Electronic Supplementary Material (ESI) for Chemical Science.


# Supplementary Information

## Martensitic Organic Crystals as Soft Actuators

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## Materials and Methods

***Material*.** Hexamethylbenzene (HMB) was purchased from a commercial supplier (Sigma-Aldrich) and further purified by sublimation to remove an unidentified highly fluorescent impurity. The sublimed compound was recrystallized by slow evaporation from benzene solution layered on the top of a layer of water. Growing the crystals on top of a layer of water dramatically increased crystallization reproducibility and crystal quality.

***Optical microscopy.*** Optical images were acquired using a Nikon LV 100 motorized optical microscope. The images were acquired using a *z*-stacking program to obtain an image that is in focused at varying levels of height.

***Force measurements.*** The load-time profiles of the crystals were measured using a tensile tester MTII/Fullam Semtester (MTI Instruments) equipped with a 5 N-load cell. The crystals were placed in between the two tensile arms and the arms were closed until contact with the crystal was reached. The steel stage of the tensile tester supporting the crystal was heated with a Thorlabs TECD2 2.4 dual-stage heating element until the phase transition was observed. The force of the measurement was calculated by determining the difference in force before and after the phase transition (Figures S2 and S3).

***Differential Scanning Calorimetry (DSC).*** Measurements were performed with a TA Q2000 DSC system using sealed aluminum pans and the temperature ranges from 315 K to 400 K with a rate of heating/cooling of 10 K $min^{-1}$.

***Single crystal X-ray Diffraction.*** The X-ray diffraction data were collected by using a Bruker APEX DUO diffractometer equipped with a Cobra cooling device (Oxford Cryosystem) with graphite-monochromated Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) or Cu$K_\alpha$ radiation ($\lambda$ = 1.54178 Å) and CCD as area detector. Data collection, integration, scaling and absorption corrections were performed by using Bruker Apex II software.[1] The integration and scaling of the data were performed by using the program SAINT.[2] The X-ray diffraction data were corrected for absorption effects using SADABS.[3] The structure was solved by direct methods, implemented in SHELXS-97.[4] The structure refinement, using the OLEX2 interface[5] was performed by using the full-matrix least-squares method, based on $F^2$ against all reflections as implemented in SHELXL-2014/7. The basic crystallographic and refinement details, and the CCDC deposition number are provided in Table S1.

## Supplementary Notes

**Note S1.** The compound as received initially contained an extremely small amount of a highly fluorescent impurity that prevented reproducible recrystallization. Several of the crystals' mechanical effects were only observed by recrystallization after sublimation to remove the impurity.

**Note S2**. This pressure-induced phase change was not observed when crystals were grown directly from the commercially obtained material.

## Supplementary Tables

**Table S1.** Crystallographic and refinement details of HMB used in this work

| | |
|---|---|
| Temperature / K | 296(1) |
| Formula weight | 162 |
| Space group | $P\bar{1}$ |
| $a$ / Å | 5.322(8) |
| $b$ / Å | 6.293(10) |
| $c$ / Å | 8.099(12) |
| $\alpha$ / ° | 104.05(2) |
| $\beta$ / ° | 99.08(2) |
| $\gamma$ / ° | 99.34(2) |
| Volume / Å$^3$ | 254.1(7) |
| $Z$ | 1 |
| Density / (g cm$^{-3}$) | 1.06 |
| $\mu$ / mm$^{-1}$ | 0.059 |
| $F_{000}$ | 90 |
| $h_{min}$, $h_{max}$ | -6,6 |
| $k_{min}$, $k_{max}$ | -7,7 |
| $l_{min}$, $l_{max}$ | -9,9 |
| No. of measured reflections | 3101 |
| No. of unique reflections | 990 |
| No. of reflections used | 833 |
| $R_{all}$, $R_{obs}$ | 0.0753, 0.0675 |
| $wR_{2,all}$, $wR_{2,obs}$ | 0.2318, 0.2211 |
| $\Delta\rho_{min,max}$ / (e Å$^{-3}$) | -0.18, 0.304 |
| *GooF* | 1.123 |
| CCDC No. | 1936559 |

**Table S2**. Comparison of maximum force-to-body weight ratio between HMB and some animals

| Animals | Force-to-weight ratio |
|---|---|
| Horse[6] | 0.2 |
| Elephant[7] | 1.7 |
| Oribatida[8] | 530 |
| Ant[9] | 1000 |
| Horned beetle[10] | 1141 |
| HMB | ~10,000 (this work) |

## Supplementary Figures

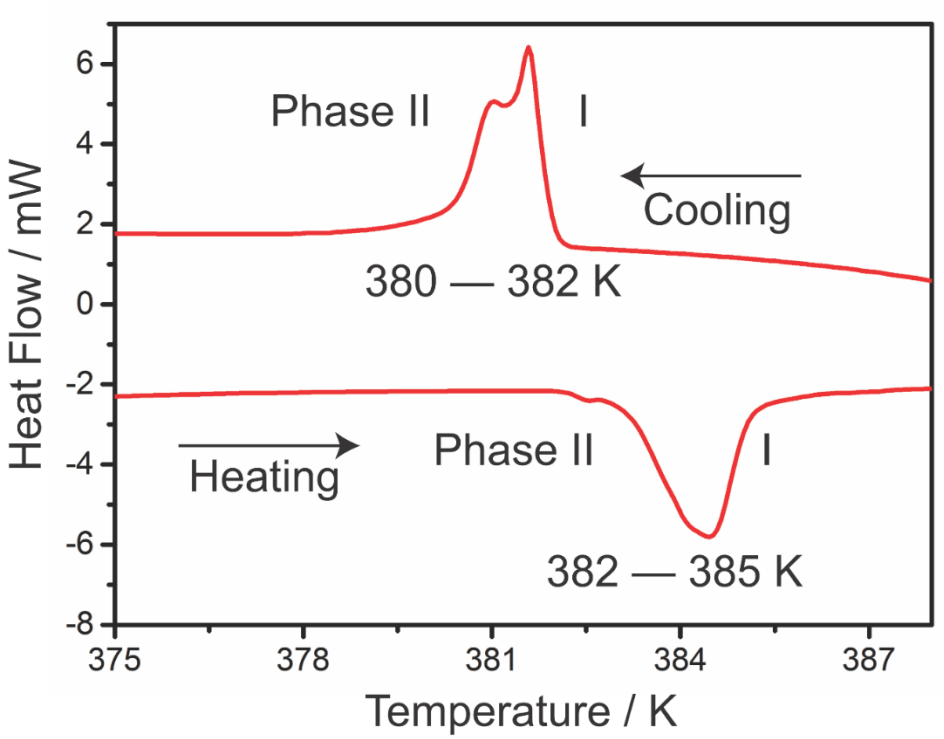


**Figure S1.** DSC of a single crystal sample of HMB scanned from 375–390 K. The shoulder at 381 K on cooling is attributed to splitting of the crystal during the transition during heating. The heating and cooling rate were 10 K $min^{-1}$.

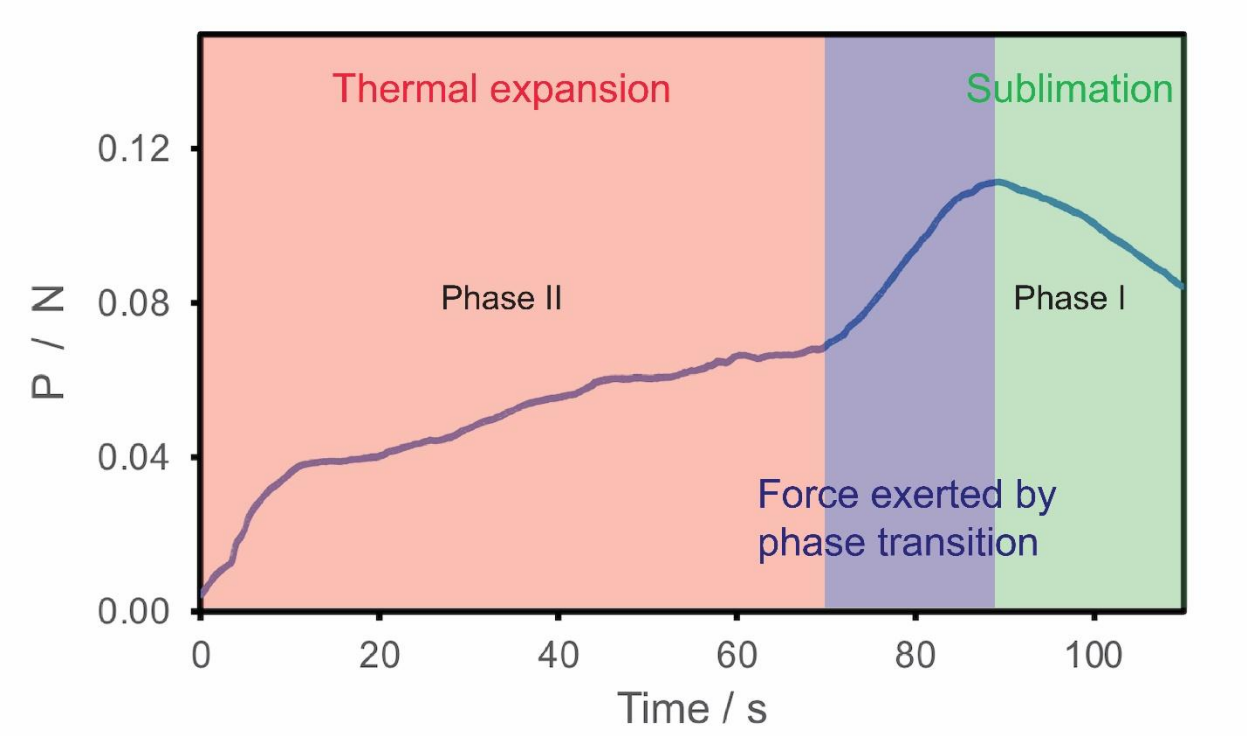


**Figure S2.** Load-time profile of a single HMB crystal measured by heated tensile tester (sample #2).

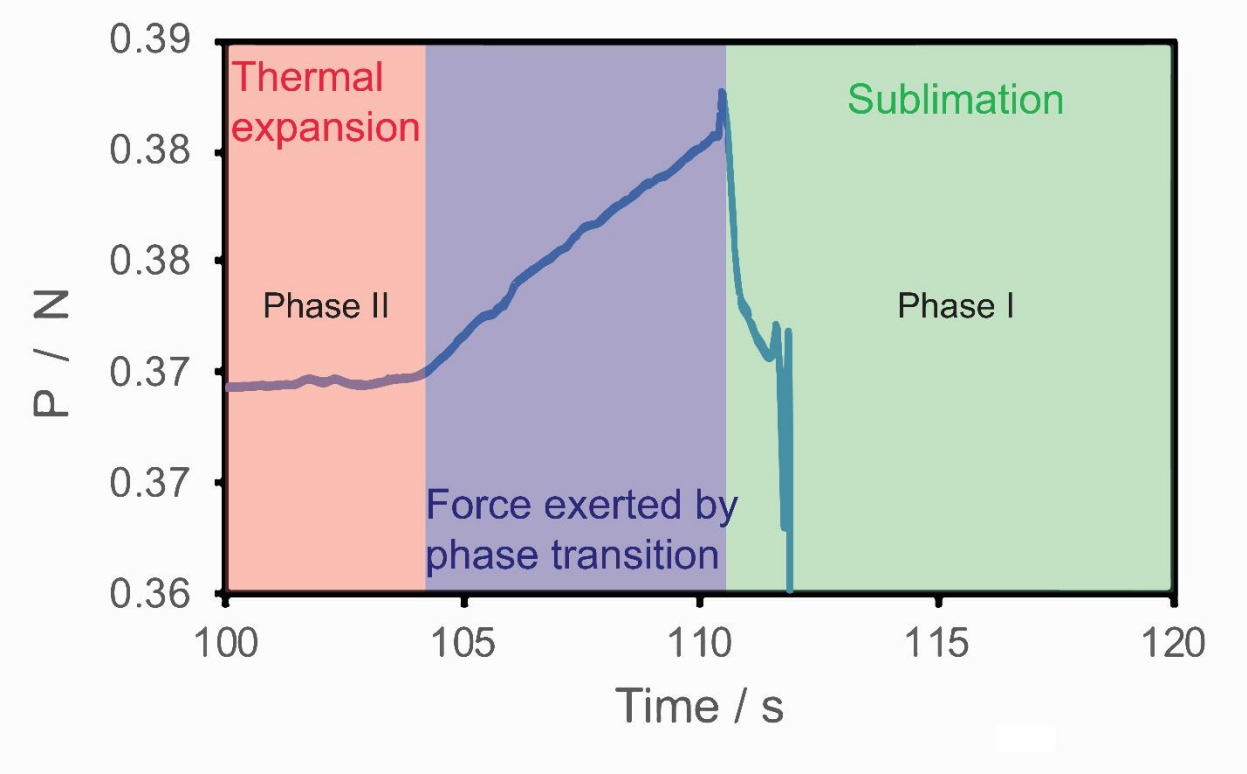


**Figure S3**. Load-time profile of a single HMB crystal measured by heated tensile tester (sample #3).

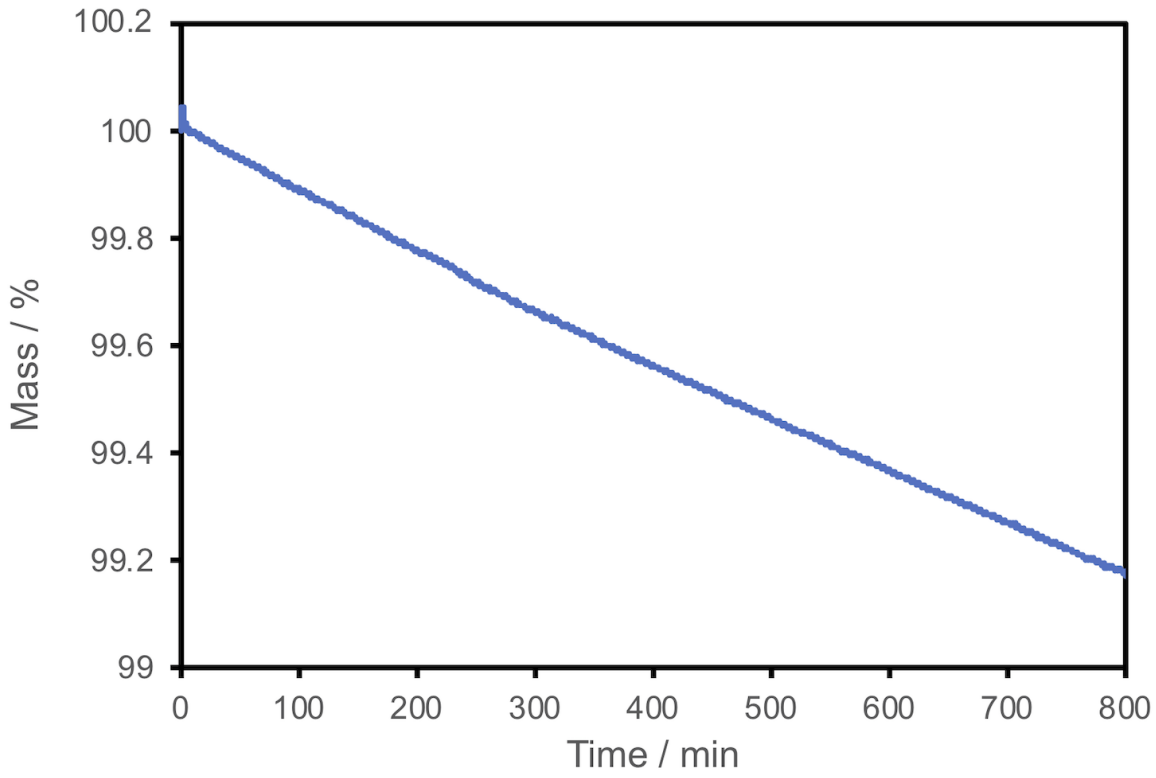


**Figure S4.** Thermogravimetric analysis of HMB at 293.15 K for 800 min at ambient pressure under a nitrogen atmosphere. The sample lost 0.8% mass.

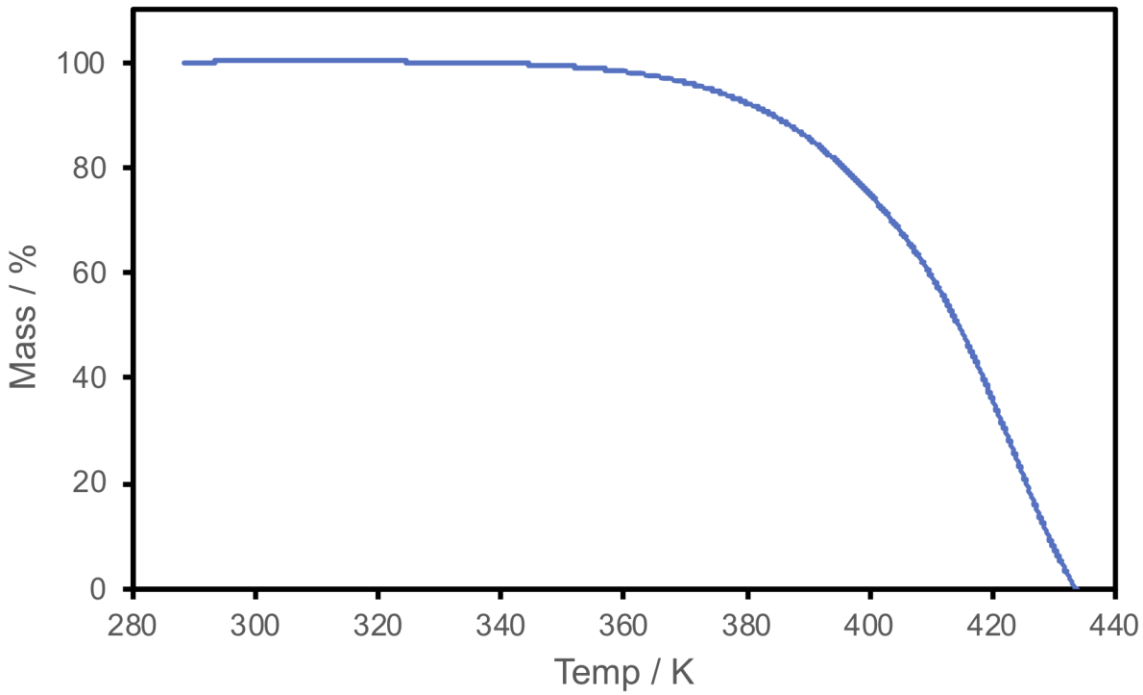


**Figure S5.** Thermogravimetric analysis of HMB between 293.15 and 473.15 K heated at a rate of 10 K/min at ambient pressure under nitrogen.

## Supplementary References


1. APEX2, Bruker AXS, Inc., Madison, WI **2007**.

2. SAINT, Bruker AXS, Inc., Madison, WI **2006**.

3. SADABS, Bruker AXS, Inc., Madison, WI **2006**.

4. G. Sheldrick, *Acta Crystallogr. A,* **2008**, *64*, 112.

5. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl Crystallogr.,* **2009**, *42*, 339.

6. R. D. Stevenson, R. J. Wassersug, *Nature,* **1993**, *364*, 195.

7. J. Shoshani, *Trends Ecol. Evol.,* **1998**, *13*, 480.

8. M. Heethoff, L. Koerner, *J. Exp. Biol.,* **2007**, *210*, 3036.

9. J. Wojtusiak, E. J. Godzińska, A. Dejean, *Tropical Zool.,* **1995**, *8*, 309.

10. R. J. Knell, L. W. Simmons, *Proc. R. Soc. B,* **2010**, *277*, 2347.

## Captions to the Supplementary Videos

**Movie S1.** A high speed camera video of an HMB crystal heated to 382 K undergoing the transition from phase II to phase I. The video was recorded at 1500 frames per second.

**Movie S2.** Measurement of the mechanical force induced by a crystal of HMB synchronized with the video of the crystal as it undergoes the phase transition from phase II to phase I.

**Movie S3.** Measurement of the mechanical force induced by a crystal of HMB synchronized with the video of the crystal as it undergoes the phase transition from phase II to phase I.

**Movie S4.** Measurement of the mechanical force induced by a crystal of HMB synchronized with the video of the crystal as it undergoes the phase transition from phase II to phase I.

**Movie S5.** Application demonstration of HMB working as actuator.

**Movie S6.** In-plane bending of a crystal of HMB using a pair of foreceps.

**Movie S7.** Out-of-plane bending of a crystal of HMB using a pair of foreceps.

**Movie S8.** Formation of twin domains using mechanical force.

**Movie S9.** Reformation of orginal crystalline domain from twin using mechanical force.