Supporting Information

Direct Quantification of Rapid and Efficient Single-Stroke Actuation by a Martensitic Transition in a Thermosalient Crystal

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Methods

Preparation and crystallization. Palladium(II) hexafluoroacetylacetonate (product no. 401471, Sigma-Aldrich), azobenzene (product no. 424633, Sigma-Aldrich) and butyronitrile (product no. 538264, Sigma-Aldrich) were used to prepare the (phenylazophenyl)palladium(II) hexafluoroacetylacetonate (PHA) crystals. The compound was prepared by cyclometalation of azobenzene with palladium(II) hexafluoroacetylacetonate.[1] In a typical procedure, 1 mmol of palladium(II) hexafluoroacetylacetonate and azobenzene were dissolved in 12 mL butyronitrile. The solution was slowly stirred and refluxed for 10 hours at 100 °C. Once the reaction completed, the hot solution was filtered five times and transferred to a crystallization dish which was then covered with an aluminium foil and left undisturbed at room temperature for nearly 35 days. This resulted in formation of PHA crystals, 0.1 – 10 mm in size, with hexagonal prismatic morphology. Most of the crystals could be categorized into one of the two habits, habit 'type 1' and 'type 2'. The habit type 1 crystals, which comprised nearly 70% of the total yield were mostly single crystals with nearly identical length (*l*) and width (*w*) ranging from 0.5 to 1 mm and thickness (*h*) ranging from 0.2 to 0.5 mm. The habit type 2 crystals, nearly 30% of the total yield, were polycrystalline, and had an identical *w* and *h* ranging from 1 to 2 mm and *l* ranging from 3 to 6 mm.

Structural and microscopic analysis. The phase identity (Table S1) of the PHA crystals was confirmed by single crystal X-ray diffraction analysis using a Bruker APEX DUO diffractometer equipped with a Cobra cooling device (Oxford Cryosystems), graphite-monochromated MoK_α radiation (λ = 0.71073 Å) and CCD as area detector. Cell measurements, data collection, integration, scaling and absorption corrections were performed by using Bruker Apex II software.[2] The diffraction images were integrated by using Bruker's SAINT program.[3] Multi-scan absorption corrections were applied to the data by using SADABS.[4] The structure was solved by direct methods, implemented in SHELXS-97.[5] The structure refinement, using the OLEX2 interface[6] was performed by using the full-matrix least-squares method, based on F^2 against all reflections as implemented in SHELXL-2014/7. The hydrogen atoms bonded to carbon atoms were fixed using the HFIX command in SHELX-TL. A check of the final CIF using PLATON[7] as part of WinGX[8] did not show any missing symmetry. The structure has been deposited within the Cambridge Structure Database with reference 1873831. The ORTEP diagram of PHA molecule at 50% probability level is shown in Figure S1.

The quality of the crystals was also analyzed by using polarized optical microscopy (microscope Nikon LV 100). In order to compensate for the thickness effects, the imaging was performed both in reflection and transmission modes. In case of type 1 crystals, the crystals were almost dark and hard to distinguish from the background when the longest crystal axis was oriented parallel and perpendicular to the cross polarizer, and exhibited maximum brightness and clear contrast from the background when the longest crystal axis was oriented at 45° with respect to the cross polarizer which confirmed their single-crystal nature. The face indexing for type 1 crystals is shown in Figure S2. On the contrary, type 2 crystals displayed mixed contrast when oriented either parallel, perpendicular or at 45° with respect to the cross-polarizer which confirmed their polycrystalline nature. For the force measurements, a total of 48 crystals (24 of each type) were selected. Out of the 24 crystals of each type, 12 crystals were used to record the longitudinal force and the other 12 crystals were used to record the lateral expansion force.

Heat capacity. The specific heat capacity at 25 °C for PHA crystals was measured using modulated differential scanning calorimetry on DSC Q2000 (TA Instruments). The temperature modulation and period were set to 1 °C and 60 s, respectively, whereas the temperature ramping rate was fixed at 1 °C min^{-1}.

Elastic modulus. The elastic modulus of PHA crystals was estimated using a tensile stage (SEMTester DAQ- linear, model 8000-0014, MTI instruments) in a three-point bending configuration at room temperature. The tensile tester was equipped with a 5 N load cell and a bending span of 1.5 mm. A crosshead speed of 0.05 mm min^{-1} was used. The tensile stage was mounted under an optical microscope fitted with camera to record the crystal deformation. The elastic modulus of the crystal, E_{cryst}, was calculated as a ratio of the bending stress σ and the bending strain ε:

$$E_{cryst} = \sigma / \varepsilon \qquad \text{(Eq 1)}$$

where

$$\sigma = 3Pl / 2wh^2 \qquad \text{(Eq 2)}$$

$$\varepsilon = 6dh / l^2 \qquad \text{(Eq 3)}$$

In the above equations, P is the load applied at the middle of the crystal causing a deflection d, and l, h and w are the crystal length, thickness and width, respectively. For the crystal used in this experiment, the dimensions were l = 8 mm, w = 1 mm and h = 0.5 mm. The σ–ε diagram obtained is shown in Figure S3 where the linear region AB returned E_{cryst} = 3.27 GPa.

Measurement of the crystal expansion force. The expansion force of the crystals were measured using AE801 sensor (Kronex). The detailed design and operating principles of the AE801 sensor can be found elsewhere.[9] The sensor is essentially a cantilever beam composed of single crystal N-type silicon sandwiched between ion-implanted P-type resistors. The deflection of the beam causes mechanical stress which affects the resistor due to piezoresistive effect and results in proportional change in the output voltage. The sensor operates on the Wheatstone bridge principle where the two sensor resistors act as one half of the bridge and the two external resistors provided by the signal conditioning device act as the other half of the bridge. The signal conditioning device also provides the excitation voltage necessary to operate the sensor. Under zero strain condition of the cantilever, the Wheatstone bridge is balanced with zero output voltage. A deflection and hence imposing strain in the cantilever causes imbalance in the Wheatstone bridge and a proportional change in the output voltage. The specified maximum deflection of the cantilever is ~70 µm, corresponding to maximum output signal of 30 mV per unit excitation volt. To compensate for sensor-to-sensor variation and to improve the accuracy, each sensor was individually calibrated by applying controlled deflections via micrometer stage and by recording the change in output voltage while ensuring good linearity between the input deflection and the output voltage. Any offset in the sensor value was recorded and taken into account during the experiments. Once the sensor was calibrated with known voltage-deflection characteristics, the expansion force for the PHA crystals was calculated using the force-deflection relationship for the cantilever beam (Eq 4):

$$d = Fa^2(3s - a) / 6EI \quad \text{(Eq 4)}$$

where d = maximum tip deflection of the cantilever, F = applied force, s = cantilever length, a = point of action of the applied force measured from the fixed end ($a \leq s$). E and I are the elastic modulus and the moment of inertia of the cantilever beam, respectively. Here, s, E and I are constants with the values of 5 mm, 160 GPa and 2.67×10^{-16} m^4, respectively. When $a = s$, the above expression simplifies to

$$d = Fs^3 / 3EI \quad \text{(Eq 5)}$$

Before starting the force measurements, the position of the crystal with respect to the cantilever was observed using optical microscope to take into account the value of a. The beam deflection upon crystal expansion was converted into force using Eqs 4 and 5, as appropriate. To measure the longitudinal expansion force, the crystal was placed between the block of brass, fixed to the heating stage, and the sensor cantilever such that the length l of the crystal was perpendicular to the block face as well as to the cantilever axis. For measurement of the lateral expansion force, the crystal was placed between the heating stage and the sensor cantilever such that the thickness h of the crystal was perpendicular to the heating stage as well as to the cantilever axis.

The signal conditioner NI-9219 (National Instruments)[10] was used to operate the AE801 in the half bridge configuration and to supply the excitation voltage of 2.5 V. The signal conditioner was connected to the compact data acquisition device NI-cDAQ9174 (National Instruments)[11] which acquires the signals from the signal conditioner and transmits the data to computer for in-situ display and recording using LabVIEW software (National Instruments). The data was acquired in the high-speed mode at the rate of 10 samples per second. The complete setup used for measuring the PHA crystal expansion force is shown schematically in Figure S4. Due to very high sensitivity of AE801 sensor, the output force signals under idle state varied between ±0.05 mN (Figure S5) which can be considered as the maximum uncertainty in the reported force values.

Tables

Table S1. Basic crystallographic data for a PHA crystal

Para-meter	*a* / Å	*b* / Å	*c* / Å	*α* / °	*β* / °	*γ* / °	*V* / Å^3	*ρ* / (g cm^{-3})	R_{int} / %
Value	8.437(3)	13.211(5)	15.740(6)	86.979(5)	86.428(5)	84.577(5)	1741.2(11)	1.887	3.18

Figures

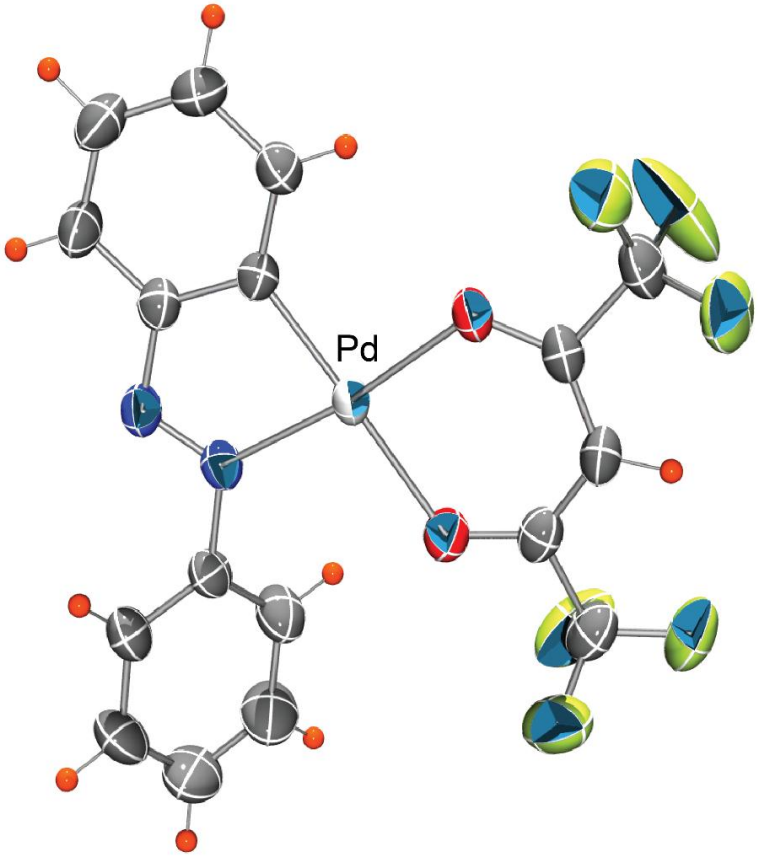

Figure S1. ORTEP diagram of PHA molecule showing thermal ellipsoids plotted at the 50% probability level.

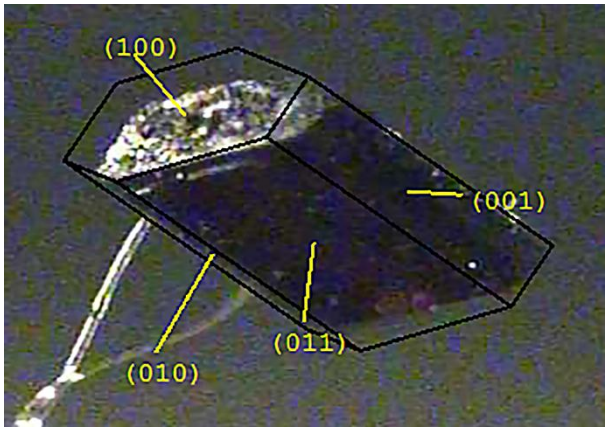

Figure S2. Face indices for type 1 crystal.

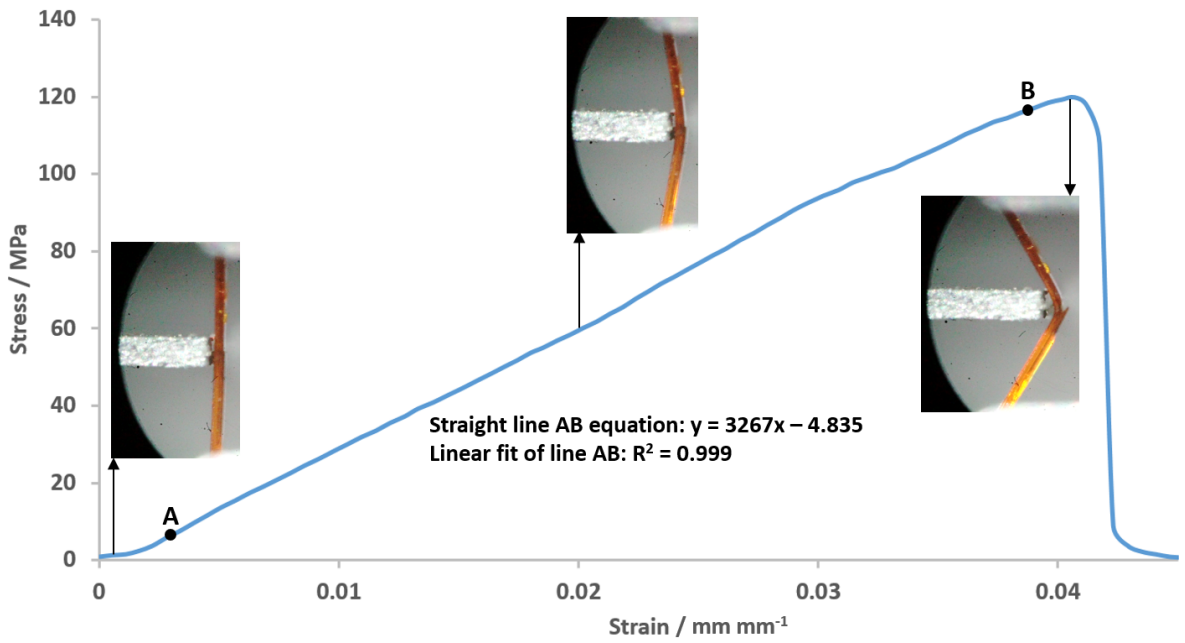

Figure S3. Stress-strain curve for a PHA crystal obtained by a three-point bending test. The insets show optical micrographs of the crystal during at different stages of the test: contact between the crystal and the jig (left), during bending (middle) and at fracture (right). The linear region between points A and B was used to calculate the approximate elastic modulus of the crystal.

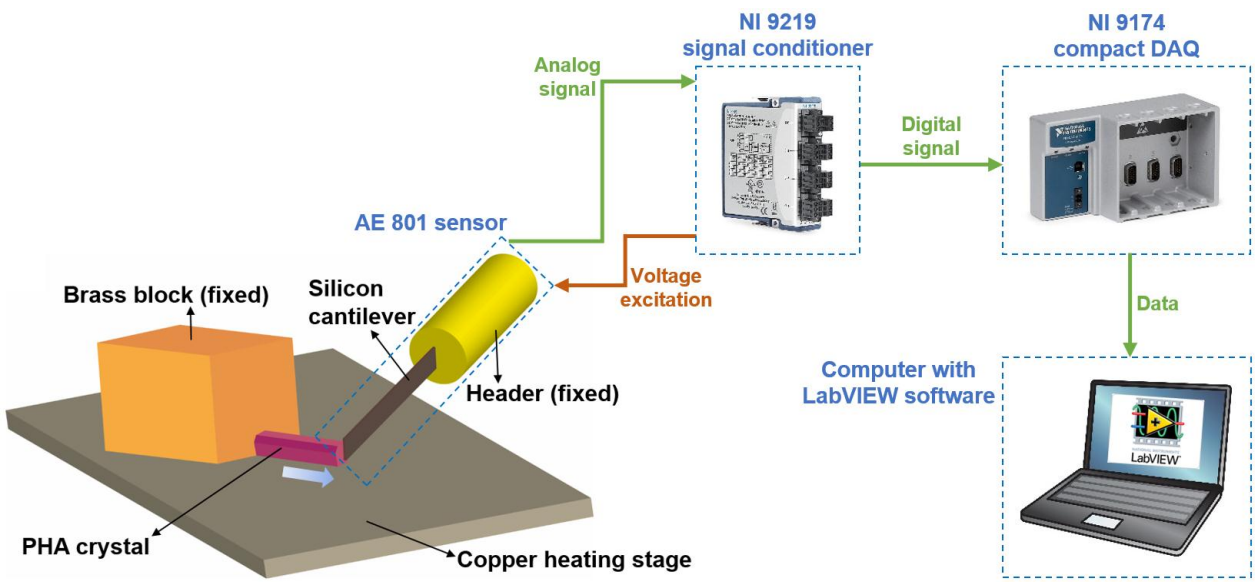

Figure S4. Block-diagram of the setup used for measurement of the crystal expansion force. The images of NI 9219 and NI 9174 are used with permission from National Instruments.

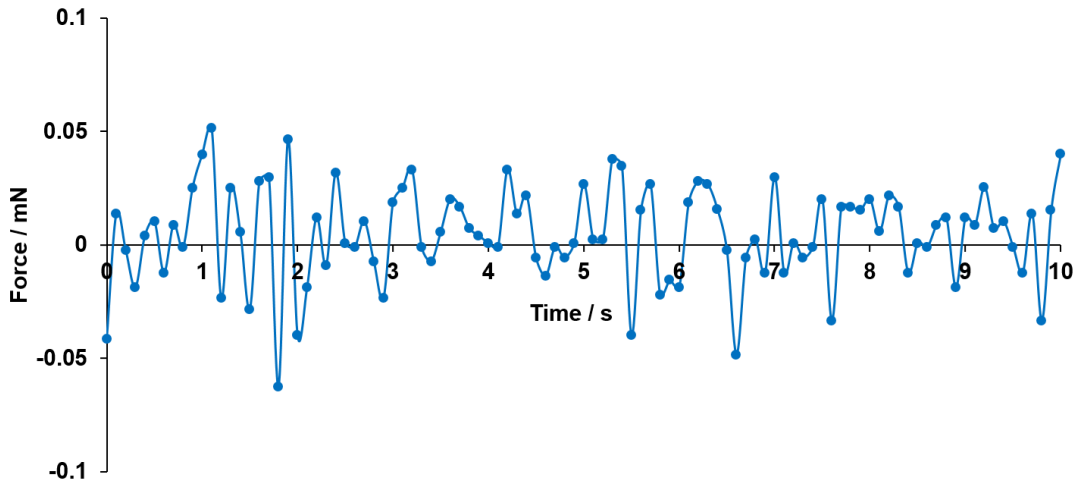

Figure S5. Typical variation in the sensor signal in idle state.

Legends to the Supporting Movies

Movie S1. Phase transformation of habit type 1 PHA crystal.

Movie S2. Phase transformation of habit type 2 PHA crystal.

Movie S3. Longitudinal force measurement for PHA crystal of habit type 2.

Movie S4. Lateral force measurement for PHA crystal off habit type 1.

Movie S5. Cyclic longitudinal force measurement for PHA crystal of habit type 1.

Movie S6. Cyclic longitudinal force measurement for PHA crystal of habit type 2.

References

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