Modelling ultrafast fluorescence dynamics: dependence of the solvent response dynamics on the fluorophore nature

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Abstract

- The spectral fluorescence dynamics of two dyes, covalently linked perylene dimethylaniline (**PeDMA**) and coumarin 153 (**C153**), was analyzed using similar theoretical approaches [1, 2].
- The approaches incorporates the description of the solvent relaxation and redistribution/relaxation of intramolecular high-frequency vibrations proceeding in parallel with the pumping.
- Experimental spectra of both dyes were obtained at the same setup [3].
- A comparison of the solvent response to different dyes shows that the solvation dynamics depends on the fluorophore.

Stationary and non-stationary spectra of PeDMA
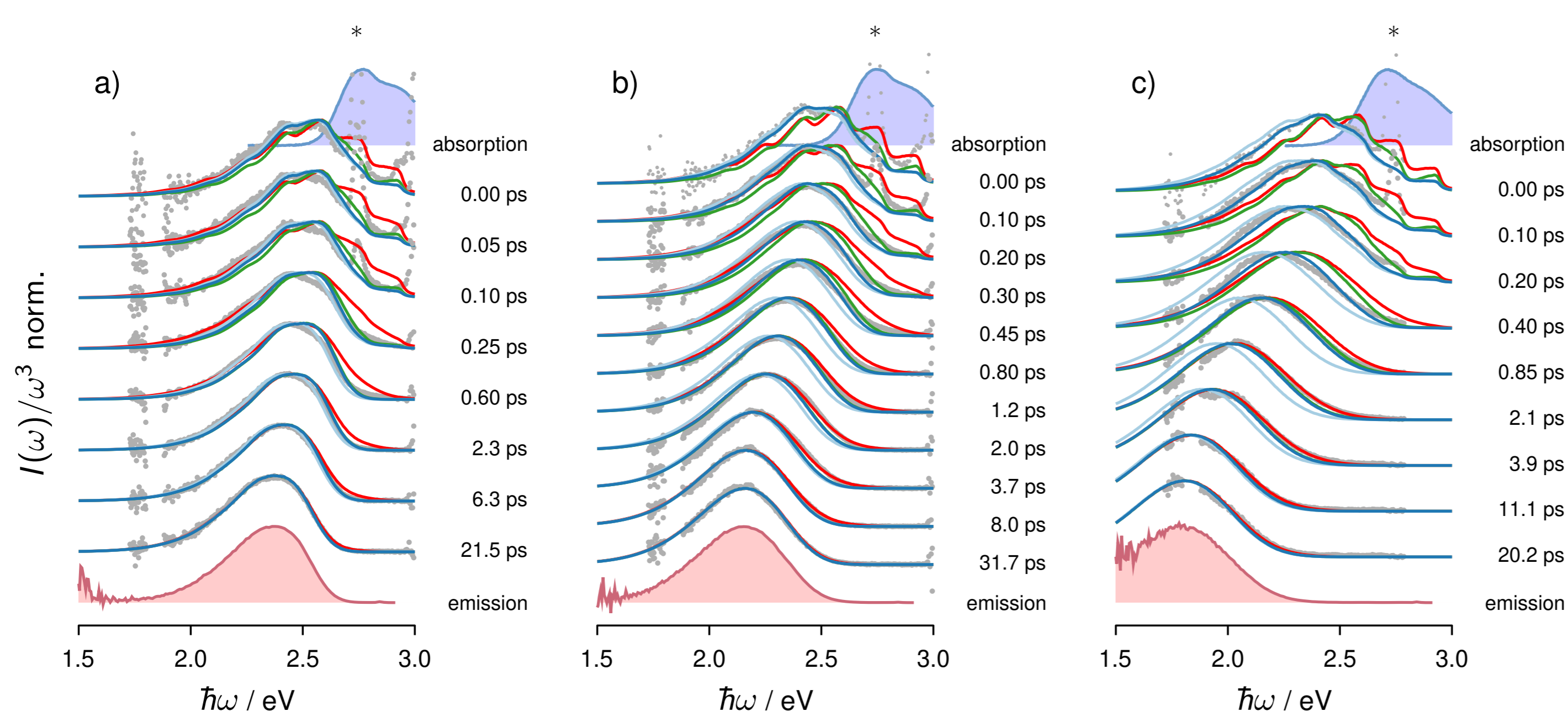
*Solvents:* a) iso-propyl-ether, b) tetrahydrofuran and c) dimethylsulfoxide.

Experimental data: the grey dots are spectral dynamics of fluorescence; the blue and red filled curves represent stationary absorption and fluorescence spectra, respectively.

The red and green lines represent the simulation results using the solvent relaxation function, $X(t) = \sum_i x_i e^{-t/\tau_i}$, obtained by using **C153**. The red and green lines differ only in the intramolecular vibrational relaxation time constants of **PeDMA**. The red lines show slower vibrational relaxation than the green lines. The time constants of slow vibrational relaxation were estimated from the spectra of nonstationary fluorescence of **PeDMA** in weakly polar n-hexane.

The light and dark blue lines represent the simulated spectral dynamics when going from **C153** to **PeDMA** solvent response. The light blue lines correspond to $\widetilde{X}_a(t) = 0.3e^{-t/\tau_0} + 0.7\,X(t)$ and the dark blue lines correspond to $\widetilde{X}_b(t) = x_1\left(0.6e^{-t/\tau_0} + 0.4e^{-t/\tau_1}\right) + \sum_{i=2} x_i e^{-t/\tau_i}$, where $\tau_0 = 0.04$ ps. Here, the vibrational relaxation time constants are the same as in the case of the green lines.

The function $X(t)$ describes the microscopic relaxation of the solvent around the fluorophore. $X(t)$ is closely related to the time dependent Stokes shift measured in experiments.
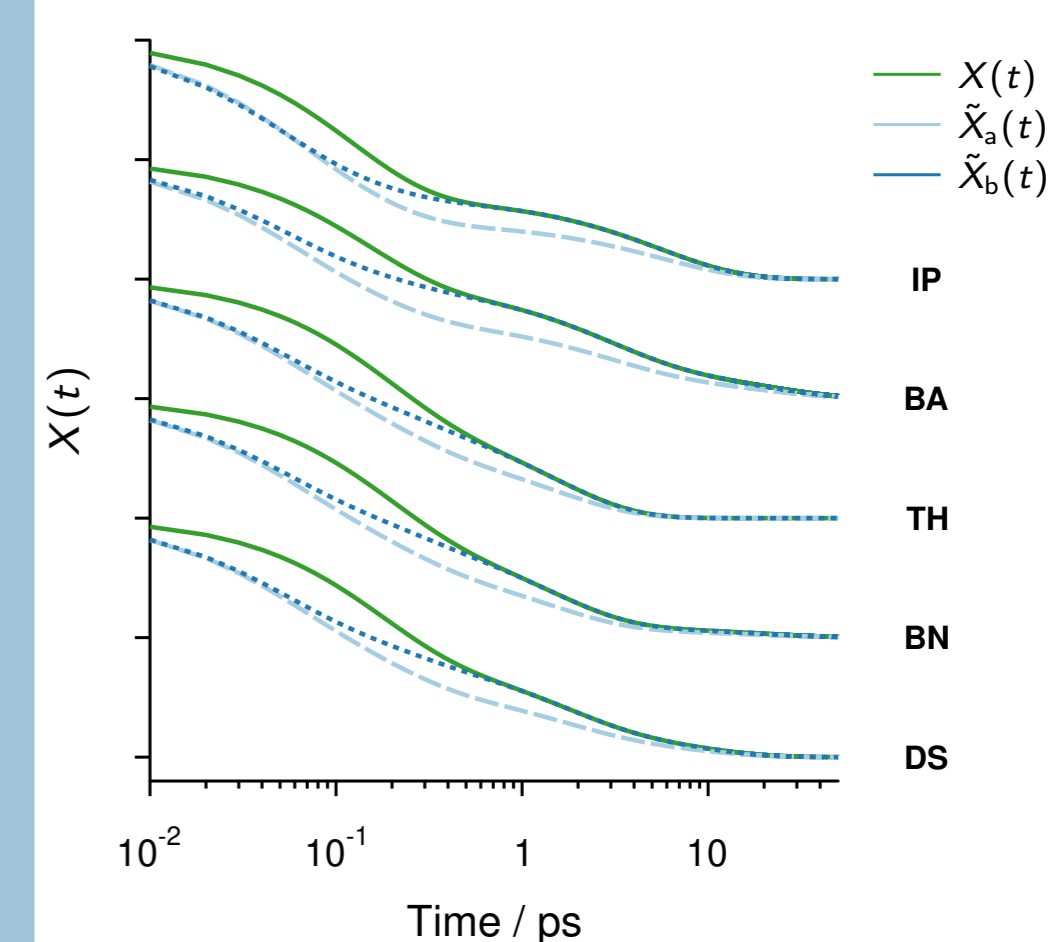
C153

Coumarin 153
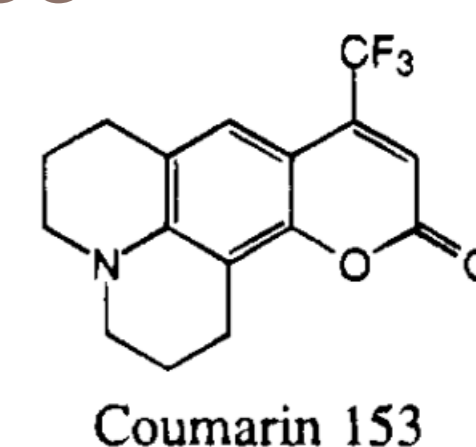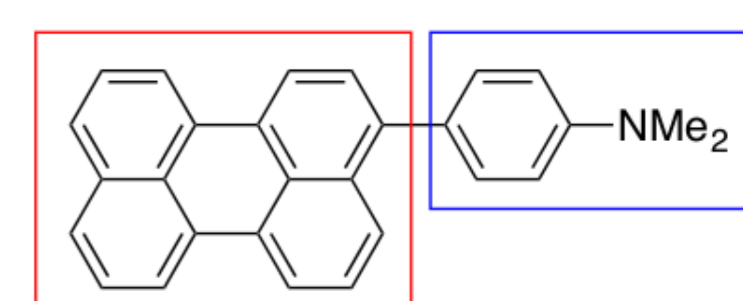
PeDMA

The red and blue boxes represent perylene and dimethylaniline, respectively.

Conclusion on the solvent response to PeDMA

- As the solvent polarity increases, the fast relaxation component of $X(t)$ becomes even faster.
- Moderately polar solvents are better described by $\widetilde{X}_a(t)$, and more polar solvents are better suited by $\widetilde{X}_b(t)$.
- Such a nonlinear change in the relaxation function indicates that the solvent response depends on the nature of the fluorophore.

Acknowledgements

References

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(2) R. G. Fedunov, I. P. Yermolenko, A. E. Nazarov, A. I. Ivanov, A. Rosspeintner and G. Angulo, *Journal of Molecular Liquids*, 2020, **298**, 112016.
(3) X.-X. Zhang, C. Würth, L. Zhao, U. Resch-Genger, N. P. Ernsting and M. Sajadi, *Review of Scientific Instruments*, 2011, **82**, 063108.

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