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SUPPORTING INFORMATION

Coherent electronic and nuclear dynamics in a rhodamine heterodimer-DNA supramolecular complex

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S1. Experimental data

S1.1 Linear characterization
S1.2 Vibrational characterization
S1.3 2D electronic spectroscopy (2DES)
S1.4 2DES measures on monochromophoric dyes
S1.5 Analysis of the oscillating contributions relevant to electronic coherence
S1.6 Analysis of the population dynamics
S1.7 Time-frequency transform analysis

S2. Computational details

S2.1 Molecular Dynamics of the BP28 complex
S2.2 Computational Details of ab-initio TD-DFT computations
S2.3 Theoretical characterisation of linear absorption spectra
S2.4 Vibronic Dimer Model
S2.5 Non-Linear Response Function of the dimer and 2D spectra

List of figures

Section 1

Figure S1.1.1 CD spectrum of BP28 deconvoluted by multi-peak fit.

Figure S1.1.2. Absorption spectra in aqueous Hepes buffer of BP28, TAMRA-DNA, and RHO-DNA.

Figure S1.1.3. Fluorescence (excitation and emission) properties of the monochromophoric samples.

Figure S1.1.4. Fluorescence (excitation and emission) properties of the BP28.

Figure S1.2.1. Raman spectra of RHO and TAMRA

Figure S1.3.1. (a) Definition of time intervals and (b) excitation geometry in 2D electronic spectroscopy (2DES).

Figure S1.5.1. Energy levels scheme.

Figure S1.5.2. Fourier maps at $\omega_2 = 970$ cm⁻¹ and related Feynman diagrams.

Figure S1.5.3. Fourier maps at $\omega_2 = 500 \text{ cm}^{-1}$ and related Feynman diagrams.

Figure S1.5.4. Comparison of the Fourier maps at 280 cm⁻¹ for the BP28 dimer and the two monochromophoric samples.

Figure S1.6.1. Dynamics of the population of the states e₅ and e₃ of BP28 dimer.

Section 2

Figure S2.1.1: Configurations from MD trajectories with different initial starting geometries.

Figure S2.2.1: Ground state equilibrium geometries of the monomers

Figure S2.2.2 : ONIOM model

Figure S2.2.3 Ground state equilibrium geometries of the H-type dimers.

Figure S2.3.1 Orbitals involved in the electronic excitations of the intense transition in the monomers.

Figure S2.3.2 Absorption spectra of the monomers.

Figure S2.3.3 Experimental and calculated Raman spectra of the monomers.

Figure S2.3.4 Coordination sites of the water molecules in RHO and in TAMRA.

Figure S2.3.5 Comparison of the experimental absorption spectra of the monomers of RHO and TAMRA.

Figure S2.3.6 Molecular orbitals involved in the electronic excitations of S_1 and S_2 of the dimer.

Figure S2.3.7 Absorption spectra of the BP28.

Figure S2.3.8 Contribution to the dispersion of the band (in %) of each hard mode for two dimers with different orientation of the substituents.

Figure S2.3.9 RHO vibrational modes which contribute to the localized active vibrational modes of the dimer.

Figure S2.3.10 RHO and TAMRA vibrational modes which contribute to the active 1627 cm⁻¹ delocalized vibrational mode of the dimer.

Figure S2.3.11 Dimer low-frequency vibrational modes with and without significant modulation of the intermolecular distance.

Figure S2.3.12 Top view on the geometry of dimer, calculated using PCM and ONIOM models for the environment.

Figure S2.3.13 Absorption spectra of the BP28 computed with the ONIOM model.

Figure S2.3.14 Computed $S_1 - S_2$ transition density for the most stable dimer.

Figure S2.4.1 Simulated absorption spectra of the monomers and the dimer with the excitonic model.

Figure S2.4.2 Simulated absorption spectra of the monomers and the dimer with different excitonic models.

S1. Experimental data

S1.1 Linear characterization

The linear absorption spectra were recorded using a Varian Cary 5 UV-visible-NIR spectrophotometer. Fluorescence emission and excitation spectra were recorded with a Horiba Jobin Yvon Fluoromax-4 using 1 nm excitation and emission beam slit width. Circular Dichroism analysis were performed on a JASCO J-600A spectropolarimeter All the linear measurements were performed at room temperature in quartz cells of 1-mm path length using the same solutions analyzed in 2D ES experiments.

The comparison between absorption and CD spectra of BP28 allowed identifying the energy of the bands involved in the photophysics of the sample, as reported in Fig. S1.1.1 and Table S1.1, and guided the interpretation of simulations and nonlinear responses. CD spectra of monochromophoric samples have also been recorded, but no signal was detected.



Scheme S1. Chemical structures of the DNA-bound rhodamine dyes.



Table S1.1. Summary of the relevant energy bands of the BP28 dimer as deduced from linear characterization. The states involved in the dynamics captured in the 2D spectra are highlighted in grey.

band	(nm)	(cm ⁻¹)
e ₆	498	20080
e ₅	527	18980
e ₄	540	18500
e ₃	556	17990
e ₂	568	17610
e ₁	588	17010

Figure S1.1.1 CD spectrum of BP28 (black line) deconvoluted by multi-peak fit (upper panel). The result of the fitting procedure is represented by the red line. The absorption spectrum is also reported (lower panel). The experimental spectrum (black) has been fitted with the same parameters used for the deconvolution of the CD spectrum, reported in Table S1.1.



Figure S1.1.3. (a) Mirror symmetry relation for a TAMRA-DNA solution ¹ Corrected absorption spectrum $\varepsilon(\tilde{\nu})/\tilde{\nu}$ (right-hand dashed line); corrected fluorescence spectrum $F(\tilde{\nu})/\tilde{\nu}^3$ (left-hand solid line) and its reflection $F(2\tilde{\nu}_0 - \tilde{\nu})/(2\tilde{\nu}_0 - \tilde{\nu})^3$ (right-hand dotted line) about the mean wavenumber $\tilde{\nu}_0$; fluorescence excitation spectrum (right-hand grey line) is also reported for comparison. (b) Same as before but for a RHO-DNA solution.



Figure S1.1.4. Bi-dimensional excitation-emission fluorescence plot of BP28.

For the monochromophoric samples (Figure S1.1.3), the absorption and fluorescence emission spectra, suitably corrected as reported in ref. 1, confirm that the mirror symmetry rule is approximately valid, as typically expected for isolated organic aromatic molecules.

Fig. S1.1.4 shows a two-dimensional excitation-emission fluorescence spectrum for BP28. The emission spectrum does not show any variation (except for amplitude) in the whole region of exciting wavelengths investigated.

In contrast with the monochromophoric samples, the spectroscopic properties of BP28 present all the typical features expected for an H-type dimer ²: the maximum in the absorption is shifted to

higher energies compared to the monochromophoric samples; a clear dichroic signal appears in the CD spectrum; the fluorescence emission is strongly suppressed with respect to the one of the monochromophoric dyes, it does not resemble the mirror image of the absorption spectrum, and the fluorescence excitation spectrum does not fully correspond to the absorption.

All these properties can be easily justified in the framework of the excitonic theory ³ for H-aggregates, predicting that (i) the strongly allowed absorption transition is not the one at lower energies, promoting an efficient non-radiative relaxation towards lower energy exciton states; and (ii) the fluorescence of an H-type aggregate is mainly emitted by a vibronic state with v=1 since the 0-0 transition is dipole forbidden².

The possible contribution of other minority species (such as dimers in different configurations or where the chromophores are not fully coupled) in the absorption and emission spectra cannot be completely ruled out, but they are not expected to have a significant contribution in the coherent dynamics recorded in the 2D spectra.

S1.2 Vibrational characterization

Resonance Raman spectra (Fig. S1.2.1) were collected using a home-built micro-Raman system, based on a Triax-320 ISA spectrograph. The excitation sources are an Ar+ laser operating at 514.5 nm and a CW Ti:sapphire laser operating at 785 nm. An Olympus BX 40 optical microscope equipped with a 20× objective was optically coupled to the spectrograph. The measurements were carried out on microcrystalline powder of DNA-free TAMRA and RHO because it was not possible to raise the concentration of the dye-DNA sample solutions above the detection limit of our experimental apparatus. The DNA duplex is not expected to perturb in a significant way the vibrational properties of the rhodamine moieties, thus the spectra can be considered representative also of the dye-DNA samples. For RHO the Resonance Raman spectrum at 514 nm has been recorded, whereas for TAMRA both the Resonance (at 514 nm) and Non-resonance (at 785 nm) Raman spectra have been recorded. Non-resonant conditions allowed for a better characterization of the TAMRA vibrational modes at low frequency.



Raman Shift (cm ⁻¹)				
TAMRA	RHO	TAMRA	RHO	
286	297	1136	1137 (w)	
335	351	1194	1198	
387	423	1222	1224 (w)	
447	449	1291	1297 (w)	
505	481	1356	1355	
557 (w)	557*	1418		
587 (w)	582*	1458 (w)	1455	
628	616*	1508	1506	
	654*	1536		
745	757	1541	1553	
826	843	1577	1587	
963	947	1648	1647	
	1027			

(w) = weak intensity band

* = belonging to the not fully resolvable set of signals between 600 and 650 cm⁻¹.

Figure S1.2.1 (left) Raman spectra of RHO (blue) and TAMRA (red) powders in resonant (solid lines) and non-resonant (dashed line) conditions. (right) Table summarizing the frequencies of the Raman active vibrational modes.

S1.3 2D electronic spectroscopy

In 2D electronic spectroscopy, like in other four wave mixing techniques, three excitations pulses interact with the sample to create a nonlinear polarization of third order in the field, which acts as a source term for the emerging signal.^{4, 5} The exciting pulses are produced by a non-collinear optical parametric amplifier (TOPAS-white, Light Conversion) pumped by an amplified Ti:sapphire oscillator (Libra, Coherent) at 3KHz repetition rate. The central wavelength of the exciting band was selected in order to be slightly tuned to the red with respect to the maximum of peak e_5 . Given the strong transition dipole moment of the associated transition, the contribution of peak e_5 would tower all other contributions. For this reason, measuring the dynamics of off-diagonal couplings between e_4 and the other transitions is better achieved by shifting the excitation spectrum towards the red.

The resulting pulse is temporally compressed and spectrally shaped by a pulse shaper (Dazzler, Fastlite). The pulse duration is compressed down to a temporal FWHM of sub-15 fs, determined by frequency resolved optical gating (FROG) measures on the solvent. Neutral density filters attenuated the pulses energy until 5 nJ per pulse at the sample position. The 2DPE experiment relies on the passively phase stabilized setup with a transmission grating already described in the literature.⁶⁻¹¹ Briefly, the laser output is split into four identical phase-stable beams (three exciting beams and a fourth beam further attenuated of about 3 orders of magnitude used as Local Oscillator, LO) in a BOXCARS geometry using a suitably designed 2D grating. Time delays between pulses were modulated by pairs of 1° fused silica wedges. One glass wedge of each pair is mounted onto a translation stage (Aerotech), providing a temporal resolution of 0.07 fs. The time delays definition and the exciting geometry are illustrated in Fig. S1.3.1. During the experiment, for fixed values of t_2 , the echo signal is measured while scanning the coherence time t_1 , by means of a spectrometer and a CCD camera (ANDOR). Thus, the signal evolution over the echo time t_3 is indirectly measured through its Fourier analogue, ω_3 . Double modulation lock-in detection for additional noise reduction and sensitivity enhancement was also implemented.⁸ The signal field is thus measured as a function of t_1 , t_2 , and ω_3 . Fourier transformation along t_1 yields finally the signal as a function of ω_1 , t_2 , and ω_3 , so that the final result is a 2D map in which the signal is plotted as a function of the corresponding coherence frequency ω_1 , representing the initial excitation, and the rephasing frequency ω_3 , which can be interpreted as the ensuing emission.

During the experiment, the relative pulse ordering of beams E_1 and E_2 can be varied to access additional non-rephasing pathways (t₁<0, E_2 coming before E_1), not generating any echo, but providing complementary information with respect to the properly time ordered pathways giving rise to the photon echo signal (t₁>0, E_1 coming before E_2). The total signal can thus be separated into rephasing and non-rephasing contributions. See ref. ^{6-8, 11} for a more detailed technical description.

Moreover, heterodyne detection, performed by interfering the signal with the LO pulse, allows measurement of both the real and imaginary part of the signal electric field. The separation of the real and the imaginary requires an additional processing, known as phasing, typically performed applying the projection-slice theorem.¹² However, proper phasing determination is not a trivial task and thus sometimes is preferable to consider the absolute 2DPE spectrum, free from any possible artifact introduced by the phasing procedure. In the following sections, the absolute components of the complex signal will be shown and commented.

In our experiments, t_2 was scanned from 0 to 600 fs in steps of 5 fs and for each value of t_2 the coherence time t_1 was scanned from 0 to 70 fs in steps of 0.26 fs. Both the rephasing and non rephasing parts of the 2D signal were acquired.¹³ At each given delay time, the signal is averaged over approximately 10³ shots per spectrum. Moreover, to ensure the reliability of the measures, at least 3 different sets of measures in different days were performed on each sample and then averaged. The experimental error on the 2D map intensity intensities is estimated to be about 5% from repeated measurements. All measurements were performed under ambient temperatures (295 K).



Figure S1.3.1 (a) Definition of time intervals and (b) excitation geometry in 2D electronic spectroscopy (2DES).

S1.4 2DES measures on monochromophoric dyes

As expected, the mono-chromophoric TAMRA-DNA and RHO-DNA spectra are dominated by diagonal features, whose positions are in good agreement with the position of the main S_0-S_1 electronic transition and the relative vibronic shoulder appearing in the absorption spectra. In both samples the diagonal signal can thus be safely assigned to the S_0-S_1 dynamics (ground state bleaching and stimulated emission). Signals at cross-peaks positions are also present, due to the dynamics of vibrational modes.

As already studied in a previous publication, in TAMRA-DNA a cross peak becomes more distinguishable especially on the upper diagonal portion of the maps, approximately 660 cm⁻¹ far from the diagonal, at longer values of t_2 (CP1'). Given its position and its dynamic evolution during t_2 , this signal was attributed to a vibrational state of S_0 or S_1 .¹⁴

The situation is similar in RHO-DNA. In addition, a strong cross-peak in lower diagonal region is clearly recognizable and can be attributed to stimulated emission (SE) from S₁ (v=0) to S₀ (v=1). Previous ultrafast studies confirm indeed that a stimulated emission peaked at 576 nm is observed in RHO with a rise time of about 200fs, in good agreement with the dynamics recorded in our 2D spectra.¹⁰ The SE phenomenon is more evident in RHO-DNA than in TAMRA-DNA because of the well-known emitting performances of the former, as proved by the intensive use of RHO in lasing applications,¹⁵⁻¹⁷ also when associated with DNA.¹⁸

The analysis of the dynamics of the signal as a function of t_2 reveals a complex beating behavior. To identify the main frequencies contributing to the beating behavior in the evolution of the 2D maps, we performed a Fourier transform (FT) along the t_2 time coordinate $t_2 \rightarrow \omega_2$ to the oscillating residuals. The result is a three-dimensional (ω_1 , ω_2 , ω_3) spectrum. In Fig. 4a (main text) we plot the results obtained integrating this 3D (ω_1 , ω_2 , ω_3) spectrum along the ω_1 and ω_3 dimensions. This provides a 1D spectrum showing the components that in average contribute more to the beating behavior of the whole 2D maps. For both monochromophoric samples, the frequencies found are in good agreement with the Raman spectra of the dyes, confirming their attribution to vibrations. (Table S1.2).^{19, 20}

	2DES ω_2 (cm ⁻¹)	Raman (cm ⁻¹)	
	298	286	
TAMRA	510	505	
	666	628	
	290	297	
	410	423	
RHO	670	654	
	847	843	
	1040	1027	
	280	286(T); 297(R)	
BP28*	510	505(R)	
	670	628 (T); 654(R)	
	970	\	

Table S1.2 Comparison between oscillations frequencies found in 2DES spectra and Raman signals.

* the 2DES frequencies of BP28 are compared with Raman modes of the TAMRA (T) and RHO (R).

S1.5 Analysis of the oscillating contributions relevant to electronic coherence

Before providing a detailed analysis of the different kinds of coherence that we identified in the BP28 dimer, we define the terminology that we use to name them. 2D photo echo spectroscopy allows differentiating between two kinds of coherences. There can be coherences that involve vibrational states of two different electronic states. In the following, we call them electronic coherences to emphasize that they involve two different electronic states. These are coherences between vibronic states, that is, excitonically mixed vibrational and electronic states.²¹ When the two electronic states involved are localized on different charge beating between the two moieties, but no population or charge transfer. There can also be coherences between vibrational states on the same electronic state. In the paper, we refer to them as vibrational coherences. As widely discussed in the literature,^{11, 22-24} electronic and vibrational coherences present different signatures in 2D spectra.

The electronic and vibrational contributions to the beating signals at 970 and 500 cm⁻¹ are reported in full details below (Fig. S1.5.2 and 1.5.3, respectively). The complete energy level scheme (Fig. S1.5.1), taking also the ground state of the dimer, is also reported for a more convenient interpretation of the Feynman diagrams in the two figures.



Figure S1.5.1 (b) Diagram of the energy levels derived from experiments and from *ab-initio* modelling. As in Fig. 2 of the main text, S_1 (S_2) vibronic sublevels are reported in blue (red) to highlight the higher degree of localization on RHO (TAMRA) moiety. Solid (dashed) lines denote ground (excited) vibrational states.

The peculiar energy level structure of the dimer makes the interpretation of the responses particularly complex. The e_3 level, which is a vibrational sublevel of S_1 , is located at about 1000 cm⁻¹ above e_1 (vibrational ground state of S_1) and at about 1000 cm⁻¹ below e_5 (vibrational ground state of S_2), as depicted in Fig.1.5.1. Therefore both the electronic coherence e_3 - e_5 and the vibrational coherence e_1 - e_3 could give rise to oscillations at the same 1000cm⁻¹ beating frequency. An additional complication, as described on p. 7 of the main text, comes also from a vibrational coherence in the ground state (g_0 - g_2) and from the fact that the energy of the transition e_5 - g_2 (18010cm⁻¹) corresponds, within our experimental resolution, to the energy difference between e_3 - g_0 (17990cm⁻¹).

In order to disentangle the electronic and the vibrational contribution, we took advantage of the spectral filtering action of the exciting bandwidth together with the knowledge that electronic and vibrational coherences present different signatures in 2D spectra.

The analysis of the Feynman pathways contributing to the 2D signal in the spectral range covered by the exciting bandwidth allowed identifying specific positions at which the two kinds of coherences (electronic e_3-e_5 and vibrational e_1-e_3 and g_0-g_2) would contribute (Fig.1.5.2): the presence of a cross peak at position CP35 with an amplitude oscillating at about 1000cm⁻¹ could only be justified with an electronic e_3-e_5 coherence. Note that this is strictly true thanks to the spectral filtering action operated through the careful choice of the exciting laser bandwidth, which is excluding from the investigated range the state e_1 , i.e. the ground vibrational level of S₁ state. This particular choice excludes all the possible vibrational contributions at 970 cm⁻¹ in the region above the diagonal. REPHASING

NON REPHASING



Figure S1.5.2 (Upper panel) Fourier maps at $\omega_2 = 970 \text{ cm}^{-1}$ obtained analyzing the rephasing and non-rephasing portion of the signal, respectively. The contributions in the 2D maps arising from the ground state vibrational coherence g_0 - g_2 are denoted by red dots, whereas white dots pinpoint the contributions of the e_3 - e_5 electronic coherence (in the rephasing map, the signal covered by the black box is due to a spurious contribution). (Lower panels) Feynman diagrams contributing at the different diagonal and off-diagonal positions. The states are named like in Fig. 2b in the main text.

NON REPHASING

REPHASING



Figure S1.5.3 (Upper panel) Fourier maps at $\omega_2 = 500 \text{ cm}^{-1}$ obtained analyzing the rephasing and non-rephasing portion of the signal, respectively. The contributions in the 2D maps arising from the ground state vibrational coherence g_0 - g_1 are denoted by red dots, whereas white dots pinpoint the contributions of the e_4 - e_5 and e_3 - e_4 electronic coherences (in the rephasing map, the signal covered by the black box is due to a spurious contribution). (Lower panels) Feynman diagrams contributing at the different diagonal and off-diagonal positions. The states are named like in Fig. 2b in the main text.

As in Fig.4(b), spurious contributions in Fig.S1.5.2 and S1.5.3 are delimited by black boxes. These spurious contributions appear in Fourier maps at the boundaries of the spectra where the echo signal is very low or absent and therefore the fit to obtain the oscillating residual and the ensuing FT are less reliable. In order to verify the spurious nature of these signals, the residuals and the respective FT at these positions have been checked and no meaningful features could be identified above the noise level.

To further support the assignment of the cross peak CP35 and the relative 970 cm⁻¹ beating to an electronic coherence, we show below the frequency maps for the vibrational mode at 280 cm⁻¹, present in the dimer and both monomers.

Differently from the mode at 970cm⁻¹, in all the maps signals out of the diagonal could be easily associated to vibrational contributions [ref. 39 main text].



Figure S1.5.4 Comparison of the Fourier maps at 280 cm⁻¹ for the BP28 dimer and the two monochromophoric samples. Red dots indicate the positions at which signal from ground and excited state vibrations are expected to contribute. Light-red dots denote positions outside the spectral bandwidth and therefore not fully captured in the reported spectra.

S1.6 Analysis of the population dynamics

The dynamics of the populations of states e_3 (17990 cm⁻¹) and e_5 (18980 cm⁻¹) (see Fig.2) is studied analyzing the time evolution of horizontal and vertical slices of the 2D maps centered at e_3 and e_5 energy, respectively. Fig. S1.6.1 shows that there is no population transfer between e_3 and e_5 on the 600 fs span of t_2 .

S1.7 Time-frequency transform analysis

The time-frequency analysis was performed using the smoothed-pseudo Wigner-Ville transform (SPWV):²⁵

$$SPWV = \int_{-\infty}^{+\infty} h(t') \int_{-\infty}^{+\infty} g(t'' - t) s\left(t'' + \frac{t'}{2}\right) s^* \left(t'' - \frac{t'}{2}\right) e^{-i2\pi\nu t'} dt'' dt'$$
(E1.1)

g and h windows are described as gaussian functions with width $\sigma_h = 50$ fs, $\sigma_g = 100$ fs. These values have been chosen after an optimization procedure as described in ²⁶.



Figure S1.6.1 Dynamics of the population of the states e_5 (panels a) and e_3 (panels b) of BP28 dimer. In each panel: the first row reports on the left the mean 2D map with lines indicating where the slices have been cut and on the right the decay of the echo signal at the diagonal position corresponding to (a) e_5 energy and (b) e_3 energy; the second row shows the evolution along t_2 of vertical slices cut at (a) $\omega_1=18980$ cm⁻¹(= e_5) and (b) $\omega_3=17990$ cm⁻¹(= e_3); the third row shows the evolution along t_2 of horizontal slices cut at (a) $\omega_3=18980$ cm⁻¹(= e_5) and (b) $\omega_3=17990$ cm⁻¹(= e_3). Grey lines highlight the energy of the states.

S2. Computational details

S2.1 Molecular dynamics of the BP28 complex

Molecular dynamics (MD) was performed to sample the configurational space of the BP28 complex. The MD calculations were carried out with the program package Amber 12.²⁷ The PARM99/BSC0 force field²⁸ was used for DNA while the force field for the chromophores and the aliphatic linkers have been set-up within Antechamber using the GAFF force field parameters ²⁹. To derive the corresponding atomic charges the dyes were capped with the NME residue³⁰ while the linkers were capped with the residue ACE on the end connected to the dve and with a phosphate group for subsequent attachment to DNA.³¹ Charges were calculated with the Restrained Electrostatic Potential (RESP) method³² which consists of fitting atomic charges to the molecular electrostatic potential generated at the HF/6-31G(d) level. The geometries of the dyes and the linker were optimized separately at the CAM-B3LYP/6-31G(d,p) level using the program package Gaussian 09.³³ The structure of the linker was optimized in vacuum while the effect of solvent on the charge distribution of the chromophores was accounted by PCM.³⁴⁻³⁶ After separate geometry optimization the structures of the dye and linker were merged, the initial structures of the DNA duplexes were constructed with the program NAB³⁷ in B-DNA form. The dyes were attached to the corresponding DNA nucleotide and three starting geometries with different configurations of the two chromophores were prepared. In one configuration the two dyes were spatially separated (runA) while in the other two configurations (runB, runC) the dyes were prepared in a nearly cofacial position. The initial geometries were subsequently solvated in a cubic periodic box of TIP3P water model ³⁸, with a minimum distance of 10 Å between any DNA or dye atom and the closest box edge. Sodium counterions were added to establish charge neutrality. Each resulting structure was energy minimized using steepest descent and conjugate gradient methods to relax any residual unfavourable steric interactions introduced during the solvation procedure. First, the DNAchromophores complex was constrained (500 kcal/mol-Å²) while the water and counterions were subjected to 10000 cycles of minimization. Then, the full system was allowed to relax during an additional 10000 cycles of unrestrained minimization. The DNA system were restrained (25 $kcal/molÅ^2$) during a 100 ps, constant volume MD simulation (NVT), during which water and the Na+ atoms were allowed to move freely and the temperature was raised from 0 to 300K using a Langevin temperature control. Next, the system was subjected to 150 ps of constant pressure (NPT) MD to achieve proper density and 5ns of relaxation before production runs. During MD the longrange electrostatic interactions were treated with the particle-mesh Ewald method³⁹ using a realspace cut-off distance of $r_{\text{cuttoff}} = 9$ Å. The SHAKE algorithm⁴⁰ was used to constrain bond vibrations involving hydrogen atoms, which allowed a time step of 2 fs.

For each starting geometry, 30 ns of molecular dynamics in explicit solvent were generated. In *runA*, where the two chromophores were initially far apart (see Fig S2.1.1A), we observed the tendency of the two dyes to aggregate (see Fig. S2.1.1B). However, the two chromophores do not reach the structure of a stable dimer since the configurational space is not completely sampled in 30 ns due to the motional freedom allowed by the linker. *RunB* and *runC*, whose initial configurations were closer to the structure of a dimer, show the stabilization and persistence of dimeric structures. In particular, *runB* (Fig. S2.1.1C) led to the stable dimeric structure showed in panel A) of Fig. S2.2.3 while *runC* (Fig. S2.1.1D) led to the stable dimeric structure shown in Fig. S2.2.3C. For these two cases we run additional 30ns of molecular dynamics in explicit solvent that confirmed the stability of the dimeric structures at room temperature.



Figure S2.1.1 Configurations from MD trajectories with different initial starting geometries. Panel A-B) shows nondimeric structures of the dyes from *runA*, panel C-D) shows the two different stable dimeric structures from *runB* and *runC*, respectively.

S2.2 Computational details of ab initio computations

DFT and TD-DFT methodologies were used to determine the equilibrium geometries and spectral properties of the bare chromophoric monomers, RHO and TAMRA and of their dimer (Fig. S2.2.1). These model structures do not include linkers and DNA environment, but provide qualitative information on the chromophore properties in a polar media. All DFT/TD-DFT calculations were carried out within Gaussian09 package.³³



Figure S2.2.1 Ground state equilibrium geometries of the monomers of RHO (A), TAMRA (B) and of the most stable dimer (C). Hereafter the color of the atoms corresponds to the labels of the atoms.

The equilibrium geometries and vibrational frequencies ω_j of the ground electronic states of the monomers and the dimer were obtained at the CAM-B3LYP-D/6-311G(d,p) level of theory^{41, 42} with van-der-Waals dispersion correction as implemented in the Gaussian09 package³³. This functional is shown to give errors within 0.3 eV range for local and charge-transfer transitions for various organic chromophores.^{43, 44} Our benchmarking with other functionals (PBE, PBE0) indicates that for the dimer, CAM-B3LYP-D is the best compromise both from vibrational analysis (Raman spectra) and excited state calculations. As it was previously shown,^{44, 45} the error in the TD-DFT excitation energy correlates with the degree of spatial overlap between the occupied and virtual orbitals involved in the excitations. We analysed the spatial overlap for the S₀-S₁ and S₀-S₂ transitions using the following measure: ^{44, 45}

$$\Lambda = \frac{\sum_{i,a} \kappa_{ia}^2 O_{ia}}{\sum_{i,a} \kappa_{ia}^2}$$
(T2.1)

$$O_{ia} = \int |\varphi_i(\mathbf{r})| |\varphi_a(\mathbf{r})| d\mathbf{r}$$
(T2. 2)

where $\varphi_i(\mathbf{r})$ and $\varphi_a(\mathbf{r})$ are occupied and virtual orbitals, respectively, κ_{ia} - is the contribution of the pair of orbitals to the TD-DFT excitation. In both monomers Λ was found to be larger 0.5 (0.64 and 0.61 for RHO and TAMRA, respectively, and 0.55 and 0.51 for S₀-S₁ and S₀-S₂ transition in the dimer), which means that the error in excitation energies calculated using TDDFT/CAM-B3LYP-D functional is expected to be within 0.5 eV. One should mention that in the dimer low-lying states of interest have the same orbitals involved in the main excitations, which means that both states will be described at the same level of accuracy, so that the S₁-S₂ energy gap is described correctly.

To better understand the influence of the DNA scaffold, linkers and solvent we studied the electronic and vibrational structure of the dimer with the ONIOM approach.⁴⁶ We used the same force field as for the MD simulations (see Section S2.1 for the details).

A two-layer ONIOM model was built: (I) MM-layer with DNA (14 base pairs) and the tail of the TAMRA linker, 6958 water molecules (where 6688 were fixed and 270 were not, see Fig. S2.2.2) and 27 sodium ions; (II) QM-layer with chromophores and RHO linker. The atoms of the linker of RHO were included in the QM part, because of their proximity to the chromophores. For the QM part CAM-B3LYP-D/6-311G(d,p) method with electrostatic embedding was used. Active modes were analysed in the same manner as for the structures optimized with DFT. Parameters for the lineshape function were obtained from the same ONIOM layer structure with gradients and modes determined for the whole system (QM+MM layers).



Figure S2.2.2 ONIOM model: (a) the whole system; (b) the part which was relaxed during the optimization: QM layer atoms depicted in 'ball-and-stick' manner.

In order to describe the displacements along normal coordinates, excited state gradients were calculated taking into account the Hessian of the ground state. All excited state properties were

computed at the TD-DFT⁴⁷ level with the same functional and basis set. The effect of solvent was taken into account by applying the continuum solvation model (PCM)⁴⁸ for water (dielectric constant ϵ =78.35). This solvation model is only an approximation to the real environment that results also from the effect of DNA, which has a lower dielectric constant, and of the ion concentration (HEPES buffer). However the major effect on the excitation energies is expected to be governed by the polar water medium. In order to estimate how the S₁-S₂ energy gap in the dimer can change upon solute-solvent interaction we calculated the energies of the excited states of the dimer within the non-equilibrium state-specific solvation model⁴⁹ and reaction field of the solvent, corresponding to the ground state. In this model the solvent electronic polarization (fast component of the solvent relaxation) is in equilibrium with the excited state electron density of the solute, while the slow solvent degrees of freedom remain equilibrated with the ground state electron density. We refer to this model as state-specific solvation PCM below.

Four H-type dimers were built taking into account different orientations of the phenyl substituent in the xanthene ring (Fig. S2.2.3). Hereafter we discuss only the most stable one (Fig. S2.2.3A) except when it is not specifically stated otherwise.



Figure S2.2.3 Ground state equilibrium geometries of the H-type dimers. The relative energy, compare to the dimer (A) of the lowest energy are (B) 2.4 kcal/mol; (C) 5.4 kcal/mol; (D) 4.8 kcal/mol. Equilibrium geometries and energies are calculated within CAM-B3LYP-D functional and 6-311G(d,p) basis set.

The optically active modes in the linear absorption profiles were then characterized. Linear absorption spectra were simulated for vertical electronic transitions within the Condon approximation starting from the equilibrium geometry of the ground electronic state. Vibronic structure simulation both for monomers and dimers were obtained through a time-domain formalism⁵⁰ based on Fourier transform of the Lax's autocorrelation function⁵¹ within the multi-mode parallel harmonic oscillator model of the potential energy surfaces.^{52, 53} Within the parallel approximation it is assumed that the oscillators of the excited electronic state can be regarded as displaced harmonic oscillators of the ground state. This approximation was shown to give qualitative description of the vibronic progression for various systems in crystals, solution and bioorganic media.⁵⁴⁻⁵⁶ Parameters for the absorption lineshape calculation were taken from the TD-DFT calculations according to the general methodology developed in Refs.^{57, 58}. All the spectra were simulated at 298 K.

The absorption cross-section, $\sigma(\omega)$, is calculated using Eqs. T2.3 to T2.5 below. $\sigma(\omega)$ is defined

using vibronic profile, $I_{ab}(\omega)$, of each electronic transition from ground state *a* to the excited state *b*. $I_{ab}(\omega)$ is the Fourier transform of the lineshape function G(t) calculated for a set of uncoupled harmonic oscillators⁵¹:

$$\sigma(\omega) = \frac{4\pi^2 \omega}{3cn} \sum_{b} I_{ab}(\omega)$$
(T2.3)

$$I_{ab}(\omega) = \frac{\left|\mu_{ab}^{0}\right|^{2}}{2\pi} \int_{0}^{\infty} G(t)e^{-i\omega t}dt$$
(T2.4)

$$G(t) = \exp\left[\frac{it}{\hbar}E_{ab}^{0}\right]\prod_{j}\exp\left[-S_{j}\left\{\coth\frac{\hbar\omega_{j}}{2kT}\left(1-\cos\omega_{j}t\right)-i\cdot\sin\omega_{j}t\right\}\right]$$
(T2.5)

where E_{ab}^{0} and μ_{ab}^{0} are the excitation energy and transition dipole moment between electronic states a and b, \Box_{j} the harmonic vibration frequencies of the ground state, T is temperature, and \hbar and k the Planck and Boltzmann constants. The S_{j} 's are the Huang-Rhys (HR) factors of each vibrational mode defined as:

$$S_{j} = \frac{\omega_{j} \left(\Delta Q_{j} \right)^{2}}{2\hbar}$$
(T2.6)

where ΔQ_j are the harmonic potential energy minima shifts expressed in mass-weighted displacements along normal coordinates. Thus, one can define the dispersion of the band⁵⁷ which accounts for temperature, the corresponding displacements, and frequencies:

$$(\delta v)^2 = \sum_j (\delta v_j)^2 = \sum_j S_j \omega_j^2 \operatorname{cth}\left(\frac{\hbar \omega_j}{2kT}\right)$$
(T2.7)

We analyse HR factors and the fraction of the contribution of each normal mode $(\delta v_j)^2 / \sum_i (\delta v_j)^2$

to the dispersion of the spectrum in order to determine the optically active modes which contribute to the width of the spectra. These modes are essentially hard modes, with a vibrational frequency above 200 cm⁻¹. Active modes with frequency lower than 200 cm⁻¹ (soft modes) mainly affect the broadening at each hard mode frequency. The density of states of the soft modes is underestimated in the harmonic approximation.

S2.3 Theoretical characterisation of linear absorption spectra

Spectral properties of the monomers.

The intense transition in the monomers is localized on the xanthene ring and involves mainly $\pi\pi^*$ excitations from the p_z molecular orbital (MO) of nitrogen in amino-groups conjugated with the π -system to the π^* MO of the xanthene ring (Fig. S2.3.1).



Figure S2.3.1 Orbitals involved in the electronic excitations of the intense transition in the monomers.

Fig. S2.3.2A shows the line-shape obtained from the vibrational analysis of the two monomers compared to the experimental spectra. The position of the shoulder in the calculated spectra is in qualitative agreement with the experimental absorption profile. The broadening of each vibronic feature of the spectra is systematically too narrow for both chromophores. Anharmonic coupling effects will significantly affect the quality of the soft mode description and consequently would lead to a more significant broadening of the hard modes.⁵⁹



Figure S2.3.2 A) Absorption spectra of the monomers of RHO (blue) and TAMRA (Red): In the experiment (continuous lines), the monomers are attached to the DNA scaffold. The computed spectra (dashed lines) are obtained from vibrational analysis of the monomers. The intensity of each spectrum is scaled to its maximum. The calculated profiles are shifted to the positions of the experimental maxima. B) Huang-Rhys factors (Eq. T2.6) of the high frequency modes. C) Contribution to the dispersion of the band (in %) (Eq. T2.7) from each mode.

From the calculation of the HR factors and dispersion associated to specific vibrations (Fig. S2.3.2B-C) we identify a set of high frequency vibrational modes in the range between 600 cm⁻¹-1700 cm⁻¹ that are responsible for the typical vibronic shoulder in the absorption spectra of the rhodamine dyes. Vibrations in the region of <1000 cm⁻¹ are breathing vibrations of the ring coupled with C-H in-plane rocking and out-of plane vibrations. Active modes at 1213 cm⁻¹, 1402 cm⁻¹ and modes around 1600 cm⁻¹ mainly involve C-C-C in-plane stretching vibrations in the xanthene moiety coupled to rocking of the C-H bonds. These active modes are also present in all the conformers of the dimers studied (see for example, Fig. S2.3.8 below). The 1213 cm⁻¹, 1402 cm⁻¹ and modes around 1600 cm⁻¹ were also identified in pyrene and other π -conjugated chromophores^{55, 60, 61} with some difference of their frequencies (for example for pyrene 1132 cm⁻¹, 1444 cm⁻¹ and

1660 cm⁻¹). The specific umbrella-type 1025 cm⁻¹ vibration of SO₃ group of the RHO substituent also contributes to the width of the spectra, however this vibration could be locked by the interaction with media, see Fig. 2.3.5C below. Calculated vibrational modes qualitatively reproduce the Raman spectra of the monomers (Fig. S2.3.3).



Figure S2.3.3 Experimental (red) and calculated (black) Raman spectra for RHO (A) and TAMRA (B). (For the experimental spectra see also Fig. S1.2.1). The insets show a zoom in the frequency range below 1000 cm⁻¹. The frequencies are unscaled.

The effect of the coordination of water molecules with the monomers was investigated for both dyes at the DFT/CAMB3LYP-D/PCM level. In RHO, the number of coordination centers is larger than in TAMRA: 3 water molecules in the vicinity of the sulfo-groups were considered in the case of RHO (Fig. S2.3.4A), and 1 molecule (on a carboxylic group) in the case of TAMRA (Fig. S2.3.4B). The calculated excitation energies for both monomers are very slightly shifted (by less than 0.05 eV) to lower values due to coordination with water molecules. The oscillator strengths exhibit minor changes only (see table S3.1). In the dimer, these coordination sites of the water molecules are located far from the pi stacking interaction region. For these reasons, the computation of the excited states of the dimer does not include specific water molecules. The effect of the solvent is described at the PCM level.

B)

A)





Figure S2.3.4 Coordination sites of the water molecules in RHO (A) and in TAMRA (B) determined by a DFT/CAM-B3LYP-D/PCM calculation.

Table S3.1. Energies and oscillator strengths of the S0-S1 transitions for RHO and TAMRA as calculated within (A) PCM model for monomers, (B) PCM model for their complexes with water molecules, as shown in Figure 2.3.4.

	А		В	
	E (S ₀ -S ₁), eV Oscillator strength		E (S ₀ -S ₁), eV Oscillator strength	
RHO	2.62	1.44	2.59	1.42
TAMRA	2.83	1.32	2.77	1.36

The broadening of the main features in the absorption spectra decreases upon the coordination with water molecules for both dyes, see Fig. S2.3.5. In the case of RHO the width is narrower than experimental absorption spectrum, and also than the spectrum computed without water molecules. This computational result suggests that no specific solvation is observed in the chromophores studied.



Figure S2.3.5 Comparison of the experimental absorption spectra of the monomers of RHO (A) and TAMRA (B) attached to DNA double helix (continuous lines) with absorption profiles calculated within PCM for monomers (dashed lines) and PCM for complexes of the monomers with water molecules (dotted lines). Each spectrum is scaled by its maximum. The calculated profile is shifted to the position of the experimental maximum. C) Contribution to the dispersion of the band (in %) from each mode for RHO (blue) and TAMRA (red) in the calculated spectra within PCM for complexes of the monomers with water molecules. The patterns is very similar to those of fig. S2.3.2C above, except for the vibrational motion for the SO₃ group at 1025 cm⁻¹ which is indeed locked by coordination to water molecules.

Spectral properties of the dimer. In the DFT calculations of the equilibrium geometry of the ground state of the most stable conformer (Fig. S2.2.1C above), the occupied orbitals in the dimer (HOMO and HOMO-1) are delocalized over two chromophores (Fig. S2.3.6 below). For a weaker interaction between two chromophores in the dimer these orbitals could have more localized nature. In the other hand the LUMO and LUMO+1, also shown in Fig. S2.3.6, are mainly localized on the RHO and TAMRA moieties respectively. The first excited state of the dimer is characterized by HOMO-1 and HOMO transitions to the LUMO, localized on RHO. For the second excited state, the main excitations are from the same occupied orbitals to the LUMO+1, localized on TAMRA. Both transitions exhibit weak intramolecular charge transfer character (Λ =0.55 and 0.51 for S₀-S₁ and S₀-S₂ transitions, respectively, see Eq. T2.1 above). The orbitals involved in the electronic excitations of S₁ and S₂ are shown in Fig. S2.3.6. These main excitations represent 96.2 and 95.1% of the composition of the S₁ and S₂ excited states of the dimer, which involve also higher excitations with two orders of magnitude lower weights, see Table S3.2.

	\mathbf{S}_1	S_2
Excitation	Weight, %	Weight, %
(HOMO-1)-LUMO	47.8	< 0.5
HOMO-LUMO	25.7	36.9
(HOMO-1)-	7.4	30.9
(LUMO+1)		
HOMO-(LUMO+1)	15.3	26.8

Table S3.2. Composition of the first (S_1) and second (S_2) excited states. See Fig. S2.3.6 for molecular orbitals characterisation.

The absorption spectrum obtained from the vibrational analysis of the dimer with S_1 - S_2 energy gap and transition dipoles obtained from the state-specific solvation TDDFT/PCM calculation is shown in Fig. S2.3.7. Linear response and the state-specific solvation scheme largely affect both the gap and transition dipoles of the $S_0 \rightarrow S_1$ excitation. We obtain a value of 2450 cm⁻¹ for the gap using the linear response model with oscillator strengths from the GS to S_1 of 0.16 and to S_2 of 1.47. The state specific solvation model leads to a smaller gap of 1640 cm⁻¹ with oscillator strength of 0.57 and 1.95 to S₁ and S₂ respectively. The numerical error on transitions frequencies computed at the TD-DFT level is usually estimated to be 0.5 eV (about 4000 cm⁻¹). The linear response computed value of the gap overestimates the experimental one (1970 cm⁻¹) while the state specific one (non equilibrium PCM) gives a too low value compared to the experimental one. Both values are within 0.05 eV of the experimental one and are well within the expected numerical accuracy for such a large system in a complex environment. They provide lower and upper bounds to the value of the gap between S₁ and S₂. As stated above, our benchmarking with other functionals (PBE, PBE0) indicates that for the dimer, CAM-B3LYP-D is the best compromise for excited state calculations. As discussed below, including explicitly the effect of the DNA backbone and the solvation by water molecule at the ONIOM level does not affect the value of the S_1 - S_2 gap.



Figure S2.3.6 Molecular orbitals involved in the electronic excitations of S_1 and S_2 of the dimer.



Figure S2.3.7 A) Absorption spectra of the BP28: experimental (continuous line) and computed from vibrational analysis of the lowest energy conformer of the dimer (dashed lines). The intensity of each spectrum is normalized by its maximum. The calculated profile is shifted to the position of the second experimental maximum (18980 cm⁻¹). The laser spectral profile used for the excitation in the 2D-spectra is also reported (shaded grey area). B) Huang-Rhys factors of the high energy modes from vibrational analysis of the first excited state of the dimer.

The analysis of the hard modes of the first excited state of the lowest energy conformer of the dimer identifies two groups of high-frequency modes contributing to the spectral width of the absorption spectrum. The first group includes the modes in the range between 600 cm⁻¹-1000 cm⁻¹, while the second group is formed by higher frequency modes in the range 1200 cm⁻¹-1650 cm⁻¹. Considering the experimental S_1 - S_2 energy gap of about 2000 cm⁻¹ these modes can contribute to the low-frequency beating (around 500 and 970 cm⁻¹), observed in the 2D-echo spectra. These vibrations have the same nature as the vibrations in RHO (Fig. S2.3.9) but the vibrational mode at 1627 cm⁻¹ is delocalized over TAMRA, see Fig. S2.3.10. These hard modes are also present in less stable conformers, see Fig. S2.3.8B.



Figure S2.3.8 Contribution to the dispersion of the band (in %) of each hard mode for two dimers with different orientation of the substituents: A) lowest energy dimer and B) a less stable (higher in energy than dimer (A) by 5.4 kcal/mol, see panel (C) in Fig. S2.2.3). The 1024 cm⁻¹ active mode for the latter involve SO₃ group umbrella-type vibrations which can be locked by the specific interactions with protic solvent.

The high frequency modes in the range $[1200 - 1650 \text{ cm}^{-1}]$ (see Fig.S2.3.9 and Fig.S2.3.10) as well as low-frequency modes above 50 cm⁻¹(see Fig.S2.3.11C-D) do not lead to a change in the distance between the two monomers. For example, the mode with frequency 280 cm⁻¹ corresponds to the out-of-plane C-C twisting vibration in the phenyl ring of the substituent in TAMRA, the mode around 500 cm⁻¹ to C-H rocking vibration. The nuclear motions corresponding to these modes will therefore not affect the value of the electronic coupling between the two monomers in the dimer. On the other hand, the modes below 50 cm⁻¹ have an intermolecular character and correspond to relative motion of the two monomers that modify the distance between them (see Fig. S2.3.11A-B). For example, the mode with 27 cm⁻¹ frequency has contributions from both torsional vibration of the amino-group and vibration of the RHO xanthene moiety as whole. The vibrational mode at 30 cm⁻¹ has a major contribution from the vibration of the two xanthene moieties of both dyes. These modes are therefore likely to lead to non adiabatic coupling and population transfer between the two monomers. However, this coupling takes place on a much longer time scale (> 670 fs), that is on a ps time scale, which is not probed in the present experiment and is much longer that the beating of the electronic frequency (970 cm⁻¹ corresponds to 34 fs) and its damping time of 150 fs.



Figure S2.3.9 RHO(A, B, C) vibrational modes which contribute to the localized active vibrational modes of the dimer (D, E, F). The frequencies of the modes are: A) 963 cm⁻¹; B) 1210 cm⁻¹; C) 1570 cm⁻¹; D) 965 cm⁻¹; E) 1210 cm⁻¹; F) 1569 cm⁻¹.



Figure S2.3.10 RHO (A) and TAMRA(B) vibrational modes which contribute to the active 1627 cm⁻¹ delocalized vibrational mode of the dimer (C, D). C – view on RHO side, D – on TAMRA side. The frequencies of the monomer modes are: A) 1618 cm⁻¹; B) 1622 cm⁻¹.



Figure S2.3.11 Dimer low-frequency vibrational modes with significant modulation of the intermolecular distance (A, B), and low-frequency modes (C,D) which can be assigned to 280 cm⁻¹ and 510 cm⁻¹ of the experimental Fourier spectra (Fig. 4a) and do not lead to a variation of the intermolecular distance. Frequency of the modes: A) 27 cm⁻¹; B) 30 cm^{-1} ; C) 280 cm⁻¹; D) 503 cm⁻¹.

The TD-DFT line shape computation does not fully reproduce the shoulder in the experimental spectrum at 18000 cm⁻¹. This discrepancy might be due to the fact that the broadening of the hard modes by the soft modes is not large enough due to anharmonicity and effects of the environment. Taking into account a more realistic environment description using the ONIOM model affects the equilibrium geometry of the dimer, mainly the torsional angles of the phenyl substituents and relative orientation of the xanthene moieties (see Fig. S2.3.12). The distance between two monomers is increased: 3.41 Å (PCM) and 3.72 Å (ONIOM).



Figure S2.3.12 Top view on the geometry of dimer, calculated using PCM (A) and ONIOM (B) models for the environment. Distance between two monomers: 3.41 Å (PCM) and 3.72 Å (ONIOM). Torsion angles of the phenyl substituents are: Ph_RHO(PCM)=-90.4, Ph_RHO(ONIOM)=-109.8; Ph_TAM(PCM)=113.7, Ph_TAM(ONIOM)=66.6.

However, the energy gap between S_1 and S_2 computed within linear response solvation scheme is not affected by these geometry changes. $\Delta E(PCM)$ for the isolated dimer is 2450 cm⁻¹ while $\Delta E(ONIOM)=2340$ cm⁻¹ and oscillator strengths 0.16/0.22 and 1.47/1.22 for the S₀-S₁ and S₀-S₂ PCM/ONIOM models respectively. Note that one cannot compute the gap using the state specific solvation scheme at the ONIOM level. The computed line shape (dots) is plotted in Fig. S3.2.13A and compared to the computed line shapes of the isolated dimer (linear PCM (thick dashes) and state-specific (thin dashes)). The ONIOM lineshape is very similar to the linear PCM one, with slightly narrower peaks.

Including realistic solvation in the model does not have a significant effect on the vibrational frequencies (no more than 30 cm⁻¹ shift compare to the PCM model). The difference is that the solvation shell leads to more similar potentials in the Franck Condon region for S_0 and S_1 for the bending and wagging C-C vibrations in the frequency range of 500-700 cm⁻¹. In other words, there are less changes in the gradient for the S1 state computed in the ONIOM model than in the isolated dimer. Consequently, the Huang-Rhys factors of the 1200-1650 cm⁻¹ hard modes are not significantly affected by the medium while those in the 600-1000 cm⁻¹ range are more affected, see Fig. S2.3.13. Note also that the effect of the medium is at the level of the solvation shell as a whole, not due to interactions with specific water molecules.



Figure S2.3.13 A) Absorption spectra of the BP28: experimental (continuous line) and computed from vibrational analysis of the same conformer of the BP28 dimer in CAM-B3LYP-D/PCM linear response solvation scheme (dashed thick lines) and state-specific solvation scheme (dashed thin lines), CAM-B3LYP-D/ONIOM linear response scheme (dotted lines) models of the environment. The intensity of each spectrum is normalized by its maximum. The calculated profile is shifted respective to the position of the second experimental maximum (18980 cm⁻¹). B) Huang-Rhys factors of the high energy modes (200-1800 cm⁻¹) from vibrational analysis of the first excited state of the BP28 dimer in PCM (black) and ONIOM (red) models of the environment.

Transition density.

Fig. S2.3.14 shows the delocalization of S_1 - S_2 transition density over the two moieties. Such a delocalization is responsible for the electronic coherence between TAMRA and RHO.



Figure S2.3.14 Computed S₁ - S₂ transition density for the most stable dimer (isocontour amplitude value 0.0004 au).

Triplet states.

The existence of triplet states that could contribute to the dynamics has been examined, the energies of the excited states with triplet spin multiplicity are compared to the singlet energies in Table S3.3 computed at the TDDFT/PCM level.

We find a triplet state which lies close to the second singlet state (E(T₅)=2.93 eV, while E(S₁)=2.99 eV). This state corresponds to the excitation from the π -orbitals on the RHO and TAMRA xanthene moities mixed with the n-orbitals of the COO⁻ group of TAMRA to the π^* -molecular orbital, localised on TAMRA. For the heteroaromatic molecules the intersystem crossing rate is proportional to the strength of the spin-orbit coupling, and the coupling between singlet and triplet π - π^* states is less than 1-3 cm^{-1.62} Contribution from the n- π^* -excitation of the COO⁻ group of TAMRA will not enhance the spin-orbit coupling since they are not localised on the same molecular fragment implying a vanishing contribution to the one-center integrals of the spin-orbit coupling⁶³. Only significant deviation of the xanthene moieties of the dyes from the planarity will ensure effective intersystem crossing, the process can be effective on the nanosecond time scale (if one assume an high intersystem crossing constant of ~ 10⁹ s⁻¹). Therefore, we expect the intersystem crossing to be much slower than the timescale relevant to the 2D photon-echo experiment.

E(Singlets), eV	E(Triplets), eV
2.68	1.71
2.99	2.00
3.17	2.69
3.36	2.84
3.58	2.93

Table S3.3 Energies of the singlet and triplet excitations in the dimer

S2.4 Vibronic Dimer Model

Previous studies indicate that an exciton-vibrational model Hamiltonian can provide understanding of the increase in intensity of the vibronic shoulder in the dipole-forbidden H-type homo- and hetero-dimers.^{2, 24} The vibronic dimer model is built by including explicitly one or more vibrational modes into the Hamiltonian of two electronically coupled chromophores.^{64, 65} In this model, mixing between electronic states and active Frank-Condon vibrations creates vibronic excitons. These states have vibrational characteristics and enhanced transition dipole moments because of intensity borrowing from the stronger electronic transition.^{21, 66}

We have built for each monomer an effective three state model that reflects the salient features of the electronic structure of the monomers, as determined by the *ab initio* computations and the vibrational analysis of the most intense optical transition (see Section S2.3 above). For each monomer, the model includes the ground electronic state, S₀, the first excited electronic state, S₁, in its vibrational ground state at energy E_V from S₀, and one vibrational excited state of a single harmonic mode of frequency ω_0 on S₁. The system is coupled to a bath characterized by a continuous spectral density⁶⁷ including a fast component with reorganisation energy λ_f and relaxation rate Γ_f and a slower component accounting for the inhomogeneous broadening with reorganisation energy λ_s and relaxation rate Γ_s . We assume that the coupling with the bath does not depend on the vibrational state. Assuming $k_B T < \hbar \omega_0$, the linear absorption of each monomer is given as:

$$S(\omega) = \omega |\mu_{10}|^2 \operatorname{Re} \int_{0}^{\infty} dt \left(\exp\left(-i\left(\omega - \omega_{eg}\right)t - g\left(t\right)\right) + F_{0,1} \exp\left(-i\left(\omega - \omega_{eg} - \omega_{0}\right)t - g\left(t\right)\right) \right)$$

$$MERGEFOR$$

$$MAT (T4.1)$$

where μ_{10} is the S₀ \rightarrow S₁ transition dipole, $\omega_{eg} = E_V / \hbar$, $F_{0,1} = |\langle 0|1 \rangle|^2$ is the Frank-Condon factor of the 0 \rightarrow 1 transition for the ω_0 mode and the line-shape function g(t) describing relaxation is explicitly given as the sum of the faster (*f*) and the slower (*s*) components:

$$g(t) = \sum_{i=f,s} \frac{\lambda_i}{\Gamma_i \hbar} \left(\frac{2k_B T}{\Gamma_i \hbar} - i \right) \left(\exp\left(-\Gamma_i t\right) + \Gamma_i t - 1 \right)$$
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MAT (T4.2)

Parameters that characterized the spectral density of the environment in the two chromophores, the reorganization energy, λ , and relaxation rate, Γ , can be estimated from *ab initio* simulation ⁶⁸⁻⁷⁰. However, these models were developed for a uniform polar medium with a predefined dielectric constant. In our case the dielectric constant of the DNA and water solution, as well as relaxation rate are qualitatively different. Therefore, we chose to determine these parameters empirically, in order to have a good agreement between experimental and calculated absorption profile. The reorganization energy of the fast bath component, λ_{f} is taken to be half of the measured Stokes shift, the other parameters defining the relaxation model for each monomer are chosen to reproduce the experimental absorption profile and they are reported in Table S4.1. The transition dipoles are

those calculated at the TD-DFT level. The frequency of the single vibrational mode included in the three level model of the dyes is an effective representation of the manifold of high frequency vibrations calculated at the TD-DFT level (see Fig. S2.3.5B). The spectra calculated according to equations * MERGEFORMAT (T4.1) and * MERGEFORMAT (T4.2) are compared with the experimental absorption in Fig. S2.4.1A (dashed lines).

Table S4.1 Parameters used in the three-state model of the monomers. μ : ground to excited state transition electric dipole moment (atomic unit, from TD-DFT); E_v : vertical excitation energy (absorption maximum of the experimental spectrum of the monomer); HR: Huang Rhys factor (chosen as effective representation of the manifold of the monomer); ω_0 : energies of effective vibrational mode; λ , Γ : reorganisation energy and relaxation rate of bath components (fast component from the experimental Stokes shift, slow component to match experimental linewidth)

RHO	TAMRA		
$ \mu = 4.5$	$ \mu = 3.6$		
$E_v = 17597 \text{ cm}^{-1}$	$E_v = 18011 \text{ cm}^{-1}$		
HR = 0.22	HR = 0.22		
$\omega_0 = 1350 \text{ cm}^{-1}$	$\omega_0 = 1350 \text{ cm}^{-1}$		
$\lambda_{\rm s} = 300 \ {\rm cm}^{-1}$ $\Gamma_{\rm s} = 10^{11}$	$\lambda_{\rm s} = 200 \ {\rm cm}^{-1}$ $\Gamma_{\rm s} = 10^{11}$		
$\lambda_f = 566/2 \text{ cm}^{-1}$ $\Gamma_f = 1.5 \cdot 10^{14}$	$\lambda_{\rm f} = 859/2 \ {\rm cm}^{-1} \ \Gamma_{\rm f} = 0.6 \cdot 10^{14}$		



Figure S2.4.1 A) Simulated absorption spectra of the monomers and the dimer (blue and red lines for RHO and TAMRA, respectively, black line for the dimer): the spectra of the monomers are obtained by the effective three state model system and eq. $\$ MERGEFORMAT (T4.1) while the absorption profile of the dimer is computed using eq. T4.10. All the parameters used for simulations are reported in Table S4.1. The spectral region covered by the laser bandwidth is shaded in grey. B) Diagram of the energy levels taken into account in the simulation of the dimer response. C) Transition dipoles calculated according to eqs. (T4.6-T4.8) and used for simulation of the dimer response.

Starting from the three-state model describing the monomers we build the dimer Hamiltonian in the so called one-particle representation. Under these assumptions the model Hamiltonian can be represented in the following basis set: $|e_v^M\rangle = \{e_v^R\rangle |e_1^R\rangle |e_1^T\rangle \}$. Each basis set vector $|e_v^M\rangle$ represents the monomer *M* in its electronic excited state at the vibrational level v while the other chromophore is in its ground electronic and vibrational state. The four by four Hamiltonian reads:

$$H = \begin{pmatrix} E_{V}^{R} & 0 & J\langle 0|0\rangle^{T}\langle 0|0\rangle^{R} & J\langle 0|1\rangle^{T}\langle 0|0\rangle^{R} \\ 0 & E_{V}^{R} + \omega_{0}^{R} & J\langle 0|0\rangle^{T}\langle 0|1\rangle^{R} & J\langle 0|1\rangle^{T}\langle 0|1\rangle^{R} \\ J\langle 0|0\rangle^{T}\langle 0|0\rangle^{R} & J\langle 0|0\rangle^{T}\langle 0|1\rangle^{R} & E_{V}^{T} & 0 \\ J\langle 0|1\rangle^{T}\langle 0|0\rangle^{R} & J\langle 0|1\rangle^{T}\langle 0|1\rangle^{R} & 0 & E_{V}^{T} + \omega_{0}^{T} \end{pmatrix}$$

$$MERGEFOR MAT (T4.3)$$

where E_V^M is the vertical electronic transition energy of monomer M, J is the electronic coupling parameter and ω_0^M is the energy of the optically active effective vibrational mode of monomer M with Huang-Rhys factor HR that determines the overlap integrals:

$$\langle 0|0\rangle^{M} = \exp(-HR/2)$$

$$\langle 0|1\rangle^{M} = \sqrt{HR} \exp(-HR/2)$$
MERGEFOR
MAT (T4.4)

We use an electronic coupling constant J=1100 cm⁻¹. In a purely electronic exciton model the exciton splitting equals 2J, therefore the chosen value of the coupling parameter is consistent with the experimental value of the electronic gap ($\sim 2000 \text{ cm}^{-1}$) and the TDDFT computations (1640 cm⁻¹ or 2450 cm⁻¹ depending on the model of solvation, see Section 2.3).

The diagonalization of the Hamiltonian $*$ MERGEFORMAT (T4.3) gives four one-exciton eigenstates of the dimer that can be expressed in the local representation as:

$$\left| \mathbf{e}_{k} \right\rangle = \sum_{m} c_{m,k}^{T} \left| \mathbf{e}_{m}^{T} \right\rangle + \sum_{n} c_{n,k}^{R} \left| \mathbf{e}_{n}^{R} \right\rangle$$
MERGEFOR
MAT (T4.5)

with m=0,1 and n=0,1 denoting the vibrational state. Table S4.2 reports the energies and the amplitudes of the one exciton eigenstates in the local states obtained by the diagonalization of the model Hamiltonian * MERGEFORMAT (T4.3). Contributions higher than 20% to the composition of the eigenstate are explicitly reported next to the corresponding amplitude.

Table S4.2 Energies (shifted to match the abs	sorption maximum) and compos	osition of the dimer st	ates in the local states
obtained by the diagonalization of the model	Hamiltonian * MERGEFORM	MAT (T4.3).	

	$ \mathbf{e}_1\rangle$	$ \mathbf{e}_2\rangle$	$ \mathbf{e}_{3}\rangle$	$ \mathbf{e}_4\rangle$
	(16302 cm^{-1})	(17959 cm^{-1})	(18504 cm^{-1})	(19087 cm^{-1})
$\left e_{0}^{R} \right\rangle$	-0.7670 (59%)	-0.5679 (32%)	-0.0825	-0.2871
$ e_1^R\rangle$	-0.1316	0.4954 (25%)	-0.7534 (57%)	-0.4119 (17%)
$\left e_{0}^{T} \right\rangle$	0.6133 (38%)	-0.6383 (41%)	-0.3813	-0.2664
$ e_1^T\rangle$	0.1349	0.1568	0.5294 (28%)	-0.8228 (68%)
%RHO	60%	57%	57%	25%
%TAM	40%	43%	43%	75%

The transformation matrix defines transition dipoles and decoherence line-shapes for each transition in the dimer as linear combination of transition dipoles and decoherence line-shapes of the two monomers. In particular, the transition dipole moment between the one-exciton state e_k and the ground state reads

$$\mu_{e_{k}g_{0}} = \left|\mu_{R}\right|\sum_{m} c_{m,k}^{R} \left|\left\langle m\right|0\right\rangle^{R}\right| + \left|\mu_{T}\right|\sum_{n} c_{n,k}^{T} \left|\left\langle n\right|0\right\rangle^{T}\right|$$
MERGEFOR
MAT (T4.6)

To account for the contributions of ground state vibrations in the beating pattern of the 2D-response we explicitly include in the model three effective vibrational modes of the ground state having the same frequencies of the modes we identified in the first excited state S1 (600cm⁻¹, 980cm⁻¹, 1490cm⁻¹ see table S1.1). Following the same identification we used for S1, the modes at 600cm⁻¹ and 980cm⁻¹ are considered to belong to the first manifold of vibrations (see Fig. S2.3.7B and Fig. 2 of the main text) mainly localized on the rhodamine moiety. Therefore, we assume for them the same transition dipole calculated as

$$\mu_{e_k,g_{1,2}} = \left| \mu_R \right| \sum_m c_{m,k}^R \left| \left\langle m \right| 1 \right\rangle^R \right|$$
MERGEFOR
MAT (T4.7)

The vibrational analysis of Section S2.3 shows that the higher frequency modes involve also TAMRA vibrations (see Fig. S2.3.10). On this basis, the transition dipole for g_3 is assumed to be

$$\mu_{\mathbf{e}_{k},g_{3}} = \left|\mu_{T}\right| \sum_{m} c_{m,k}^{T} \left|\left\langle m \right| \mathbf{1} \right\rangle^{T} \right|$$
(T4.8)

Notice that the identification of g_3 as mainly due to TAMRA is purely formal since the model Hamiltonian does not describe the mixing of the ground state vibrations. This assumption, however, does not affect the modelling of the non-linear response since the transitions involving the g_3 level fall outside the laser excitation bandwidth.

The resulting set of transition dipoles are reported in Fig. S2.4.1C. The decoherence between the state e_k and e_j is described by the line-shape function:

$$g_{kj}(t) = \sum_{mm'} \left| c_{m,k}^{T} \right|^{2} \left| c_{m',j}^{T} \right|^{2} g_{mm'}^{T}(t) + \sum_{nn'} \left| c_{n,k}^{R} \right|^{2} \left| c_{n',j}^{R} \right|^{2} g_{nn'}^{R}(t)$$
(T4.9)

where the monomer line-shape function $g_{mm'}^{M}(t) = \int_{0}^{t} d\tau \int_{0}^{t} d\tau' C_{mm'}^{M}(\tau')$ is the double time integral of

the correlation function between the fluctuation of the *m* and the *m*' monomer states,⁵ defined in eq. * MERGEFORMAT (T4.2) for the $S_0 \rightarrow S_1$ transition. Assuming $k_B T < \hbar \omega_0$, the linear absorption spectra of the dimer can be calculated as:

$$S(\omega) = \omega \sum_{k} \left| \mu_{kg_0} \right|^2 \operatorname{Re} \int_{0}^{\infty} dt \exp\left(-i\left(\omega - \omega_{kg_0}\right)t - g_{kk}\left(t\right)\right)$$
(T4.10)

The absorption spectra are reported in Fig. S2.4.1A and compare well with the experimental ones especially within the region covered by the laser bandwidth. While the 4 state model Hamiltonian * MERGEFORMAT (T4.3) together of the parameter values gathered in Table S4.1 for the monomers gives a good description of the intensity enhancement caused by the mixing of the monomer transition dipoles, Eqs. (T4.6 - T4.8), it does not reproduce quantitatively the electronic energy gap and the transition frequencies observed in the experiment. We stress that the model is based on an effective, coarse-grained description of the vibrational structure of the monomers.

Considering two states for each monomer also implies an over simplification of the description of their interaction. For these reasons, comparison with TD-DFT results provides molecularly detailed information that is complementary to the effective description provided by the vibronic dimer model Hamiltonian. The vibrational analysis described in Section S2.3 points out that the effective vibration of the monomer corresponds to a bunch of molecular vibrations that are likely to be involved in the non-linear optical response. Moreover, the TD-DFT analysis shows that while indeed four excitations are mainly involved in the S₁-S₂ transition of the dimer, excitations involving other electronic states of the monomers also contribute (see Table S3.2). Ideally, one would need a more complicated coupling scheme with more than 2 vibronic states of the monomers to fully reproduce the TD-DFT and experimental results. Establishing such a model is beyond the scope of this paper. However, to verify whether a different choice of the states of the monomer improves the agreement with the experimental absorption in the whole range of energy, other possible choices were tested. In Figure S2.4.2 we show the results of including two vibrational modes of the RHO moiety (eR0, eR1, eR2) and only the GS of TAMRA (eT0) within a four-state (panel B) and two five-state (panels C-D) model Hamiltonians ((eR0, eR1, eR2, eT0, eT1) as specified in the figure caption. Panel A reports the four-state model (eR0, eR1, eT0, eT1) with a single active mode on each monomer used for calculating the 2D response for comparison.

In the first case (B), we included two effective vibrational states (eR1, eR2) in the rhodamine dve and only the electronic excited state of TAMRA (eT0). The frequency of the additional mode on RHO was chosen to be 600 cm⁻¹ as suggested by the analysis of harmonic modes with significant HR factors reported in figure S2.3.2. Other choices are equally likely because such low frequency modes do not change sensibly the calculated absorption profile of the rhodamine dye (dashed blue line in figure S2.4.2). It is instead important to maintain the high frequency mode to reproduce the vibronic shoulder (1450cm⁻¹ in the model of panel B). In this four-state model, the vibronic shoulder of TAMRA cannot be reproduced because no active modes of TAMRA are present. The black lines show the dimer spectrum for different coupling parameters (J=800, 900 and 1000) compared with the experimental spectrum (black solid line) and the spectrum obtained with the original four-state model parametrized as reported in Table S4.1 (magenta line). The peak around 18000 cm⁻¹ of the dimer is not well reproduced by the four-state model with two modes on rhodamine. This confirms that it is important to also include active vibrations of the TAMRA moiety to obtain a good agreement of the dimer spectrum in the region of interest. We have therefore considered five-state model Hamiltonians by keeping the two active modes on Rhodamine and the high frequency active mode on Tamra. The spectra obtained with two five-state models where the frequency of the additional mode on RHO has energy 600 cm⁻¹ and 300 cm⁻¹ are shown in panel C) and D) respectively for different values of the electronic coupling constant. The inclusion of the second mode on rhodamine does not significantly improve the agreement of the model with the experimental data compared to the minimal model where only one mode in each monomer are considered. Therefore, we conclude that four-state model representing a vibronic dimer gives the best balance between the quality of the obtained results and the number of fitting parameters.



Figure S2.4.2: Simulation of the absorption spectra of the monomers (RHO in blue, TAMRA in red) and the dimer (in black) resulting from model Hamiltonians with two vibrational active modes in the RHO moiety. Solid line are the experimental spectra, dashed/dotted lines are the simulated spectra, panel A shows the results obtained with the original four state model as parametrized in Table S4.1 for reference with the simulated spectra of the dimer in magenta. The spectrum obtained for the dimer with the four-state model of Table S4.1 is also reported in the other panels for comparison (magenta line). B) Four-state model where the two active vibrational modes on RHO have frequencies 600 cm⁻¹ (Huang Rhys factor 0.15) and 1450 cm⁻¹ (Huang Rhys factor 0.2) while TAMRA has only one electronic state. Due to the explicit consideration of an additional mode, the reorganisation energy of the slow part of the environment of RHO is decreased to $\lambda s = 250$ cm⁻¹. The coupling J=800 cm⁻¹ (dash-dotted line), 900 cm⁻¹ (dotted line) and 1000 cm⁻¹ (dashed line). All the other parameters are the same as in Table S4.1. C) Five-state model where RHO is described as in A) and TAMRA as in Table S4.1. The spectra of the dimer are obtained with coupling parameter J equals to 1100 cm⁻¹ (dashed line), 1000 cm⁻¹ (dotted line) and 900 cm⁻¹ (dotted line).

S2.5 Non-Linear Response Function of the dimer and 2D spectra

The rephasing part of the third order response function of the dimer can be written as a sum of two different types of the so-called Liouville pathways. They can be represented by the corresponding double-sided Feynman diagrams. Explicitly, the Ground State Bleaching contributions can be written as:

$$R_{g_{0}\alpha,g_{0}g_{v},\beta g_{v}}^{GSB}(t_{3},t_{2},t_{1}) = \left| \mu_{g_{0}\alpha} \right| \left| \mu_{\alpha g_{v}} \right| \left| \mu_{g_{0}\beta} \right| \left| \mu_{\beta g_{v}} \right| \exp\left\{ -i\omega_{\beta g_{v}}t_{3} + i\omega_{g_{v}g_{0}}t_{2} + i\omega_{\alpha g_{0}}t_{1} \right\} F^{GSB}(t_{3},t_{2},t_{1}) \\ F^{GSB}(t_{3},t_{2},t_{1}) = \exp\left\{ -g_{\alpha\alpha}^{*}\left(t_{1}\right) - g_{\beta\beta}\left(t_{3}\right) + g_{\alpha\beta}^{*}\left(t_{1} + t_{2} + t_{3}\right) - g_{\alpha\beta}^{*}\left(t_{1} + t_{2}\right) - g_{\alpha\beta}^{*}\left(t_{2} + t_{3}\right) + g_{\alpha\beta}^{*}\left(t_{2}\right) \right\}$$
(T5.1)

and the Stimulated Emission contributions are:

$$R_{g_{0}\alpha,\beta\alpha,\betag_{v}}^{SE}(t_{3},t_{2},t_{1}) = \left| \mu_{g_{0}\alpha} \right| \left| \mu_{g_{0}\beta} \right| \left| \mu_{ag_{v}} \right| \exp\left\{ -i\omega_{\beta g_{v}}t_{3} - i\omega_{\beta\alpha}t_{2} + i\omega_{\alpha g_{0}}t_{1} \right\} F^{SE}(t_{3},t_{2},t_{1})$$

$$F^{SE}(t_{3},t_{2},t_{1}) = \exp\left\{ -g_{\alpha\alpha}^{*}(t_{1}+t_{2}) - g_{\beta\beta}(t_{2}+t_{3}) + g_{\alpha\beta}^{*}(t_{1}+t_{2}+t_{3}) - g_{\alpha\beta}^{*}(t_{1}) - g_{\alpha\beta}^{*}(t_{3}) + g_{\alpha\beta}(t_{2}) \right\}$$
(T5.2)

The first part of each contribution is the product of four transition dipoles describing the amplitude of the specific non-linear optical transition. The complex exponential reflects the coherences involved during the three time periods t_1 , t_2 and t_3 and indicates the spectral regions where the pathway contributes and its behaviour during the population time t_2 . Finally, the third term indicated as $F^j(t_3, t_2, t_1)$ is a complex but decaying function, essentially determining the line-shape of the features in the 2D maps. The explicit form in terms of combination of coherence line-shape function, eq. T5.2, is obtained by applying the cumulant expansion methods to the evolution operator corresponding to the system-bath interaction Hamiltonian.⁵ Given the response function as the sum of all the contributions

 $S\left(t_{3},t_{2},t_{1}\right) = \sum_{\alpha\beta\nu} \left[R_{g_{0}\alpha,g_{0}g_{\nu},\beta g_{\nu}}^{GSB}\left(t_{3},t_{2},t_{1}\right) + R_{g_{0}\alpha,\beta\alpha,\beta g_{\nu}}^{SE}\left(t_{3},t_{2},t_{1}\right) \right]$

The third order polarization is obtained as a triple convolution of the system response function and the sample exciting electric field.⁷¹ In the limit of short pulses and for a well defined time ordering of the light-matter interactions, the spectra in the impulsive limit can be calculated directly from the response function as double Fourier transform with respect to t_1 and t_3 :

(T5.3)

$$S_{PE}(\omega_{1},t_{2},\omega_{2}) = \iint dt_{1}dt_{2} \exp(-i\omega_{1}t_{1})\exp(i\omega_{2}t_{3})S(t_{3},t_{2},t_{1})$$
(T5.4)

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