Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Mechanical Stimulation of Energetic Materials at the Nanoscale

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S1 Face indexing

Figure S1 shows results of the face indexing performed on single crystals of 34-DNP, PA, PETN, and CL-20.

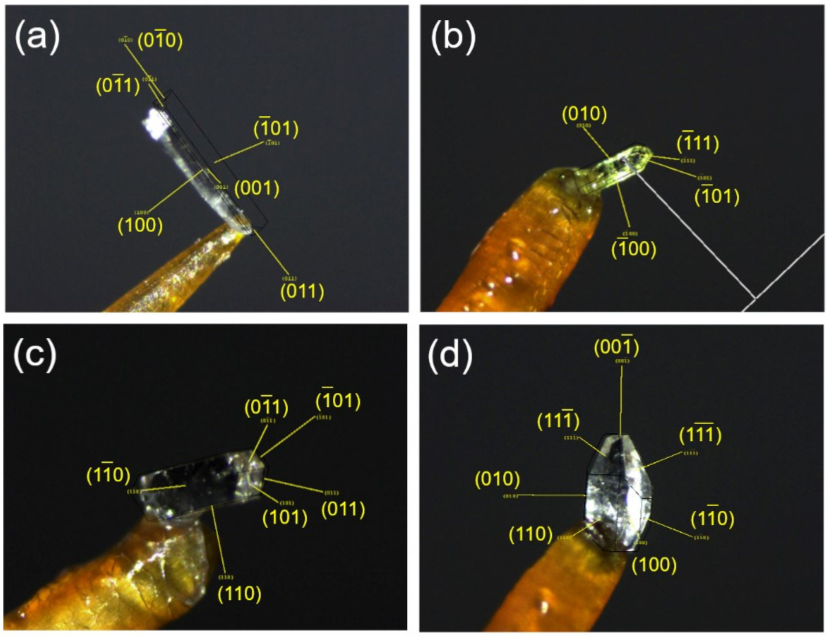

Figure S1. Results of face indexing of model EMs: (a) 34-DNP, (b) PA, (c) PETN, and (d) CL-20.

S2 Spontaneous PA surface dynamics

Figure S2 summarizes the results of prolonged investigation of the (100) face spontaneous rearrangements (RH ≈ 30%). AFM images of the same small region, 2x2 µm, obtained with 1.5 hours interval, show disappearance of the growth steps and flattening of the surface, Figure S2 a-b. However, on a larger scale, it can be seen that, together with the rearrangement of the growth steps, the surface is covered with cubic particles. While growth steps disappearing, particle size and number increase, which indicates the transfer of the material within crystal, Figure S2 c-d.

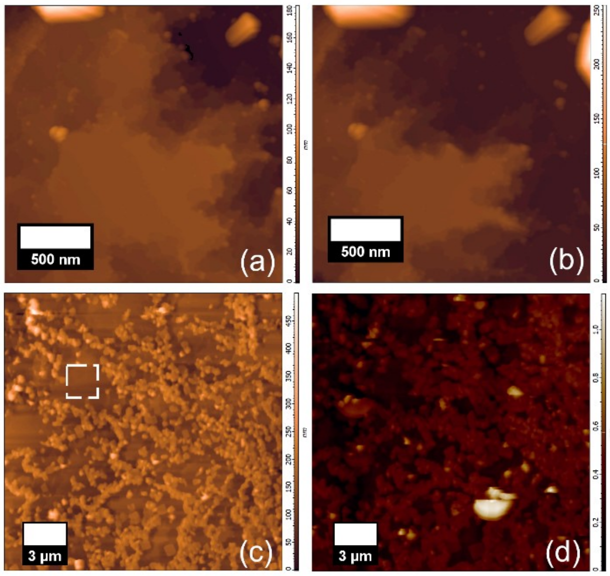

Figure S2. (a-b) AFM images of the same region separated by 1.5 hours and (c-d) AFM images of a larger region separated by 3 hours indicate the spontaneous rearrangements of the PA crystal (100) face. Note that (a) is highlighted region from (c).

S3 Applied force influence on picric acid response to friction stimulation

To gain more insights into the material response to friction stimulation, we investigated the growth dynamics of the hole volume against the magnitude of the friction force. To this end, two scratch tracks were monitored simultaneously: one was created by applying a force close to the threshold force, 0.67 µN, and another was created by a much higher force, about 6 µN. The volume of each hole grows with its own rate if taken in absolute units: 143 ± 16 nm^3 s^{-1} for the first scratch and 1120 ± 140 nm^3 s^{-1} for the second. However, when the values are normalized by the initial V_0 volume of the scratch, the grow rates become close for the both scratches: $(5.3 \pm 0.3)\cdot 10^{-4}$ s^{-1} from the 0.67 μN scratch, and $(5.9 \pm 0.4)\cdot 10^{-4}$ s^{-1} from the 6 μN scratch, Figure S3. Hence, the energy imparted by the scratch plays negligible role in the dynamics of the surface.

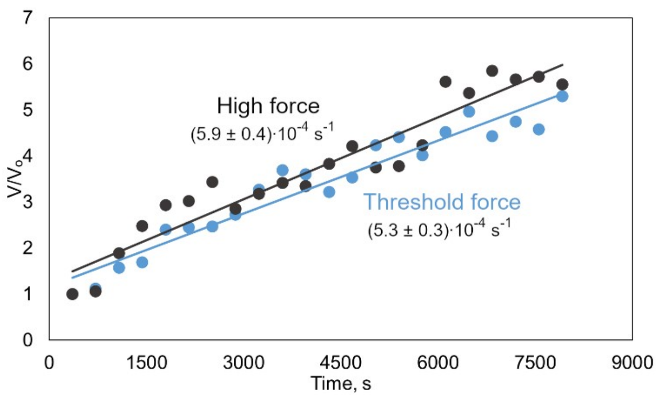

Figure S3. Influence of the force applied during friction stimulation. Despite significant force difference, 0.67 and 6 μN, volume growth rate is similar for both scratch tracks.

S4 Morphology of 34-DNP, PETN, and CL-20 samples

Figure S4 shows surface structure of model EMs obtained by AFM. Similar to PA, 34-DNP, PETN and CL-20 crystal surfaces consist of the grow steps with height of 1.47 ± 0.17 nm, 1.16 ± 0.15 nm and 1.21 ± 0.16 nm, respectively.

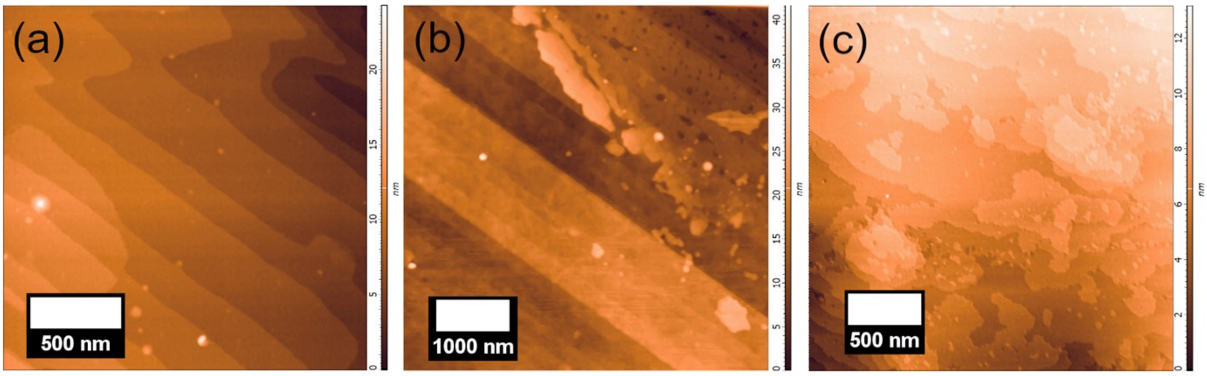

Figure S4. Surface structure of model EMs measured by AFM. (a) 34-DNP, (b) PETN, and (c) CL-20.

S5 Threshold force values for model EMs

Table S1 shows the threshold force and pressure values obtained during indentation experiments along with the experimental and calculated yield strength values for 34-DNP, PA, PETN and CL-20. The threshold force needed to visually affect the surface naturally increases with increasing the mechanical strength of crystal.

Table S1. Calculated threshold forces, pressure and yield strength values of 34-DNP, PA, PETN, and CL-20

Compound	**Threshold force, μN**	**Threshold pressure, GPa**	**σ, MPa**
PA	0.48 ± 0.07	2.4 ± 0.4	52 [b]
34-DNP	<0.07	<0.4	29 [a]
PETN	1.34 ± 0.14	6.6 ± 0.7	60 [b]
CL-20	9.1 ± 1.0	45 ± 5	104 [a]

[a] Calculated, see discussion in the introduction. [b] Experimental values.[1]

S6 Friction stimulation of 34-DNP at a high humidity

Figure S5 shows the result of scratching experiment performed on 34-DNP crystal. After scratching, nanoparticles from several tens of nanometers to 150 nm in size appeared on and near the scratch track. The total volume of nanoparticles is $0.85 \cdot 10^{-3}$ μm^3, which coincides in order with the volume of the scratch track observed in previous experiments, $0.39 \cdot 10^{-3}$ μm^3. Thus, these particles are probably the material removed from the crystal surface during the experiment.

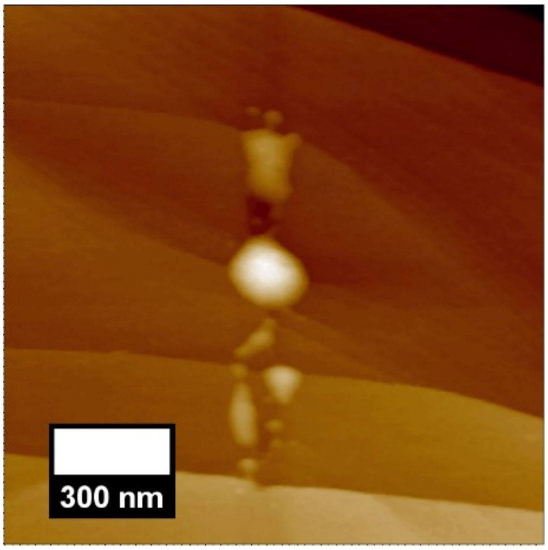

Figure S5. Result of the friction stimulation of 34-DNP at high humidity, RH 63%.

References

(1) Afanas'ev, G. T.; Bobolev, V. K. *Initiation of Solid Explosives by Impact*, Nauka.; Moscow, 1968.