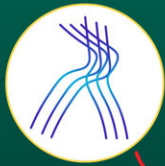


Unraveling the mechanism of green emission peaks in single polyfluorene chains

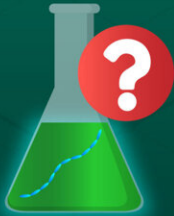
April 26 2023

Unveiling the Spectral Features of Single Conjugated Polyfluorene Chain

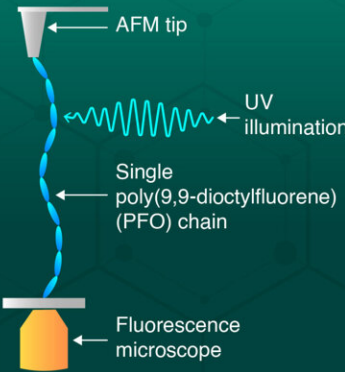
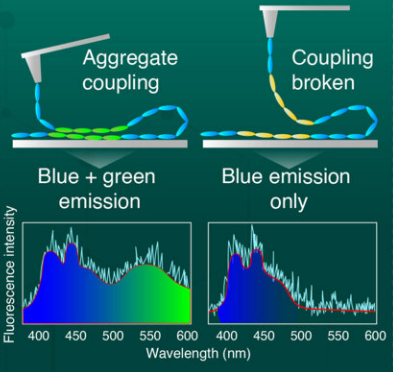
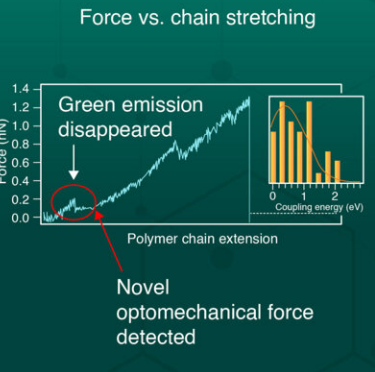
Molecular aggregation in conjugated polymers gives rise to unique spectral properties



Polyfluorene, a conjugated polymer, occasionally shows a green emission whose origin is unknown




Simultaneous atomic force microscopy (AFM) and fluorescence measurement on a single polyfluorene chain

Mechanical manipulation with AFM	Fluorescence spectroscopy	AFM measurements
 <p>Labels: AFM tip, UV illumination, Single poly(9,9-dioctylfluorene) (PFO) chain, Fluorescence microscope</p>	 <p>Labels: Aggregate coupling, Coupling broken, Blue + green emission, Blue emission only</p>	 <p>Labels: Force vs. chain stretching, Green emission disappeared, Polymer chain extension, Novel optomechanical force detected</p>

Intra-chain aggregation of light-absorbing molecules is responsible for the generation of additional spectral peaks that can be controlled with mechanical manipulation

Simultaneous Force and Fluorescence Spectroscopy on Single Chains of Polyfluorene: Effect of Intra-Chain Aggregate Coupling
Nakamura et al. (2023) | ACS Nano



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Tokyo Institute of Technology

Graphical abstract. Credit: Tokyo Tech

Molecular aggregates are clusters of small molecules held together by relatively weak forces believed to be originating from electronic interactions between the molecules. Owing to their exceptional photophysical properties, molecular aggregates find unique applications in many areas of technology and continue to be a subject of intense research. In fact, researchers have utilized molecular aggregates to engineer a variety of functional materials, biomedical tools, and nanodevices.

However, the phenomenon of molecular aggregation is not limited to small molecules alone. Individual polymer segment chains can also interact with one another and give rise to phenomena that are very similar to those found in molecular aggregates. One such example is polyfluorene, a conjugated polymer that, when excited by UV radiation or an appropriate electric field, emits a bright blue light in solution.

Despite being a well-researched polymer, the spectral peaks for polyfluorene have long been the subject of speculation. It turns out that, in addition to the blue emission, it occasionally also emits a green emission, the cause of which has been debated in the scientific community. One plausible explanation for the green emission is that it results from the occurrence of photooxidation reaction. However, there is also evidence that favors the interchain aggregation of chain segments as a cause.

A group of researchers from Tokyo Institute of Technology, Japan, led by Professor Martin Vacha, recently developed an innovative experimental protocol that aimed to resolve this knowledge gap. In their study published in *ACS Nano*, the researchers combined two microscopy

techniques to perform precise photomechanical measurements in poly(9,9-dioctylfluorene) (PFO), a prototypical kind of polyfluorene.

First, a single PFO chain was chemically attached to the tip of an atomic [force](#) microscope (AFM) on one end and to a transparent substrate on the other end. Initially folded, the PFO chain was then stretched slowly by precisely controlling the position of the AFM tip.

As a result, the AFM could constantly gauge the amount of mechanical force required for the PFO chain to stretch. Simultaneously, the team measured the spectra of the light emitted by PFO upon UV illumination using a fluorescence microscope placed beneath the substrate. This helped them study the changes in emission spectrum of the PFO chain with mechanical stretching.

They observed a green emission band accompanying the blue emission band during the initial stage of stretching. The green emission band disappeared eventually as the folded chain was stretched and the intra-chain aggregates broke up, which was confirmed by the AFM measurements.

Explaining these observations, Prof. Vacha says, "Our work presents a direct evidence that the green emission band is observed due to intra-chain aggregation of PFO, which undergoes breakup on mechanical unfolding, and results in the disappearance of the green emission."

Additionally, the team also observed additional spectral features, suggesting a novel optomechanical force acting on some of the PFO chains. On further analysis, they found this force to be originating from the breakup of intra-chain aggregate coupling upon UV illumination. The nature of this coupling was determined through precise analyses.

Prof. Vacha highlights, "The force by which the aggregate was coupled

and the length for which the coupling was effective revealed that this optomechanical force results from van der Waals interactions and excitonic coupling."

These pioneering techniques could find intriguing applications in a variety of fields, including energy conversion in molecular motors or the nano-mechanical manipulation of molecular properties in [polymer chains](#) and molecular nanofibers.

More information: Tomonori Nakamura et al, Simultaneous Force and Fluorescence Spectroscopy on Single Chains of Polyfluorene: Effect of Intra-Chain Aggregate Coupling, *ACS Nano* (2023). [DOI: 10.1021/acsnano.2c09773](#)

Provided by Tokyo Institute of Technology

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