

## Photoreactivity of functionalized dithienylethenes for supramolecular assembly: from the solution to the photoresponsive thin film

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Photochromism is the reversible phototransformation of a chemical species between two forms having different absorption spectra. Industrial applications are numerous from optical memories to opto-mechanics devices including light driven actuators [1,2].

Concerning this last topic, professor Takeshita (Saga University, Japan) inspired by Meijer works [3] has elaborated new photosensitive elastomeric films based on supramolecular assembly between bistable dithienylethene A (molecular switch) and elastomeric units B bearing similar hydrogen bonding 2-Ureido-4[1H]-pyrimidinone moieties (see fig. 1). [3,4] Thin films are prepared by mixing in solution the elastomer and the dithienylethene A switched in the closed conformation by UV light irradiation, and then drop casting the blend. In such a way, a photoresponsive thin film is obtained for which macroscopic shape can be modulated by UV or Visible light as shown in figure 1. We have undertaken a long term multi-physics and multi-scale study which is necessary to rationalize the behavior of this this complex system. We present in this paper some results mainly based on ultrafast spectroscopy and *ab initio* calculations and dealing with the photochemistry and photophysics of this system with the aim of establishing relationship with its optomechanical behavior.

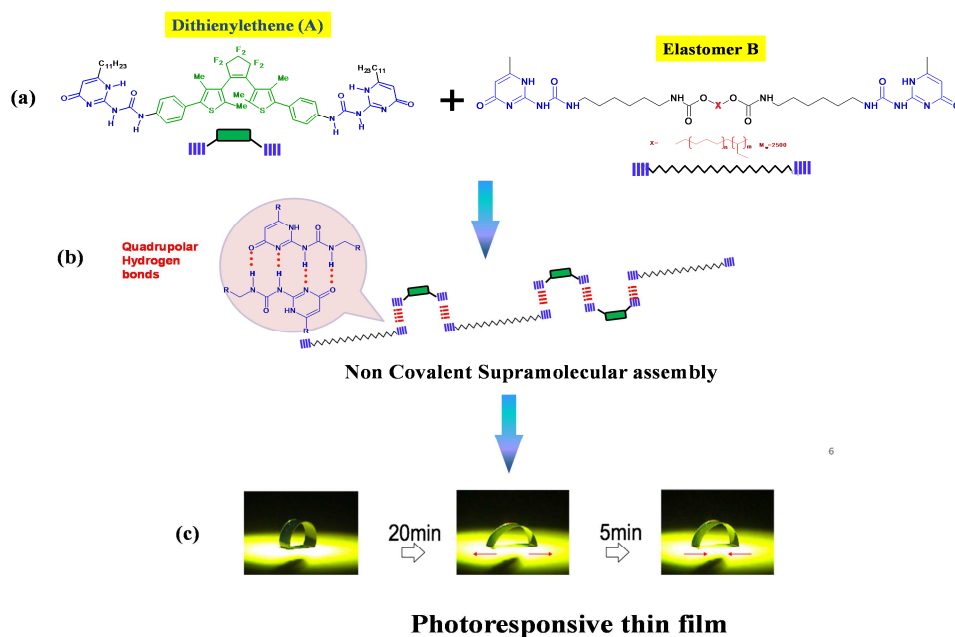


Figure 1: (a) Dithienylethene A and elastomeric units B. (b) Quadrupolar hydrogen bonds site able to link as A-A, B-B or A-B. (c) Thin CF blue film under visible irradiation

We first investigated the kinetics of supramolecular assemblies by DLS, NMR, AFM, and DFT calculation. Concerning the self-assembly A-A-A-A, a strong sensitivity to initial conditions and a typical kinetics showing lag time and overshoot have been interpreted in terms of nucleation and 3D growth of nano-objects. After addition of B, these effects disappear in favor of a mixture which homogenizes within several hours.

Then, from photochemical studies conducted by nano/femtosecond absorption spectroscopy and TD-DFT calculations, we have investigated the photocommutation mechanisms of A in different environments (monomers, oligomers, large assemblies). Considering the  $S_1$  states, the characteristic times of photoreversion ( $\sim 5$  ps) and photocyclization ( $\sim 150$  fs) processes appear to agree with literature data: Two triplet states have been identified (antiparallel and parallel conformers), one of which is photoactive ( $\sim 10$   $\mu$ s). Compared to the photoreversion process which is insensitive to changes in the environment, the photocyclisation process appears to be very sensitive. This interface between the open and closed forms within the films (A : B) is probably one of the keys to understand the opto-mechanical effect.

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