Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Superlinear amplification of the first hyperpolarizability of linear aggregates of DANS molecules

Somananda Sanyal,[a] Cristina Sissa,[a] Francesca Terenziani,[a] Swapan K. Pati[b] and Anna Painelli[a†]

[a] *Department of Chemistry, Life Science and Environmental Sustainability, Parma University, 43124 Parma, Italy*
[b] *New Chemistry Unit and Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore-64, India.*
† e-mail: anna.painelli@unipr.it

Supporting Information

Experimental procedure

UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 650 spectrometer on solutions having concentration approximately 10^{-5} M. Fluorescence spectra were measured with a Fluoromax-3 Horiba Jobin Yvon spectrofluorometer on diluted solutions having maximum optical density < 0.1. Emission spectra were corrected for the wavelength-dependent efficiency of the detection system.

The two-state model for D-π-A dyes in solution

We shortly summarize the two-state model for D-π-A dyes, as discussed in refs 17-19 (main text). The electronic structure of a D-π-A dyes dye is described in terms of two orthogonal basis states, |N⟩ and |Z>, corresponding to the neutral D-π-A and to the zwitterionic D^+-π-A^- resonating structures, respectively (see Fig. 2, main text). The two states are separated by an energy gap 2*z* and are mixed by a matrix element *τ*, the relevant Hamiltonian being:

$$H_{el} = 2z\hat{\rho} - \tau\hat{\sigma} \tag{1}$$

where $\hat{\rho} = |Z\rangle\langle Z|$ is the ionicity operator and $\hat{\sigma} = |Z\rangle\langle N| + |N\rangle\langle Z|$. The dipole moment operator is defined as $\hat{\mu} = \mu_0\hat{\rho}$, where μ_0 is the dipole moment of the zwitterionic state.

The coupling between electronic and vibrational degrees of freedom is important to reproduce spectral bandshapes and the model must be extended in this direction. Accordingly, we introduce an effective vibrational coordinate, *Q*, accounting for the different equilibrium geometry associated with the two electronic basis states. The coupled Hamiltonian is written as:

$$H_{mol} = 2z\hat{\rho} - \tau\hat{\sigma} + \omega_v\sqrt{2\varepsilon_v}Q + \frac{1}{2}\left(P^2 + \omega_v Q^2\right) \tag{2}$$

where *Q* and *P* are the harmonic coordinate and conjugate momentum, characterized by a frequency ω_v and a relaxation energy ε_v. The coupled electronic and vibrational problem described by the Hamiltonian in Eq. 2 is solved in a non-adiabatic approach. In short, the Hamiltonian matrix is written on the basis obtained as the direct product of the electronic states times the eigenstates of the harmonic oscillator described by the last term in Eq. 2, and then diagonalized to get numerically exact non-adiabatic eigenstates. Of course the infinite basis of the harmonic oscillator is truncated to the first *M* states, with *M* large enough to reach convergence (typically M = 10 is enough). The eigenstates of the non-adiabatic Hamiltonian enter the sum-over-states expressions for linear and nonlinear optical spectra, as described below.

Finally we introduce the interaction with the solvent. As discussed in previous literature [*A. Painelli, Chemical Physics 1999,* ***245****, 185*], we explicitly account for the slow, orientational component of the reaction field, F_{or}. The fast electronic component of the reaction field enters into the model with a renormalization of molecular parameters. However, thanks to the marginal variability of the refractive index of common organic solvents, we adopt solvent-independent molecular parameters. The orientational component of the reaction field enters the molecular Hamiltonian as follows:

$$H = H_{mol} - F_{or}\mu_0\hat{\rho} + \frac{\mu_0^2}{4\varepsilon_{or}}F_{or}^2 \tag{3}$$

where ε_{or} is the solvent relaxation energy, a parameter that increases with the solvent polarity. Because of the second term in Eq. 3, the Hamiltonian acquires a dependence on F_{or}. Accordingly, we diagonalize the Hamiltonian matrix written on the non-adiabatic basis for different values of F_{or} obtaining F_{or}-dependent eigenstates and eigenvectors. These quantities enter into the calculation of F_{or}-dependent optical spectra. The overall spectra are finally obtained summing up spectra calculated for different F_{or} values, weighting each spectrum according to the Boltzmann distribution of the relevant state. Specifically, for linear and nonlinear absorption spectra as well as for the HRS spectra we consider the Boltzmann distribution relevant to the F_{or}-dependent ground-state energy, while for fluorescence spectra we consider the Boltzmann distribution relevant to the F_{or}-dependent energy of the fluorescent state. This procedure allows to quantitatively account for the (highly non-trivial) inhomogeneous broadening effects in linear and nonlinear spectral properties of DA dyes (see refs. 17, 18 of the main text).

The model for aggregates of DA dyes

The Hamiltonian for an aggregate of DA dyes reads (see refs. 2, 13 in the main text):

$$H = \sum_{i=1}^{N}\left[2z\hat{\rho}_i - \tau\hat{\sigma}_i + \omega_v\sqrt{2\varepsilon_v}Q_i + \frac{1}{2}\left(P_i^2 + \omega_v Q_i^2\right)\right] + V\sum_{i}^{N-1}\hat{\rho}_i\hat{\rho}_{i+1} \tag{4}$$

where the first sum is the sum of the molecular Hamiltonians for the N dyes in the aggregate. The second sum accounts for the electrostatic interactions between nearest-neighbour dyes (V measures the interactions between two adjacent molecules in their zwitterionic state). The Hamiltonian matrix for the aggregate can be written on the basis obtained as the direct product of the non-adiabatic basis on each molecule, for a grand total of $(2M)^N$ states, a number that increases fast with N. To handle the problem of large aggregates we explore the possibility to account only for the in-phase combination of molecular modes:

$$Q_0 = \frac{1}{\sqrt{N}}\sum_{i=1}^{N} Q_i \tag{5}$$

With this approximation the aggregate Hamiltonian reduces to:

$$H_{reduced} = \sum_{i=1}^{N}\left[2z\hat{\rho}_i - \tau\hat{\sigma}_i + \frac{\omega_v\sqrt{2\varepsilon_v}}{\sqrt{N}}Q_0 + \right] + V\sum_{i}^{N-1}\hat{\rho}_i\hat{\rho}_{i+1} + \frac{1}{2}\left(P_0^2 + \omega_v Q_0^2\right) \tag{6}$$

Where P_0 is the linear momentum conjugated to Q_0. Accounting for a single oscillator reduces the dimension of the basis to $2^N M$, making the non-adiabatic solution of the aggregate problem possible for aggregates up to $N = 14$. The approximation is expected to work well for delocalized excitons, as demonstrated by results in Fig. S1, where we compare linear absorption and HRS spectra calculated for a dimer described by the reduced Hamiltonian in Eq. 6 (black lines), with those obtained accounting for the full Hamiltonian in Eq. 4 (red lines). The agreement is very poor for $V = -0.5$ eV, but it improves upon increasing the absolute value of V. Specifically, for $V = -1.35$ (as relevant to the present work) the comparison between the two approaches suggests that the adopted approximation works well. We underline that the reduced vibrational model is expected to work better upon increasing the chain length, due to the more extended delocalization (ref. 23, main text).

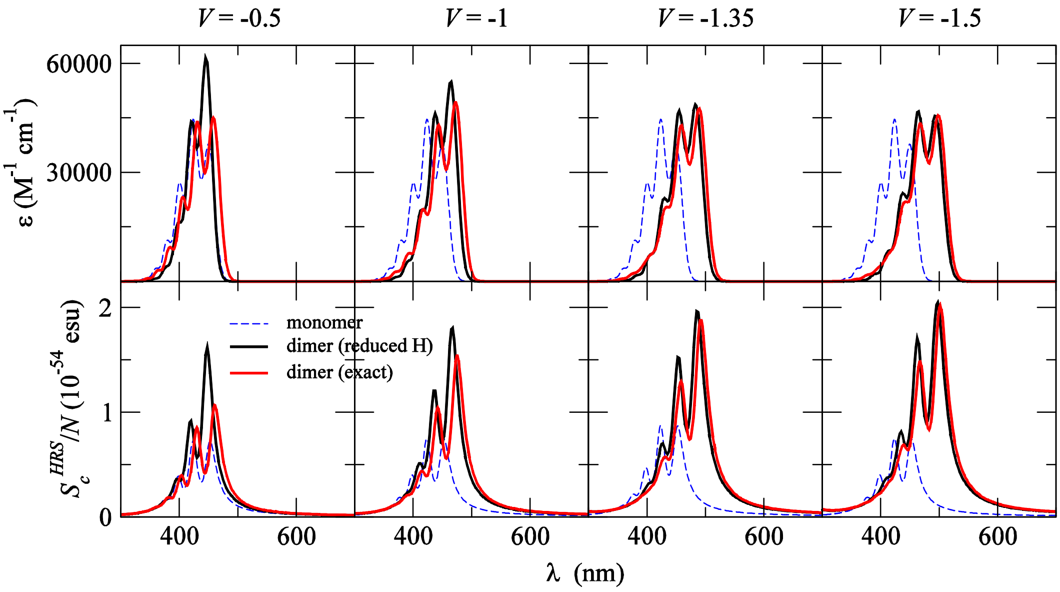

Fig. S1. Linear absorption (top panels) and HRS spectra (bottom panels) calculated for a DANS linear dimer (molecular model parameters in Table 1, in the main paper) with V = -0.5, -1, -1.35, -1.5 eV from left to right. Red lines: results obtained with the complete Hamiltonian; Black lines: results obtained with the reduced Hamiltonian only accounting for the in-phase motion of all Q_i coordinates; Blue dashed lines: results for the monomer (ε_{or}=0).

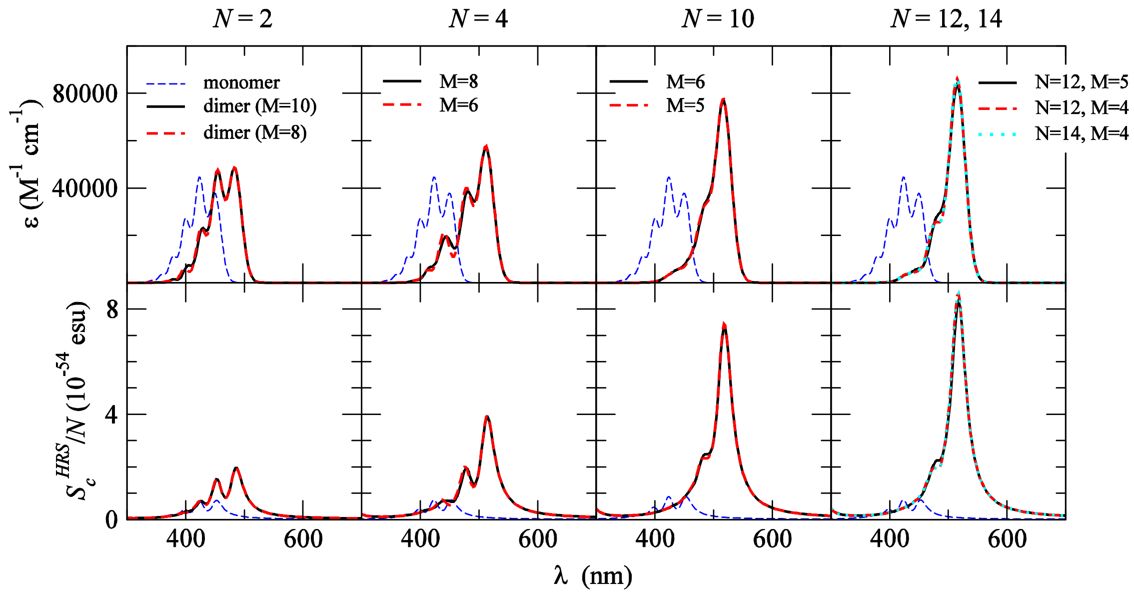

Fig. S2. Linear absorption (top panels) and HRS spectra (bottom panels) calculated for DANS linear aggregates of increasing dimension (N = 2, 4, 10, 12 and 14, from left to right), as reported on the figure labels. Black and red lines refer to a different number of phonon states (*M*, see legends). In the rightmost panels, the cyan dotted line shows results obtained for $N = 14$, $M = 4$. In all panels the blue dashed line refers to the monomer.

We are now in the position to address aggregates of increasing size, adopting the reduced Hamiltonian in Eq. 6. We expect that the effect of the coupling decreases with increasing the aggregate length; accordingly, to maintain the problem tractable for long chains, we progressively reduce the number of vibrational states included in the calculation, M. Results reported in Fig. S2 show that upon increasing the chain length from $N = 2$ to $N = 12$, M can be decreased from 10 to 4, without altering the quality of the calculated spectra. Moreover, results for $N = 12$ and 14 are superimposed, suggesting a delocalization length of about 12 molecular sites. Results in Fig. 5 (main text) correspond to the black curves in Fig. S2.

Aligning molecules with a zwitterionic ground state

As discussed in the main text, the ground state of DANS is dominated by the neutral D-π-A structure while the excited state is mainly zwitterionic (D^+-π-A^-). Accordingly, upon excitation the molecular dipole moment increases sharply, explaining the observed normal solvatochromism, i.e. the red-shift of the linear absorption and fluorescence spectra with increasing solvent polarity (refs. 3, 17, 18 in the main text). The opposite behaviour is observed for chromophores whose ground state is dominated by the zwitterionic structure: the decrease of the molecular dipole moment upon excitation leads in these dyes to a negative solvatochromism, i.e. a blue-shift of the absorption and emission bands in solvents of increasing polarity (refs. 3, 17, 18 in the main text). In ref. 18 (main text) we investigated and parameterized a well-known dye having an almost zwitterionic ground state, and in Fig. S3 we use the molecular model parameters as derived in Ref. 18 for that dye, and compare the behaviour of a monomer with an aligned dimer, assuming exactly the same $V = -1.35$ eV as adopted for DANS. Because of the attractive intermolecular interactions ($V < 0$), the ground state of this mainly zwitterionic dye is more stabilized than the excited state, leading to a largely blue-shifted absorption band with respect to the monomer, in line with the inverse solvatochromism. Moreover, the zwitterionic character of the dye further increases in the dimer because the attractive intermolecular interactions favour charge separation, leading to a huge reduction of the intensity of the linear absorption band of the aggregate (the intensity of the absorption band in fact vanishes in the two limits of a pure neutral and zwitterionic state, corresponding to a system with $\tau=0$). The suppression of the β response is however much more pronounced, in line with early predictions about static NLO responses (ref. 13, main text).

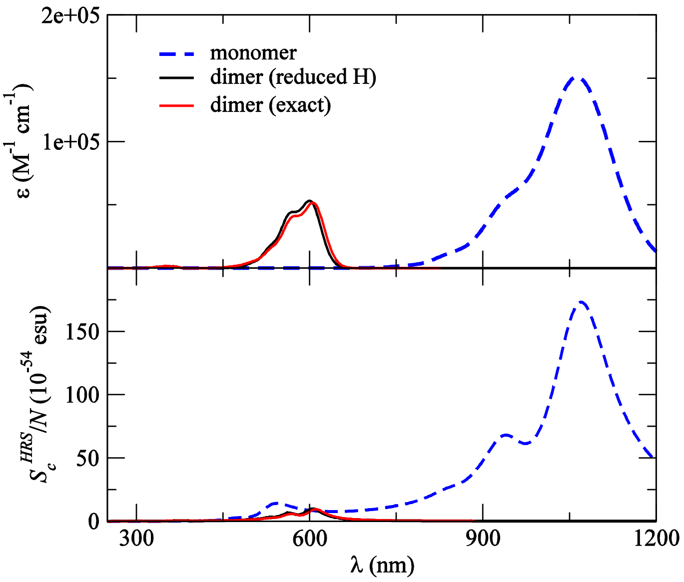

Fig. S3. Linear absorption spectra (top panel) and HRS spectra (bottom panel) calculated for a molecule having an almost zwitterionic ground state (z = -0.25 eV, τ = 0.47 eV, ω_v = 0.14 eV, ε_v = 0.17 eV, γ = 0.07 eV, μ_0 = 40 D). Blue dashed lines: results for the monomer; Red and black lines: results for a dimer with V = -1.35 eV, obtained with the complete Hamiltonian (Eq. 4), and with the reduced Hamiltonian (Eq. 6), respectively.

Sum-over-states expressions for linear and nonlinear spectral properties

The linear absorption coefficient (M^{-1} cm^{-1} units) is calculated as:

$$\varepsilon(\tilde{\nu}) = \frac{10\pi N_A \tilde{\nu}}{3\ln 10 hc\varepsilon_0} \frac{1}{\sigma\sqrt{2\pi}} \sum_n \mu_{gn}^2 \exp\left[-\frac{1}{2}\left(\frac{\tilde{\nu}_{gn}-\tilde{\nu}}{\sigma}\right)^2\right]$$

where $\tilde{\nu}$ is the wavenumber (cm^{-1} units), N_A the Avogadro number, c the light velocity, ε_0 the vacuum dielectric constant; σ is the width of the Gaussian bandshape assigned to each vibronic transition, related to the intrinsic linewidth as σ = 2γ/2.354. Moreover, μ_{gn} and $\tilde{\nu}_{gn}$ are the transition dipole moment and energy from the ground state (g) to the excited state (n) and the sum runs over all excited states.

The fluorescence spectrum is calculated as:

$$I(\tilde{\nu}) \propto \frac{\tilde{\nu}^3}{\sigma\sqrt{2\pi}} \sum_n \mu_{fn}^2 \exp\left[-\frac{1}{2}\left(\frac{\tilde{\nu}_{fn}-\tilde{\nu}}{\sigma}\right)^2\right]$$

where f is the fluorescent state and the sum runs over all states with energy lower than the fluorescent state.

In HRS measurement, a focused laser beam is shone on a solution and the intensity of the field generated at the second-harmonic frequency is recorded as a function of the frequency of the incoming light. The calibrated HRS signal S_c^{HRS}, per dye molecule, is obtained with reference to the response of the pure solvent as [Ref. 18 of main text]:

$$S_c^{HRS} = \frac{N_{solvent}}{N_{dye}} \left(\frac{S_{sample}^{HRS} - S_{solvent}^{HRS}}{S_{solvent}^{HRS}} \right) \beta_{solvent}^2$$

where $N_{dye/solvent}$ is the number density of the dye and of the solvent, respectively; $S_{sample/solvent}^{HRS}$ is the HRS signal measured for the sample and the solvent, respectively. The calibrated HRS signal S_c^{HRS} is related to the β tensor, or better to the orientational average of its square. For linear molecules, a single component of the β tensor (arbitrarily set to the along the z direction) survives, so that:

$S_c^{HRS} = \beta_{zzz}^2$

with

$$\beta_{zzz}(-2\omega;\omega,\omega) = \frac{1}{3\hbar^2} \sum_{m,n} \left(\frac{\langle g|\mu_z|m\rangle\langle m|\bar{\mu}_z|n\rangle\langle n|\mu_z|g\rangle}{(\Omega_{mg} - 2\omega)(\Omega_{ng} - \omega)} + \frac{\langle g|\mu_z|m\rangle\langle m|\bar{\mu}_z|n\rangle\langle n|\mu_z|g\rangle}{(\Omega_{mg}^* + \omega)(\Omega_{ng} - \omega)} + \frac{\langle g|\mu_z|m\rangle\langle m|\bar{\mu}_z|n\rangle\langle n|\mu_z|g\rangle}{(\Omega_{mg}^* + \omega)(\Omega_{ng}^* + 2\omega)} \right)$$

where the sums run over all excited states; ω is the laser frequency and $\Omega_{mg} = \omega_{mg} - i\gamma_{mg}$, with ω_{mg} the transition frequencies from the ground state (g) to the excited state (m) and γ_{mg} the associated bandwidth. The dipole moment difference operator is defined as: $\bar{\mu}_z = \mu_z - \langle g|\mu_z|g\rangle$.

All the calculated β results are shown in the B* convention as defined by Willetts et al. (J. Chem. Phys. 97, 1992, 7590).

The two-photon absorption cross section is calculated as (cgs units):

$$\sigma_2(\omega) = \frac{4\pi^2\hbar\omega^2}{c^2 n^2} \mathrm{Im}\langle\gamma(-\omega;\omega,\omega,-\omega)\rangle$$

where

$$\begin{aligned}\gamma_{ijkl}(-\omega;\omega,\omega,-\omega) = \frac{1}{\hbar^3}\sum_{lmn} \Bigg\{ & \frac{\langle g|\mu_i|l\rangle\langle l|\bar{\mu}_j|m\rangle\langle m|\bar{\mu}_k|n\rangle\langle n|\mu_l|g\rangle}{(\Omega_{lg} - \omega)(\Omega_{mg} - 2\omega)(\Omega_{ng} - \omega)} + \\ & \frac{\langle g|\mu_j|l\rangle\langle l|\bar{\mu}_i|m\rangle\langle m|\bar{\mu}_k|n\rangle\langle n|\mu_l|g\rangle}{(\Omega_{lg}^* - \omega)(\Omega_{mg} - 2\omega)(\Omega_{ng} - \omega)} + \\ & \frac{\langle g|\mu_i|l\rangle\langle l|\bar{\mu}_j|m\rangle\langle m|\bar{\mu}_l|n\rangle\langle n|\mu_k|g\rangle}{(\Omega_{lg} - \omega)(\Omega_{mg} - 2\omega)(\Omega_{ng} - \omega)} + \\ & \frac{\langle g|\mu_j|l\rangle\langle l|\bar{\mu}_i|m\rangle\langle m|\bar{\mu}_k|n\rangle\langle n|\mu_l|g\rangle}{(\Omega_{lg}^* - \omega)(\Omega_{mg} - 2\omega)(\Omega_{ng} - \omega)} \Bigg\}\end{aligned}$$