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Mechano-responsive fluorescent polydiacetylene-based materials: towards quantification of shearing stress at the nanoscale

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An OFF to ON mechano-responsive fluorescent polydiacetylene derivative has been prepared by photopolymerisation of a diacetylene covalently linked to a tetrazine fluorophore. This system has been studied at the nanoscale and shows a fluorescence emission intensity that increases with the intensity of the mechanical stimulation in the 20–200 nN range.

Mechano-responsive fluorescence is defined as a change in the fluorescence properties (emission colour, quantum yield or lifetime) upon mechanical stimulation.¹ Functional materials based on this phenomenon have attracted considerable attention over the past decade and a variety of mechano-responsive fluorescent compounds have been developed either based on organic molecules² or on transition metal complexes.³ However, in most of the studies on mechano-responsive molecular materials, the force necessary to trigger the fluorescence change is not quantified, which is a severe limitation for the development of force sensors. Furthermore, study at nanoscale has been limited to a few examples,^{4–7} although spatial⁸ and photophysical⁹ amplification of the fluorescence response could be foreseen.

Polydiacetylenes (PDAs) have been widely studied in the past years because of their photophysical responsiveness to different stimuli.¹⁰ PDAs can be obtained via topochemical polymerisation by γ -rays, heat, or UV irradiation, which can be applied to self-assembled diacetylene monomers in the form of thin films,¹¹ aggregates in solution (micelles or liposomes),¹² or embedded in a polymer matrix.¹³ It is well known that the polymerised form of diacetylenes undergoes dramatic chromogenic transitions, switching from a so-called blue form ($\lambda_{\text{abs}} = 630 \text{ nm}$) to a red form ($\lambda_{\text{abs}} = 540 \text{ nm}$) which is also weakly fluorescent.¹⁴ The mechanism of transition is still matter of debate, but there is evidence that supramolecular

arrangements and electronic structures are linked together: the blue chains are strictly planar (strained arrangement) and the red chains are twisted (relaxed arrangement).¹⁵ A wide variety of stimuli such as temperature, chemo- or bio-specific binding, pH, ions,^{16–18} and mechanical forces^{4, 13, 19, 20} have been shown to trigger the transition. Furthermore, we have shown that it is possible to obtain a thermofluorochromic system with an excellent off to on contrast²¹, despite a low polymerisation rate, by covalently attaching the diacetylene to an appropriate fluorophore, namely tetrazine (Tz)²². Before polymerisation, tetrazine is fluorescent in solid state. When the polymer is in the blue form, the fluorescence of tetrazine is quenched by energy transfer, resulting in a *non-emissive state*. When the blue-to-red transition has occurred upon external stimulation, the energy transfer is blocked and the system goes back to its *emissive state*.

Because of the reported properties of PDA-Tz systems, we decided to extend the study to mechano-responsive fluorescence. We synthesised a new compound that can self-assemble more easily, **TzDA** (Fig. 1), and we describe here its off to on fluorescence switch upon mechanical stimulation at macro and nanoscale. We show for the first time that the fluorescence recovery can be directly correlated to the applied mechanical stress, at the nanoscale.

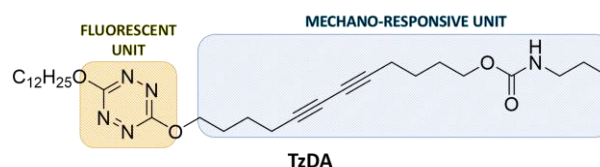


Figure 1. Molecular design of **TzDA**

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The diacetylene **TzDA** has a specific molecular design to meet the requirements of fluorescence quenching and polymerisation efficiency. Therefore, a urethane moiety on one side of the molecule as well as an alkyl chain on the other side are introduced to favour self-assembly of the monomers, thus facilitating the polymerisation.²³ The fluorophore is covalently attached to the diacetylene through a flexible spacer so as to ensure an efficient topotactical polymerisation while enabling energy transfer from the tetrazine to the blue PDA phase. The synthesis is performed in three steps from commercially available 5-hexynol (full details are given in ESI): 6-bromohex-5-yn-1-ol is obtained by bromination with Br_2 in alkaline aqueous medium at 0°C ²⁴ and hex-5-yn-1-yl propylcarbamate is obtained by reaction with propyl isocyanate. The two alkynes are then coupled asymmetrically by a Cu(I) -catalysed Cadiot-Chodkiewicz coupling. The last step consists in the introduction of the tetrazine fluorophore, bearing a C12 alkyl chain on one side, by aromatic nucleophilic substitution.²⁵

Photophysical properties for the monomeric **TzDA** both in solution and in thin films are typical of a tetrazine derivative (see ESI), with a broad fluorescence emission centred at 565 nm. After vacuum evaporation on microscopy slides (80 nm thickness), polymerisation of the sample (**poly-TzDA**) was performed by UV-irradiation. Upon irradiation at 254 nm, a new band forms with a maximum at 600 nm (Fig. 2A), corresponding to a high energy shifted blue form, so called "purple", sometimes observed in PDAs.^{14, 15} It can be noticed that the peak at 600 nm increases progressively until a plateau is reached (see Fig. 2C), indicating that the maximum of polymer fraction is obtained after irradiating 20 min at 1.4 mW cm^{-2} . As explained thoroughly in²⁶, it is incorrect to assume a complete polymerisation of the sample. Indeed, taking a value of $\alpha = 2 \times 10^5 \text{ cm}^{-1}$ for the absorption coefficient of the PDA gives an order of magnitude of 10% polymer percentage. As the polymer fraction increases, a shape modification of the absorption band towards lower wavelengths is also noticed. This effect is ascribable to plastic deformation of the crystals that steps in beyond a certain polymer fraction, causing a slight increase of the exciton energy.²⁶

In Fig. 2B, the fluorescence spectra after each irradiation of the same sample are shown. As the polymer fraction in the film increases during irradiation, the luminescence of the tetrazine is progressively quenched by energy transfer. Plotting the fluorescence intensity versus the irradiation energy allows tracing the kinetics of quenching (Fig. 2C). For the first irradiation steps, the fluorescence decreases very efficiently until a plateau is reached after 1300 mJ cm^{-2} . Residual fluorescence could tentatively be attributed to a less efficient energy transfer to the chains formed at the end of the irradiation, which absorb at higher energy, thus limiting the maximum quenching to 93%. It is worth noting that the fluorescence quenching is more pronounced than the concomitant absorption change, as highlighted in Fig. 2C: most of the fluorescence drop is reached after 200 mJ cm^{-2} , corresponding to only 50% of the absorption increase. This non-linear effect is evidenced in Fig. 2D, displaying the correlation of the fluorescence intensity with the polymer absorbance (λ_{abs} at

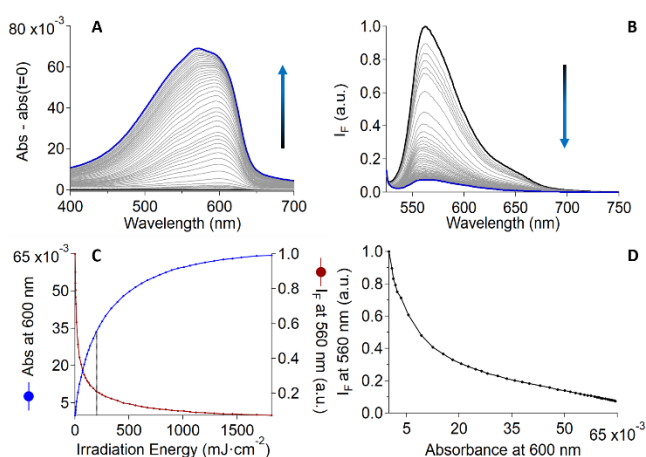


Figure 2. Absorbance and fluorescence spectra for consecutive irradiations at 254 nm of vacuum evaporated **TzDA**. (A) UV-vis spectra for each irradiation: the initial spectrum of the non-irradiated sample, where the only absorption in the visible is due to the tetrazine, is subtracted to all the others to let us analyse only the PDA contribution; (B) Fluorescence spectra ($\lambda_{\text{exc}} = 510 \text{ nm}$) for each irradiation; (C) evolution of the PDA absorbance peak at 600 nm and tetrazine fluorescence peak at 560 nm in respect to the irradiation energy at 254 nm; (D) correlation of fluorescence intensity with blue polymer absorption for progressive irradiation. See ESI for details on irradiation energy.

600 nm) after each irradiation period, attesting the highly efficient intermolecular energy transfer from multiple tetrazine donors to a PDA chain.

poly-TzDA responsiveness to heating and mechanical stress was investigated qualitatively by UV-Vis and fluorescence spectroscopy on vacuum evaporated thin films on glass slides (drop casted films on paper substrate were used to monitor the fluorescence recovery after mechanical stimulation). By heating the polymerised thin film, the typical absorption spectrum of a red-PDA is obtained (Fig. 3A, blue and red curves respectively). Simultaneously, Fig. 3B shows that the ON state of the monomeric form (black curve) is efficiently switched to the OFF state where the tetrazine fluorescence is quenched by energy transfer towards the blue-PDA (blue curve). Upon heating, the conversion to the red-PDA causes a strong weakening of the energy transfer, resulting in the efficient restoration of the tetrazine fluorescence (red curve). Similarly, when the blue polymer film is subjected to mechanical stress, here performed by hand with a spatula, the red-PDA is obtained, which is confirmed by the absorption spectra shown in Fig. 3C. Therefore, mechanical stress, like heating, restores tetrazine fluorescence as shown in Fig. 3D. Additionally, this mechanism is pseudo-reversible if cycles of UV irradiations and mechanical stimulations are performed. Fig. 3D shows that a second irradiation forms more blue polymer thus the fluorescence intensity decreases (purple curve), and that a subsequent mechanical stimulation restores again the quenched fluorescence intensity (brown curve). This qualitative spectroscopic study constitutes also a strong proof of the quenching by energy transfer mechanism that occurs efficiently towards the blue PDA only. In fact, the tetrazine fluorescence spectrum (in **TzDA** monomer, Fig. 3A, black line) overlaps strongly with blue PDA absorption (blue line) and much less with red PDA absorption spectrum (red line). Fluorescence spectra at low temperature (-180°C) acquired for monomeric and

polymeric films supported the hypothesis of energy transfer (see ESI, Fig. S1).

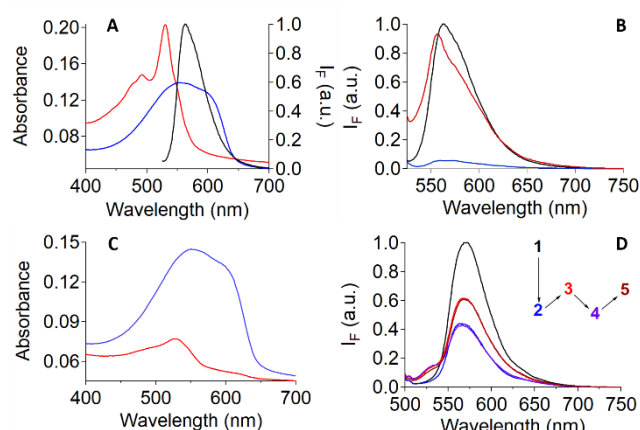


Figure 3. (A) Absorbance spectra before (in blue) and after (in red) heating at around 70°C superimposed with the fluorescence emission spectrum of the monomer (in black); (B) Fluorescence emission spectra before polymerisation (black), after irradiation (blue) and after heating (red); (C) Absorbance spectra before (in blue) and after (in red) mechanical shearing with a spatula. It has to be noticed that mechanical shearing removes some PDA material which induces a decrease in absorption; in (A), (B) and (C) **TzDA** is deposited on glass slides support; (D) Fluorescence emission spectra of a thin film dropcasted on paper before polymerisation (black), and after two consecutive cycles of irradiation (blue, purple) /shearing (red, brown).

In order to achieve a more detailed understanding of the mechanofluorochromic behaviour of **poly-TzDA** and to quantify its fluorescence response to forces, we decided to investigate the thin films at the nanoscale using an Atomic Force Microscope (AFM) coupled with a fluorescence microscope. With this set-up (see ESI for a detailed description), morphology, shearing and fluorescence images could be recorded for the same zone.⁷

Morphology images, obtained in tapping mode, show that **TzDA** monomer assembles in rod-like micrometric monocrystals, which appear to accumulate on top of the film (Fig. 4A and S6). In addition, the size and shape of the crystals is not homogeneous, ranging in height from about 100 nm in the background to 400 nm for the sporadic big crystals on the surface. However, the same morphology is common to different areas of the sample (see ESI). In agreement with a topotactical polymerisation of diacetylenes, where monomers do not diffuse to react and their crystallographic positions and symmetry in the polymer crystals do not change^{27,28,29}, the morphology is well retained after photopolymerisation, as shown in Fig. 4B. After heating, however, the size and shape of the crystals are modified (see ESI, Fig. S8). The AFM constitutes also a powerful tool to shear the film at the nanometre scale. Squared 3x3 μm^2 shears are performed on the sample surface setting the AFM in contact mode. The applied vertical force of the tip on the surface can be adjusted over a range of several nN (20 to 500 nN for the experiments here presented). Tip velocity was fixed at 6.1 $\mu\text{m s}^{-1}$ which appeared as optimal for this particular compound (see ESI, Fig. S3). After applying a shearing stress, a fluorescence image of the exact same area is acquired. Upon stimulation, the morphology of the thin film is altered and the modification becomes more evident for higher applied nominal vertical forces up to a maximum level (estimated to be between

200 and 300 nN) from which the AFM tip indents deep in the film and causes material displacement on the sides and on top of the sheared area (Fig. 4C). When looking at the corresponding fluorescence image (Fig. 4D and S7), it is concluded that **poly-TzDA** restores its fluorescence emission locally where the film was scratched.

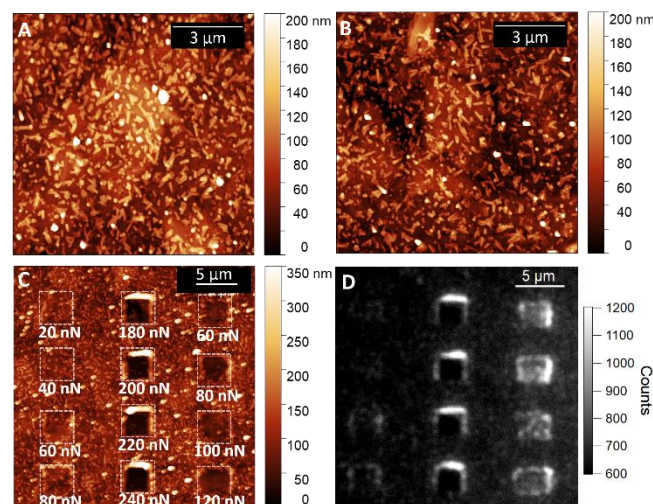


Figure 4. AFM morphology images of the (A) monomer, (B) polymer and (C) polymer after mechanical shears of **poly-TzDA** in different areas at increasing nominal forces (20 – 240 nN), the areas were scanned from bottom to top and from left to right at a tip velocity of 6.1 $\mu\text{m s}^{-1}$ (see ESI, fig. S2); (D) corresponding fluorescence image of sheared **poly-TzDA**.

Fluorescence recovery images are obtained by subtraction of the fluorescence images taken before and after shearing stress. Therefore, the background signal is eliminated and only the fluorescence restoration resulting from the mechanical stimulation appears. Integrating the signal over a fixed area in correspondence of each sheared zone gives a numerical value of fluorescence recovery that can be plotted versus the nominal applied force. The resulting trend of the measurements is shown in Fig. 5. The inset in Fig. 5 shows the fluorescence recovery images of two independent sets of mechanically stimulated films, with forces ranging from 20 nN (left) to 160 nN (right). The fluorescence recovery intensity increases progressively along with the increasing applied force in the range from 20 to 200 nN, while for more intense shears it remains almost constant, resulting in a plateau. All the mechanical stimulations were performed in the same experimental conditions, with a diamond-like carbon coated AFM tip (see ESI for specifications), the same excitation light power and image acquisition time. However, the variability in the fluorescence recovery images for a given force can be partly explained by local differences in film morphology that can cause eventually a different responsiveness to mechanical stimulation and by the AFM tip size and shape that can be affected as a consequence of scratching. The lack of fluorescence variation at high force range may be ascribable either to blue-to-red PDA conversion saturation or, most probably, to a constant applied mechanical stress. In this range, the tip indentation in the sample surface is deep, thus the actual applied force decorrelates from the vertical piezo-stage displacement.

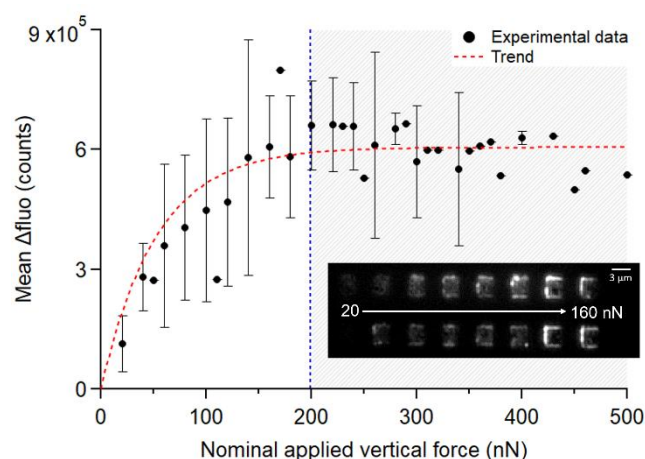


Figure 5. Graphical representation of the recovered fluorescence signal in each scraped area versus the corresponding applied vertical force expressed in nN. Each point corresponds to the mean value of different measurements, and the error bars correspond to the standard deviation. The dotted red line represents the general trend as a guide to the eye. The grey area corresponds to the plateau region, starting at 200 nN (blue dotted line). Inset: fluorescence recovery images of two independent sets of mechanically stimulated films, with forces ranging from 20 nN (left) to 160 nN (right).

In conclusion, a new ON-OFF mechano-responsive system based on polydiacetylene (**poly-TzDA**) has been synthesised. Upon UV irradiation, polymerisation of thin films of **TzDA** occurs (up to 10% of polymer formed) and results in an efficient non-linear quenching of the tetrazine fluorophore. The photophysical properties of this system upon mechanical stimulation have been inquired both at the macro and nanoscale. The introduction of the tetrazine fluorophore (non-emissive before mechanical stimulation and emissive after) allows us to probe by fluorescence the PDA forms (non-stimulated blue and stimulated red), thus with higher accuracy in respect to a simple chromogenic study. A detailed study at the nanometre scale by the use of an atomic force microscope coupled with a fluorescence microscope provided a morphological study of the films along with the possibility of evaluating the fluorescence recovery intensity upon a well-defined mechanical force applied by the AFM in contact mode. The correlation between force and fluorescence intensity is shown here for the first time.

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Conflicts of interest

There are no conflicts to declare.

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