Electronic Supplementary Material (ESI) for Materials Advances.

Supporting information

Polydiacetylene photocomposite material obtained by orthogonal chemistry: a detailed study at the mesoscopic scale

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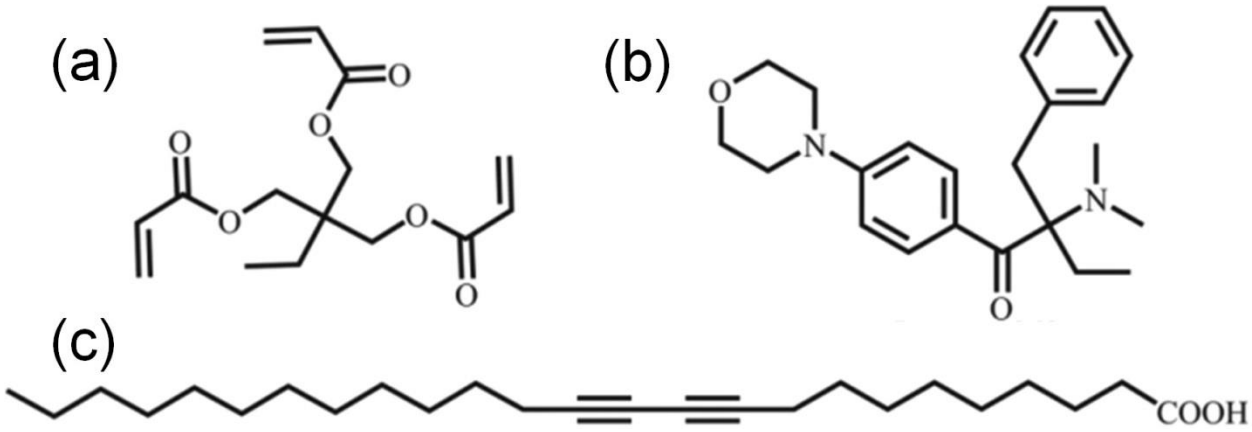

Figure S1. Molecular structures of (a) TMPTA (b) Irgacure 369 and (c) PCDA.

Film of the mixture on HOPG

In this section, the photocomposite films are analyzed by several microscopic and spectroscopic techniques. All samples characterized here are formed by drop-casting on HOPG a solution of the mixture diluted 100 times (or 10 times for a few figures). The figures in this section correspond to films in which the TMPTA has been polymerized (at 405 nm). The PCDA has been polymerized when it is indicated that the sample underwent irradiation in UV. This polymerization does not result in any noticeable change in the images, except for a very small height decrease measured in AFM for the PDA crystals, as mentioned in the main text.

In the following images, it can be noticed that the rectangular crystals of PCDA/PDA are almost always surrounded by a narrow layer of a homogeneous and amorphous material that we attribute to the polyacrylate. We can observe this in both SEM (figure S1c) and AFM topography (figure S2) images. Even when the polyacrylate is not directly observable in the topography image, such as in figure S3a, the phase image can evidence its presence around the PCDA crystals (figure S3b).

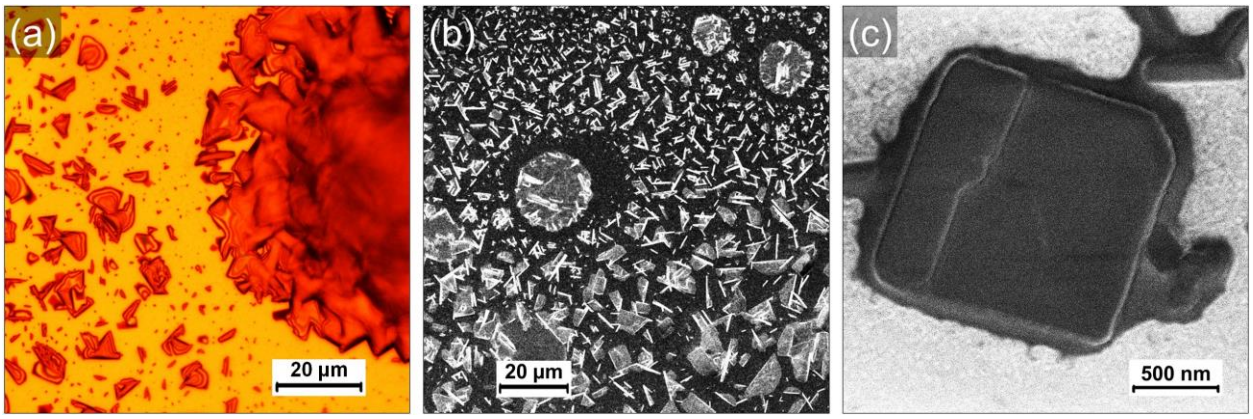

Figure S1. (a) Optical micrograph and (b, c) SEM images of the mixture (diluted 100 times) deposited on HOPG and irradiated 3 min at 405 nm.

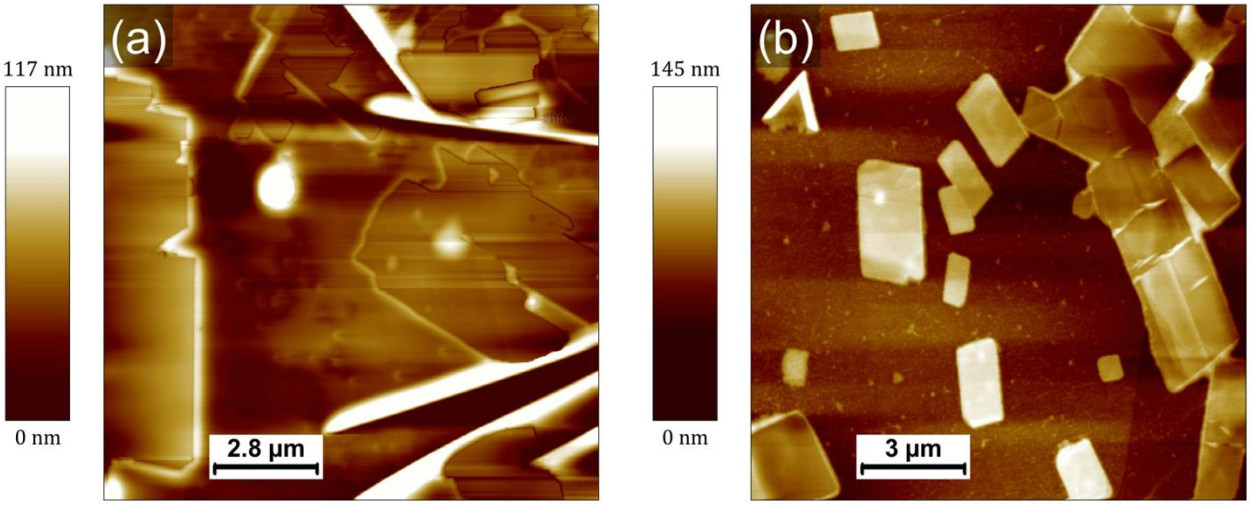

Figure S2. (a) AFM topography image of the mixture (diluted 100 times) deposited on HOPG and irradiated 3 min at 405 nm. (b) AFM topography image of the mixture (diluted 10 times) deposited on HOPG and irradiated 3 min at 405 nm and then 1 min with a UV lamp.

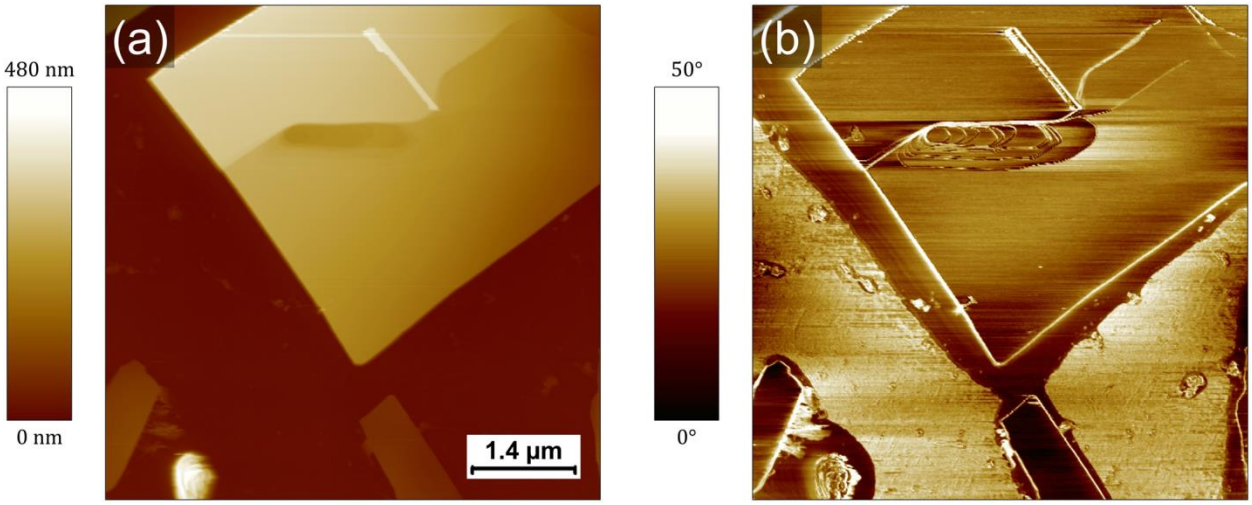

Figure S3. AFM (a) topography and (b) corresponding phase images of the mixture (diluted 10 times) deposited on HOPG and irradiated 3 min at 405 nm.

After the photopolymerization of the PCDA, the spatial distribution of the PDAs can be mapped by Raman. It allows to identify two main types of regions: thin areas where the crystals (or needles) are surrounded or on top of polyacrylate, and thick areas corresponding to polyacrylate “droplets”. In the latter, where the concentration of PDA is the highest (see figure S4), the PDA crystals are totally confined within the polyacrylate.

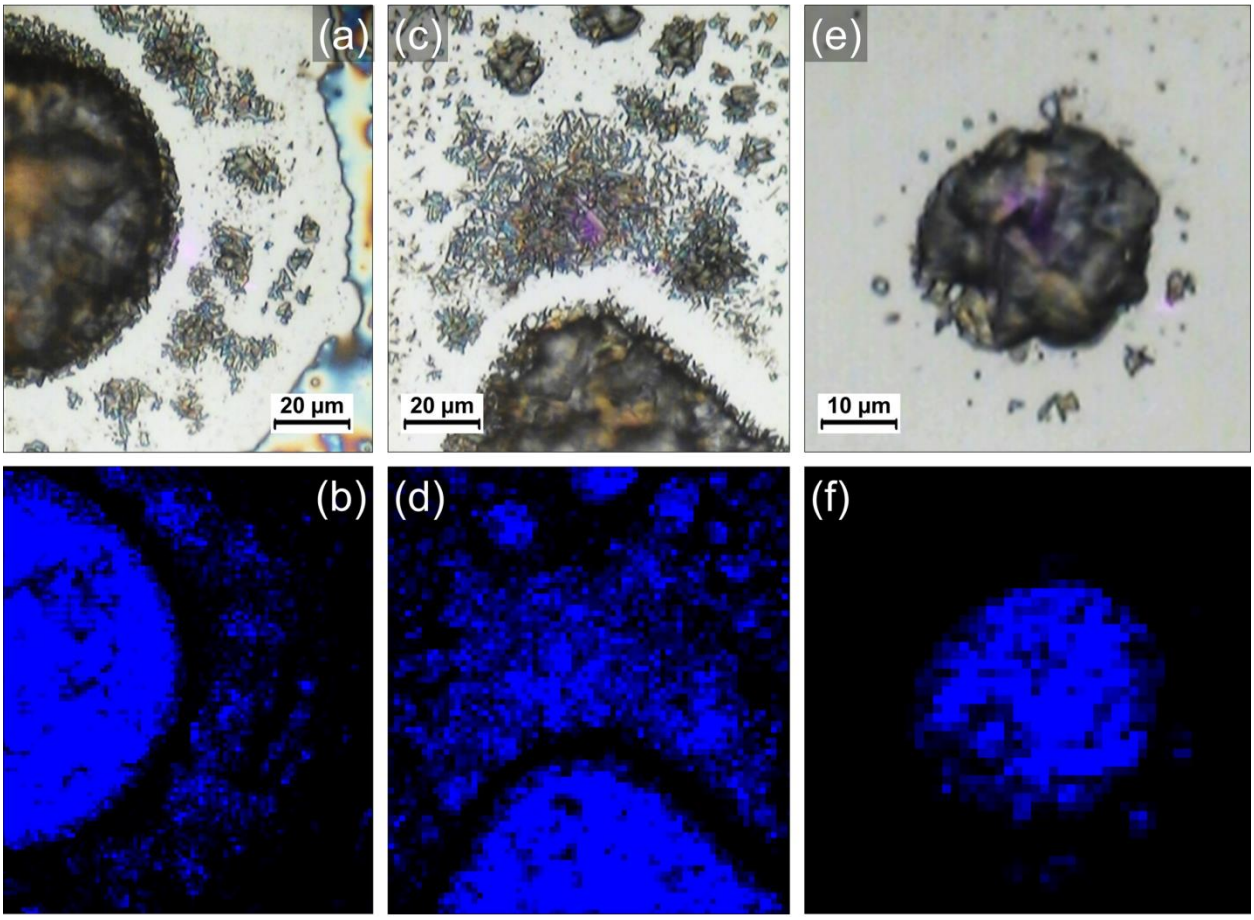

Figure S4. (a, c, e) Optical micrographs and (b, d, f) corresponding Raman maps of the density of polymerized blue PDA (*i.e.* value of the Raman peak at ≈ 2080 cm^{-1}) of the photocomposite film (diluted 100 times) on HOPG after irradiation at 405 nm and in UV. Color code: black = no PDA, blue = PDA.

Raman maps showed that there is no significant amount of PDA in the "empty" areas, but SEM (figure S1c) and AFM (figure S3b) images showed that the HOPG in these regions is covered by a layer of amorphous material probably consisting in a mixture of TMPTA, PCDA and Irgacure 369. AFM images obtained in such an area are shown in figure S5.

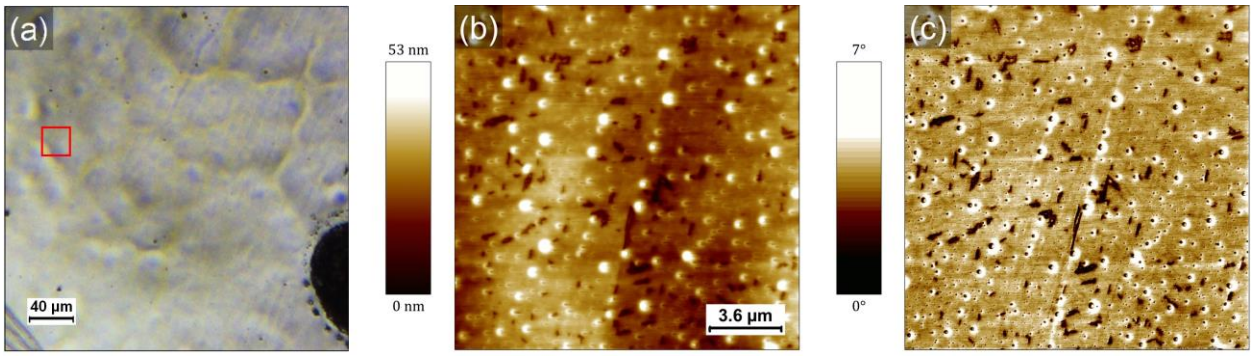

Figure S5. (a) Optical micrograph, (b) AFM topography and (c) phase images of the photocomposite film (diluted 100 times) on HOPG. The AFM images in (b) and (c) correspond to the red rectangle in (a).

Film of pure PCDA on HOPG

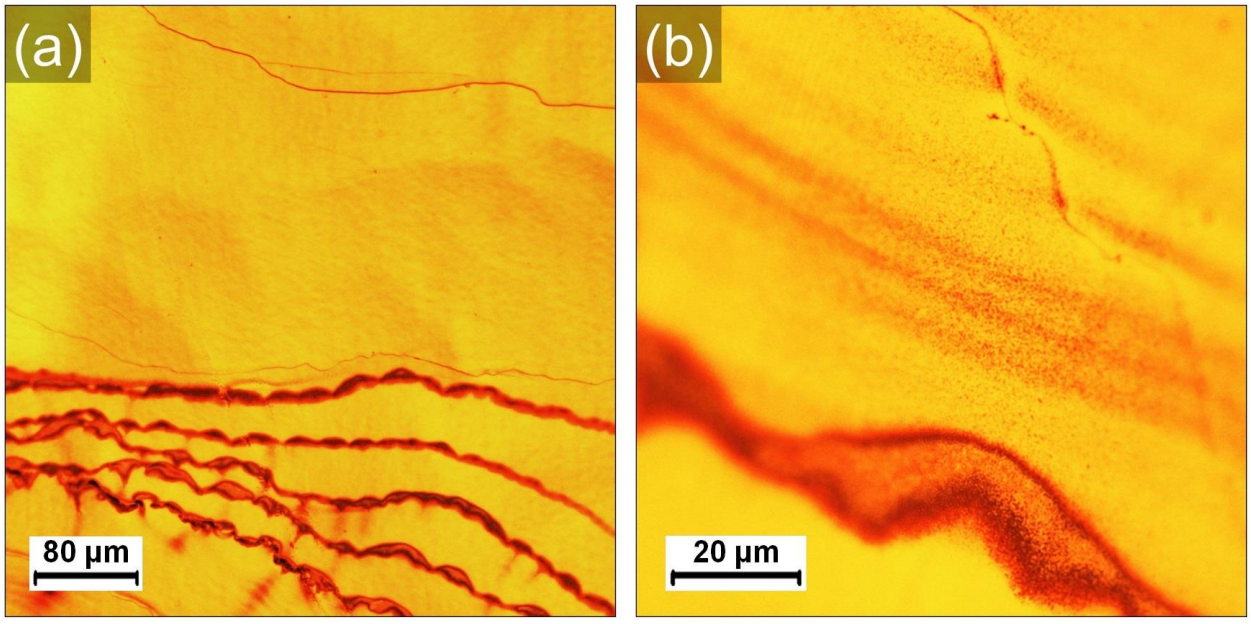

Figure S6. Optical micrographs of a pure PCDA film on HOPG prepared by drop-casting a 1.4 x 10^{-3} mol/l solution in CH_2Cl_2. No PCDA crystals can be imaged at this scale. Some concentric circles with more material (due to the drop-casting method) are observed on the sample, but the

rest of the surface is quite homogeneous.

Film of the mixture on SiO_2

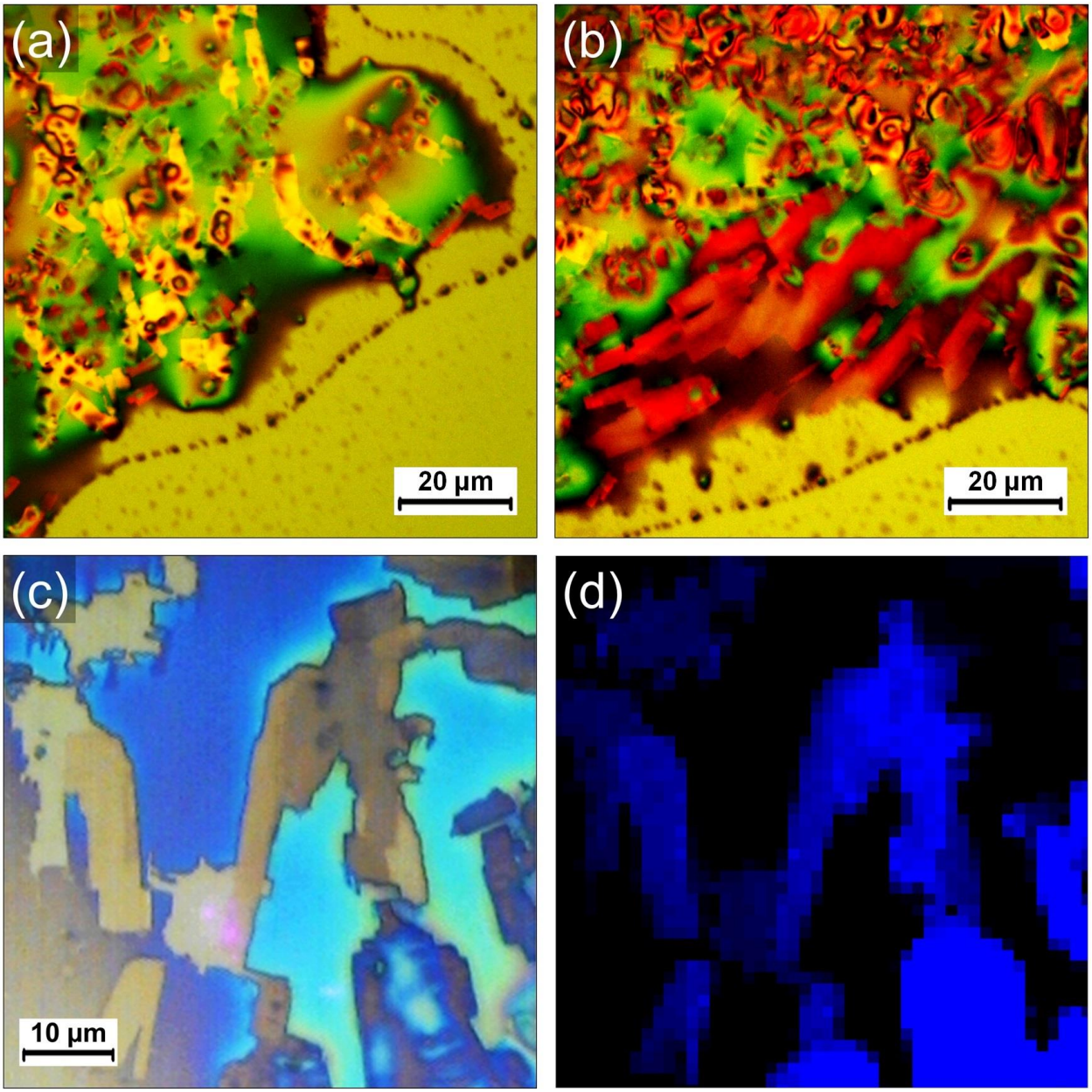

Figure S7. (a, b, c) Optical micrographs of the mixture (diluted 100 times) deposited on SiO_2 and irradiated 3 min at 405 nm and then 20 s with a UV lamp. (d) Correlative Raman map

(corresponding to image c) of the density of polymerized blue PDA (*i.e.* value of the Raman peak at ≈ 2080 cm^{-1}). PDA rectangular crystals are formed within polyacrylate droplets. Raman maps confirm that the PDA is exclusively present in the crystals.

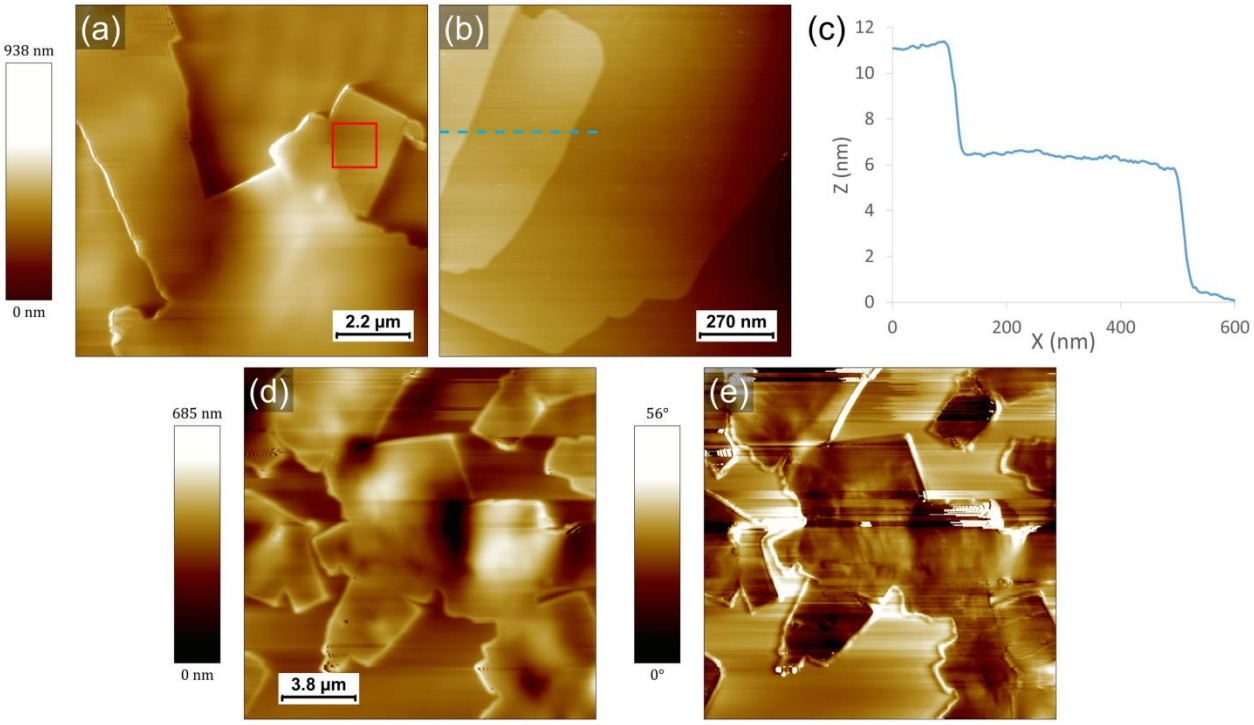

Figure S8. AFM images of the mixture (diluted 100 times) deposited on SiO_2 and irradiated 3 min at 405 nm and then 20 s with a UV lamp. (a, b) AFM topography images. The AFM image in (b) correspond to the red rectangle in (a). (c) Line profile along the blue dotted line in (b). AFM (d) topography and (e) phase images of the same area. Two types of regions can be evidenced by AFM. The polyacrylate is amorphous while flat terraces can be seen in the PDA regions. Phase images allow to discriminate both materials (with the polyacrylate showing a brighter contrast).

Kinetics of formation of the photocomposite film

In situ monitoring of the mixture deposition on HOPG allowed to directly observe the evaporation of the solvent. As shown in figure S9, it gives rise to "empty" circles around the acrylate droplets. These empty regions are therefore due to a dewetting process occurring during drop-casting.

AFM images performed before any irradiation (figure S10) demonstrate that the formation of PCDA crystals occurs/starts in the liquid TMPTA (*i.e.* before the formation of polyacrylate).

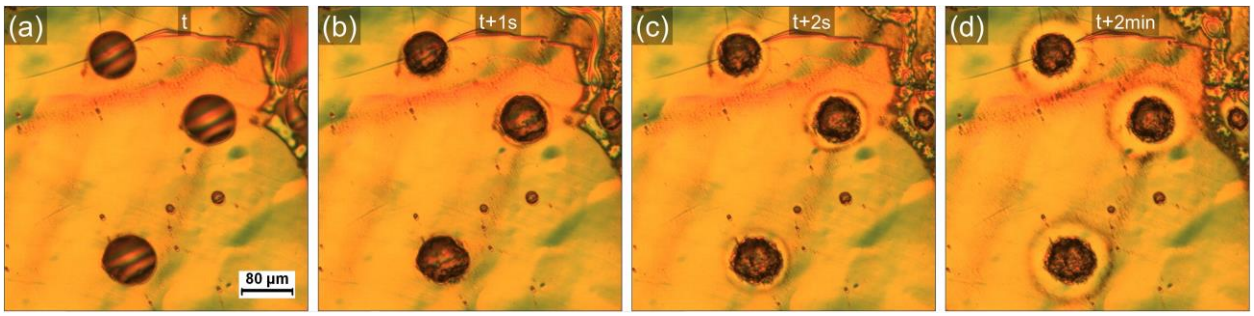

Figure S9. Optical micrographs showing the kinetics of the evaporation of the solvent during the drop-casting of the mixture (diluted 100 times) on HOPG. (a) Image taken a few seconds after deposition of the solution. Images taken respectively (b) 1 s, (c) 2 s and (d) 2 min after image (a).

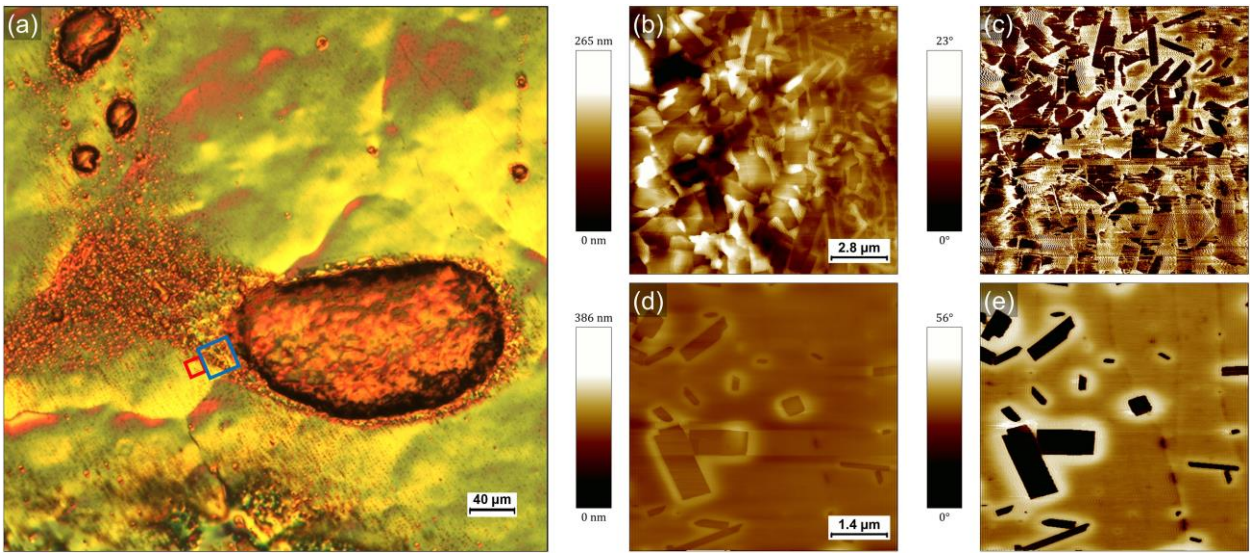

Figure S10. (a) Optical micrograph of photocomposite film (diluted 100 times) on HOPG before any irradiation. AFM (b, d) topography and (c, e) corresponding phase images. The AFM images in (b) and (c) correspond to the blue rectangle in (a). The AFM images in (d) and (e) correspond to the red rectangle in (a).

The images in figure S11 evidence the shrinkage of the TMPTA droplets during photopolymerization (due to the higher density of the polyacrylate). It reveals PCDA crystals that were hidden before, and gives also rise to a narrow dewetting area.

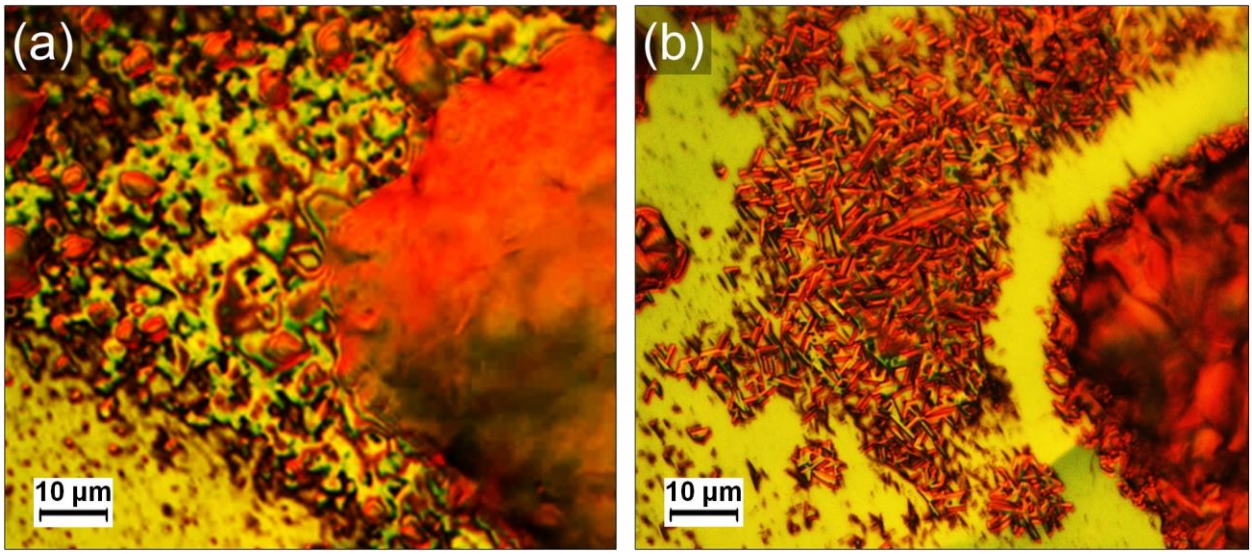

Figure S11. Optical micrographs of the mixture (diluted 100 times) deposited on HOPG (a) before and (b, c) after irradiation during 3 min at 405 nm.

Annealing of the films

The evolution of the photocomposite film under annealing can be monitored *in situ*. Optical images in figure S12 show that PDA crystals undergo a transition (causing an increase in height evidenced by a change in contrast) between 50 °C and 75 °C (the temperatures can vary from sample to sample).

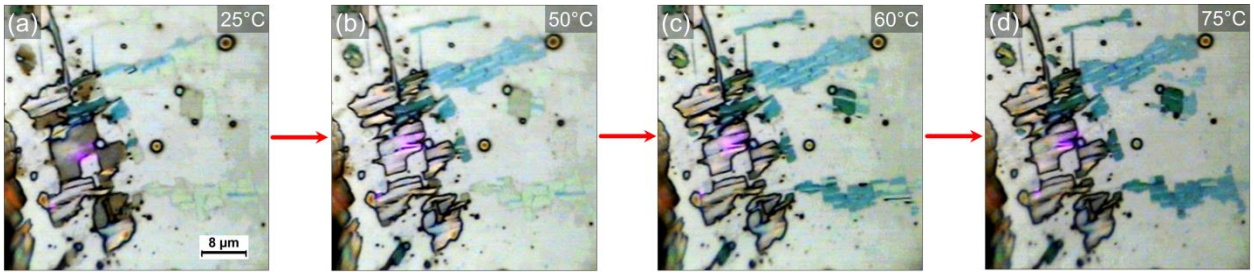

Figure S12. Optical micrographs of the photocomposite film (diluted 100 times) on HOPG during annealing. (a) Micrograph at room temperature before heating and evolution of the same area

during stepwise annealing at following temperatures: (b) 50 °C, (c) 60 °C and (d) 75 °C.

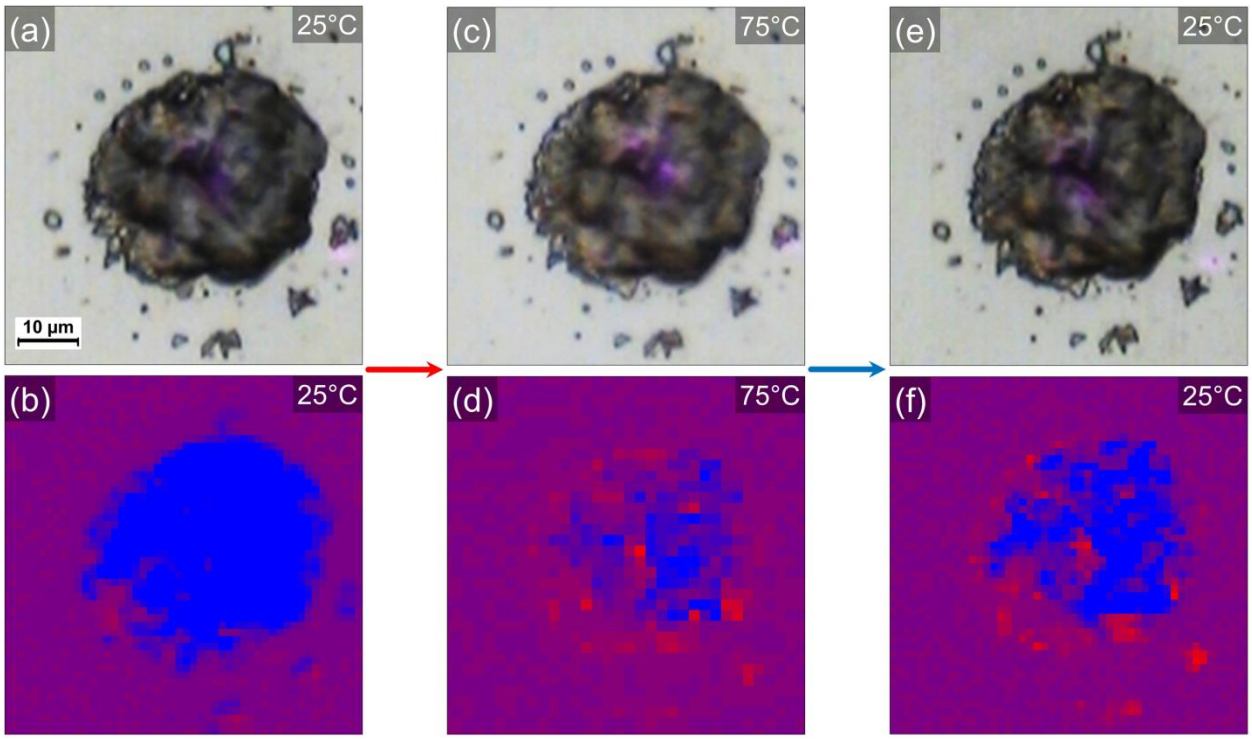

Figure S13. Optical micrographs and corresponding Raman maps of the photocomposite film (diluted 100 times) on HOPG during annealing. (a) Micrograph and (b) Raman map at room temperature before heating. (c, d) Same area during heating at 75 °C and (e, f) after return at room temperature. Blue pixels correspond to areas where the blue phase is dominant (peak at 2080 cm^{-1} higher than the one at 2120 cm^{-1}), red pixels to areas where the red phase is dominant (*vice versa*) and purple ones to regions with either no PDA or with peaks at 2080 cm^{-1} and 2120 cm^{-1} of similar intensity.

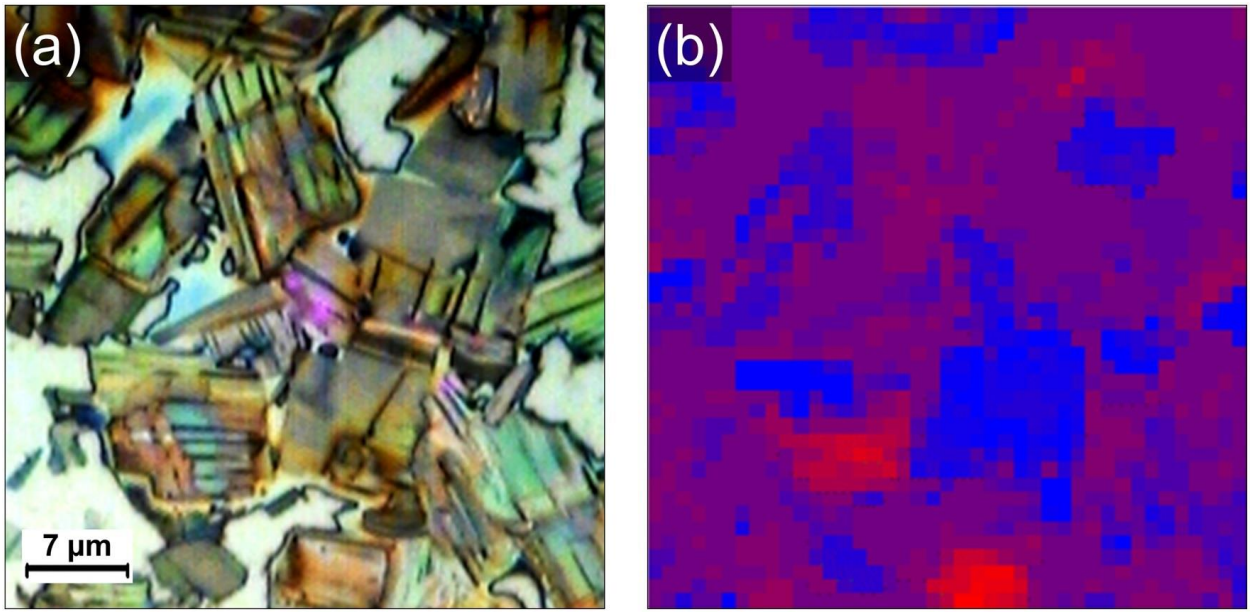

Figure S14. (a) Optical micrograph and (b) corresponding Raman map of the photocomposite film (diluted 10 times) on HOPG after annealing at 80 °C for 8 min (Raman performed at room temperature). Same color code as in figure S13.

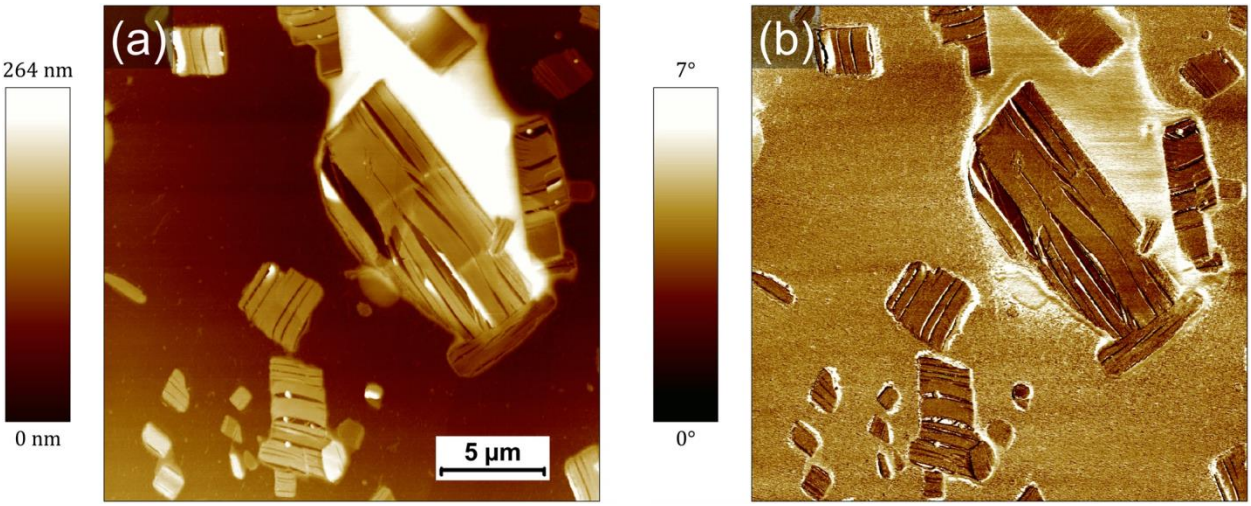

Figure S15. (a) AFM topography image of the photocomposite film (diluted 10 times) on HOPG after annealing at 80 °C for 8 min. (b) AFM phase image of the same area.

Cathodoluminescence measurements

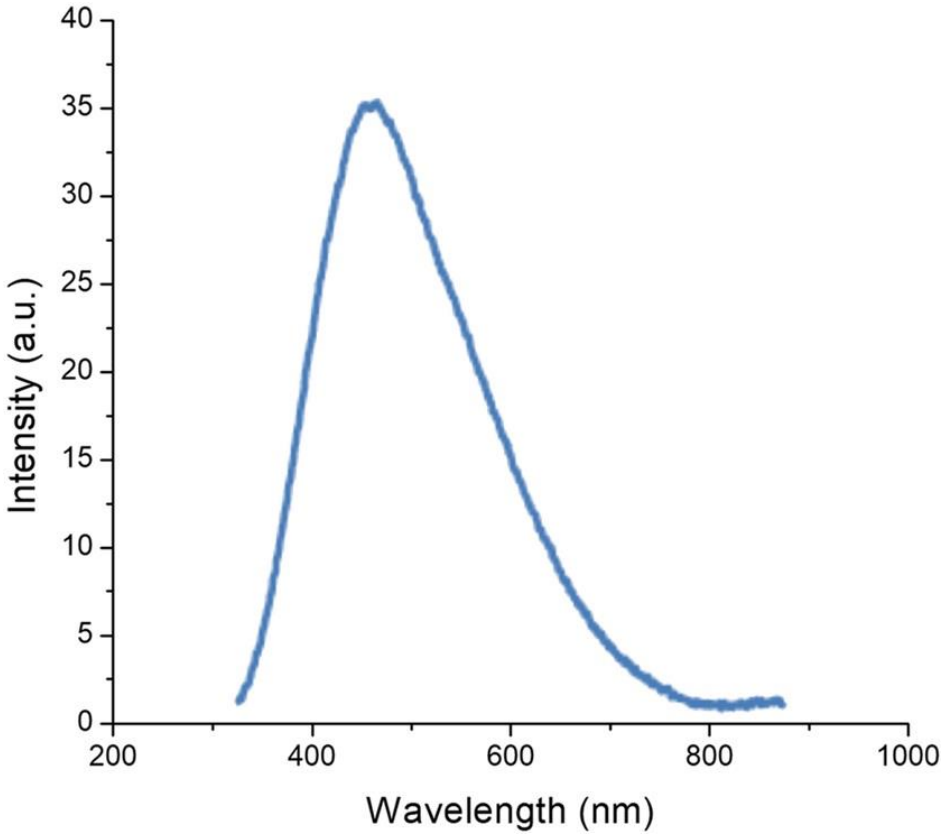

Figure S16. CL spectrum of a pure polyacrylate film (deposition of a droplet of TMPTA with 0.1 wt % of photoinitiator on HOPG and subsequent irradiation during 4 min at 405 nm).

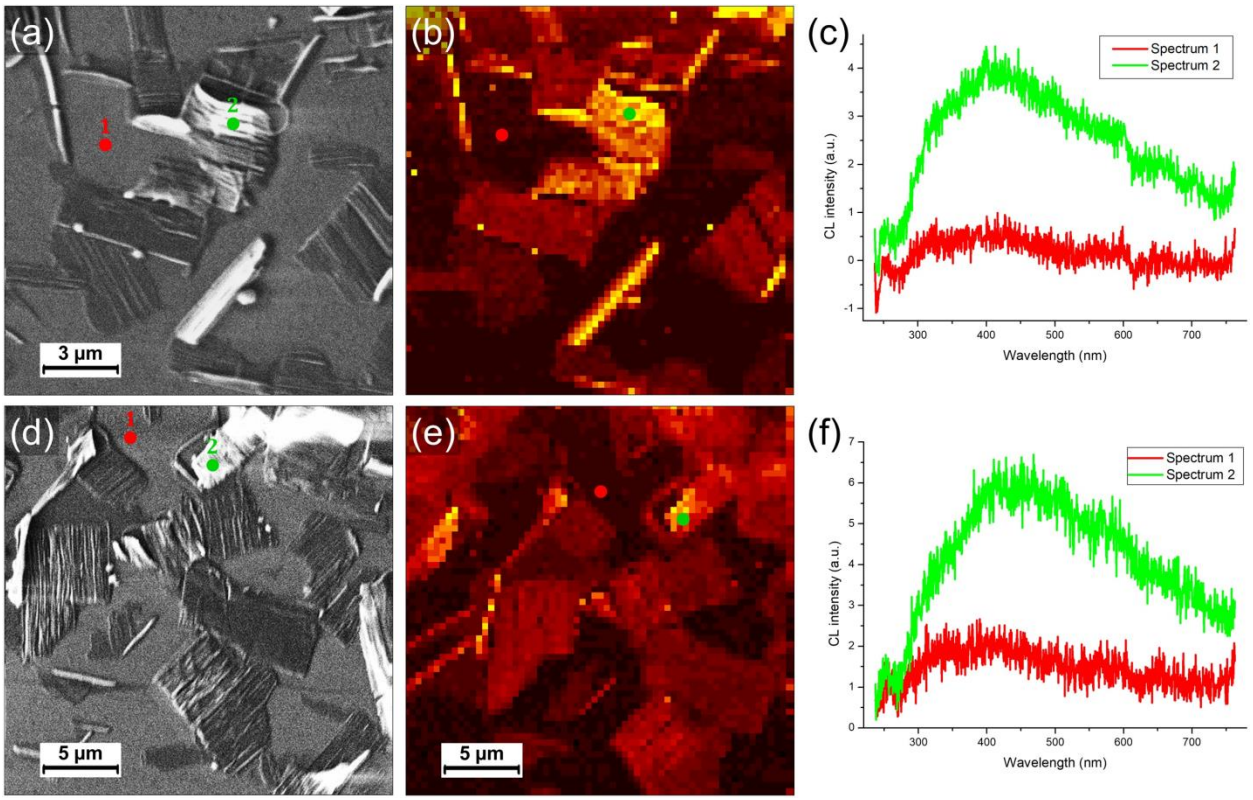

Figure S17. Correlative (a, d) SEM images and (b, e) CL maps of thin regions of the photocomposite film (diluted 10 times) on HOPG after annealing at 80 °C for 8 min. The brightness of each pixel is proportional to the intensity of the signal of the CL spectrum taken at this point (integration over the entire wavelength range). (c, f) CL spectra taken in points 1 and 2 from figures (a) and (d), respectively.

Comparison with the undiluted film

Here, a characterization by optical microscopy and by AFM of an undiluted film is presented. The film was prepared by drop-casting on a quartz slide and irradiating (at 405 nm and then in UV) the undiluted mixture formulation (5 % of PCDA and 0.05 % of Irgacure 369 in TMPTA, which acts here as the solvent). The images in figure S18 show crystalline domains similar to the PDA

domains observed in diluted films. Amorphous regions are also observed in their vicinity. This suggests that the phase separation and the crystallization of PCDA occur in the same way as in the diluted films studied in this work.

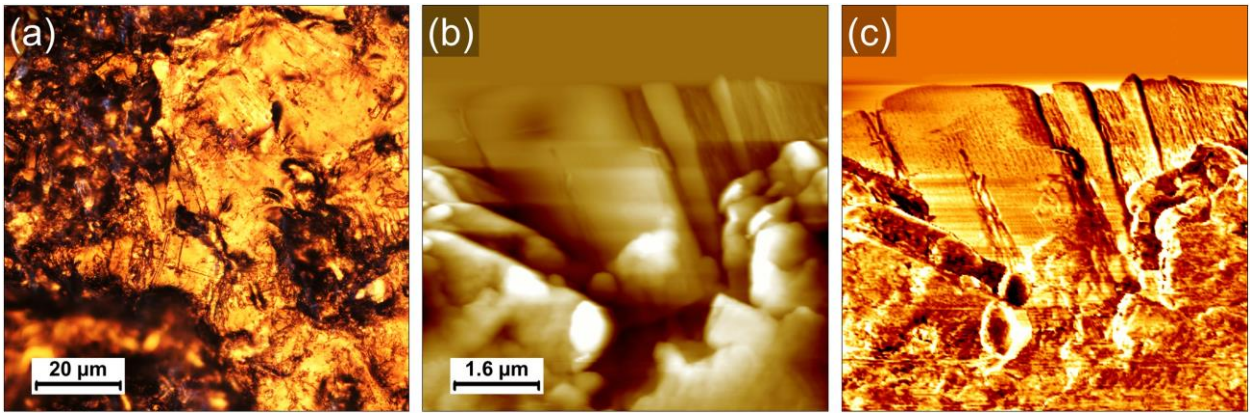

Figure S18. (a) Optical micrograph of the undiluted film drop-casted on a quartz slide. The brighter regions of the image exhibit flat, crystalline domains typical of PDA crystals. The darker regions correspond to amorphous areas that can be attributed to the polyacrylate. (b) AFM topography and (c) phase images of the same film. Typical PDA crystals can be identified in most of the image. The amorphous region on the top part of the image is attributed to the polyacrylate.