Photoinduced Peeling of Molecular Crystals

Electronic Supporting Information

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Experimental Methods:

Sample Preparation: Electrophoresis grade sodium dodecyl sulfate (SDS, purity>98.5%) was purchased from Bio Rad and used without further purification. 1-dodecanol (98%) was purchased from Sigma-Aldrich and used without further purification. N, N-dimethylformamide (DMF) was distilled before use. Milli-Q water was used for all the experiments and dilutions. *cis*-**DMAAM** (97% *cis* isomer) was prepared following a previously reported procedure.[1]

To prepare uniformly shaped microcrystals, an aqueous solution containing 0.02 molar SDS was prepared with varying amounts of 1-dodecanol. A flowchart of preparation of cis-DMAAM microblocks is provided in Figure S13. Typically, a solution of *cis*-**DMAAM** in DMF (0.13 M, 25 μL) is injected into 5 mL of the SDS/1-dodecanol solution inside a 20 mL glass vial while stirring at 800 rpm and maintaining a temperature of 40^{o}C. Once the solution formed a clear yellow color, the stirring speed is dialed down to 100 rpm to form uniform seed crystals. Without 1-dodecanol, elongated octahedral microcrystals (tetragonal dipyramidal) precipitate out after four hours of stirring at 100 rpm. For 1-dodecanol concentrations (> 0.0022 M), uniform microblocks precipitate out after one hour of stirring. The microblock dimensions are on the order of 10 μm long and 1.1 μm wide with 8% standard deviation.

To obtain large crystals of either habit, 50 μL of the *cis*-**DMAAM**/DMF solution is injected into the SDS or SDS/1-dodecanol solution (5 ml, 40^{o}C) and giving it a gentle swirl until the solution becomes clear yellow. This yielded a quasi-stable solution of the *cis*-**DMAAM** that remains clear for several hours as long as it is not

disturbed. To grow larger microblocks, a 100 μL suspension of the previously prepared microblocks is added to this quasi-stable solution in a 20 mL vial to seed crystal growth. The mixture is kept undisturbed at 40°C for at least 4 hours. Microblocks grown in this way are uniform with and roughly 30× larger in volume. When the concentration of the seed crystals is decreased, larger microblocks were observed. When the quasi-stable solution is left unseeded and undisturbed at 40°C for several days, large blocks also form but with indentations on the end faces (Figure S14). Table S4 describes the crystal size and shape outcomes from a variety of different growth conditions.

Characterization:

SEM measurements are performed using JEOL JSM-6510LV scanning electron microscope. For sample preparation, a drop of the *cis*-**DMAAM** microblock suspension in SDS/1-dodecanol is placed on a blank Anodic Aluminum Oxide (AAO) template (Whatman Anodisc inorganic filter membrane diameter 25.4 mm, pore size 0.2 μm), rinsed with water to remove residual SDS and 1-dodecanol, and dried by vacuum filtration. After further drying in air, samples are coated with a thin layer of Pt prior to SEM scanning.

Powder X-ray diffraction data are collected on a PANalytical Empyrean X-ray powder diffractometer (CuK radiation, λ = 1.540598 Å, 45 KV/40 mA power) at 296 K. For the microblocks that lay horizontally on the AAO template surface, the sample preparation process is the same as for the SEM measurements but without metal coating.

The sample was measured in Bragg-Brentano geometry. The sample holder stage was fixed horizontally and the detector (divergence slit = 0.76 mm with no monochromator) was rotated over the sample with a step size = 0.0263 degrees.

Optical microscopy studies are performed using an upright Optika fluorescence microscope equipped with an Optika 2 MP digital camera. A drop of the *cis*-**DMAAM** microblocks is deposited over a microscope glass slide then covered with a coverslip. To initiate the photomechanical response, the sample is pulsed with light from a 100 W medium pressure Hg lamp passing through a 405 nm interference filter with a full width-half max of 10 nm. A 1 sec pulse is enough to cause the microblocks to spontaneously peel after 15 to 20 s regardless of their size.

HPLC analysis of the photoproducts is performed by pulsing a 5 μL suspension of the microblocks in SDS/1-dodecanol with 405 nm light until the entire sample consisted of peels. The suspension is dissolved in acetonitrile and analyzed using HPLC (Shimadzu LC-20AD) equipped with a general purpose BDS Hypersil C18 column with a 250x4.6 mm dimensions from Thermo Scientific. An isocratic mobile phase composed of 80% acetonitrile 20% water at pH = 2.5 and a flow rate of 1.5 mL/min was used to elute the sample through the column. The detector wavelength was set at 260 nm, matching one of the isosbestic points of the *cis* and *trans*-**DMAAM** absorption spectrum. Column temperature was held at 35 ^{o}C throughout the run.

^{1}H Nuclear Magnetic Resonance (^{1}H NMR) measurements were collected via using a Bruker Avance NEO 400 spectrometer with a 5mm ^{1}H, ^{19}F-^{31}P Prodigy LN2 cryoprobe. The sample preparation process is similar to PXRD measurements, but the dried sample was dissolved in $CDCl_3$ (Sigma-Aldrich, 99.9% +) instead of left as a solid.

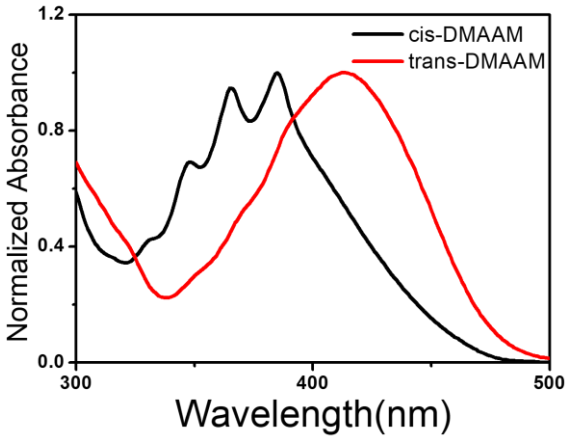

Figure S1. UV-Vis absorption spectra of *cis*-**DMAAM** and *trans*-**DMAAM** in chloroform solution.

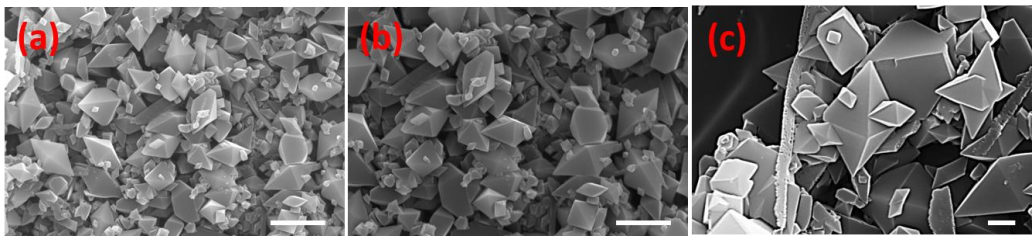

Figure S2. SEM images of *cis*-**DMAAM** octahedral crystals, [SDS] = 0.02 M, [1-dodecanol] = 0 M, scale bar: (a) 5 μm, (b) 5 μm and (c) 1 μm.

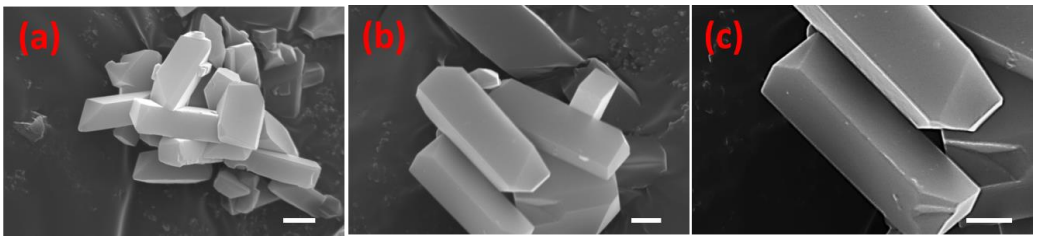

Figure S3. SEM images of *cis*-**DMAAM** crystals, [SDS] = 0.02 M, [1-dodecanol] = 0.0009 M, scale bar: (a) 2 μm, (b) 1 μm and (c) 1 μm.

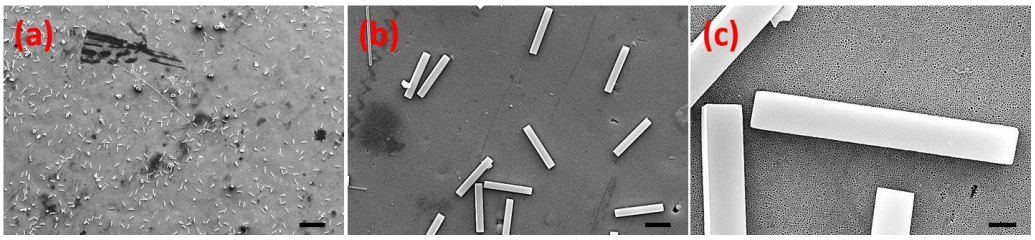

Figure S4. SEM images of *cis*-**DMAAM** crystals, [SDS] = 0.02 M, [1-dodecanol] = 0.0022 M, scale bar: (a) 100 μm, (b) 10 μm and (c) 1 μm.

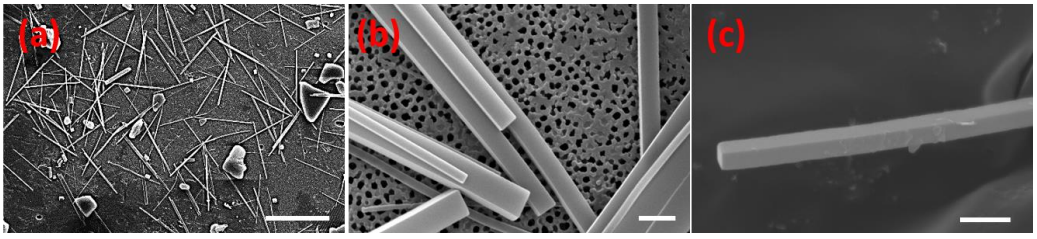

Figure S5. SEM images of *cis*-**DMAAM** crystals, [SDS] = 0.02 M, [1-dodecanol] = 0.0066 M, scale bar: (a) 50 μm, (b) 1 μm and (c) 1 μm.

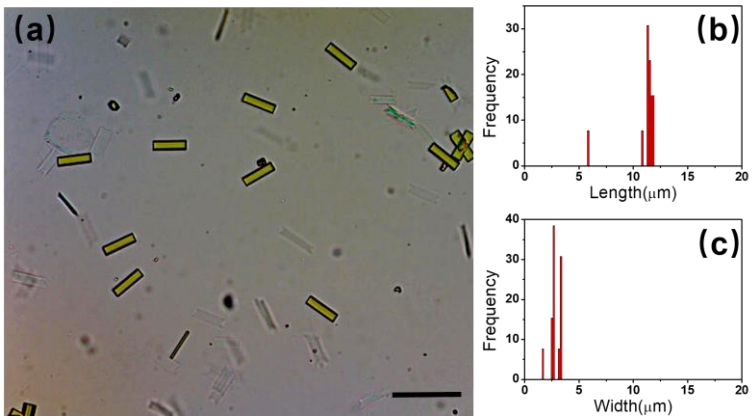

Figure S6. (a) Optical microscope images of *cis*-**DMAAM** microcrystals. Scale bar: 25 μm. (b) and (c) histograms of length and width distributions of *cis*-**DMAAM** microcrystals. Preparation conditions for these crystals are seed solution = 50 μL, SDS = 0.02 M and 1-dodecanol = 0.0022 M. Note that a larger amount of seed solution was used for this preparation than for Figure 2 in the text.

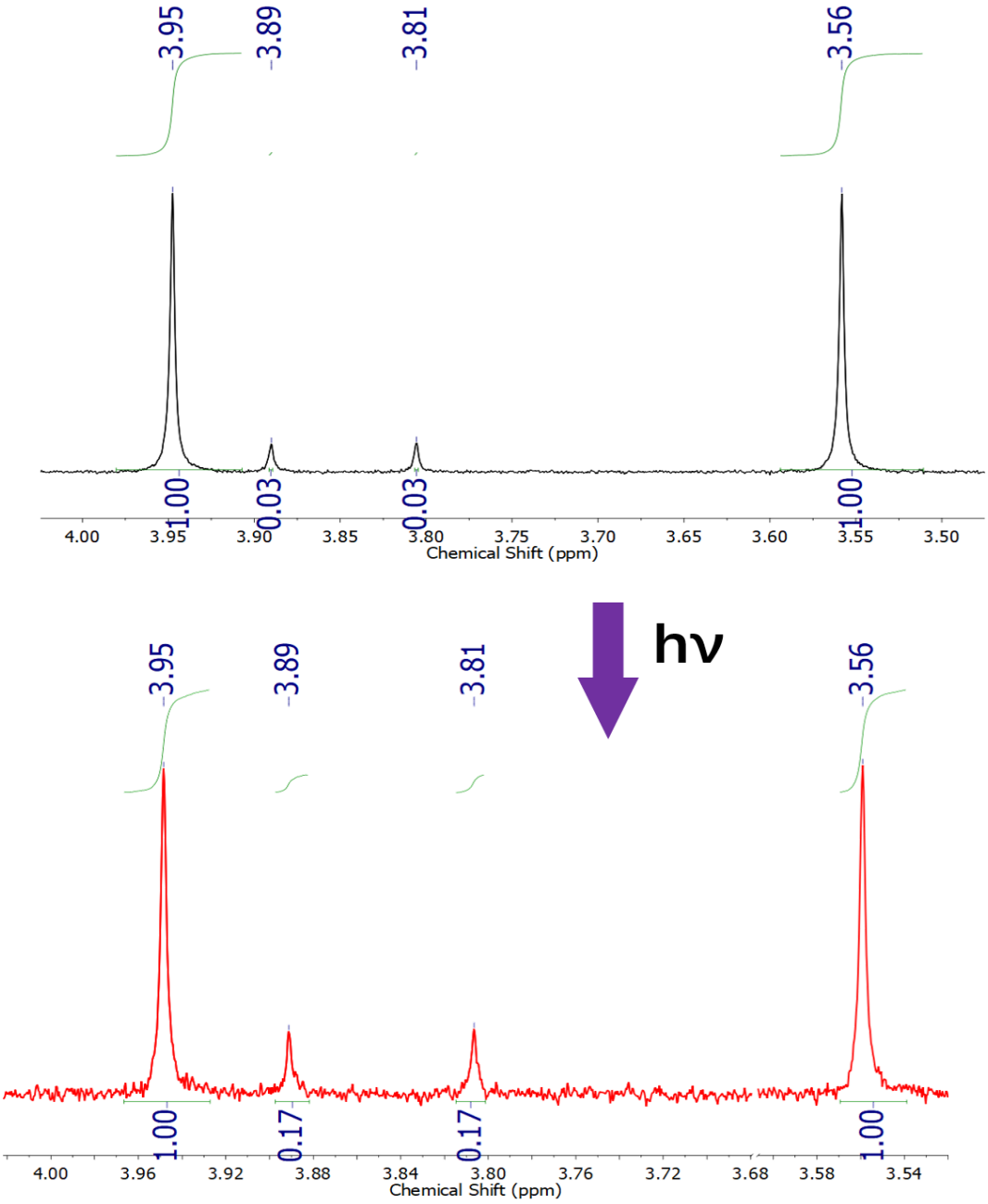

Figure S7. [1]HNMR data of *cis*-**DMAAM** octahedral crystals before and after 20 min UV irradiation (chloroform-d as the solvent).The peaks at 3.81 and 3.89 ppm are due to *trans*-**DMAAM** isomers. The ratio of trans-DMAAM according to the peak integration is about 14.5% and *cis*-**DMAAM** is about 85.5% after UV light irradiation, which showed agreement with our HPLC data of *cis*-**DMAAM** microblocks in Figure S11.

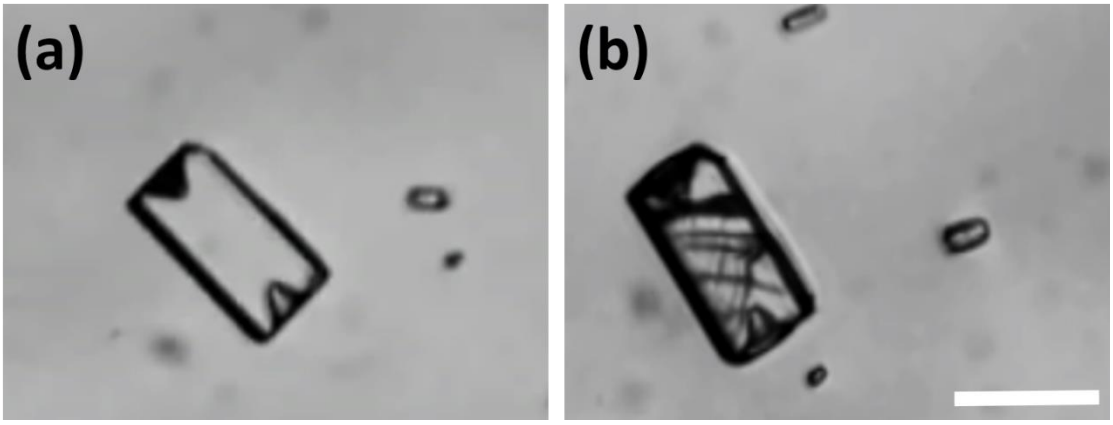

Figure S8. Optical microscopy images of a large *cis*-**DMAAM** crystal (a) before light irradiation and (b) after light irradiation. Scale bar: 100 μm

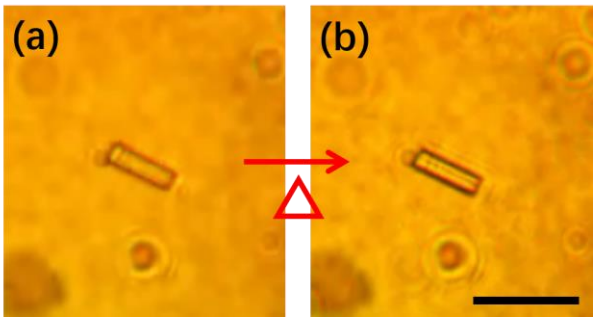

Figure S9. (a) Optical microscope image of *cis*-**DMAAM** microblock before heating and (b) optical microscope image of *cis*-**DMAAM** microblock after heating at 60°C for 1 min. Scale bar: 30 μm.

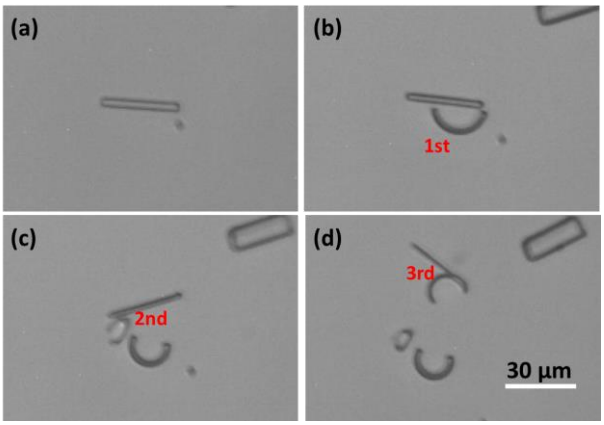

Figure S10. Optical microscope images to show multiple peeling sequences of the *cis*-**DMAAM** microblock under UV light irradiation. (a) Before UV light pulse, (b) first peeling, (c) second peeling, and (d) third peeling. A total of 4 peels is obtained for a 2s light pulse from a 2.4 micron thick block, allowing us to estimate that each peel is 0.6 microns thick. Data for other pulse durations is shown in movie S6.

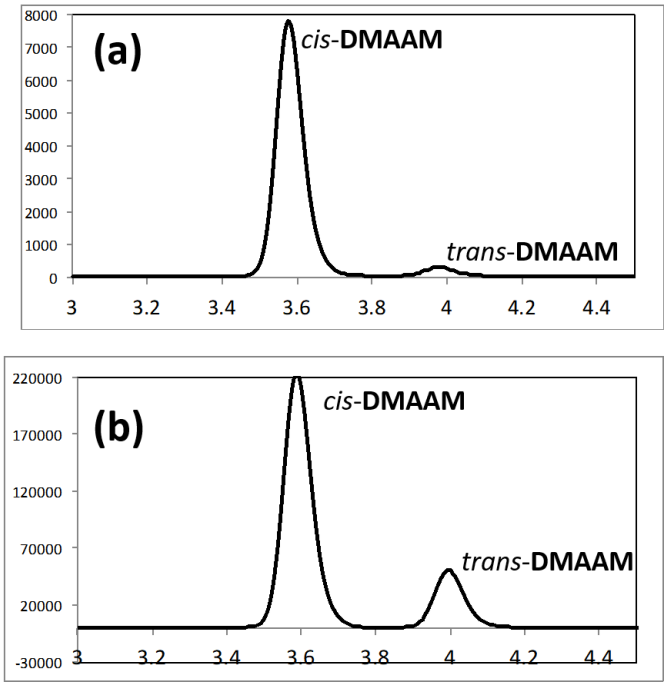

Figure S11. HPLC data of peeled cis-**DMAAM** microblocks (a) before UV light irradiation and (b) after UV light irradiation. *cis*-**DMAAM** comprises 97% (central peak at 3.6 min) and *trans*-**DMAAM** comprises 3% (central peak at 4.0 min) of the total sample before light irradiation. After the blocks are completely peeled apart by multiple cycles of 405 nm irradiation, the *cis*-**DMAAM** comprises 84% and trans-DMAAM comprises 16% of the total sample.

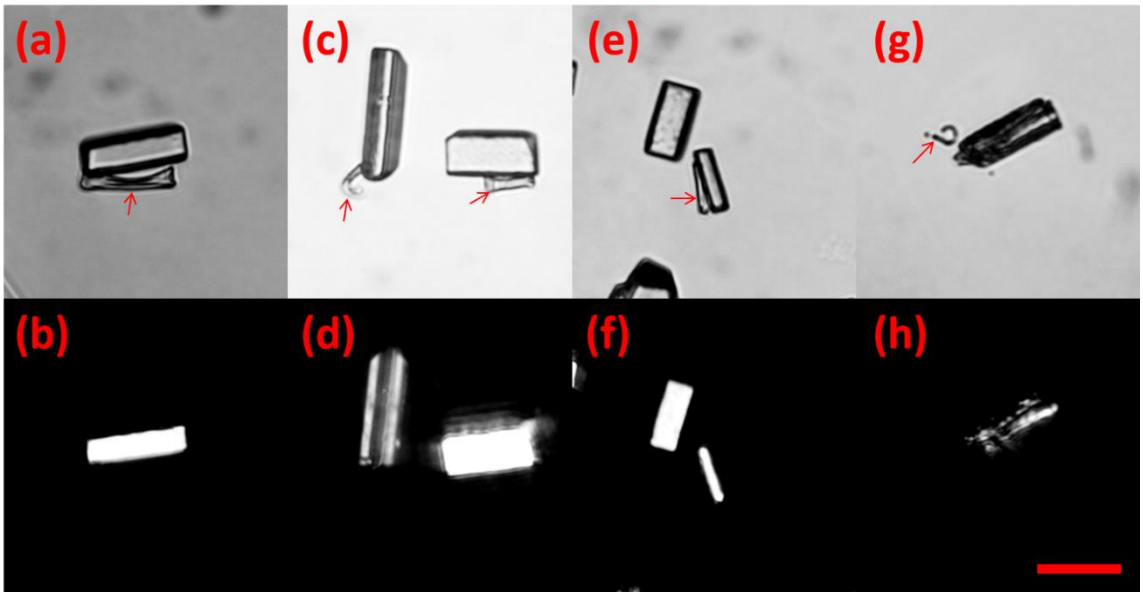

Figure S12. (a), (c), (e) and (g) optical microscopy images of *cis*-**DMAAM** microblocks with photoproduct peels. The red arrows indicate the photoinduced peels. (b), (c) (f) and (h) cross-polarized microscope images of the same samples showing that the photoproduct peels do not exhibit birefringence and show no signs of crystallinity. Scale bar: 10 μm

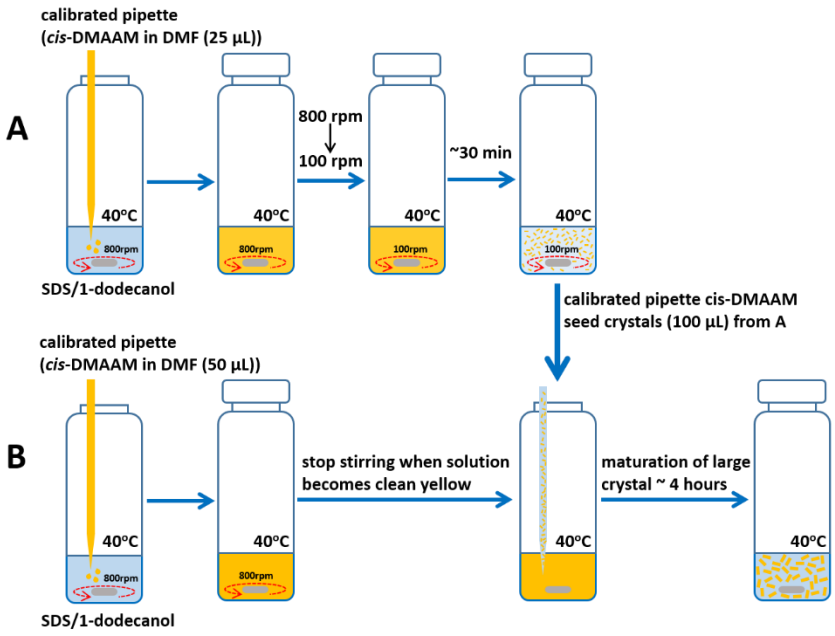

Figure S13. Flow chart of preparation of *cis*-**DMAAM** microblocks

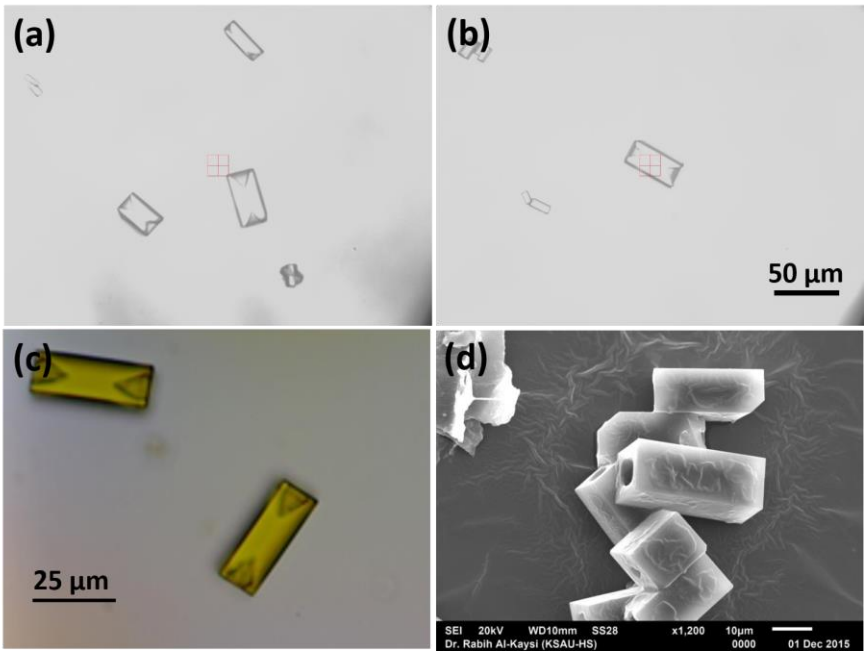

Figure S14. (a) and (b) optical microscopy images of large *cis*-**DMAAM** microblocks with indentations at the end after several days of growth at 40ºC. The red-cross maker in the center of the images is the reference maker for snapshot of camera in microscope. (c) colored optical microscope image of the large microblocks. (d) SEM image of the same microblocks.

The effects of pulse duration

Table S1

1s Irradiation pulse

Peeling times	Peeling duration (s)
1	24
2	22
3	22
4	19
5	22
6	∞

Table S2

2s Irradiation pulse

Peeling times	Peeling duration (s)
1	30
2	23
3	30
4	∞

Table S3

5s irradiation pulse

Peeling times	Peeling duration (s)
1	40
2	35
3	∞

[SDS] molar	[1-dodecanol] molar	microblocks: length × width(μm) Volume (μm^3)	Temperature (^oC)
0.02	0	micro-octahedrons	40
0.02	0.001	truncated-tetragons	60 → 40
0.02	0.0022	microblocks: 10.5 × 1.5 Volume = 24 (with 25 μL seeds)	60 →40
0.02	0.0022	microblocks: 12.1 × 2.1 Volume = 53 (with 50 μL seeds	60 → 40
0.02	0.0022	microblocks: 4 × 2 (fast mixing)	40
0.02	0.0044	microblocks: 13.2 × 1.1 Volume = 16 (slow mixing)	60 → 40
0.02	0.0022	microblocks: 6 × 1.1 Volume = 7 (fast mixing)	40
0.02	0.0022	microblocks: 15 × 4 Volume = 240 (no seeds, undisturbed growth)	40
0.02	0.0033	microblocks: 8.5 ×1.1 Volume = 10 (with 25 μL seeds)	40
0.02	0.0044	microblocks: 11 ×1.0 Volume = 11 (with 25 μL seeds)	40
0.02	0.0066	microblocks: 10.2 × 0.9 Volume = 8 (slow mixing)	40
0.02	0.02	microblocks: 10.7 × 0.9 Volume = 9 (slow mixing)	40

Table S4. Conditions that yield different size of microblocks: [*cis*-**DMAAM**] is 0.13 M unless it is stated, volume of aqueous mixture = 5 mL, and volume of *cis*-**DMAAM** solution injected for seed crystals = 25 μL and 50 μL.

Reference:

1. T. Kim, M. K. Al-Muhanna, S. D. Al-Suwaidan, R. O. Al-Kaysi and C. J. Bardeen, *Angewandte Chemie International Edition*, 2013, **52**, 6889-6893.