

TOWARDS ACCURATE FLUORESCENT FORCE SENSORS RELYING ON MECHANOFLUOROCHROMIC POLYDIACETYLENE-BASED MATERIALS

Luca Polacchi,¹ Arnaud Brosseau¹, Rémi Métivier¹, Clémence Allain¹

¹PPSM, CNRS, ENS Paris-Saclay, France

luca.polacchi@ens-paris-saclay.fr

Mechanofluorochromic materials are a recently discovered class of compounds that change their fluorescent properties when subjected to external mechanical stimulation. [1] This mechanical force produces changes in the compound structure or in its supramolecular structure, resulting in a modified radiative relaxation of the excited state, ultimately producing a different emitted light (emission wavelength, fluorescence quantum yield, fluorescence lifetime). Polydiacetylenes are ordered π -conjugated systems whose topochemical polymerization can be obtained by UV irradiation at 254 nm. [2] They are usually present in two forms, “blue” ($\lambda_{\text{abs}} = 600\text{-}630\text{ nm}$) or “red” ($\lambda_{\text{abs}} = 520\text{-}550\text{ nm}$), according to the degree, orientation and planarity of their molecular packing. [3] When an external stimulus, like a mechanical force, is applied, the molecular packing is modified and the system is converted from the blue to the red form. We are interested in the study of compounds where an appropriate fluorophore, as a tetrazine ring, is attached to the main chain (Figure 1a). In this case, an energy transfer occurs uniquely towards the blue form of the polymer: before mechanical stimulation the fluorophore’s fluorescence ($\lambda_{\text{em}} = 560\text{ nm}$) is quenched, while after mechanical stress is applied, the polymer is converted to the red form and the energy transfer is blocked, thus the emission is restored. In conclusion, a fluorescent ON-OFF switching sensor responsive to forces can be built. [4] The interest is in studying the nanoscale response to forces in the nN range aiming at providing a mechanical sensor with a well-defined correlation force-fluorescence recovery. It would therefore allow to quantify the intensity of mechanical stimulations by fluorescence. The morphologic study of vacuum-evaporated thin films of such a compound as well as its photopolymerisation properties and its photophysical response to shearing at the nanoscale, performed by an AFM coupled with a fluorescence microscope, will be presented.

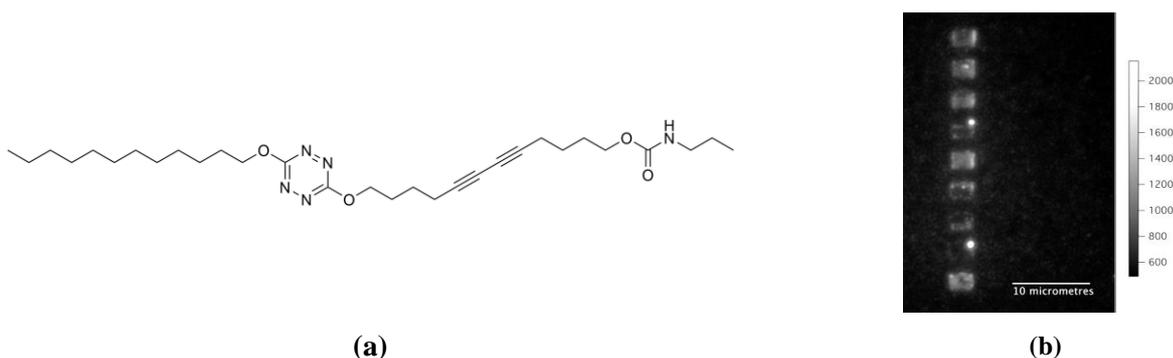


Figure 1. (a) Diacetylene chain substituted by a tetrazine ring, which was synthesized and studied; (b) tetrazine fluorescence recovery after transition of the polydiacetylene chain upon nano-shearing (nominal force 125 nN).

[1] Y. Sagara et al., *J. Am. Chem. Soc.*, 2014, 136 (11), pp 4273–4280

[2] X. Chen, G. Zhou, X. Peng, and J. Yoon, *Chem. Soc. Rev.*, vol. 41, no. 13, pp. 4610-4630, Jun. 2012.

[3] M. A. Reppy and B. A. Pindzola, *Biosensing Chem. Commun.*, 42, pp. 4317-4338, 2007

[4] T. Barisien et al., *ACS Appl. Mater. Interfaces*, vol. 5, no. 21, pp. 10 836-10 841, Nov. 2013.