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Nonlinear optical absorption of doped and undoped polyaniline

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Abstract – We measured the nonlinear optical absorption of polyaniline (PANI) in its doped and undoped state, by using white-light continuum pulses, in a spectral range spanning from 450 up to 700 nm. The excited state absorption spectrum reveals that undoped and doped PANI present no reabsorption to a higher excited state (saturable absorption), indicating that the doping changes only shift the photobleaching to IR region.

Conjugated polymers, including polyanilines (PANI), are materials of large technological interest, due to their electrical conductivity and large optical nonlinearities. For instance, PANI derivatives have already been proposed for applications in energy storage and transformation, memory storage, catalystics, sensors, membranes, etc.[1] Although there are extensive theoretical and experimental spectroscopic studies on PANI, the deep understanding of its photoexcitation mechanism still requires some effort. In order to probe the excited states of PANI, laser spectroscopic techniques have been employed. Among them, those employing white-light continuum (WLC) sources outstand in characterizing excited states, owing to its high spectral resolution and time saving. When using such techniques under resonant conditions, the WLC pulse chirp must be considered, once distinct spectral components will reach the sample in distinct times, and cumulative effects such as excited state absorption might occur. In this work we present the results on the nonlinear absorption spectrum, from 450 up to 700 nm, of doped and undoped PANI in DMSO solution. The nonlinear absorption measurement was obtained through the White-Light Continnum (WLC) Z-scan technique,[2] which experimental setup is displayed in Fig. 1. The WLC was generated by focusing 150–fs pulses at 775 nm from a Ti:sapphire chirped pulse amplified system in distilled water (3 cm path length cell). 8 μJ of WLC in the visible range was generated by employing ~ 0.3 mJ at 775 nm. The WLC beam is then recollimated using a f = 10 cm lens. The WLC spectrum used in our experiment presents roughly 250 nm band in the visible region (450–700 nm). The sample was scanned along the focused WLC beam (z-direction), being the transmitted light recollimated into a portable spectrometer. The transmittance at distinct z-positions was normalized to the transmittance far from the focus, yielding the normalized transmittance curves (Z-scan signatures) for each excitation wavelength. The linear absorption of undoped and doped polianiline is represented by the solid line in Fig. 2 a and b, respectively, while the resonant nonlinear absorption spectra are represented by the open circles. Both doped and undoped PANI present saturation of the absorption (SA) in the spectral range analysed (from 450 up to 700 nm). A set of rate equations, based on the three-energy-level was used in order to obtain the excited state absorption cross-section. The superposition of linear and nonlinear absorption, observed for both PANI's, reveals that the excited state has a low absorption cross-section. Such fast optical transparency of PANI points out it as a candidate material for photonics applications.

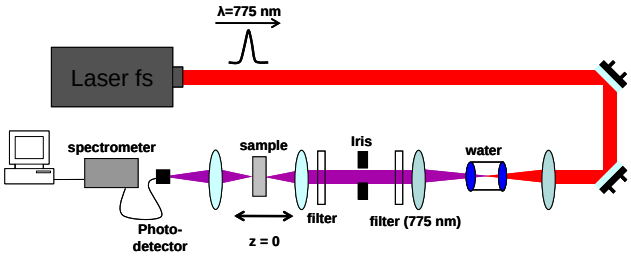

Figure 1: WLC Z-scan technique experimental setup.

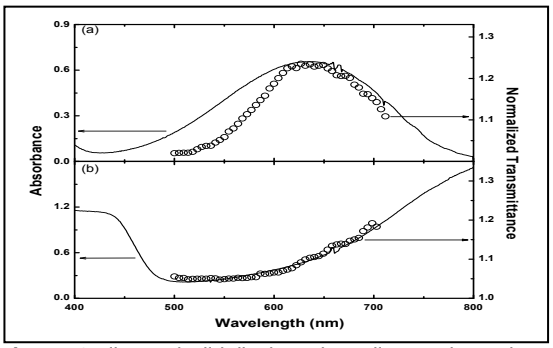

Figure 2: linear (solid line) and nonlinear absorption (open circle) of undoped (a) and doped (b) PANI.

References

[1] N. Gospodinova, L. Terlemezyan, Progress in Polymer Science 1998; 23:1443.
[2] L. De Boni, A. A. Andrade, L. Misoguti, C. R. Mendonca, S. C. Zilio, Optics Express 2004; 12:3921.