Mapping the evolution of spatial exciton coherence through time-resolved fluorescence

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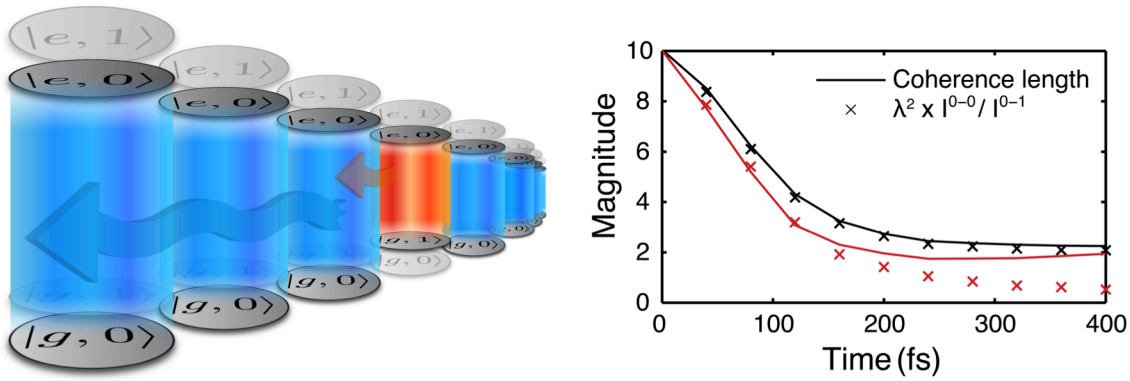
We demonstrate that time-resolved fluorescence allows one to continuously monitor exciton coherence between molecules featuring a pronounced vibronic progression. The degree of coherence is shown to be directly reflected in the spectral vibronic peaks. Fluorescence excludes ground state vibrations, which makes this excited state coherence measure unambiguous to interpret.

Exciton coherence attracts great interest due to its anticipated impact on the functioning of photosynthetic complexes and synthetic photovoltaics. Nevertheless, in order to determine its functional relevance, experiments are in demand in which signals from exciton coherence can unambiguously be distinguished from those from ground state vibrations. For 2D electronic spectroscopy, the preeminent technique for probing coherent phenomena, making this distinction has proven to be troublesome. We propose an alternative experimental means for coherence detection that is not susceptible to ground state vibrations: time-resolved fluorescence, when applied to molecular assemblies featuring a distinct (high-frequency) vibronic progression, is shown to indicate the coherent exciton sharing between distant molecules [1]. Through numerical simulations we demonstrate how an excitation, coherently prepared over a long spatial range, undergoes coherence decay, and how time-resolved fluorescence allows one to monitor this process in time (Figure). The first experimental report employing this principle has appeared in press recently [2].



(Left) Artist impression of how spatial exciton coherence is reflected in time-resolved fluorescence. The 0-0 vibronic signal (blue) experiences a coherent enhancement, whereas the 0-1 signal (red) does not. Taking the ration of the signals yields the coherence measure. (Right) Calculated evolution of the 0-0 to 0-1 peak ratio and coherence length for a J (black) and an H-aggregate (red).

[1] R. Tempelaar, F.C. Spano, J. Knoester, and T.L.C. Jansen, J. Phys. Chem. Lett. **5**, 1505 (2014).
[2] J. Sung, P. Kim, B. Fimmel, F. Würthner, and D. Kim, Nature Communications **6**, 8646 (2015).