Ultrafast nonlinear dynamics of the structure-specific fluorescence in protein structures

G. Soavi[1], S. Bourelle[2], G. Wang[1] , A. Lombardo[1], and G. Kaminski Schierle[3]

[1] *Cambridge Graphene Centre, Engineering Department, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0FA*

[2] *Optoelectronics Group, Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE*

[3] *Department of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive, Cambridge CB3 0AS*

Understanding the mechanisms associated with the formation of protein fibrils, the kinetic aspects of their aggregation in different environment and their optical properties is a subject of intense investigation, as many of these structures are associated with neurodegenerative diseases such as Alzheimer's and Parkinson's disease. The three-dimensional arrangement of protein fibrils consists to a large extent of β-sheets, which are stabilised by a dense network of hydrogen bonds (H-bonds). Upon fibrillisation, such structures reach the thermodynamically most stable state, and the ensuing H-bonds interconnecting the β-sheets have been shown to be stronger than those found in any other folded protein.

These biomolecular assemblies are attractive nanostructures due to their biocompatibility, straightforward chemical modifiability and their potential for bottom-up fabrication. We have shown [1] that peptide nanofibrils can absorb light at energies in the near UV range and exhibit a structure-specific intrinsic fluorescence in the visible range even in the absence of aromatic amino acids, a newly observed phenomenon. Our recent experimental study, in combination with molecular dynamics and TD-DFT calculations, shows that the origin of this fluorescence is due to charge delocalisation and proton transfer along the dense hydrogen bond network of the β-sheet nanofibril structure. The presence of a structure-specific fluorophore in these structures has a wide range of potential applications such as bio-inspired self-assembled optical materials and biomolecular nanoantennas for light harvesting.

Here we use time-resolved ultrafast spectroscopy to gain further insights into the origin of this intrinsic fluorescence and its temporal evolution on a ps timescale. In particular, we use excitation correlation photoluminescence (ECPL) [2] to resolve excited state dynamics in Aβ42 fibrils. In the ECPL experiment we measure the time integrated PL upon photoexcitation with two temporally delayed pump pulses of equal intensity and equal wavelength of 360nm. The presence of density-dependent competing nonradiative channels is responsible for a superlinear or sublinear behavior of the PL with intensity, resulting in a nonzero ECPL signal. Thus, ECPL specifically picks out the contribution of the limiting nonradiative channels from the overall recombination dynamics. Interestingly, we observe both super-linear and sub-linear recombination mechanisms as a function of the excitation fluence in Aβ42 fibrils and we measure a sub-ns excited state lifetime. These results suggest the presence of a complex excited state landscape where the recombination channels can be modulated by interaction with light.

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