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Supporting Information for

Performance of molecular crystals in conversion of light to mechanical work

Jad Mahmoud Halabi[a], Ejaz Ahmed[a], Samuel Sofela[b], Panče Naumov[a,c,1]

[a]Smart Materials Lab (SML), Division of Science and Mathematics, New York University Abu Dhabi, Abu Dhabi, United Arab Emirates

[b]Division of Engineering, New York University Abu Dhabi, Abu Dhabi, United Arab Emirates

[c]Radcliffe Institute for Advanced Study, Harvard University, MA 02138

[1]Corresponding author. Email: pance.naumov@nyu.edu

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1. Supporting Information Methods

1.1. Crystallization of DDAB, DMNAB, and DR1

Crystallization of 3',4'-dimethyl-4-(dimethylamino)azobenzene (DDAB): DDAB was recrystallized by dissolving 100 mg of commercially purchased DDAB in 6 mL of 1,4-dioxane/methanol mixture in a 1:1 ratio by sonication at 60 °C for 5 min to get a clear orange solution. The vial was then uncapped and the solution was left to evaporate at room temperature. After one week, needle-like single crystals of DDAB were obtained. The identity of the compound was confirmed by single crystal X-ray diffraction. The crystal structure of DDAB was deposited at the Cambridge Crystallographic Data Center (CCDC) and can be obtained as reference 1913968.

Crystallization of 4-(dimethylamino)-2-methyl-4'-nitroazobenzene (DMNAB): 20 mg of DMNAB was added into a mixture of methanol (1.5 mL) and 1,4-dioxane (0.5 mL). Initially 1.0 mL of methanol and 0.25 mL of 1,4-dioxane were added to the vial and then additional solvents were used to achieve complete dissolution while adding minimal amounts of 1,4-dioxane. The vial was placed in a sonication bath at 35 ºC and sonicated for 5 min to get the clear solution. The vial was then uncapped and the solution was left to evaporate at room temperature. After 5 days, needle-like single crystals of DMNAB were obtained.

Crystallization of N-ethyl-N-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline (DR1): Around 30 mg of DR1 solid was dissolved into a mixture of methanol and tetrahydrofuran (1:1, 4.0 mL) at 50 ºC in a sonicating bath and sonicated for 5 min, whereupon it turned into a clear red solution. Plate-like red crystals of DR1 of good quality were obtained in two days by evaporation at room temperature.

1.2. Determination of the photomechanical response

The photomechanical response of the azobenzene single crystals was recorded using a Nikon SMZ 745T microscope connected with a Nikon Coolpix P7800 digital camera. Each crystal was affixed at one end to a glass capillary. Ultraviolet (UV) irradiation was carried out using a commercial broadband UV lamp (SP8, Ushio, Japan) at a fixed distance of 1.5 cm from the sample using a heat filter. The irradiation power was measured to be 13 mW cm^{-2}. Visible light background irradiation was carried out using a SCHOTT KL 1500 LED lamp. The bending/unbending process was recorded as videos. Kinovea (experimental version) software was used to process the videos and measure the displacement generated by tracking the crystal tip (unrestrained displacement) or the top circular cross section of the PDMS micropillars (crystal subject to a load).

1.3. Fabrication of the PDMS micropillars

An acrylic mold was first fabricated through computer numerical control (CNC) by drilling holes of varying depths (1 – 3 mm) and diameters (250 – 500 µm). A mold release layer was then created by placing the mold in a desiccator under vacuum for 2 hours next to a slide containing ~3−4 drops of the trichlorosilane. The PDMS oligomer and crosslinking prepolymer of PDMS agent from a Sylgard 184 kit were mixed in a 10:1 ratio using a mixer (Thinky® ARE 250). The mixture was fully degassed in a vacuum jar for 1 hour. This mixture was poured onto the mold and left inside an oven to cure for 3 hours at 80 °C. The process yielded transparent polymer sheet with multiple cylindrical PDMS micro-pillars with a Young's modulus E_{PDMS} = 2.6 MPa (1).

1.4. Finite Element Analysis (FEA): ANSYS Simulation

The ANSYS software (2) was used to conduct a structural finite element analysis to simulate the photoresponse of DDAB single crystals. A simplified 3D analysis geometry of the single crystal

(length L = 1 mm, width W = 60 µm, thickness t = 41 µm) was first created and then preprocessed before running the simulation. Materials properties were then assigned to the structure. Meshing is an integral step in the engineering simulation process where complex structures are broken down into elements with defined shape and size which are connected with nodes. Choosing the appropriate mesh or element size helps optimize computation time while maintaining low error in the results. Different mesh sizes were tested, and the element size was reduced until the simulation results converged. Given the rectangular shape of our crystals and that the mechanical displacement simulated is that of bending, a quadrilateral mesh of size 10^{-5} m was selected.

2. Supporting Information Figures

Fig. S1. Optical image of typical single crystals of (a) DDAB, (b) DMNAB, and (c) DR1.

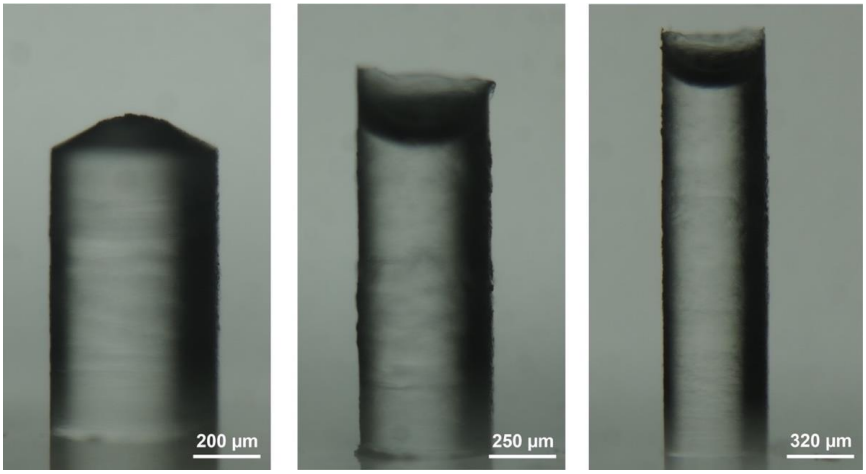

Fig. S2. Optical images of a sample of PDMS micropillars of varying stiffness custom-fabricated to suit the estimated range of force generated by photoactuated single crystals of azobenzenes.

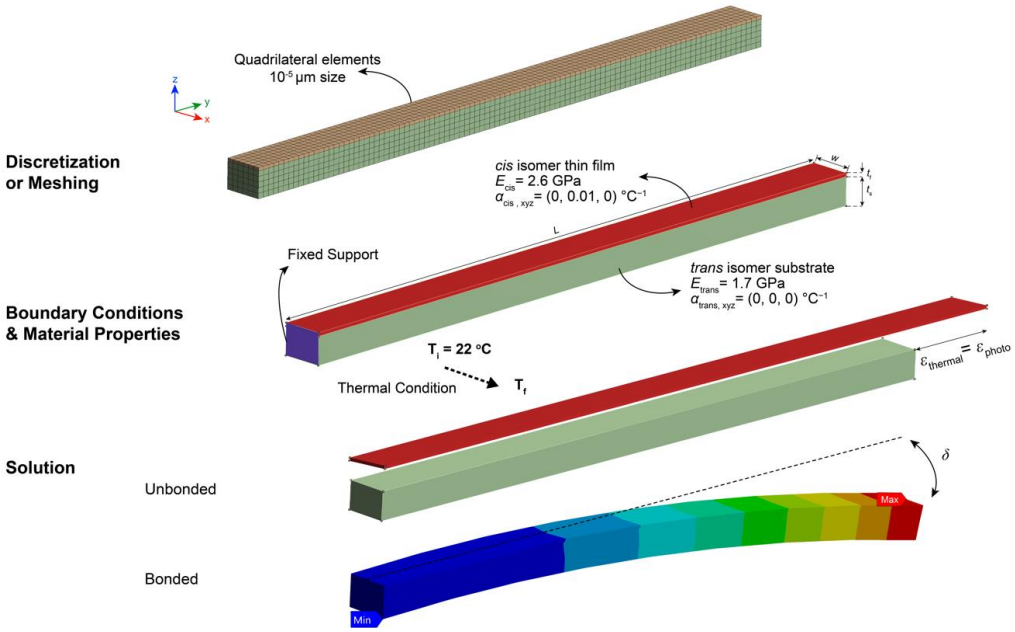

Fig. S3. ANSYS Finite Element Analysis (FEA) model, preprocessing, and solution. The geometric dimensions of the model match that of the experimentally studied DDAB single crystal, and the model has materials mechanical properties of the *trans* and *cis* DDAB isomers, E_{trans}= 1.6 GPa and E_{cis} = 2.7 GPa, respectively. The quadrilateral mesh size converged at 10^{-5} m and boundary conditions such that introducing a fixed support at the bottom of the crystal were applied to match the experimental conditions. The strain is induced by applying a thermal condition ($T_{\mathrm{i}} \rightarrow T_{\mathrm{f}}$, $T_{\mathrm{f}} > T_{\mathrm{i}}$) that only induces expansion in the thin film which is subsequently translated into bending in the structure (tip displacement, δ) through the bonded contact between the thin film and the main substrate. The maximum strain and the thickness of the thin film were then optimized by matching the FEA deformation results to the experimental results.

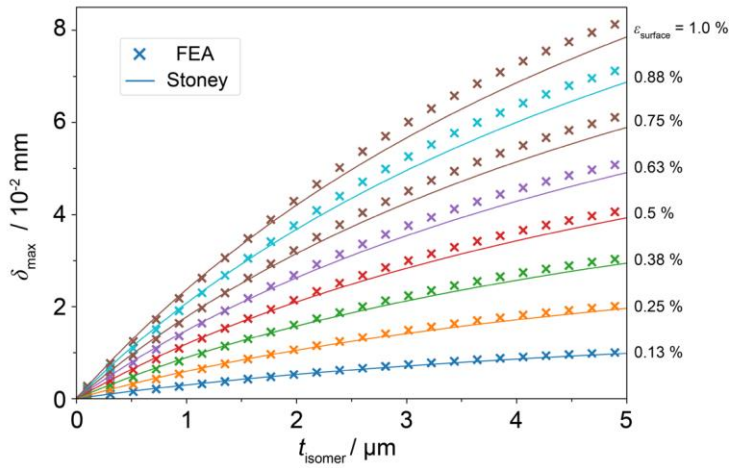

Fig. S4. Comparison between the Finite Element Analysis (FEA) displacement results and the mathematical model (Stoney equation) displacement results with respect to the depth of isomerization at different photoinduced strains. The same mechanical properties and dimensions (length and total thickness) of the DDAB crystal were used in the Stoney equation to calculate the maximum tip displacement.

3. Supporting Information Tables

Table S1. Actuating performance indices for individual photoresponsive azobenzene compounds (DR1, DMNAB, and DDAB) obtained from 15 single crystals (5 crystals of each compound)

Performance Indices	DR1				DMNAB				DDAB			
	Range		Weighted mean	Weighted STD	Range		Weighted mean	Weighted STD	Range		Weighted mean	Weighted STD
	min	max			min	max			min	max		
Nominal Length (m)	$2.0x10^{-3}$	$2.9x10^{-3}$	$2.5x10^{-3}$	$3.9x10^{-3}$	$2.8x10^{-3}$	$3.1x10^{-3}$	$2.9x10^{-3}$	$1.2x10^{-4}$	$3.2x10^{-3}$	$5.9x10^{-3}$	$4.1x10^{-3}$	$9.7x10^{-4}$
Nominal Width (m)	$1.8x10^{-4}$	$4.1x10^{-4}$	$2.8x10^{-4}$	$1.1x10^{-4}$	$1.3x10^{-4}$	$1.5x10^{-4}$	$1.4x10^{-4}$	$5.3x10^{-6}$	$7.9x10^{-5}$	$3.0x10^{-4}$	$1.7x10^{-4}$	$8.3 x10^{-5}$
Nominal Thickness (m)	$1.4x10^{-5}$	$2.3x10^{-5}$	$1.9x10^{-5}$	$3.1x10^{-6}$	$1.0x10^{-5}$	$2.3x10^{-5}$	$1.4x10^{-5}$	$5.3x10^{-6}$	$1.5x10^{-5}$	$7.2x10^{-5}$	$3.9x10^{-5}$	$2.6x10^{-5}$
Maximum Stroke (m)	$4.8x10^{-5}$	$2.3x10^{-4}$	$1.5x10^{-4}$	$6.9x10^{-5}$	$7.3x10^{-5}$	$1.2x10^{-4}$	$9.3x10^{-5}$	$2.0x10^{-5}$	$1.9x10^{-4}$	$2.7x10^{-3}$	$1.0x10^{-3}$	$1.4x10^{-3}$
Actuation Time (s)	$2.2x10^{-1}$	$5.4x10^{-1}$	$2.8x10^{-1}$	$1.1x10^{-1}$	$1.4x10^{-1}$	$2.3x10^{-1}$	$1.8x10^{-1}$	$4.6x10^{-2}$	$1.2x10^{2}$	$1.2x10^{2}$	–	–
Actuation Speed (m s^{-1})	$2.5x10^{-4}$	$4.6x10^{-3}$	$1.8x10^{-3}$	$1.7x10^{-3}$	$4.7x10^{-4}$	$6.8x10^{-4}$	$5.7x10^{-4}$	$9.5x10^{-5}$	$1.2x10^{-6}$	$9.1x10^{-5}$	$2.3x10^{-5}$	$3.7x10^{-5}$
Maximum Force Output (N)	$8.7x10^{-5}$	$6.7x10^{-4}$	$4.0x10^{-4}$	$1.1x10^{-4}$	$2.4x10^{-4}$	$3.9x10^{-4}$	$2.5x10^{-4}$	$4.3x10^{-5}$	$8.4x10^{-5}$	$4.4x10^{-3}$	$1.6x10^{-3}$	$1.8x10^{-3}$
Force Density (N m^{-3})	$1.2x10^{7}$	$4.9x10^{7}$	$2.8x10^{7}$	$2.8x10^{6}$	$4.2x10^{7}$	$7.7x10^{7}$	$5.5x10^{7}$	$9.6x10^{6}$	$7.8x10^{6}$	$2.2x10^{8}$	$7.9x10^{7}$	$9.0x10^{7}$
Work Output (N m)	$1.9x10^{-10}$	$1.1x10^{-8}$	$2.6x10^{-9}$	$2.3x10^{-9}$	$1.4x10^{-9}$	$8.2x10^{-9}$	$1.5x10^{-9}$	$5.2x10^{-10}$	$1.8x10^{-10}$	$4.9x10^{-7}$	$1.3x10^{-7}$	$2.0x10^{-7}$
Work Density (J m^{-3})	26	$8.2x10^{2}$	$2.6x10^{2}$	$1.2x10^{2}$	$2.7x10^{2}$	$2.0x10^{3}$	$3.4x10^{2}$	$1.1x10^{2}$	17	$2.4x10^{4}$	$6.6x10^{3}$	$1.0x10^{4}$
Power Output (kW)	$8.8x10^{-13}$	$3.3x10^{-11}$	$1.1x10^{-12}$	$1.7x10^{-12}$	$6.1x10^{-11}$	$6.1x10^{-11}$	$7.5x10^{-12}$	$5.3x10^{-12}$	$1.5x10^{-15}$	$4.1x10^{-12}$	$1.1x10^{-12}$	$1.7x10^{-12}$
Power Density (W m^{-3})	$1.2x10^{2}$	$2.4x10^{3}$	$1.7x10^{2}$	$2.1x10^{2}$	$1.2x10^{3}$	$1.5x10^{4}$	$1.5x10^{3}$	$9.6x10^{2}$	$1.4x10^{-1}$	$2.0x10^{2}$	55	84
Actuator Efficiency	$1.8x10^{-5}$	$2.7x10^{-4}$	$2.6x10^{-5}$	$3.1x10^{-5}$	$1.1x10^{-4}$	$1.2x10^{-3}$	$1.4x10^{-4}$	$1.0x10^{-4}$	$1.6x10^{-8}$	$1.1x10^{-4}$	$3.0x10^{-5}$	$4.8x10^{-5}$

Table S2. Actuating performance indices of photoresponsive azobenzene single crystals obtained from 15 single crystals (5 crystals of each compound)

Performance Indices	Mean	STD Dev	Minimum	Maximum	Range	Median	Variance
Nominal Length (m)	$3.2x10^{-3}$	$9.2x10^{-4}$	$2.0x10^{-3}$	$5.9x10^{-3}$	$3.9x10^{-3}$	$2.9x10^{-3}$	$8.6x10^{-7}$
Nominal Width (m)	$1.9x10^{-4}$	$9.5x10^{-5}$	$7.9x10^{-5}$	$4.1x10^{-4}$	$3.3x10^{-4}$	$1.7x10^{-4}$	$9.0x10^{-9}$
Nominal Thickness (m)	$2.5x10^{-5}$	$1.9x10^{-5}$	$1.0x10^{-5}$	$7.2x10^{-5}$	$6.2x10^{-5}$	$1.9x10^{-5}$	$3.5x10^{-10}$
Maximum Stroke (m)	$3.6x10^{-4}$	$7.4x10^{-4}$	$4.8x10^{-5}$	$2.7x10^{-3}$	$2.7x10^{-3}$	$1.4x10^{-4}$	$5.5x10^{-7}$
Actuation Time (s)	$4.5x10^{1}$	$6.0x10^{1}$	$1.4x10^{-1}$	$1.2x10^{2}$	$1.2x10^{2}$	$4.5x10^{-1}$	$3.6x10^{3}$
Actuation Speed (m s^{-1})	$7.7x10^{-4}$	$1.2x10^{-3}$	$1.2x10^{-6}$	$4.6x10^{-3}$	$4.6x10^{-3}$	$4.7x10^{-4}$	$1.5x10^{-6}$
Maximum Force Output (N)	$8.0x10^{-4}$	$1.2x10^{-3}$	$8.4x10^{-5}$	$4.4x10^{-3}$	$4.3x10^{-3}$	$3.9x10^{-4}$	$1.4x10^{-6}$
Force Density (N m^{-3})	$5.6x10^{7}$	$5.7x10^{7}$	$7.8x10^{6}$	$2.2x10^{8}$	$2.1x10^{8}$	$4.3x10^{7}$	$3.2x10^{15}$
Work Output (N m)	$5.2x10^{-8}$	$1.3x10^{-7}$	$1.8x10^{-10}$	$4.9x10^{-7}$	$4.9x10^{-7}$	$5.3x10^{-9}$	$1.7x10^{-14}$
Work Density (J m^{-3})	$2.8x10^{3}$	$6.6x10^{3}$	$1.7x10^{1}$	$2.4x10^{4}$	$2.4x10^{4}$	$4.1x10^{2}$	$4.3x10^{7}$
Power Output (kW)	$1.2x10^{-11}$	$1.7x10^{-11}$	$1.5x10^{-15}$	$6.1x10^{-11}$	$6.1x10^{-11}$	$5.1x10^{-12}$	$2.8x10^{-22}$
Power Density (W m^{-3})	$1.7x10^{3}$	$3.7x10^{3}$	$1.4x10^{-1}$	$1.5x10^{4}$	$1.5x10^{4}$	$4.8x10^{2}$	$1.4x10^{7}$
Actuator Efficiency	$1.9x10^{-4}$	$3.0x10^{-4}$	$1.6x10^{-8}$	$1.2x10^{-3}$	$1.2x10^{-3}$	$1.1x10^{-4}$	$8.9x10^{-8}$

Table S3. Actuator classes included in the materials property plots (3)

Actuator class	Type of actuators included
Electromagnetic	Magnetostrictor
	Moving coil
	Solenoid
Electromechanical	Electric cylinder
	Electrostatic
	MEMS (MicroElectroMechanical Systems)
	Mini-linear
Fluidic	Hydraulic
	Pneumatic
	Diaphragm actuator
Piezoelectric	Ceramic piezoelectric
	Piezoelectric transducer
	Piezoelectric QuickPack actuator
	Electrostrictive actuators
Smart Materials	Electroactive polymers
	Polymer gels
	Nano-muscles
	Shape memory alloys
	Thermal actuators
	Azobenzene single crystals
Hybrid	(single class)
Natural	Muscle

Table S4. Experimental, FEA, and Stoney equation tip displacement results (δ) of 5 randomly selected DDAB crystals used to test the predictive accuracy of the ANSYS-generated model*

		Crystal 1	Crystal 2	Crystal 3	Crystal 4	Crystal 5
Nominal Length (mm)		4.2	4.3	3.2	3.4	3.5
Nominal Width (μm)		180	300	200	81	80
Nominal Thickness (μm)		15	30	20	72	70
δ_{Exp} (mm)		2.70	1.00	1.02	0.19	0.25
FEA	**δ_{FEA} (mm)**	3.74	1.36	1.30	0.22	0.24
	FEA Prediction Error (%)	38.5	36.0	27.5	17.4	4.0
δ_{Stoney} (mm)		3.57	1.37	1.40	0.22	0.23

* In Fig. 4*C* in the manuscript, crystals 1−5 are presented in order from left to right.

Supporting Information Movie S1 Legend

Movie S1. Photobending response of a fixed DDAB single crystal displacing a PDMS micropillar (500 μm in diameter) upon irradiation.

Supporting References

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