SUPPORTING INFORMATION

for

Dimers of polar chromophores in solution: role of excitonic interactions on one- and two-photon absorption properties

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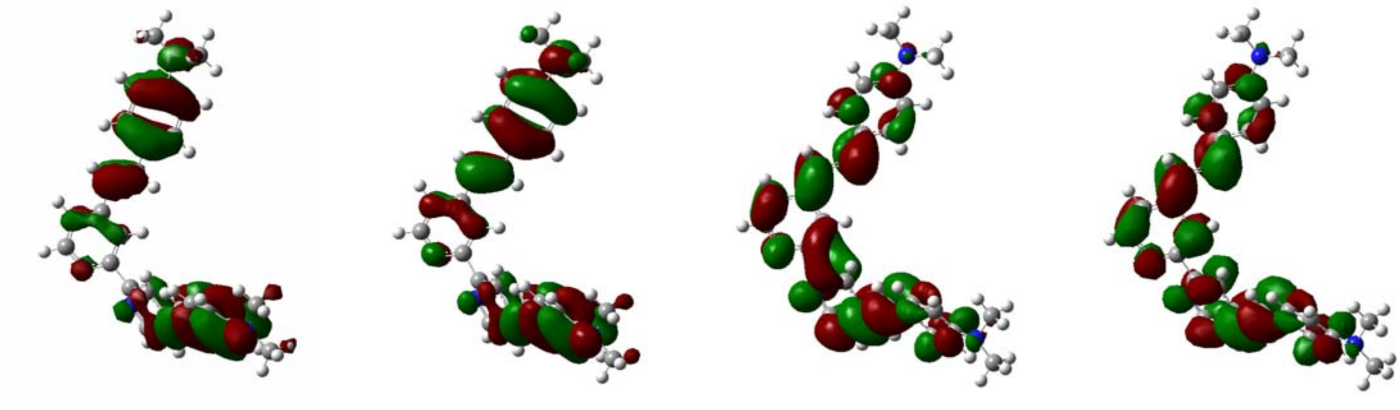
Electronic density in MO for the conformation du in CH_2Cl_2

Figure SI.1
Electronic density in four molecular orbitals: the HOMO-1, HOMO, LUMO and LUMO+1 for the conformation **du** in CH_2Cl_2.



HOMO-1 CH_2Cl_2 HOMO CH_2Cl_2 LUMO CH_2Cl_2 LUMO+1 CH_2Cl_2

Some details about the four-state model adopted for 2

The four-state electronic Hamiltonian is described by the following expression:

$$\hat{H}_{el} = \begin{pmatrix} 0 & -\sqrt{2}t & -\sqrt{2}t & 0 \\ -\sqrt{2}t & 2z & 0 & -\sqrt{2}t \\ -\sqrt{2}t & 0 & 2z & -\sqrt{2}t \\ 0 & -\sqrt{2}t & -\sqrt{2}t & 4z+V \end{pmatrix} = 2z(\hat{\rho}_1 + \hat{\rho}_2) - \sqrt{2}t\hat{\sigma}_{12} + V\hat{\rho}_1\hat{\rho}_2 \qquad \text{(SI. 1)}$$

where the relevant electronic operators are defined as:

$$\hat{\sigma}_{12} = \begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix} \qquad \hat{\rho}_1 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad \hat{\rho}_2 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad \text{(SI. 2)}$$

Following the same steps as described for the monomer, two equivalent harmonic coordinates (one for each chromophore) Q_1 and Q_2 (and the relative momenta P_1 and P_2) are introduced to account for molecular vibrations. These vibrations are defined in terms of the same frequency ω_v and relaxation energy ε_v.
Finally, including the solvent effective coordinates defined for each chromophore, q_1 and q_2, the essential-state Hamiltonian for the dimer results:

$$\begin{aligned} H_{TOT}(q_1, q_2) &= H_{el+ph+solv} \\ &= 2z(\hat{\rho}_1 + \hat{\rho}_2) - \sqrt{2}t\hat{\sigma} - \omega_v\sqrt{2\varepsilon_v}\,(Q_1\hat{\rho}_1 + Q_2\hat{\rho}_2) + q_1\hat{\rho}_1 + q_2\hat{\rho}_2 \\ &\quad + \frac{1}{2}\omega_v^{\,2}\left(Q_1^{\,2} + Q_2^{\,2}\right) + \frac{1}{2}\left(P_1^2 + P_2^{\,2}\right) + \frac{1}{4\varepsilon_{or}}\left(q_1^{\,2} + q_2^{\,2}\right) \end{aligned} \qquad \text{(SI. 3)}$$

Solvation coordinates are treated as classical coordinates and the total Hamiltonian is defined on a two-dimensional grid of q_1 and q_2 values. On each point of the grid the coupled electronic and vibrational problem is solved via direct diagonalization of the non-adiabatic basis obtained as the direct product of the four electronic basis states times the eigenstates of the two independent harmonic oscillators. Once again, linear and non-linear spectra are calculated on each point of the q_1, q_2 grid and total spectra are obtained summing up the contributions from each point in the grid weighted by the relevant Boltzmann factor.

More details about the procedure for calculating linear (absorption and fluorescence) and non linear (TPA) optical spectra calculation are described in previous work[1].

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[1] Grisanti, L., et al., *Enhancing the efficiency of two-photon absorption by metal coordination.* Physical Chemistry Chemical Physics, 2009. **11**(41): p. 9450-9457.

θ-dependence of calculated linear and non linear spectra for 2 (essential state model)

Figure SI.2

Calculated OPA (top panel) and TPA (bottom panel)spectra relevant for **2** in CH_2Cl_2 at different values of the angle θ (different color), calculated according to the essential-state model described in the paper (parameters are listed in Table 3). Spectra for **1,** multiplied by a factor two, are also reported for comparison (dashed line).