

Stilbene is an organic compound with structural formula $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$ ($\text{C}_{14}\text{H}_{12}$). It is a classic example of molecules demonstrating *trans-cis* isomerization occurring under UV irradiation and thus playing an important role in the various processes in biology and chemistry. Nevertheless, the *trans*-isomer, which is solid crystal under normal conditions, is more stable than the liquid form of the *cis*-stilbene.

Stable solid *trans*-stilbene (TS) is a promising material for sensing and electronics, because it demonstrates morphology-dependent optical properties and the ability to form quite stable noncovalent complex with 2D materials like hexagonal boron nitride.

In this work we aim to investigate thin films of TS with different morphologies. For this purpose, we prepared TS thin films in polystyrene matrix by varying both relative TS concentration (0.5%, 10%, 20%, 60% and 80%) with respect to the matrix and the film thickness (45 nm, 75 nm, 175 nm, 300 nm and 670 nm). We applied atomic force microscopy (AFM) and coherent anti-Stokes Raman scattering (CARS) in order to characterize the morphologies of the films. We observed that low concentrated films consist completely of the TS monomers, while at higher concentrations the formation of unstructured aggregates is observed and for the highest concentrations ideal μm -sized TS monocrystals are formed. All these three TS phases exhibit different optical properties (namely, fluorescence spectra and kinetics). To further investigate this effect, we measured temperature-dependent (from room temperature down to 15 K) steady-state fluorescence and decay kinetics of the films consisting of TS monomers, aggregates and monocrystals. After that we applied the global analysis of the experimental data via non-negative matrix factorization technique.

We observed a gradual shift of the optical properties of stilbene, transitioning from those characteristic of monomers to those of crystals as the TS concentration in the film increased. Thus, for applications TS properties can be easily controlled via sample preparation procedure, namely TS monomers/aggregates/crystallites formation is controlled by concentration, while their amount is controlled by the thickness of the film.

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