Supporting information

Quantification of mechanofluorochromism at the macroscale via colorimetric analysis of controlled mechanical stimulation

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1. Summary of experimental conditions

Table S1. Intensity of applied compression, H_C criterion, stress threshold and ratio of yellow pixels over the total (yellow + blue) pixels in the last snapshot for the 8 pure compression experiments.

Experiment number	Applied compression (N)	H_C	Stress threshold (MPa)	Ratio (%)
1	0-100	0.5727	13	20
2	0-100	0.5736	72	3
3	0-100	0.5694	230	4
4	0-100	0,5724	140	10
5	0-100	0.5699	38	9
6	0-100	0.5828	214	1
7	0-100	0.5748	281	1
8	0-100	0.5607	98	2

In Table S2, experiments with large crystals correspond to crystal lengths between 300 µm and 1.7 mm while small crystals are in the range from tens of µm to 300 µm.

Table S2. Sample size, type and intensity of applied compression, H_C criterion, shearing threshold for the 33 shearing experiments. The torque values recorded at the time corresponding to the shearing threshold detection and the ratio of yellow pixels over the total (yellow + blue) pixels in the last snapshot are reported for the constant force shearing experiments.

Experiment number	Sample size	Type of compression	Applied compression (N)	H_C	Shearing threshold (kPa)	Torque at corresponding time (Nm)	Ratio (%)
9	Large	Ramp	0-50	0.5720	0.194		
10	Large		0-50	0.5644	0.762		
11	Large		0-60	0.5686	1.136		
12	Large		10-60	0.5690	1.209		
13	Small		10-60	0.5717	0.835		
14	Small		20-70	0.5878	0.167		
15	Large		30-80	0.5854	2.266		
16	Large		30-80	0.5801	10.054		
17	Large		30-80	0.5755	2.353		
18	Small	Constant	5	0.5866	0.201	0.009	2
19	Small		5	0.5909	0.03	0.002	1
20	Small		5	0.5929	0.174	0.004	1
21	Small		10	0.5921	1.622	0.016	25
22	Small		10	0.5813	0.631	0.017	4
23	Small		10	0.5851	4.592	0.035	2
24	Small		10	0.5864	0.583	0.018	9
25	Small		10	0.5867	0.530	0.010	1
26	Small		10	0.5918	0.076	0.009	1
27	Small		15	0.5919	0.226	0.012	4
28	Small		15	0.5865	2.889	0.028	28
29	Small		15	0.5901	0.496	0.012	6
30	Small		15	0.5926	0.816	0.015	4
31	Small		20	0.5811	1.219	0.021	4
32	Small		20	0.5886	1.418	0.025	15
33	Small		20	0.5851	1.220	0.020	3
34	Small		30	0.5860	5.169	0.041	17
35	Small		30	0.5931	1.550	0.021	1
36	Small		40	0.5857	9.360	0.077	50
37	Small		40	0.5833	3.768	0.067	9
38	Small		40	0.5921	2.529	0.037	2
39	Small		60	0.5679	3.309	0.065	6
40	Small		60	0.5793	3.927	0.070	5
41	Small		60	0.5887	3.677	0.093	17

2. Data processing

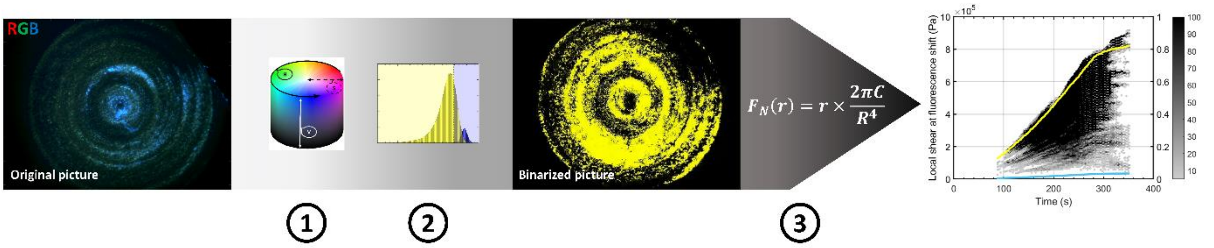

Figure S1. Schematics summarizing the three steps of data processing for shearing experiments. First and second steps correspond respectively to conversion from RGB to HSV colour space and determination of H_C criterion based on H histograms. Third step consists in associating each new yellow pixel to a local shearing value.

3. Conversion from RGB to HSV colour space

HSV colour space is comprised of three coordinates H, S and V that can be attributed respectively to circumference, radius and axis of a cylinder (Figure S2). H, S and V coordinates can be calculated from R, G and B values with the following equations [1] :

$$H = \left(\frac{G-B}{max-min} + 0\right)/6 \text{ if } R = max$$
$$H = \left(\frac{B-R}{max-min} + 2\right)/6 \text{ if } G = max$$
$$H = \left(\frac{R-G}{max-min} + 4\right)/6 \text{ if } B = max$$

$$S = \frac{max-min}{max}$$

$$V = max$$

with $max = \max(R, G, B)$ and $min = \min(R, G, B)$

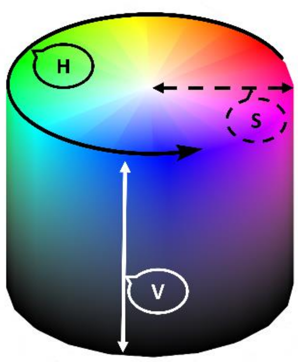

Figure S2. HSV colour space.

4. Removal of the background

In order to avoid reflectance of the LED on the pestle surface and to ensure a rough enough surface to shear the crystals, the pestle was covered with a piece of weakly fluorescent paper. The movie background is removed to avoid counting these pixels in the following step of the data processing. To do so, a threshold S_C is defined on the sum $S = R + G + B$ because dark pixels present a significantly lower value of this sum than fluorescent ones. As shown in Figure S3, when the applied S_c threshold is low (until $S_c = 5,000$), the mean H value is centred around 0.65, which corresponds to blue fluorescence of the paper stuck on the pestle. Indeed, a snapshot taken only with the paper (without **DFB-H** on the glass-window) revealed a mean H value of 0.645 when Sc = 0. When S_c is increased, this residual fluorescence is removed, resulting in a mean H value of 0.61 representing fluorescence of **DFB-H** blue crystals. Thus, according to Figure S3, $S_C = 10,000$ is a suitable threshold to remove dark background pixels and keep only fluorescent ones.

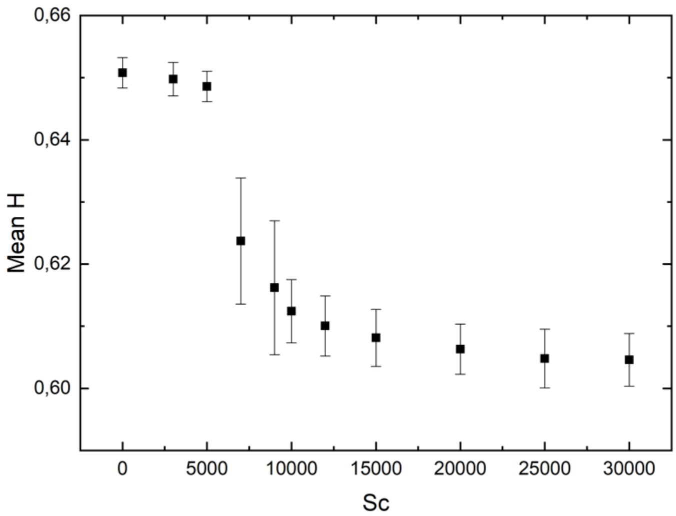

Figure S3. Mean H value of first picture from each movie versus applied S_c threshold.

In the case of pure compression experiments, the pestle was used without paper. The crystals were initially placed under the pestle and out of the reflectance areas in order not to interfere with subsequent detection of pixels turning to yellow.

5. Control experiment for H histograms

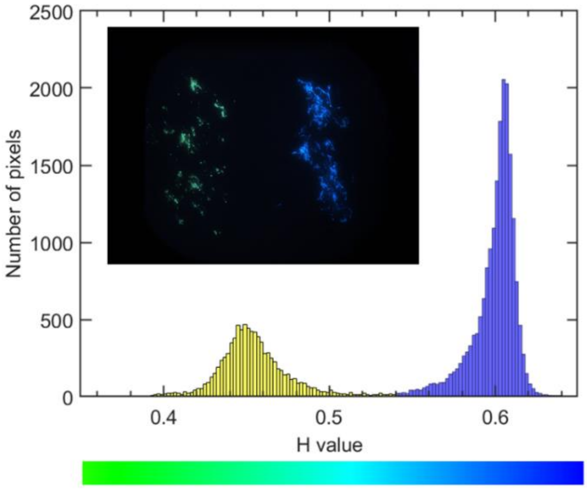

Figure S4. Histogram of H coordinate for manual grinding experiment with the corresponding picture in inset.

6. Pure compression experiments

All the pure compression experiments are performed on a single large crystal each time.
The compressive stress for a given time t, σ_t (in Pa) is calculated as follow:

$$\sigma_t = \frac{F_t}{S_t}$$

with F_t the force recorded by the sensor and S_t the surface of the crystal at a given time t. In the field of mechanics σ_t corresponds to the true stress.
The surface of the crystal S_t is determined by adding up the area of all the pixels that are fluorescent (blue + yellow) on each image, to take into account the modification of the surface with compression.
The fluorescent pixels are the ones having an S_C > 10 000 as previously shown in section 4 of ESI.

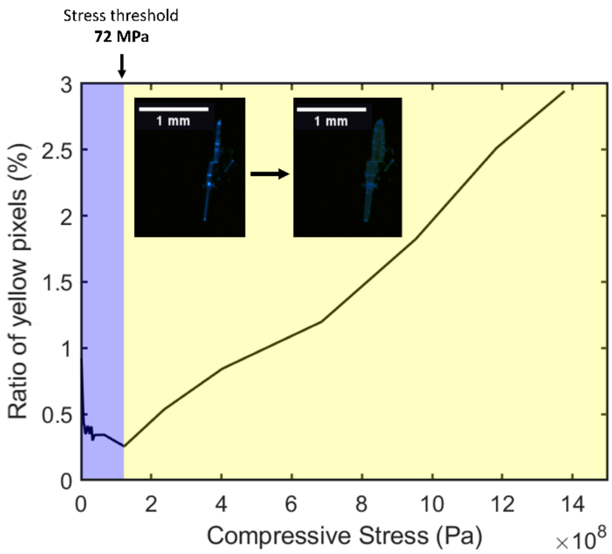

Figure S5. Ratio of yellow pixels over total of fluorescent pixels (blue + yellow) against pure compressive stress for experiment #2. The corresponding snapshots before (left) and after (right) compression are in inset. The stress threshold is defined as the point from which the ratio starts increasing, meaning that yellow phase appears.

7. Local shearing definition

The shear is here locally determined on each pixel using equation (1) below while the compression was deduced from the area of the whole crystal for the pure compression experiments.
In order to detect a reasonable change of fluorescence colour, only the pixels that belong to a cluster of 4 contiguous pixels turning to yellow were effectively detected. Then, the local shearing for each pixel detected as yellow was calculated as follows.

- C corresponds to the torque resulting from all shears and recorded by the sensor. Only the crystals that are in contact between the glass-window and the pestle experience a shearing and then contribute to C.
- r is the distance of a given pixel to the centre of the pestle.
- $\overrightarrow{F_N}$ corresponds to the shearing force on one pixel of given r and θ coordinates in the cylindrical coordinate system.
- R is the radius of the pestle.

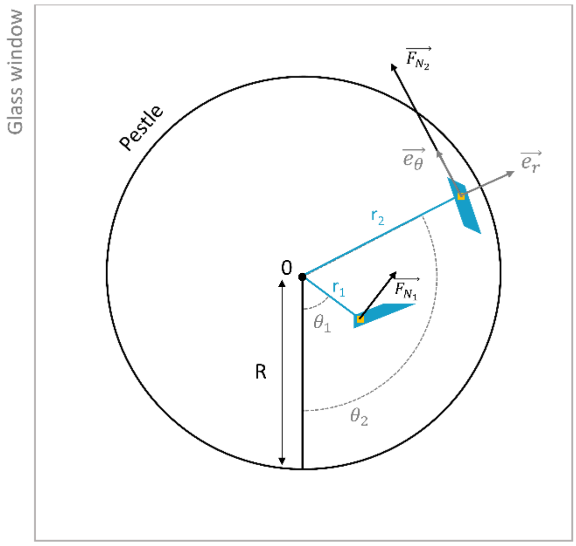

Figure S6. Schematics of coordinates and applied local shearing force.

The hypotheses are the following:

- $\overrightarrow{F_N}$ is linear and equal to zero at the centre of the pestle.
- $\overrightarrow{F_N}$ is independent of θ.

Thus: $r = 0 \rightarrow F_N = 0$

$r = R \rightarrow F_N = F_{N_{max}}$

Then, the shearing force on one pixel can be expressed as: $F_N(r,\theta) = F_N(r) = \frac{r}{R} F_{N_{max}}$

On the other hand, the torque resulting from all shear is:

$$C = \int_S F_N(r,\theta) \times r dS = \int_0^{2\pi} \int_0^R F_N(r,\theta) \times r \times r dr d\theta$$

$$C = \frac{F_{Nmax}}{R} \times 2\pi \times \frac{R^4}{4}$$

$$F_{N_{max}} = \frac{2C}{\pi R^3}$$

Finally, $$\boxed{F_N(r) = r \times \frac{2C}{\pi R^4}}. \qquad (1)$$

8. Definition of sample size and shearing threshold

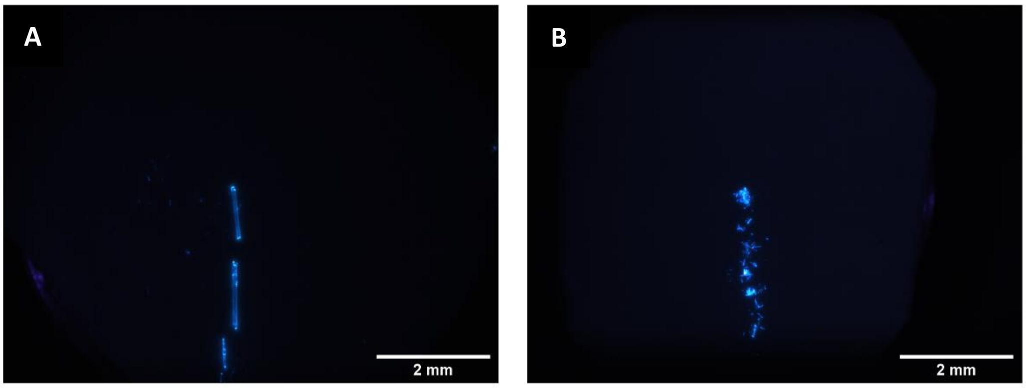

Figure S7. Pictures of (A) large crystals and (B) microcrystalline **DFB-H** powder before shearing in experiments #11 and #24 respectively.

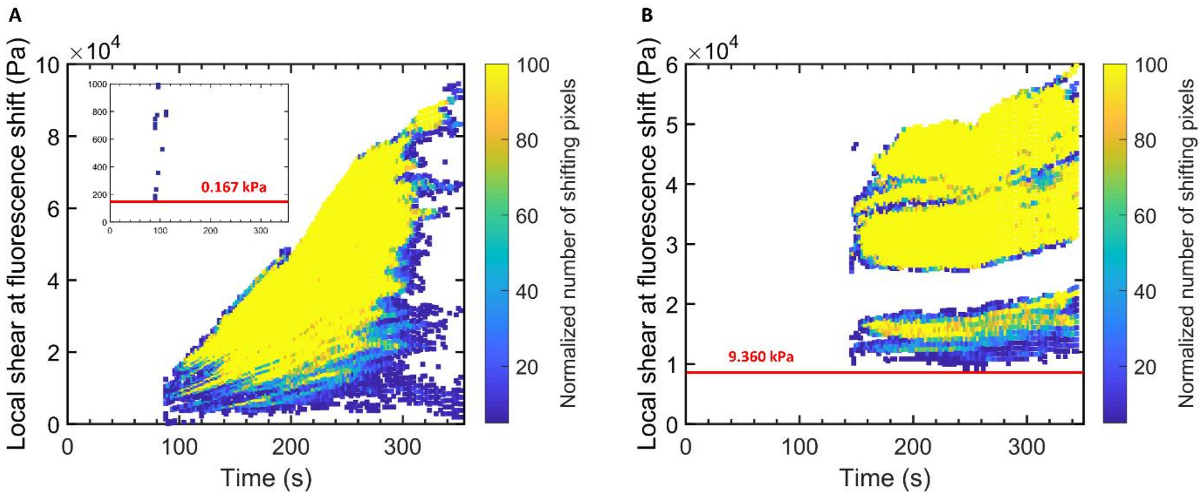

Figure S8. Plot of local shear at fluorescence shift for (A) a compression ramp (experiment #14) and (B) a constant compression experiment (experiment #36). Inset in (A) corresponds to a zoom. The horizontal red line represents the threshold of the experiment and corresponds to a local shear value.

9. Shearing experiments at constant vertical force

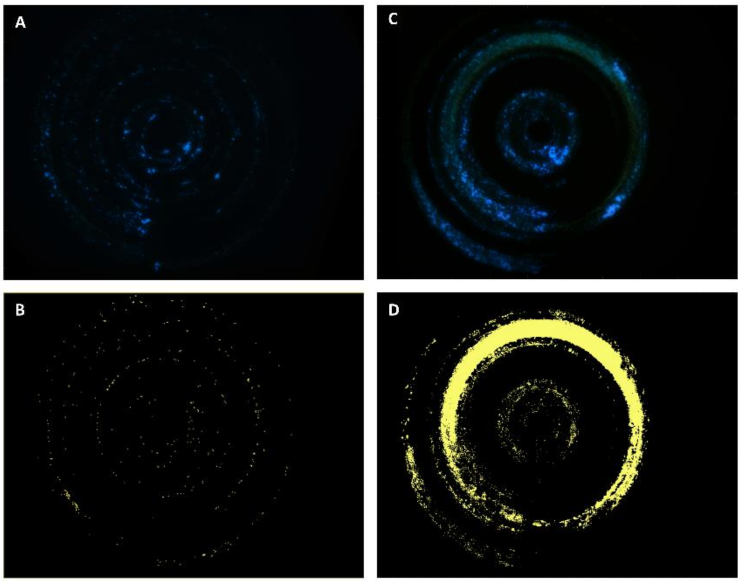

Figure S9. (A, C) Last snapshots of the movie and (B, D) corresponding binarized pictures for shearing experiments at constant vertical compressions. (A, B) correspond to an experiment (#20) with a final ratio of yellow pixels of 1 % (blue area of Figure 6 main text) and (C, D) correspond to an experiment (#41) with a final ratio of 17 % (red area of Figure 6 main text). Final ratio is defined as the ratio of yellow pixels over the total number of fluorescent pixels (yellow + blue) in the last snapshot.

10. Reversibility and impregnated papers

After one complete rotation of the pestle (experiments #42 and #44), the glass-window, on which the powder was sheared, is annealed in an oven at 110°C for 20 min. Good recoverability of the blue phase allowed us to run a second shearing experiment on the annealed samples (experiments #43 and #45). The yellow phase could still be obtained after the second stimulation, as indicated in Fig. S10.

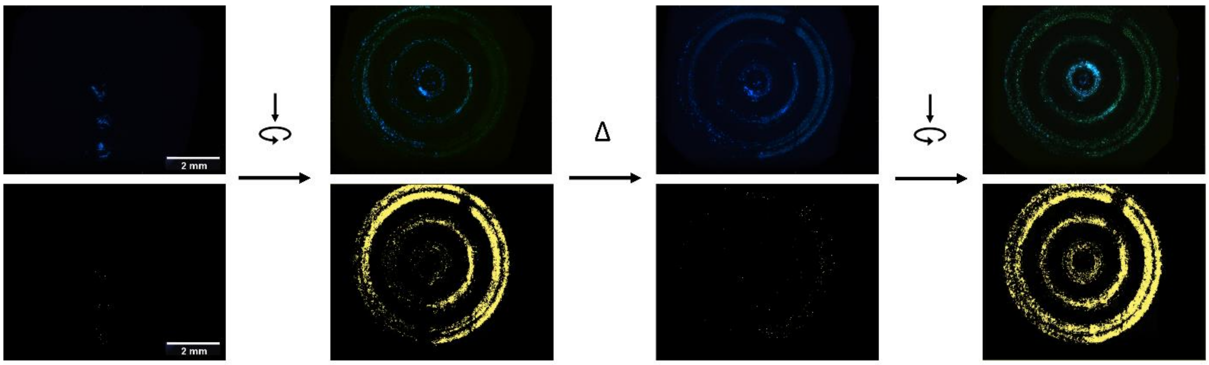

Figure S10. Pictures (top) and binarized images (bottom) of a shearing experiment on pristine powder sample (left, experiment #44) and after thermal annealing (right, experiment #45).

Papers were prepared by painting a piece of cellulose paper with a cotton soaked with a solution of **DFB-H** (0.18 M) in $CHCl_3$. The papers were then annealed in an oven at 110°C for 90 min to obtain exclusively the blue phase of **DFB-H**. Applying shearing stress on the papers yielded the yellow phase, as shown on the last snapshot of the movie and the corresponding binarized image (Fig. S11).

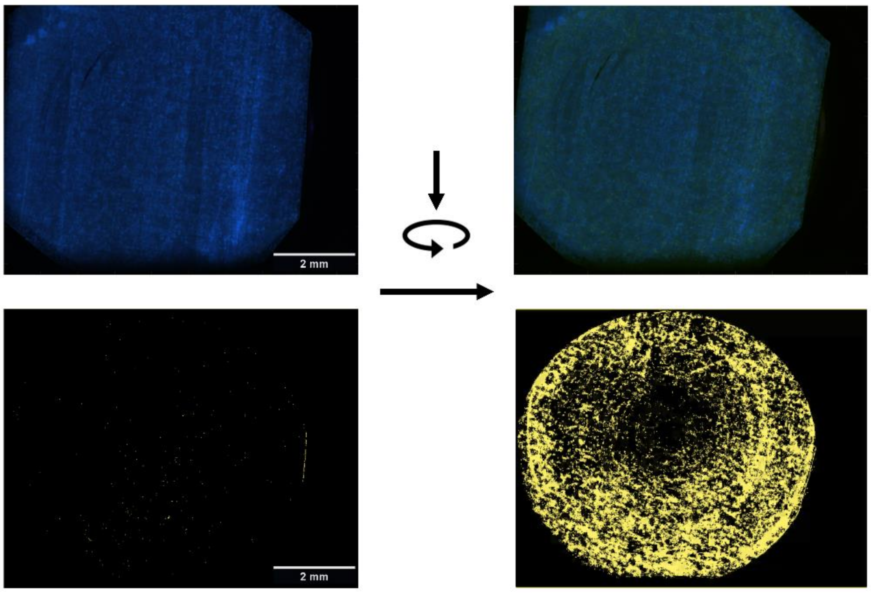

Figure S11. Pictures (top) and binarized images (bottom) before (left) and after (right) a shearing experiment on an impregnated paper (experiment #46).

Table S3. Type and intensity of applied compression, H_C criterion, shearing threshold for the shearing experiments on annealed powder samples and impregnated papers.

Experiment number	Experiment type	Type of compression	Applied compression (N)	H_C	Shearing threshold (kPa)
42	Pristine	Constant	30	0.5837	2.357
43	Annealed		30	0.5692	1.732
44	Pristine		30	0.5846	2.516
45	Annealed		30	0.5669	2.050
46	Paper		20	0.5944	0.044
47	Paper	Ramp	0-50	0.5981	0.473
48	Paper		0-50	0.5953	0.202

11. Additional references

(1) A. R. Smith, *Comput. Graphics* 1978, **12,** 12–19.