

## Supplementary Materials

### Transient-Absorption Spectroscopy of Dendrimers via Nonadiabatic Excited-State Dynamics Simulations

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#### S1. DEDUCTION OF THE ORIENTATIONAL AVERAGING PUMP-PROBE SIGNAL

According to<sup>1</sup>

$$C_{abcd} \equiv \overline{(\mathbf{s}_1 \mathbf{d}_a)(\mathbf{s}_2 \mathbf{d}_b)(\mathbf{s}_3 \mathbf{d}_c)(\mathbf{s}_4 \mathbf{d}_d)} = \frac{1}{30} \{g_1(\mathbf{s})(\mathbf{d}_a \mathbf{d}_b)(\mathbf{d}_c \mathbf{d}_d) + g_2(\mathbf{s})(\mathbf{d}_a \mathbf{d}_c)(\mathbf{d}_b \mathbf{d}_d) + g_3(\mathbf{s})(\mathbf{d}_a \mathbf{d}_d)(\mathbf{d}_b \mathbf{d}_c)\} \quad (\text{S1})$$

Here  $\mathbf{s}_1, \mathbf{s}_2, \mathbf{s}_3, \mathbf{s}_4$  are arbitrary unit vectors in the laboratory frame (in our case, the unit vectors of polarizations),  $\mathbf{d}_a, \mathbf{d}_b, \mathbf{d}_c, \mathbf{d}_d$  are arbitrary unit vectors in the molecular frame, overbar indicates orientational averaging, and

$$\begin{aligned} g_1(\mathbf{s}) &= 4(\mathbf{s}_1 \mathbf{s}_2)(\mathbf{s}_3 \mathbf{s}_4) - (\mathbf{s}_1 \mathbf{s}_3)(\mathbf{s}_2 \mathbf{s}_4) - (\mathbf{s}_1 \mathbf{s}_4)(\mathbf{s}_2 \mathbf{s}_3) \\ g_2(\mathbf{s}) &= 4(\mathbf{s}_1 \mathbf{s}_3)(\mathbf{s}_2 \mathbf{s}_4) - (\mathbf{s}_1 \mathbf{s}_2)(\mathbf{s}_3 \mathbf{s}_4) - (\mathbf{s}_1 \mathbf{s}_4)(\mathbf{s}_2 \mathbf{s}_3) \quad (\text{S2}) \\ g_3(\mathbf{s}) &= 4(\mathbf{s}_1 \mathbf{s}_4)(\mathbf{s}_2 \mathbf{s}_3) - (\mathbf{s}_1 \mathbf{s}_2)(\mathbf{s}_3 \mathbf{s}_4) - (\mathbf{s}_1 \mathbf{s}_3)(\mathbf{s}_2 \mathbf{s}_4) \end{aligned}$$

If we assume that the  $\mathbf{d}$ -vectors are mutually orthogonal,

$$(\mathbf{d}_a \mathbf{d}_b) = \delta_{ab} \quad (\text{S3})$$

then

$$C_{abcd} = \frac{1}{30} (g_1(\mathbf{s})\delta_{ab}\delta_{cd} + g_2(\mathbf{s})\delta_{ac}\delta_{bd} + g_3(\mathbf{s})\delta_{ad}\delta_{bc}) \quad (\text{S4})$$

According to<sup>2</sup>, any orientationally averaged four-wave-mixing signal can be evaluated by the formula

$$\bar{S} = \sum_{a,b,c,d=x,y,z} C_{abcd} S_{abcd} \quad (\text{S5})$$

where  $S_{abcd}$  are the signals evaluated according to the following prescriptions: all transition dipole moments responsible for the interaction with the pulse #1, 2, 3, and 4 are dictated along the axis  $a$ ,  $b$ ,  $c$ ,  $d$  of the molecular frame, respectively. For example,  $S_{xyyx}$  corresponds to the signal in which all transition dipole moments responsible for the interaction with pulses #1, and 4 are dictated along the axis  $x$  of the molecular frame, and all transition dipole moments responsible for the interaction with pulses #2, and 3 are dictated along the axis  $y$  of the molecular frame.

Explicitly, eqs. (S4) and (S5) yields:

$$\begin{aligned} \bar{S} &= \frac{1}{30} \sum_{ab} (g_1(\mathbf{s})S_{aabb} + g_2(\mathbf{s})S_{abab} + g_3(\mathbf{s})S_{abba}) \\ &= \frac{1}{30} g_1(\mathbf{s})(S_{xxxx} + S_{yyxx} + S_{zzxx} + S_{xxyy} + S_{yyyy} + S_{zzyy} + S_{xxzz} + S_{yyzz} + S_{zzzz}) \\ &\quad + \frac{1}{30} g_2(\mathbf{s})(S_{xxxx} + S_{yxyx} + S_{zxzx} + S_{xyxy} + S_{yyyy} + S_{zyzy} + S_{xzzx} + S_{yzyz} + S_{zzzz}) \\ &\quad + \frac{1}{30} g_3(\mathbf{s})(S_{xxxx} + S_{yxxy} + S_{zxxz} + S_{xyyx} + S_{yyyy} + S_{zyyz} + S_{xzzx} + S_{yzzz} + S_{zzzz}) \\ &= \frac{1}{30} (g_1(\mathbf{s}) + g_2(\mathbf{s}) + g_3(\mathbf{s}))(S_{xxxx} + S_{yyyy} + S_{zzzz}) \\ &\quad + \frac{1}{30} g_1(\mathbf{s})(S_{yyxx} + S_{zzxx} + S_{xxyy} + S_{zzyy} + S_{xxzz} + S_{yyzz}) \\ &\quad + \frac{1}{30} g_2(\mathbf{s})(S_{yxyx} + S_{zxzx} + S_{xyxy} + S_{zyzy} + S_{xzzx} + S_{yzyz}) \\ &\quad + \frac{1}{30} g_3(\mathbf{s})(S_{yxxy} + S_{zxxz} + S_{xyyx} + S_{zyyz} + S_{xzzx} + S_{yzzz}) \end{aligned}$$

That is, in general we need 21 components of  $S_{abcd}$ .

For pump-probe,  $S_{abcd}$  is symmetric with respect to the perturbation of the indexes within first and second pair. It means that

$$S_{yxyx} = S_{xyxy} = S_{yxxy} = S_{xyyx},$$

$$S_{zxzx} = S_{xzzx} = S_{zxxz} = S_{xzzx},$$

$$S_{zyzy} = S_{yzyz} = S_{zyyz} = S_{yzzz},$$

We thus have

$$\begin{aligned}
\bar{S} &= \frac{1}{30} (g_1(\mathbf{s}) + g_2(\mathbf{s}) + g_3(\mathbf{s})) (S_{xxxx} + S_{yyyy} + S_{zzzz}) \\
&+ \frac{1}{30} g_1(\mathbf{s}) (S_{yyxx} + S_{zzxx} + S_{xxyy} + S_{zzyy} + S_{xxzz} + S_{yyzz}) \\
&+ \frac{1}{15} (g_2(\mathbf{s}) + g_3(\mathbf{s})) (S_{yxyx} + S_{zxzx} + S_{zyzy})
\end{aligned}$$

In addition,

$\mathbf{s}_1 = \mathbf{s}_2 = \mathbf{s}_{pu}$  and  $\mathbf{s}_3 = \mathbf{s}_4 = \mathbf{s}_{pr}$ , so that

$$\begin{aligned}
g_1(\mathbf{s}) &= 4 - 2(\mathbf{s}_{pu}\mathbf{s}_{pr})^2 \\
g_2(\mathbf{s}) &= g_3(\mathbf{s}) = 3(\mathbf{s}_{pu}\mathbf{s}_{pr})^2 - 1
\end{aligned}$$

Hence we obtain eq. (15).

## S2. FRENKEL EXCITON HAMILTONIAN MODEL

We consider the Frenkel exciton model of a system given by a central unit with energy  $E_0$  and four equivalent branches with energy  $E_1$ . We denote the coupling between the core and the branches as  $V_0$ , the coupling between two adjacent branches  $V_1$ , and the coupling between opposed branches as  $V_2$ . The corresponding Hamiltonian is given by:

$$H = \begin{pmatrix} E_0 & V_0 & V_0 & V_0 & V_0 \\ V_0 & E_1 & V_1 & V_2 & V_1 \\ V_0 & V_1 & E_1 & V_1 & V_2 \\ V_0 & V_2 & V_1 & E_1 & V_1 \\ V_0 & V_1 & V_2 & V_1 & E_1 \end{pmatrix}, \quad (S6)$$

The corresponding eigenvalues are given by:

$$\begin{pmatrix} E_{S_1} \\ E_{S_2} \\ E_{S_3} \\ E_{S_4} \\ E_{S_5} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} \left( E_0 + E_1 + 2V_1 + V_2 - \sqrt{16V_0^2 + (E_1 - E_0 + 2V_1 + V_2)^2} \right) \\ E_1 - 2V_1 + V_2 \\ E_1 - V_2 \\ E_1 - V_2 \\ \frac{1}{2} \left( E_0 + E_1 + 2V_1 + V_2 + \sqrt{16V_0^2 + (E_1 - E_0 + 2V_1 + V_2)^2} \right) \end{pmatrix}, \quad (S7)$$

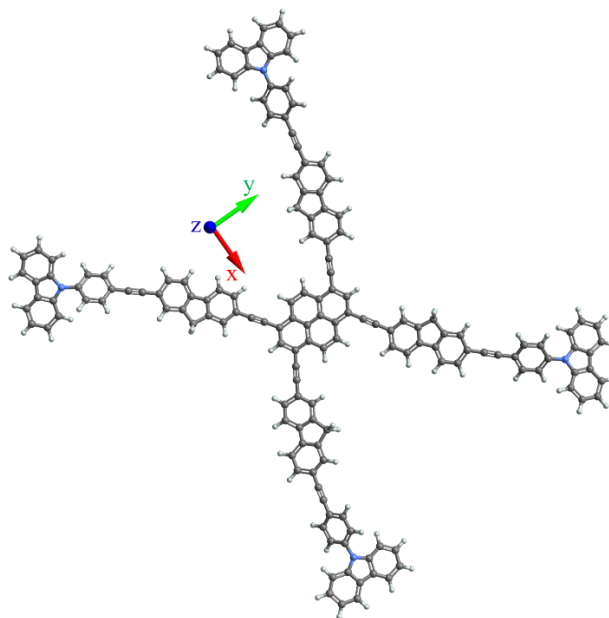
And the corresponding eigenvectors are given by:

$$\begin{pmatrix} \mathbf{X}_{S_1} \\ \mathbf{X}_{S_2} \\ \mathbf{X}_{S_3} \\ \mathbf{X}_{S_4} \\ \mathbf{X}_{S_5} \end{pmatrix} = \begin{pmatrix} \frac{E_0 - E_1 - 2V_1 - \sqrt{16V_0^2 + (E_1 - E_0 + 2V_1)^2}}{2V_0} & 1 & 1 & 1 & 1 \\ 0 & -1 & 1 & -1 & 1 \\ 0 & -1 & 0 & 1 & 0 \\ 0 & 0 & -1 & 0 & 1 \\ \frac{E_0 - E_1 - 2V_1 + \sqrt{16V_0^2 + (E_1 - E_0 + 2V_1)^2}}{2V_0} & 1 & 1 & 1 & 1 \end{pmatrix}, \quad (\text{S8})$$

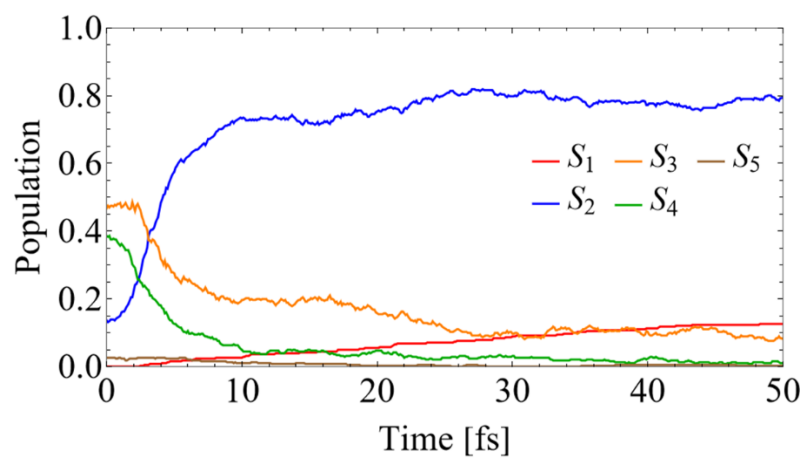
Here, it results convenient to note that the  $S_1$  localization depends on the relative magnitudes of energies and couplings. In particular,  $S_1$  is localized in the central core when:

$$\left| \frac{E_0 - E_1 - 2V_1 - \sqrt{16V_0^2 + (E_1 - E_0 + 2V_1)^2}}{2V_0} \right| \gg 1, \quad (\text{S9})$$

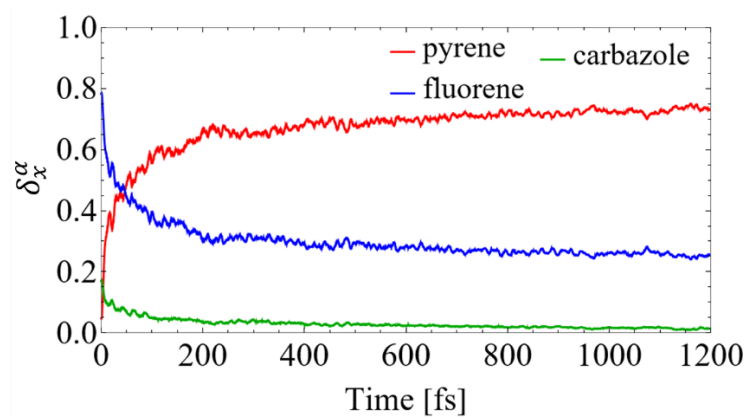
### S3. SUPORTING INFORMATION FIGURES



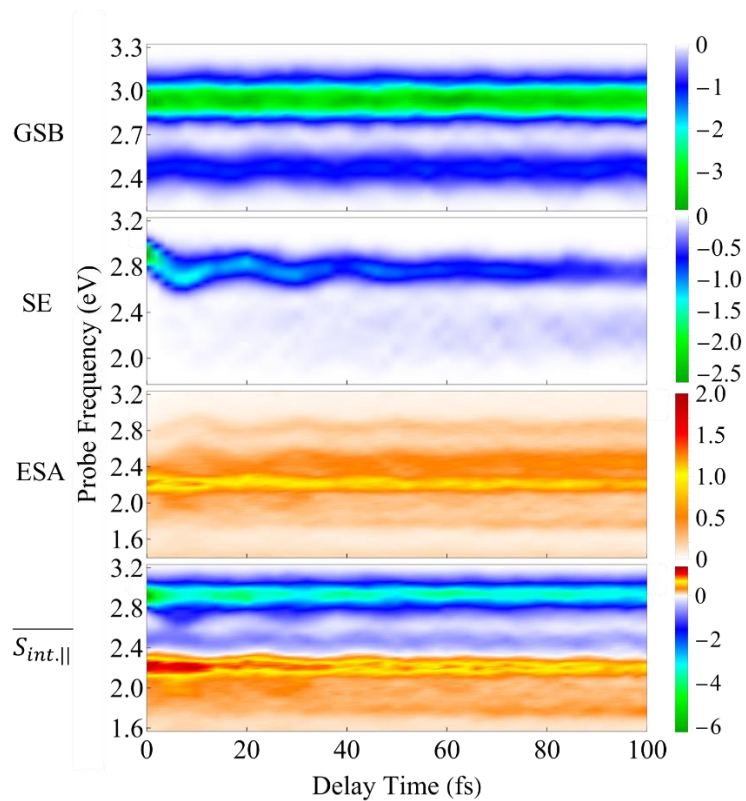
**Figure S1.** Chemical structure of the dendrimer T1 indicating the x,y,z directions of the body-fixed reference frame.



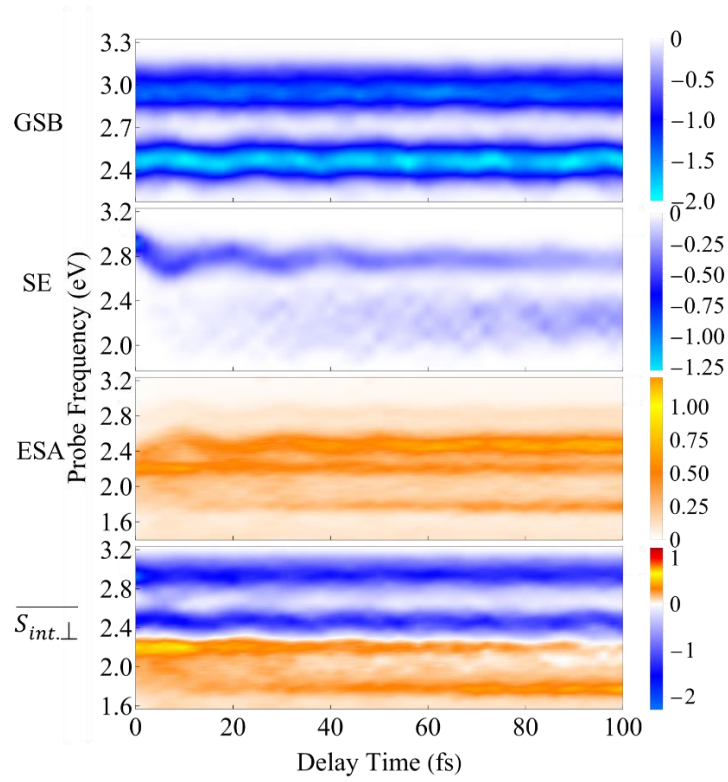
**Figure S2.** Evolution at short times of average populations of electronic states calculated from the fraction of trajectories in a particular state at a given time after the initial laser excitation.



**Figure S3.** Evolution of the average fraction of the transition densities  $\delta_{carbazole}^\alpha(t)$ ,  $\delta_{fluorene}^\alpha(t)$ , and  $\delta_{pyrene}^\alpha(t)$ .

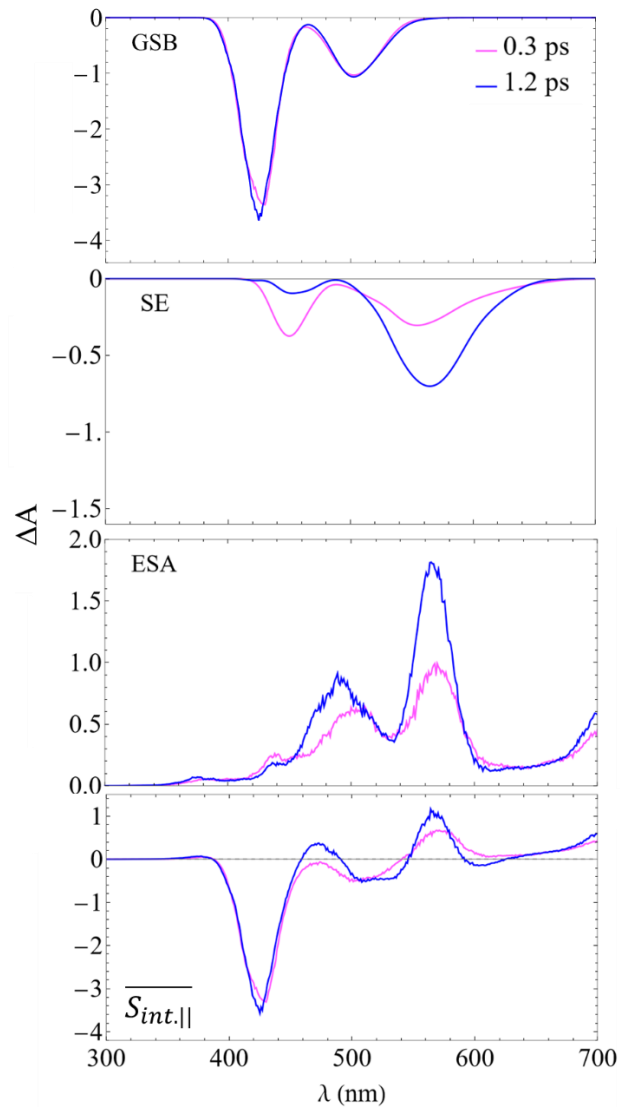


**Figure S4.** Evolution at short times of GSB, SE, and ESA contributions to  $\overline{S_{int,||}}$  using the orientational averaging total pump-probe signal with parallel pulses, i.e.,  $\mathbf{s}_{pu} = \mathbf{s}_{pr}$ .

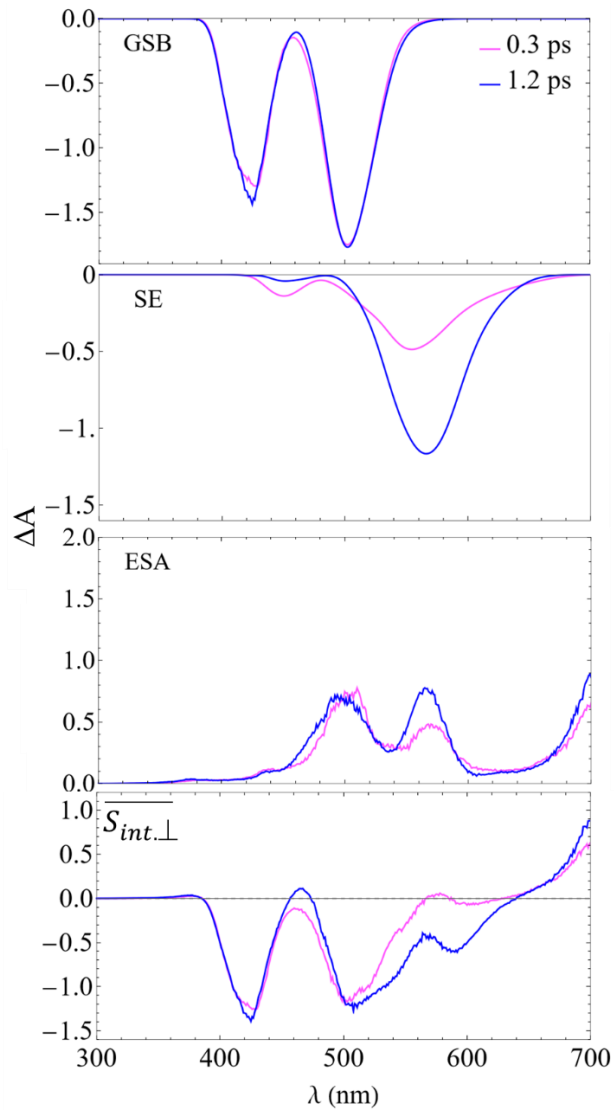


**Figure S5.** Evolution at short times of GSB, SE, and ESA contributions to  $\overline{S_{int,\perp}}$  using the orientational averaging total pump-probe signal with orthogonal pulses, i.e.,  $\mathbf{s}_{pu} \perp \mathbf{s}_{pr}$ .





**Figure S6.** GSB, SE, ESA and  $\overline{S_{int,||}}$  signals at two different times with parallel pulses, i.e.,  $s_{pu} = s_{pr}$ .

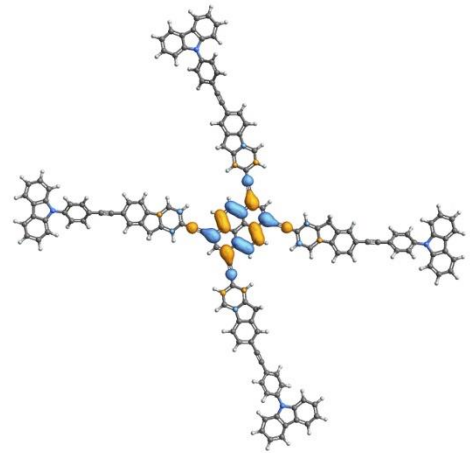
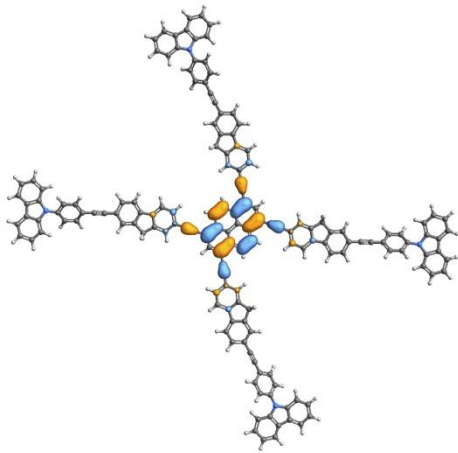


**Figure S7.** GSB, SE, ESA and  $\overline{S_{int,\perp}}$  signals at two different times with orthogonal pulses, i.e.,  $s_{pu} \perp s_{pr}$ .

Hole

$S_1$   
Weight = 0.831623

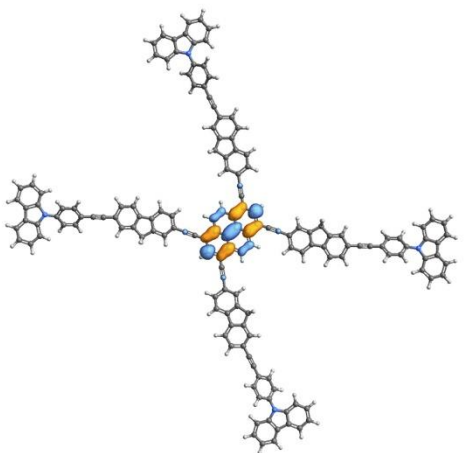
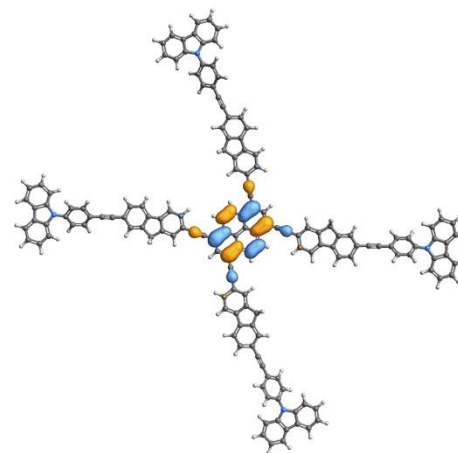
Particle



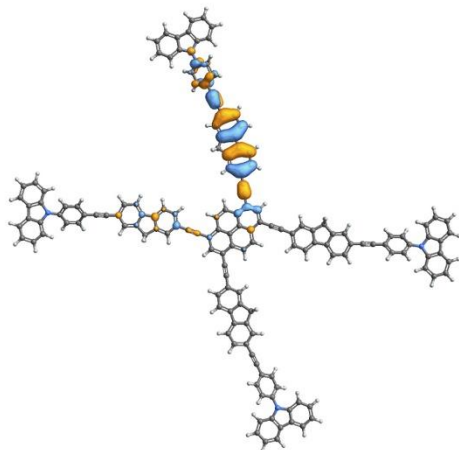
Hole

$S_2$   
Weight = 0.699593

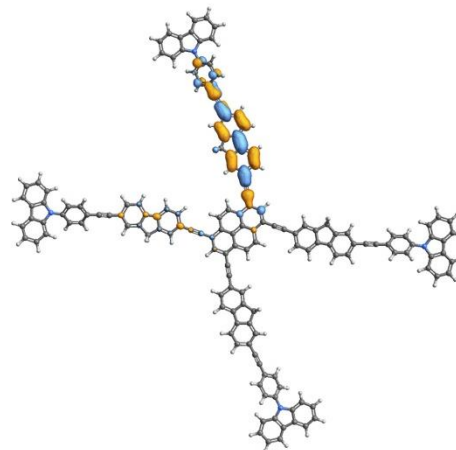
Particle



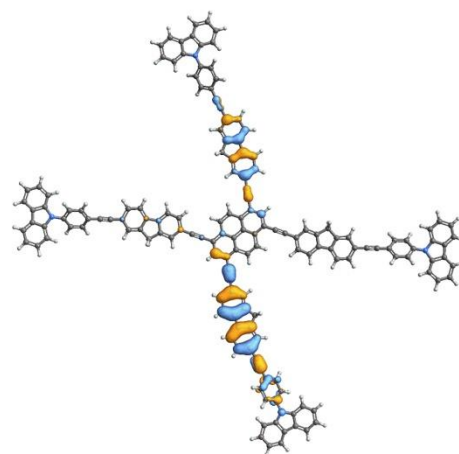
Hole  $S_3$   
Weight = 0.416298



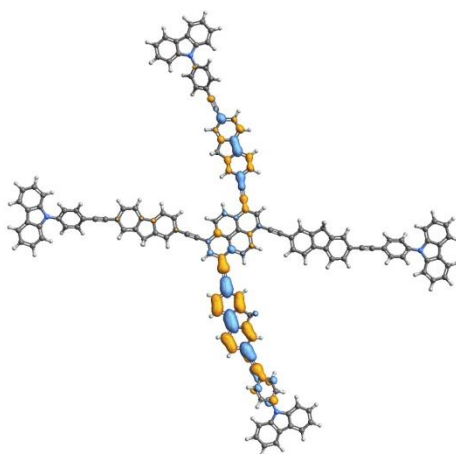
Particle

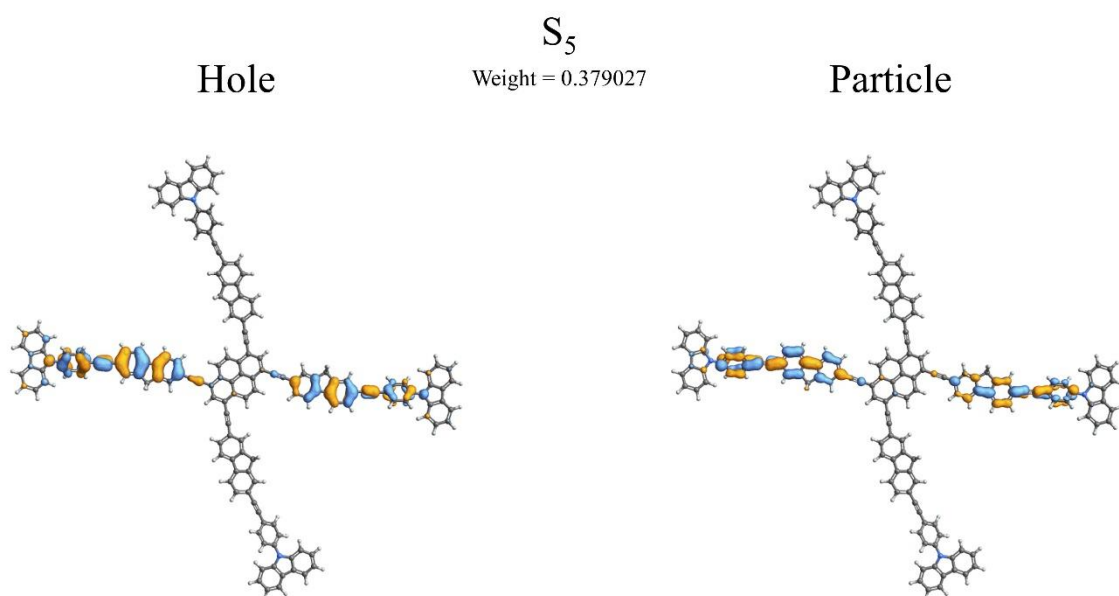


Hole  $S_4$   
Weight = 0.41056

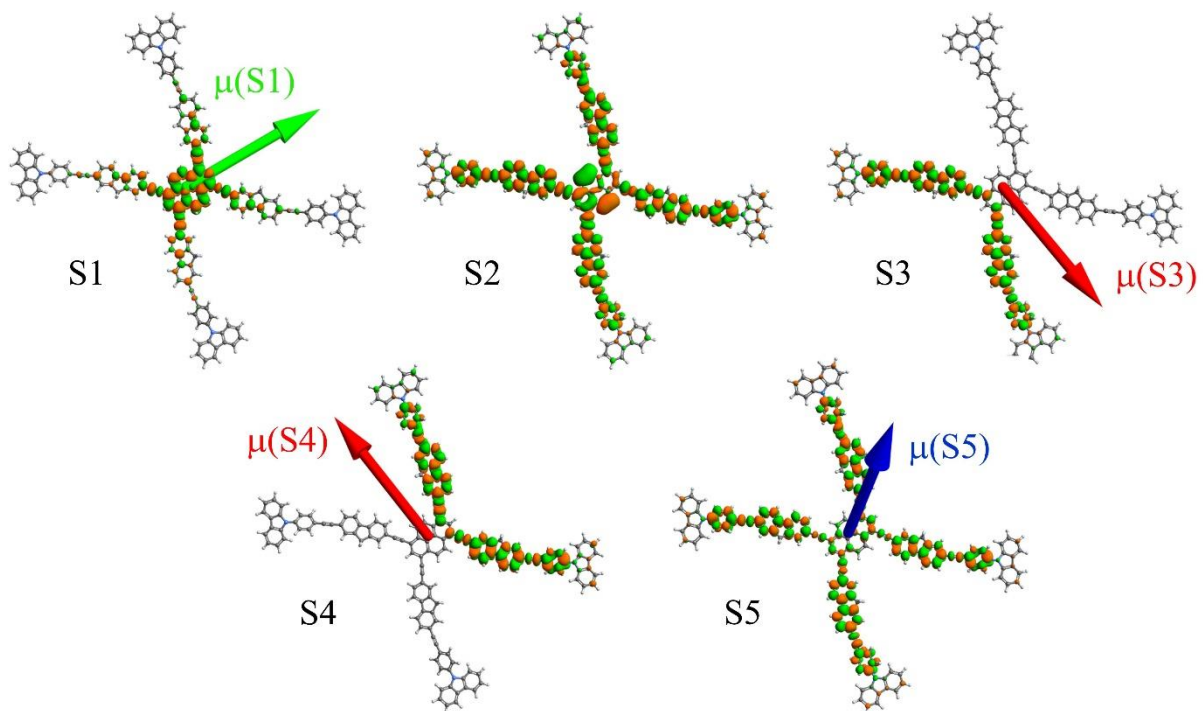


Particle

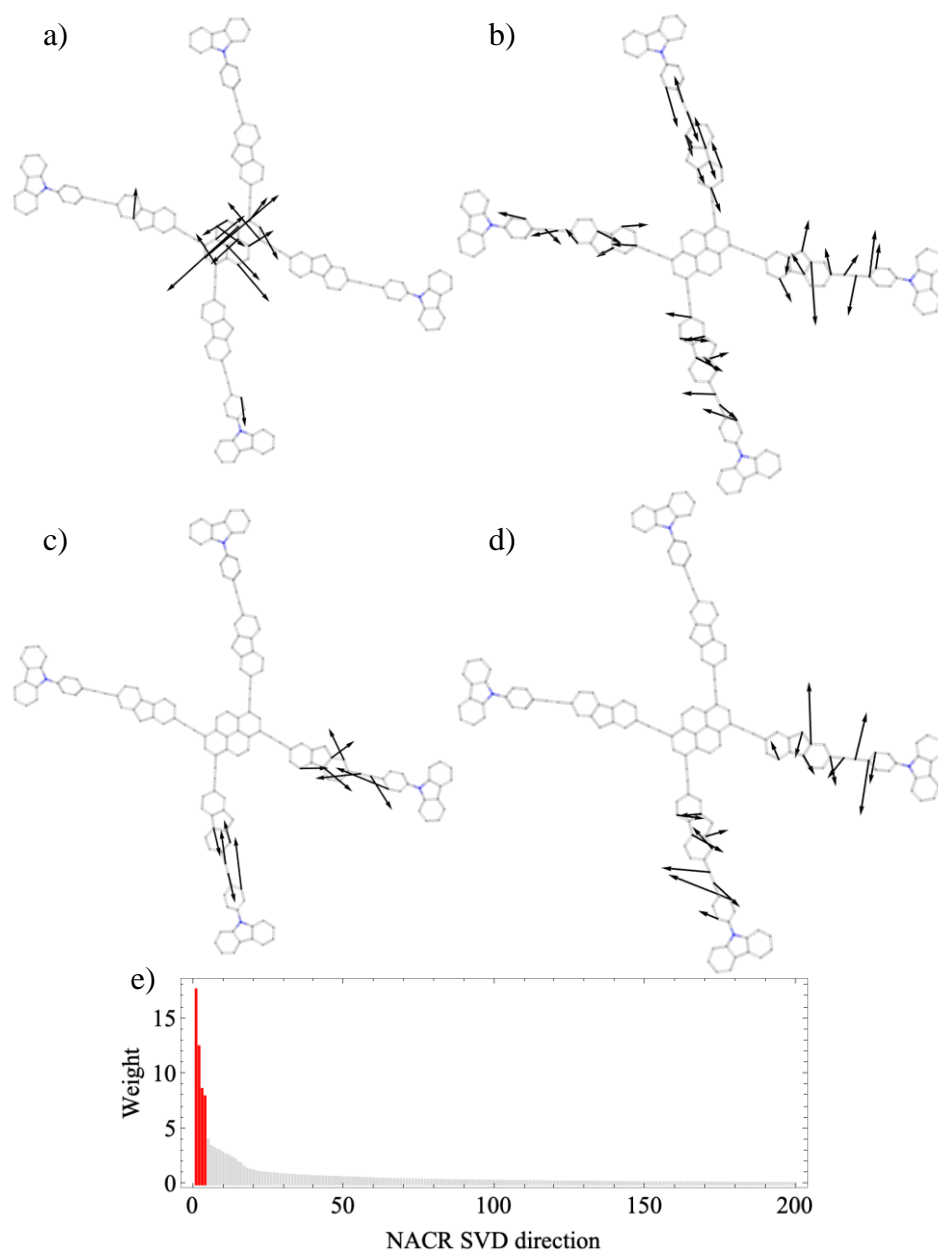




**Figure S8.** Hole-electron pairs calculated for the first 5 excited states.



**Figure S9.** Spatial distributions of electronic transition densities indicating the orientation of their corresponding transition dipole moments ( $\mu$ ) for the five lowest energy electronic states.



**Figure S10.** Singular value decomposition for the non-adiabatic coupling vectors from  $S_{3/4}$  to  $S_2$ . The four bigger contributions are represented from (a) to (d), while (e) shows the corresponding weights.