{3\pi\hbar c^3} |\vec{\mu}_{if}^0|^2 \int_{-\infty}^{+\infty} d\tau \exp(iE_{if}\tau) Z^{-1} \rho_{fi}^{FC}(t,T)$$
(S2.11)

$$\sigma(\omega)_{i \to f}^{FC/HT} = \frac{2\omega^3}{3\pi\hbar c^3} \sum_k \vec{\mu}_{if}^0 \vec{\mu}_{fk} \int_{-\infty}^{+\infty} d\tau \exp(iE_{if}\tau) Z^{-1} \rho_{fi}^{FC}(t,T)$$
(S2.12)

$$\sigma(\omega)_{i \to f}^{HT} = \frac{2\omega^3}{3\pi\hbar c^3} \sum_{k,k'} \vec{\mu}_{fk} \vec{\mu}_{fk'} \int_{-\infty}^{+\infty} d\tau \exp(iE_{if}\tau) Z^{-1} \rho_{fi}^{HT}(t,T)$$
(S2.13)

With:

$$\rho_{fi}^{FC}(t,T) = Tr \left[ e^{-iE_{f,v_f} \tau_f} e^{-iE_{i,v_i} \tau_i} \right]$$
(S2.14)

$$\rho_{fi}^{FC/HT}(t,T) = Tr \left[ Q_{fk} e^{-iE_{f,v_f} \tau_f} e^{-iE_{i,v_i} \tau_i} \right]$$
(S2.15)

$$\rho_{fi}^{HT}(t,T) = Tr \left[ Q_{fk} e^{-iE_{f,v_f} \tau_f} Q_{fk'} e^{-iE_{i,v_i} \tau_i} \right]$$
(S2.16)

the so-called *thermal vibration cross-correlation functions* (TVCFs), which represents the thermal modulation of the vibrational wavefunctions overlap.  $\tau = \tau_f = t/\hbar$  and  $\tau_i = -\tau_f - i\beta$ , with  $\beta = (k_B T)^{-1}$  and Z the partition function of the Boltzmann distribution.

The analytical expression for the TVCFs has been derived by Ianconescu and Pollak<sup>[6]</sup> within the harmonic approximation.

The stick spectra have been computed following a Time-Independent approach, within the *undistorted displaced harmonic approximation*, i.e. neglecting the Duschinsky rotation and assuming equal frequencies and normal modes for the ground and excited state. The intensity associated with each vibronic transition, starting from the lowest vibrational level of the initial electronic state can be written as:

$$I_{i,0\to f,\nu_f} \propto |\vec{\mu}_{if}^0|^2 \prod_k^{TS} \frac{(S_k)^{n_k}}{n_k!} exp^{[i0]}(-S_k)$$
(S2.17)

in which  $n_k$  is the vibrational quantum number and  $S_k$  is the Huang-Rhys (HR) factor associated with the *k*-th vibrational normal mode, defining the projection of the geometry displacement between state i and f along the *k*-th totalsymmetric normal mode:

$$S_{k} = \frac{1}{2} \left\{ \sqrt{\frac{\omega_{k}}{\hbar}} [X_{i} - X_{f}] M^{\frac{1}{2}} L_{k}(f) \right\}^{2}$$
(S2.18)

in which  $\omega_k$  is the vibrational frequency of the k-th normal mode,  $X_i$  and  $X_f$  are the cartesian coordinates of the equilibrium geometry of state state *i* and *f*, *M* is the diagonal matrix whose elements are the atomic masses,  $L_k(f)$  is the vector containing the normal coordinates written in terms of mass-weighted cartesian coordinate of the final state.

The resulting "stick spectra" is the convolution of each vibronic transition<sup>[6]</sup>:

$$I(\omega) \propto \sum_{n_1 = 0} \dots \sum_{n_n = 0} I_{i,0 \to f,v_f}$$
 (S2.19)

For the simulation of the stick spectra only the HR factors > 0.01 have been taken into account considering only two vibrational quantum number (n = 0,1).

The Huang-Rhys factors, used to compute the stick spectra, have been obtained with Q-Chem 5.4.



Figure S17: Duschinsky rotation matrix for 2T-b (a), 2T-d (b) and 2T-f (c).



*Figure S18*: normal mode at 1609 cm<sup>-1</sup> for 2T-b (a) and at 1473 cm<sup>-1</sup> 2T-f (b)



**Figure S19:** Contributions of the Herzberg-Teller effect associate with each normal mode (  $(\partial \mu_{if} / \partial Q_{fk}) \langle v_i | Q_{fk} | v_f \rangle$ ) for **2T-b** (a), **2T-d** (b) and **2T-f** (c) compound.



*Figure S20*: normal modes with the highest HT contribution for 2T-b (a), 2T-d (b) and 2T-f (c).

*Table S16*: unperturbed transition dipole moment, Herzberg-Teller terms and total transition dipole moment computed at TD-DFT-PBE0/def2-SVP for 2T-b, 2T-d, 2T-f and 2N-Uthrene

	2Т-b	2T- <i>d</i>	2T-f	2N-Uthrene
$\mu_{if}^{0}$ [a.u.]	0.261	0.160	0.448	0.285
$\mu^{HT}$ [a.u.]	0.939	1.090	1.387	1.757
$\mu^{TOT} = \mu^0 + \mu^{HT}$ [a.u.]	1.200	1.250	1.835	2.042



*Figure S21*: Duschinsky rotation matrix between  $S_0$  and  $S_1$  normal modes of 2N-uthrene (left) and 2B-uthrene (right) compound.



**Figure S22**: a) contributions of the Herzberg-Teller effect associate with each normal mode (  $(\partial \mu_{if}/\partial Q_{fk})\langle v_i | Q_{fk} | v_f \rangle$ ); b) normal mode at 1638 cm<sup>-1</sup> for **2N-Uthrene** compound; c) contributions of the Herzberg-Teller effect associate with each normal mode for **2B-uthrene**.

27	<b>-</b> <i>b</i>	21	[- <i>d</i>	2	Г- <i>f</i>	2N-1	uthrene	2B-1	ıthrene
Freq	HR	Freq	HR	Freq	HR	Freq	HR	Freq	HR
246	0.0030	123	0.0912	121	0.0390	48	0.0540	59	0.7387
255	0.0016	405	0.0010	253	0.0400	55	0.5989	104	1.0446
384	0.0019	489	0.0121	280	0.3615	105	0.1370	157	0.2511
438	0.1643	514	0.0102	431	0.0074	210	0.0944	181	0.0331
459	0.1927	689	0.0626	446	0.1417	247	0.2616	249	0.0960
511	0.0304	805	0.0027	453	0.0015	490	0.0211	409	0.0136
565	0.0933	933	0.0027	522	0.0013	512	0.0143	451	0.0708
619	0.0050	1139	0.0024	561	0.0331	590	0.0345	464	0.0589
728	0.0068	1318	0.0048	604	0.1114	684	0.0116	470	0.0711
755	0.0043	1359	0.0109	649	0.0021	729	0.0135	494	0.1567
795	0.0011	1456	0.0608	783	0.0094	1092	0.0133	606	0.0119
1050	0.0047	1535	0.2067	788	0.0021	1127	0.0176	741	0.0125
1121	0.0121	1652	0.0254	948	0.0034	1168	0.0279	776	0.0338
1153	0.0013	1672	0.0037	1103	0.0052	1345	0.0298	782	0.2303
1242	0.0240	2341	0.0024	1224	0.0018	1390	0.0242	832	0.0137
1329	0.0131	3210	0.0010	1294	0.0598	1420	0.0239	1177	0.0994
1366	0.0042			1347	0.0011	1451	0.0257	1198	0.0173
1436	0.0572			1386	0.0445	1582	0.1519	1300	0.0328
1463	0.0548			1473	0.1599			1325	0.1561
1609	0.0609			1558	0.0580			1356	0.0197
1643	0.0031			1648	0.0554			1399	0.0185
1666	0.0165			1670	0.0788			1422	0.0107
1688	0.0150			1693	0.0067			1526	0.0293
3611	0.0056			2336	0.0011			1632	0.0103
				3633	0.0304				
				3750	0.0040				

*Table S17:* frequencies and Huang-Rhys factors for 2T-b, 2T-d, 2T-f (>0.001), 2N-uthrene and 2B-uthrene (>0.01).

# 4. Non-radiative decay rates

#### 4.1. Rate expression derivation

The calculation of the non-radiative decay rates, internal conversion (IC) and (reverse)intersystem crossing ((R)ISC), is based on a time-dependent approach, similar to the one employed to derive the expression for the emission cross-section.

The internal conversion rate constant  $\binom{k_{IC}}{k_{IC}}$  can be written at first according to the Fermi's golden rule:

$$k_{IC} = \frac{2\pi}{\hbar} |H_{NA}|^2 \delta(E_{if} + E_{i,v_i} - E_{f,v_f})$$
(S3.1)

in which  $H_{NA}$  is the non-adiabatic coupling defined as follows:

$$H_{NA} = -\hbar^{2} \sum_{k} \left\langle \Psi_{f} \left| \frac{\partial}{\partial Q_{fk}} \right| \Psi_{i} \right\rangle =$$

$$= -\hbar^{2} \sum_{k} \left\langle \psi_{f} \Theta_{f,v_{f}} \left| \frac{\partial}{\partial Q_{fk}} \right| \psi_{i} \Theta_{i,v_{i}} \right\rangle =$$

$$= -\hbar^{2} \sum_{k} \left\langle \psi_{f} \left| \frac{\partial}{\partial Q_{fk}} \right| \psi_{i} \right\rangle \left\langle \Theta_{f,v_{f}} \left| \frac{\partial}{\partial Q_{fk}} \right| \Theta_{i,v_{i}} \right\rangle =$$

$$= \sum_{k} \left\langle \psi_{f} \left| \mathcal{P}_{fk} \right| \psi_{i} \right\rangle \left\langle \Theta_{f,v_{f}} \left| \mathcal{P}_{fk} \right| \Theta_{i,v_{i}} \right\rangle$$
(S3.2)

With  $\mathcal{P}_{fk} = (-\hbar)^{-1} (\partial/\partial Q_{fk})$ . In the last step, we employed the Born-Oppenheimer approximation. The sum runs over the vibrational normal modes, so that the non-adiabatic coupling can be written as

$$H_{NA} = \sum_{i} H_{NA,k}$$

the sum of each contribution associated with each normal modes: k Consequently, by inserting eq.S3.2 into eq.S3.1, the total internal conversion rate can be written as the sum of different

contribution:  $k_{IC} = \sum_{kk'} k_{IC,kk'}$ , with  $|H_{NA,kk'}|^2$  defined as:

$$|H_{NA,kk'}|^{2} = H_{NA,k}H_{NA,k'} =$$

$$= \langle \psi_{f} | \mathcal{P}_{fk} | \psi_{i} \rangle \langle \psi_{i} | \mathcal{P}_{fk'} | \psi_{f} \rangle \langle \Theta_{f,v_{f}} | \mathcal{P}_{fk} | \Theta_{i,v_{i}} \rangle \langle \Theta_{i,v_{i}} | \mathcal{P}_{fk'} | \Theta_{f,v_{f}} \rangle$$
(S3.3)

We label the product between the integral involving the electronic wavefunctions as  $R_{kk'}$  (the diagonal elements  $R_{kk}$  have been labelled as  $NAC_k$  in the main text) and the one involving the vibrational wavefunction as  $V_{kk'}$ . The expression of the internal conversion rate receiving contributions from the *k*-th and *k'*-th normal mode can be written as follow:

$$k_{IC,kk'} = \frac{2\pi}{\hbar} R_{kk'} Z^{-1} \sum_{v_i,v_f} e^{-E_{i,v_i}\beta} V_{kk'} \delta(E_{if} + E_{i,v_i} - E_{f,v_f})$$
(S3.4)

in which we included the Boltzmann distribution function associated with the initial state  $e^{-E_{i,v_i}\beta}/Z$ . Now, we move to the time domain employing the Fourier transform of the delta function. The argument of the sum becomes:

$$\left\langle \Theta_{i,v_{i}} \middle| \hat{V}_{fk} e^{-iE_{f,v_{f}}\tau} \middle| \Theta_{f,v_{f}} \right\rangle \left\langle \Theta_{i,v_{i}} \middle| \hat{V}_{fk'} e^{-(\beta - i\tau)E_{i,v_{i}}} \middle| \Theta_{f,v_{f}} \right\rangle$$
(S3.5)

It follows that the internal conversion rate constant can be written as:

$$k_{IC,kk'} = \frac{2\pi}{\hbar} R_{kk'} Z^{-1} \sum_{v_i, v_f} \int_{-\infty}^{+\infty} d\tau \exp(iE_{if}\tau) \times$$

$$\times \left\langle \Theta_{i,v_i} \middle| \hat{V}_{fk} e^{-iE_{f,v_f}\tau} \middle| \Theta_{f,v_f} \right\rangle \left\langle \Theta_{i,v_i} \middle| \hat{V}_{fk'} e^{-(\beta - i\tau)E_{i,v_i}} \middle| \Theta_{f,v_f} \right\rangle$$
(S3.6)

Or, in the more compact form, defining the *thermal cross-correlation function* for the internal conversion as:

$$k_{IC,kk'} = \frac{2\pi}{\hbar} R_{kk'} \int_{-\infty}^{+\infty} d\tau \exp(iE_{if}\tau) Z^{-1} \rho_{if}^{IC}(t)$$
(S3.7)

with

$$\rho_{fi}^{IC}(t,T) = Tr \left[ V_{fk} e^{-iE_{f,v_f}\tau_f} V_{fk'} e^{-iE_{i,v_i}\tau_i} \right]$$
(S3.8)

The electronic non-adiabatic couplings,  $R_k$ , have been computed according to the following expression:

$$R_{k} = \left\langle \psi_{f} \left| \frac{\partial}{\partial Q_{fk}} \right| \psi_{i} \right\rangle = \frac{\left\langle \psi_{f} \left| \frac{\partial V}{\partial Q_{fk}} \right| \psi_{i} \right\rangle}{E(\psi_{f}) - E(\psi_{i})}$$
(S3.9)

with V the electrostatic potential. The numerator of eqS3.9 can be written as follows<sup>[8,9]</sup>:

$$\left| \psi_f \left| \frac{\partial V}{\partial Q_{fk}} \right| \psi_i \right| = -\sum_{\sigma} \frac{Z_{\sigma} e^2}{\sqrt{M_{\sigma_j}}} \sum_{k, y, z} F_{if, \sigma j} L_{f\sigma j, k}$$
(S3.10)

with  $Z_{\sigma}$  the charge of the  $\sigma$ -th nucleus, e the electron charge,  $M_{\sigma}$  the mass of the  $\sigma$ -th nucleus,  $L_{f\sigma j,k} = \frac{\partial q_{\sigma j}}{\partial Q_{fk}}$  is the *j*-th components of the Hessian matrix associated with the  $\sigma$ -th atomic center,  $F_{if,\sigma j}$  is the *j*-th component of the transition electric field at the atomic center  $\sigma$  which is proportional to the transition density matrix ( $\Omega_{if}^{0}$ ) evaluated at the equilibrium geometry of the initial state:

$$F_{if,\sigma j} = \langle \psi_f \left| F_{\sigma j} \right| \psi_i \rangle = \int dr \Omega_{if}^0 \frac{e(r_{\sigma j} - R_{\sigma j})}{|r_{\sigma} - R_{\sigma}|^3}$$
(S3.11)

The (R)ISC rate expression is simpler than the one derived for IC. Assuming that the SOC is not dependent on the nuclear coordinates, the  $k_{(R)ISC}$  can be written as:

$$k_{(R)ISC} = \frac{2\pi}{\hbar} |H_{SOC}|^2 \delta(E_{if} + E_{i,v_i} - E_{f,v_f})$$
(S3.12)

Thus, moving to the time domain, the eqS3.12 can be rewritten as:

$$k_{(R)ISC} = \frac{1}{\hbar} |H_{SOC}|^2 \int_{-\infty}^{+\infty} d\tau \ e^{iE_{if}\tau} Z^{-1} \rho_{if}^{ISC}(t,T)$$
(S2.13)

with

$$\rho_{if}^{ISC}(t,T) = Tr \left[ e^{-iE_{f,v_{f}}\tau_{f}} e^{-iE_{i,v_{i}}\tau_{i}} \right]$$
(S2.14)

#### 4.2. Symmetry consideration on spin-orbit coupling calculations.

It is possible from symmetry considerations to determine if the spin-orbit coupling (SOC) driving (Reverse) Intersystem Crossing ((R)ISC) would be vanishing or not.

The spin-orbit operator  $H_{SOC}$  is defined:

$$H_{SOC} = A_{SOC}(r)L \cdot S$$

With  $A_{SOC}(r)$  a scalar function of the position,  $\vec{L}$  the orbital momentum operator and  $\vec{S}$  the spin momentum operator

By definition of the scalar  $\vec{L} \cdot \vec{S}$  is a scalar.

The components  $L_{x,y,z}$  and  $S_{x,y,z}$  of the orbital and the spin momentums transform like rotations  $R_{x,y,z}$ . From a symmetry perspective,  $\vec{L} \cdot \vec{S}$  thus belongs to the totally symmetric irreducible representation whatever the point group considered.

The SOC matrix element between  $S_1$  and  $T_n$  excited states  $\langle \psi_{S_1} | H_{SOC} | \psi_{T_n} \rangle$  will be non-vanishing if the product of the representations of  $S_1$  and  $T_n$ ,  $\Gamma(\psi_{S_1}) \otimes \Gamma(\psi_{T_n})$  includes the totally symmetric representation.

The first singlet excited state wavefunction writes:

$$\begin{split} \psi_{S_1} &= \psi_{S_1}^{space} \times \psi_{S_1}^{spin} \\ \psi_{S}^{spin} \end{split}$$

 $\psi_{S_1}^{spin}$  representation is the totally symmetric representation so that the representation the first singlet

excited state wavefunction  $\Gamma(\psi_{S_1}) = \Gamma(\psi_{S_1}^{space})$ . The n-th triplet excited state wavefunction writes:

$$\psi_{T_n} = \psi_{T_n}^{space} \times \psi_{T_n}^{spin}$$
$$\psi_{T}^{spin}$$

 $T_n$  representation is associated to the rotations.



**Figure S23**: molecular orbitals computed at HF/def2-TZVP for 2T-b (a), 2T-d (b) and 2T-f (c) (isocontour  $\sigma$ =0.02 e·Bohr-3).

**Table S18**:  $S_1$ ,  $S_2$ ,  $T_1$  vertical excitation energies computed at SCS-ADC(2)+COSMO/def2-TZVP and electric dipole moment in vacuum for cyclazine, 2T-f and 2B-uthrene.

Cyclazine	Vacuum	Toluene	Acetonitrile	μ <sup>vac</sup> <sub>el</sub> [D]
S <sub>0</sub> tot. en. [hartree]	-516.502846	-516.506480	-516.510689	0.0010
S <sub>1</sub> tot. en. [hartree]	-516.463143	-516.466449	-516.471042	0.0005
T <sub>1</sub> tot. en. [hartree]	-516.454760	-516.458078	-516.462779	0.0005
S <sup>vert</sup> <sub>1</sub> exc. [eV]	1.080	1.089	1.079	
T <sup>vert</sup> 1 exc. [eV]	1.308	1.317	1.304	
$\Delta^{E_{ST}^{vert}}$ [eV]	-0.228	-0.228	-0.225	
2T-f				
$S_0$ tot. en. [hartree]	-811.319582	-811.334481	-811.353224	10.50
S <sub>1</sub> tot. en. [hartree]	-811.245327	-811.257052	-811.271410	8.79
T <sub>1</sub> tot. en. [hartree]	-811.240213	-811.252873	-811.270153	10.30
S <sup>vert</sup> <sub>1</sub> exc. [eV]	2.020	2.107	2.226	
T <sup>vert</sup> 1 exc. [eV]	2.160	2.221	2.260	
$\Delta^{E_{ST}^{vert}}$ [eV]	-0.140	-0.114	-0.034	
2B-uthrene				

S <sub>0</sub> tot. en. [hartree]	-894.876107	-894.835752	-894.842980	0.322
$S_1$ tot. en. [hartree]	-894.830893	-894.791649	-894.798594	1.485
S <sub>2</sub> tot. en. [hartree]	-894.826801	-894.788507	-894.795081	0.092
$T_1$ tot. en. [hartree]	-894.823987	-894.784364	-894.791403	0.566
S <sup>vert</sup> <sub>1</sub> exc. [eV]	1.201	1.200	1.208	
S <sup>vert</sup> <sub>2</sub> exc. [eV]	1.276	1.286	1.303	
T <sup>vert</sup> <sub>1</sub> exc. [eV]	1.418	1.398	1.403	
$\Delta^{\mathrm{E}_{\mathrm{S1T1}}^{\mathrm{vert}}}$ [eV]	-0.217	-0.198	-0.196	
$\Delta^{\mathrm{E_{S2T1}^{vert}}}[\mathrm{eV}]$	-0.142	-0.113	-0.100	

For cyclazine the solvent effect has a negligible impact on the excited state energies and the  $\Delta E_{ST}$ , acquiring values close to those obtained in vacuum, in line with the vanishing electric dipole moment ( $\mu^{vac}_{el}$ ) of S<sub>0</sub>, S<sub>1</sub> and T<sub>1</sub> (see Table S18). On the contrary, 2T-*f* is more affected by the change of the dielectric constant due to the stronger push-pull character brought by the amino and cyano groups. Moving from toluene to acetonitrile, the vertical excitation energies are blue-shifted because of the larger stabilization of S<sub>0</sub> ( $\mu^{vac}_{el} = 10.50$  Debye) with respect to S<sub>1</sub> ( $\mu^{vac}_{el} = 8.47$  Debye) and T<sub>1</sub> ( $\mu^{vac}_{el} = 10.30$  Debye). Moreover, the larger  $\mu^{vac}_{el}$  of T<sub>1</sub> than S<sub>1</sub> results in a larger stabilization of the former in acetonitrile, closing the gap between the excited states and leading to a less negative  $\Delta E_{ST}$ . As for cyclazine, the small and similar electric dipole moment exhibited in the ground- and excited-states of 2B-uthrene translates in a small and similar modulation of their energy, leading to a slight blue-shift of the vertical excitation energies, ensuring the negative  $\Delta E_{ST}$  between S<sub>1</sub> (S<sub>2</sub>) and T<sub>1</sub>.

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