

DETERMINATION OF MOLECULAR ORIENTATIONS IN SINGLE POLYFLUORENE NANOWIRES USING POLARISATION DEPENDENT NONLINEAR MICROSCOPY

Pierre Lovera, Gareth Redmond

Tyndall National Institute, Lee Maltings, Prospect Row, Cork, Ireland

pierre.lovera@tyndall.ie

One-dimensional (1D) nanostructures based on molecular and polymeric materials are attracting significant research interest due to the many novel chemical, physical and electronic properties that may arise in such systems and the possibility for exploitation of their properties in a variety of applications. In terms of useful polymeric materials, polyfluorene based π -conjugated polymers are attractive due to their excellent charge transport properties, high photoluminescence (PL) quantum efficiencies and chemically tuneable emission wavelengths. Poly(9,9-dioctylfluorene) (PFO) is a prototypical main chain liquid crystalline homopolymer that emits in the blue and can exhibit a variety of different phases. Incorporation of PFO into 1D nanostructures would be an important advance since it would offer the potential to exploit the diverse benefits of this unique polymer in nanowire based photonic and electronic devices. To this end, we developed a novel way to synthesise PFO nanowires with semi-crystalline internal morphologies by exploiting the method of melt-assisted template wetting. The resulting wires exhibited regular cylindrical morphologies with well-defined end facets allowing nanowire active waveguiding, Fabry-Pérot microcavity behaviour and optically pumped lasing to be achieved ^[1-3].

More recently, we extended these studies to demonstrate that PFO nanowires can also be synthesized by solution-assisted template wetting and that these wires also exhibit attractive properties ^[4]. For example, investigation using linear optical methods revealed that the wires contained a significant fraction of β -phase PFO, in which polymer chain segments adopt a planarised and extended conformation, and that, as a consequence, the wires essentially acted as self-doped 1D nanostructures in which the β -phase dominated the luminescence behaviour following optical, electrochemical or electrical excitation. However, given the diverse range of potential applications available to these novel structures, one topic of great importance merits significant attention, namely, the development of an understanding of the effects of processing conditions on the extent of internal molecular organisation within PFO nanowires.

To address this challenge, we selected β -phase containing PFO nanowires as model 1D organic nanostructures and, for the first time, studied the internal molecular arrangements within single wires using a combination of third harmonic generation (3HG) and three photon excited luminescence (3PEL) imaging and spectroscopy. The dependence of three photon effects on the cube of the incident laser intensity provides for higher spatial resolution as compared with one photon methods and the use of a

near-IR laser as the excitation source (1064 nm) minimises both optical damage and scattering background at the sample. These advantages are critical for imaging potentially fragile organic nanostructures. Another benefit is that three photon methods may show superior sensitivity to molecular anisotropy, relative to linear methods, as a result of the directionality induced by the multiphoton interaction.

In this talk, I will present results that demonstrate, for the first time, 3HG in single conjugated polymer, PFO, nanowires. Notably, by measuring polarisation dependent 3HG spectra, a pronounced dependence of excitation polarisation angle on 3HG signal intensity is observed. When the polarisation of the excitation beam is parallel to the long axis of a nanowire, the magnitude of the 3HG signal is found to be about 20 times greater than when the polarisation of the excitation beam and the nanowire long axis are mutually orthogonal. By assuming that $\chi_{||}^{(3)}$, i.e., the component of the third-order susceptibility tensor with all indices parallel to the direction of the internal polymer molecular chains, dominates the 3HG signal response, a fit which incorporates a Gaussian distribution of polymer chain orientations about a net alignment direction may be made to the measured angular variation in 3HG signal intensity. A best fit to the data is found to correspond to a distribution of chain orientations about the long axis of the nanowires with a FWHM of 19° indicating that the polymer molecules within the wires are predominantly axially oriented.

I will also demonstrate 3PEL in PFO nanowires for the first time and show that, by analysing the dependence of 3PEL intensity images and spectra on both excitation and collection polarisations at the single nanowire level, values for the spread in molecular orientations about the nanowire long axis similar in magnitude to those obtained by 3HG methods, may be obtained. Importantly, by measuring both excitation and collection polarisation dependent data independently, it is possible to identify distinct orientation distributions for the populations of molecules that absorb the three photon excitation light and that subsequently emit the resulting luminescence, i.e., the nature of energy transfer processes within the wires may be probed. To conclude my talk, the implications of these results for the design of new optical methods to monitor nanowire internal structure and, also, for tailoring synthetic methods to achieve specific wire morphologies will be discussed.

References:

- [1] Physica E, DOI: [10.1016/j.physe.2007.10.009](https://doi.org/10.1016/j.physe.2007.10.009).
- [2] Small, **3**, 1178 (2007)
- [3].Nat. Nanotech., **2**, 180 (2007).
- [4] Adv. Mater. **20**, 42 (2008).