SUPPLEMENTARY INFORMATION

Two-Dimensional Electronic Spectroscopy Discloses Dynamics and Mechanisms of Solvent-Driven Inertial Relaxation in Polar BODIPY Dyes

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S1. Additional spectroscopic characterizations

S1.1 Time-resolved fluorescence

Time-resolved fluorescence measures show a clear decrease of the fluorescence lifetime going from THF to MeOH solutions. The presence of the nitro group quenches further the emission of the NO2-PHDB molecule, which is almost completely suppressed in MeOH. The quenching of the emission in more polar solvents and in the presence of electron withdrawing groups can be explained considering (i) the ICT nature of the excited states and (ii) the presence of photoinduced electron transfer (PET) processes.

![Fluorescence decay of NO2-PHDB (black) and PHDB (red) in THF (solid lines) and MeOH (dashed lines). Excitation at 390 nm. The table summarizes the results of a bi-exponential fit of the decay traces.](image)

|            | THF       | MeOH      |
|------------|-----------|-----------|
| NO2-PHDB   | 0.50 (85%)| 0.13 (94%)|
| PHDB       | 1.29 (39%)| 0.75 (94%)|
| NO2-PHDB   | 2.13 (15%)| 1.62 (6%)  |
| PHDB       | 2.28 (61%)| 2.99 (6%)  |

Figure S1.1. Fluorescence decay of NO2-PHDB (black) and PHDB (red) in THF (solid lines) and MeOH (dashed lines). Excitation at 390 nm. The table summarizes the results of a bi-exponential fit of the decay traces.

S1.2 Temperature dependence

In order to exclude possible factors causing the fluorescence quenching in MeOH, as the formation of aggregates or dimers, a solution of NO2-PHDB in MeOH has been warmed at 50 and 60°C. No relevant changes can be detected in UV-vis spectra.

![UV-vis and RLS spectra of NO2-PHDB in MeOH upon heating.](image)

Figure S1.2. (a) UV-vis and (b) RLS spectra of NO2-PHDB in MeOH upon heating.
**S1.3 pH dependent spectral changes in MeOH**

To exclude the presence of fully or partially protonated forms of BODIPY (involving amine groups in para position on the distyryl moieties), a spectroscopic characterization as a function of pH has been performed. This investigation confirmed that in the experimental conditions adopted in this work the amine groups in both NO2-PHDB and PHDB are in the free base form. Note that at acidic conditions, more emissive species are formed, in agreement with previous findings on similar structures\(^1\). These results can be interpreted with the presence of PET processes occurring when the amine is unprotonated, causing fluorescence quenching.\(^2-5\)

![Figure S1.3](image)

**Figure S1.3.** (a) UV-vis, (b) emission decay profiles, (c) fluorescence excitation and (d) emission spectra of NO2-PHDB in MeOH upon HCl addition.
Figure S1.4. (a) UV-vis, (b) emission decay profiles, (c) fluorescence excitation and (d) emission spectra of PHDB in MeOH upon HCl addition.
S2. Quantum Mechanical Calculations.

S2.1 Absorption and emission vertical energies via TDDFT-PCM calculations.

As reported in the main test the solvent effects have been included by using the PCM method. In this method, solvent is represented as a homogeneous dielectric medium surrounding the solute molecule that is placed in a cavity built as the envelop of spheres centered on the atomic positions. The solution of a proper Poisson’s equation allows mutual polarization between the solute and solvent in a cost effective way.

In the investigation of absorption and emission problems with the PCM method two approaches are usually employed, that is, state specific (SS) and linear responses (LR) approaches. 6,7

In the former, solvent reaction field is variationally determined together with all the other parameters in the electronic method used (i.e. MOs and CIs coefficients). This method can result quite expensive and it has been implemented in G09 code only for single point calculations and thus the cheaper LR formalism is usually used.

In the latter approach, the excitation energies are determined including a PCM correction dependent on the electron density variation associated with the ground-to-excited state transition.

To describe the solvent degrees of freedom during electronic excitations (absorption) and de-excitation (emission) processes in PCM calculations the non-equilibrium (NEQ) and the equilibrium (EQ) time regimes are usually employed.

In the former, only the solvent electronic polarization is in equilibrium with the excited state electron density of interest whereas in the latter all the solvent degrees of freedom are in equilibrium with the electron density. NEQ-PCM is most suitable for the calculation of absorption processes in solution whileEQ-PCM is the preferred choice for the study of excited state structural relaxation processes.

In this work, the calculation of vertical excitation and emission processes of the three molecules in methanol have been carried out by employing the NEQ-LR-PCM and EQ-SS-PCM approaches, respectively.

Table S2.1 reports the absorption and emission transition energies for the two molecules investigated together with the experimental $\lambda_{max}$.

|          | Abs. $\lambda_{S0,S1}$ (nm) | Emi. $\lambda_{S1,S0}$ (nm) | Stokes’ shift $\Delta\lambda$ (nm) |
|----------|-----------------------------|-----------------------------|---------------------------------|
|          | Calc.           | Exp.           | Calc.           | Exp.           | Calc.           | Exp.           |
| Methanol |                |                |                  |                |                  |                |
| PHDB     | 572.0          | 680            | 640.0           | 729            | 68.0            | 49             |
| NO$_2$-PHDB | 580.7        | 676            | 632.2           | 721            | 51.5            | 45             |
| THF      |                |                |                  |                |                  |                |
| PHDB     | 576.5          | 688            | 633.6           | 714            | 57.1            | 26             |
| NO$_2$-PHDB | 585.1        | 688            | 624.5           | 711            | 39.4            | 23             |
S2.2 Ground and excited frequencies and normal modes.

The harmonic frequencies and normal modes have been computed for the PHDB and NO2-PHDB molecules for both the ground and excited state in order to determine the similarity between the two sets of normal modes of the two excited states. Figure S2.1 reports the correlation plots between the ground and excited state frequencies and Duchinsky (\(J\)) matrix defined in the Cartesian coordinates as \(J = (L_I)^T L_F\) where \(L\) is the transformation matrix from mass-weighted Cartesian to normal coordinates. I and F stands for initial (ground) and final (excited) states. The perfect correlation between the ground and excited frequencies and the diagonal form of the Duchinsky matrix confirm that for both molecules the normal modes of vibrations are very similar in the two states.

![Correlation plots](image)

Figure S2.1. Correlation plot between ground and excited states frequencies for PHDB (a) and NO2-PHDB (c). Duchinsky matrix for PHDB (b) and NO2-PHDB (d).

Figure S2.2 reports the eigenvectors of the normal modes associated to the more relevant vibrational transitions observed in the Raman spectra for the two molecules. The wavenumbers are those computed at the harmonic level without accounting for anharmonic effects.
**Figure S2.2.** Normal modes of PHDB and NO2-PHDB corresponding to the vibrational transitions individuated in the RAMAN experimental spectra. The wavenumbers are those computed at the harmonic level without any correction for anharmonic effects.

**S2.3 Vibrationally resolved spectra of PHDB molecule.**

Fig. S2.3 compares the theoretical stick absorption and emission spectra (blue) of the PHDB molecule with the experimental ones (red) in THF solvent.

The spectra have been computed by using the Franck-Condon (FC) approximation for the transition dipole moment coupled with the Adiabatic Hessian (AH) strategy without including temperature effects but assuming that only the vibrational ground state is populated in the initial electronic state ($S_0$ for the absorption spectra and $S_1$ for the emission one). To save computational time and since we have observed that the electronic
properties of the molecule do not change we have removed in vibronic calculations the ethyl groups of the bodipy core.

The agreement between the two spectra is good with the shoulders and tails present in the experimental spectra being due to vibronic transitions rather than to other electronic transitions among different states. As expected, the 0-0 transition is the dominant one in all the cases whereas the shoulders are composed of a blend of several vibrational states.

The most important vibronic contributions are assigned in the figure and are due to single quanta excitation of one normal mode. In particular, the shoulder in the absorption spectrum is given by the single quanta excitation of normal modes 35 (333 cm\(^{-1}\) with respect to the 0-0 line), 113 (1097 cm\(^{-1}\)), 132 (1315 cm\(^{-1}\)), 156 (1531 cm\(^{-1}\)) and 166 (1626 cm\(^{-1}\)) whereas the shoulder in the emission spectra is ascribed to the excitation of a single quanta of normal modes 150, 169 and 172. All these normal models are reported in Fig S2.4. Mode 35 is due to the out of plane wagging of the NH\(_2\) group; mode 113 to the breathing of the BODIPY core; mode 132 and 156 to the bending of the aromatic CH bonds of the entire molecule whereas mode 166 to the bending and stretching of hydrogen bonds of the styryl group. However, it must be kept in mind that all these normal modes involve the simultaneous oscillation of several atoms of the molecule and results extremely difficult to classify them.

**Figure S2.3.** Comparison between the experimental (red lines) and computed (blue histograms) absorption and emission vibronic spectra of PHDB molecule in THF solvent. The theoretical spectra have been shifted in order to have the best agreement with the experiments.
**Figure S2.4.** Normal modes of the S₁ (35, 113, 132, 156 and 166) and S₀ (150, 169 and 172) electronic state of PHDB in THF, at the CAM-B3LYP level of theory.

**S3. Raman spectroscopy**

Raman spectra have been performed with a home-built micro-Raman system, based on a Triax-320 ISA spectrograph, equipped with a holographic 1800 g/mm grating and a CCD detector (Spectrum One ISA Instruments). The excitation source was a He-Ne laser at 633 nm. A Kaiser Optical System holographic notch filter was used to reduce the stray-light level. An Olympus BX 40 optical microscope equipped with a 20x/0.75 objective was optically coupled to the spectrograph. To avoid optical damage to the sample, the power of the exciting radiation was maintained between 0.15 and 0.5 mW. The Raman spectra were recorded on crystalline powders of the compounds between 200 and 2000 cm⁻¹ and with an instrumental resolution of about 2 cm⁻¹.
S4. 2D electronic spectroscopy (2DES)

S4.1 Setup

2DES measurements have been performed with the setup described in ref\textsuperscript{10}. The pulses energy at the sample position is reduced until 5 nJ per pulse by a broadband half-waveplate/polarizer system. 

\( t_2 \) 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 80 fs in steps of 0.32 fs.

To characterize the temporal properties of the exciting pulses, we performed FROG measurements in the same experimental conditions of 2DES measures, only replacing the sample solution with a solvent in the same 1 mm path-length cuvette. We retrieved a pulse duration of 14.5 fs, reasonably assuming gaussian pulses (Fig. S4.1).

![FROG](image)

**Figure S4.1.** a) FROG performed in the same experimental condition of the 2DES experiment. b) FROG signal integrated along the frequency axis. The experimental curve (blue dots) is well fitted by a gaussian function with FWHM of 20.6 fs (red line), leading to a pulse duration of 14.5 fs.

To ensure the reliability of the measures, at least 3 different sets of measures in different days were performed and then averaged. All measurements were performed under ambient temperatures (295 K).

Additional 2DES spectra are reported in Fig. S4.2.

S4.2 Global fitting analysis

2DES signals are analyzed with a global complex multi-exponential fit method as proposed in \textsuperscript{11}. Briefly, the decay of the total complex signal at each point of the 2D map is fitted with a global function written as sum of complex exponentials:

\[
f = \sum_{n=1}^{N} a_n e^{i\phi_n} e^{-t_2/\tau_n e^{i\omega_n t_2}}
\]

Components with \( \omega_n=0 \) describe population decay contributions, whereas components with \( \omega_n \neq 0 \) represent oscillating components associated to coherent dynamics along \( t_2 \). The corresponding amplitude plotted in a 2D
map as a function of $t_1$ and $t_3$ builds the so-called DAS (decay associated spectra) and CAS (coherence associated spectra), respectively.

These maps allow the direct visualization of the sign and the amplitude distribution of a particular decay component along the 2D spectra. Given the $n$-th component associated to the time constant $\tau_n$, a positive amplitude (red areas) will be found at positions in the 2D maps where the signal is decaying with $\tau_n$, whereas a negative amplitude (blue areas) will be found where the signal is rising with $\tau_n$.

To avoid possible contaminations at early time due to coherent artifacts, the first 15 fs have been discarded from the fitting procedure.

**S4.3 Time-frequency transform (TFT) analysis**

The time-frequency analysis was performed using the smoothed-pseudo Wigner-Ville distribution (SPWV)\textsuperscript{12}:

$$SPWV = \int_{-\infty}^{+\infty} h(t') \int_{-\infty}^{+\infty} g(t'' - t)s \left( t'' + \frac{t'}{2} \right) s^\prime \left( t'' - \frac{t'}{2} \right) e^{-i2\pi vt'} dt'' dt'$$

where $g$ and $h$ windows are gaussian functions with standard deviation $\sigma_g=50$ fs, $\sigma_h=100$ fs. The time windows operate a smoothing of the Wigner-Ville distribution and suppress the interference terms, which would otherwise damage the overall analysis adding oscillating features in the time frequency plane.

Fig.S4.3 compares the time-frequency transform analysis of the oscillating residuals at coordinates $(14500,13800)$ cm$^{-1}$ for NO2-PHDB in THF (a) and in MeOH.
Figure S4.2. (a) Experimental and simulated 2D maps for PHDB in THF at selected values of population time T. On the right, we report the 2D decay associated spectrum (DAS1) associated to the ultrafast relaxation dynamics with time constant 13 fs. (b) Same as before but for NO2-PHDB in THF. DAS1 is associated to a time constant of 29 fs. (c) and (d) Experimental 2D maps and DAS1 for PHDB and NO2-PHDB in MeOH, respectively. Time constants associated to DAS1 are 16 and 41 fs for PHDB and NO2-PHDB, respectively.
Figure S4.3. Time-frequency transform analysis of the oscillating residuals at coordinates (14500,13800) cm$^{-1}$ for NO2-PHDB in THF (a) and in MeOH (b). Upper panels: oscillating residuals at the studied coordinates. Left panels: Fourier spectra of the oscillating residuals.

S4.4 2DES simulation

2DES rephasing spectra are calculated using a well-established framework of methods based on third order perturbation theory$^{13-15}$. The third order polarization $P^{(3)}(t)$ of the sample is given by the convolution of a response function $S^{(3)}(t_1, t_2, t_3)$ with all the exciting pulses as

$$P^{(3)}(t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 S^{(3)}(t_1, t_2, t_3) E(t - t_3) E(t - t_2 - t_3) E(t - t_1 - t_2 - t_3),$$

where $E(t)$ is the electric field of the pulses, and $t_1$, $t_2$ and $t_3$ are the times of each field interactions.

The response function is then modeled employing a two-level system, ground state ($S_0$) and excited state ($S_1$), with vertical transition energy ($\omega_0$) of 14550 cm$^{-1}$ and 14630 cm$^{-1}$ respectively for NO2-PHDB and PHDB. Nuclear degrees of freedom are included into the model as overdamped oscillation of the bath, which are responsible for the dephasing. In particular two semi-classical overdamped Brownian oscillators$^{16}$ are included into the lineshape function $g(t)$, effectively shaping the low frequency domain of the spectral density of the bath fluctuations coupled to the electronic transition. High frequency vibrational modes coupled to the electronic transition are not included in the model. The contribution of the $n$-th oscillator is specified as

$$g_n(t) = \frac{\lambda_n}{\gamma_n} \left( \frac{2k_B T}{\gamma_n} - i \right) \left( e^{-\gamma_n t} + \gamma_n t - 1 \right)$$

where $\lambda_n$ is the reorganization energy, $\gamma_n$ is the relaxation rate, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. The total lineshape function is then $g(t) = g_1(t) + g_2(t)$, with parameters reported in Table S4.1.
In a two-level system, the rephasing response function can be written as sum of two different contributions
$$R_{n}(t_1, t_2, t_3) = |\mu|^4 \exp \left( +i\omega_0 t_1 - i\omega_0 t_3 - g^*(t_1) + g^*(t_2) - g(t_3) \right)$$
$$-g^*(t_1 + t_2) - g^*(t_2 + t_3) + g^*(t_1 + t_2 + t_3)),$$
$$R_{3}(t_1, t_2, t_3) = |\mu|^4 \exp \left( +i\omega_0 t_1 - i\omega_0 t_3 - g^*(t_1) + g(t_2) - g^*(t_3) \right)$$
$$-g^*(t_1 + t_2) - g(t_2 + t_3) + g^*(t_1 + t_2 + t_3)),$$

The impulsive rephasing response function is then fully convoluted in the time domain with the experimental laser pulses using the procedure reported in Ref.\textsuperscript{16}. The parameter in Table 5.1 were tuned in order to have a good match of the experimental 2DES signal and the convolved simulated 2DES signal, keeping at the same time a good match of the linear absorption spectra calculated as
$$ABS(\omega) \propto 2\omega|\mu|^2 \Re \int_0^\infty dt \exp \left( i(\omega - \omega_0)t - g(t) \right).$$

A comparison of experimental and simulated linear and laser spectra are reported in Fig. S4.4.

**Figure S4.4.** Experimental and simulated linear absorption spectrum with superimposed experimental and simulated laser spectrum for NO2-PHDB (left) and PHDB (right).
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