Supporting Information

Using light intensity to control reaction kinetics and reversibility in photomechanical crystals

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1. 4-Fluoro-9-anthracene Carboxylic Acid (4F-9AC) crystal preparation

The **4F-9AC** crystals were made by subliming 10 mg of powered **4F-9AC** within three small cylinders, 1 cm in diameter and height, stacked vertically to collected deposited crystals. The powered compound and stack of small cylinders were covered with a vial, heated to between 180-190 ^{o}C and left for 24 hours or until most of the **4F-9AC** sublimed.

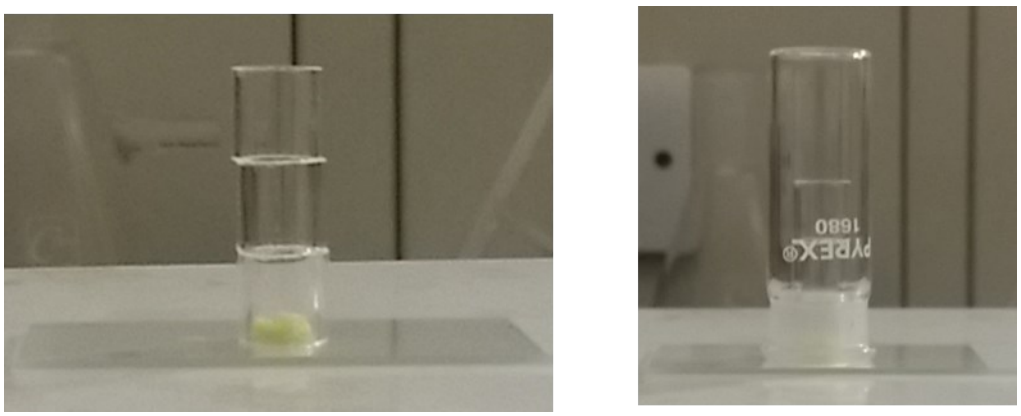

Figure S1. a) Three small cylinders stacked with 10 mg of powered raw material on a hotplate for sublimation b) These cylinders are covered with a vial to prevent loss of material.

2. Spot size measurement

The spot size was measured using a razor blade mounted to a micrometer and an OPHIR power meter. The razor blade was moved incrementally across the spot size while the power is measured, then the signal is plotted as a function of razor blade position. The integral of this data is taken and results in a Gaussian curve that can be used to determine the full width half max of the beam profile.

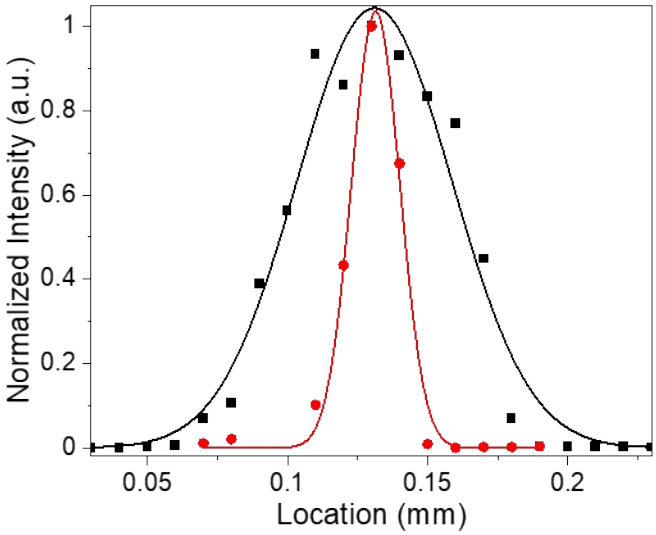

Figure S2. The integral of the beam powers fit to a Gaussian curve, the pump (black) has a radius of 55 microns, while the probe (red) has a radius of 17 microns. Under these conditions, 90% of the probe beam is encompassed inside a spatial region where the pump intensity varies by only 20%.

3. Bleach depth limitations

Increasing the photon dose increased the bleach depth linearly, until a level of 60% bleaching was achieved, at which point no further loss of signal is observed.

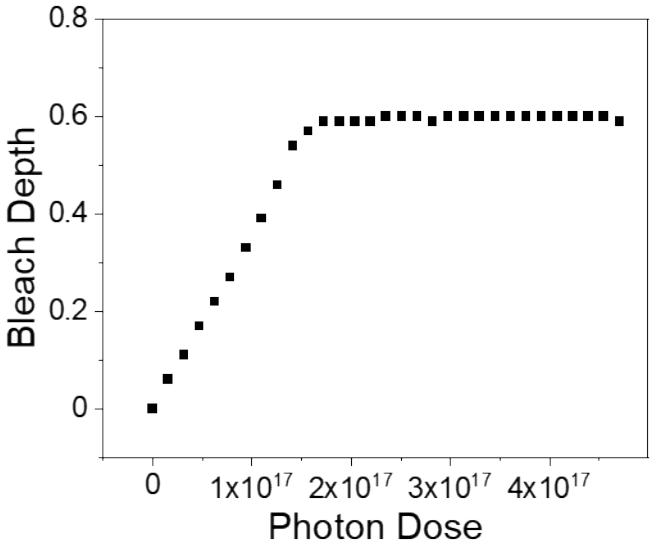

Figure S3. Bleach depth dependence on the photon dose, showing the plateau at 60% bleaching.

4. Image analysis

After a **4F-9AC** needle is irradiated in a localized spot, the photoinduced curvature relaxes after the light is switched off, and the decay of this curvature can be measured by image analysis. Two-minute recovery videos were taken using an Amscope MU900 digital microscope camera during irradiation and recovery. A still frame image was taken every second and the angle of bending was measured using ImageJ software. This was done by anchoring an angle to the end of the crystal that does not move and a second anchor to the bending location. The third point to form this angle was matched to the displaced end of the crystal to determine the acute angle of bending. The angle of bending was then plotted against time to give the curvature graphs.

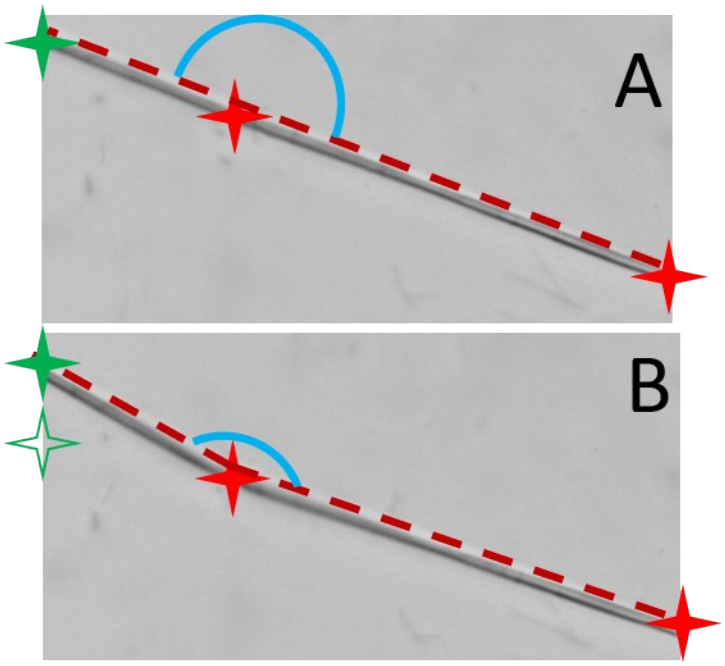

Figure S4. Two anchored points are set with two portions of the crystal that do not move, designated with red stars. The green star points are adjusted with each measurement to reflect the movement of the displaced end after bleaching (going from A to B). This then produces an obtuse angle that can be measured by ImageJ software.

5. Probe power impact on initial recovery curve $R_F(t)$

The initial recovery function RF(t) is relatively insensitive to the probe power, which just determines how far the plateau of the signal is below the signal level before time 0. In other words, different values for $F(\tau_{end})$ due to different probe beam powers do not affect the shape of $R_F(t)$.

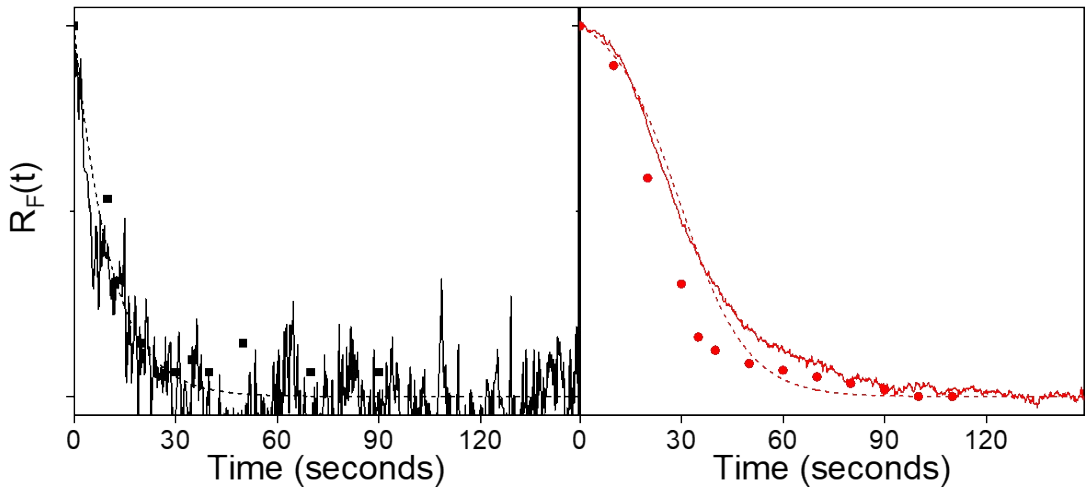

Figure S5. Left: Fluorescence recovery $R_F(t)$ curve for asmall bleach depth (10%) with a continuous probe (solid), intermittent blocking (squares), and a fit to the Finke-Watzky model (dashed). Right: Fluorescence recovery $R_F(t)$ curve for a large bleach depth (40%) with a continuous probe (solid), intermittent blocking (squares), and a fit to the Finke-Watzky model (dashed).

6. Long time scans

Over the time span of the initial recovery experiments, three minutes, there was less than a 1% change in the fluorescence signal when there was no bleach pulse. When left for an hour the unbleached signal decreased slowly over time. When compared to both small and large bleaches, the unbleached signals eventually both overlap with the bleached signals if given enough time.

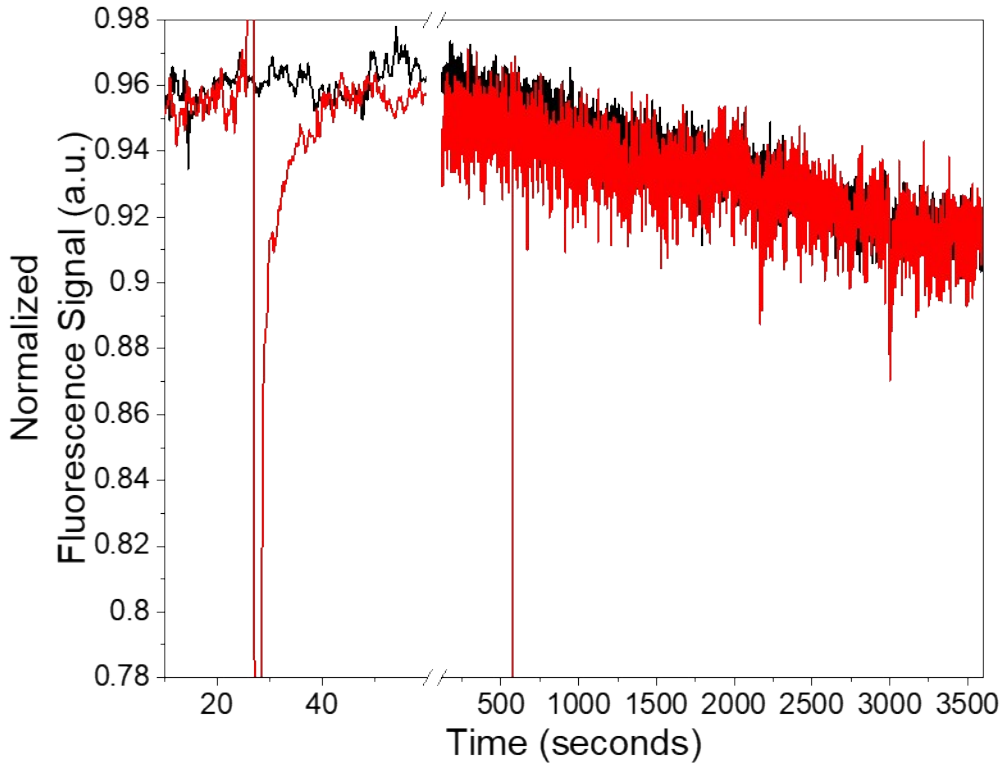

Figure S6. Fluorescence signals from an unbleached sample (black) and a sample that experienced a 20% bleach (red) are compared for an hour. The initial portion of the graph (0-60 seconds) shows the recovery of fluorescence after photobleaching, which then begins to decay slowly on longer timescales (250-3600 seconds), eventually overlapping with the decay of the unbleached sample.

7. Fluorescence recovery curves

As the photon dose increased, the loss of fluorescence also increased. To quantify the recovery behavior, the experimental results were fitted with an exponential recovery as well as curves calculated using the Finky-Watzky model. The single exponential recovery matches the smallest bleach depth, but fails to provide a reasonable fit for any of the others. The FW model fits the early time behavior for the minimum and maximum bleaches, but fails to describe the long time holding behavior or quantitatively fit the transition from single exponential to sigmoidal seen in B and C.

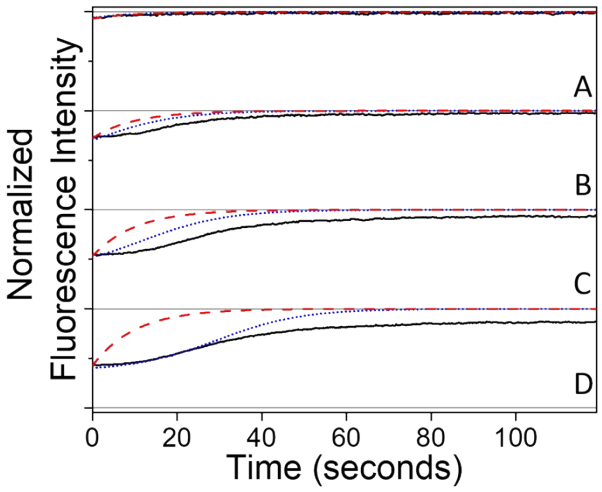

Figure S7. Experimental recovery curves (black solid lines) are stacked by increasing photon dose and therefore bleach depth (A: 0.5 seconds, B: 2.5 seconds, C: 4 seconds, D: 5 seconds). These curves are over laid with exponential curves (red dashed lines) calculated using equation (5) with I=0 and k_1=0.1 s^{-1} and curves calculated using the FW model (blue dotted lines) for different bleach depths equation (7) was used with I=0, k_1=0.1 s^{-1} and k_2=0.005 s^{-1}.

8. Solution of Kinetic Equations

A. First-order kinetic model:

$$A \underset{k_1}{\overset{\sigma I \varphi_1}{\rightleftarrows}} B$$

$$[A]+[B]=C_0$$

A represents the monomer pair that gives rise to the detected fluorescence, *B* is the non-emissive photodimer, C_0 is the total concentration of anthracene pairs, k_1 is the back-reaction rate, and $\sigma I\varphi$ is the net photodimerization rate where σ is the absorption cross section, *I* is the probe light intensity, and φ is the quantum yield. This model leads to the linear differential equation

$$\frac{d[A]}{dt} = -\sigma I\phi[A] + k_1[B] = -\sigma I\phi[A] + k_1(C_0 - [A])$$

$$\frac{d[A]}{dt} + (\sigma I\phi + k_1)[A] = k_1 C_0$$

Let $\gamma = k_1+\sigma I\varphi$, multiply both sides by $e^{\gamma t}$ and rewrite the equation as a derivative of a product:

$$\frac{d}{dt}\left([A]e^{\gamma t}\right) = k_1 C_0 e^{\gamma t}$$

$$[A]e^{\gamma t} = \frac{k_1 C_0}{\gamma} e^{\gamma t} + K$$

where *K* is a constant of integration. Rearranging and using the initial condition $[A](t=0)=[A]_0$ allows us to solve for *K* and obtain the analytical solution

$$[A](t) = \left([A]_0 - \frac{k_1 C_0}{\gamma}\right) e^{-\gamma t} + \frac{k_1 C_0}{\gamma}$$

B. Finke-Watzky Model

$$A + A \xrightarrow{\sigma I \varphi_1} A + B$$

$$A + B \xrightarrow[k_1]{} B + B$$

$$A + B \xrightarrow{\sigma I \varphi_2} B + B$$

$$A + B \xrightarrow[k_2]{} B + B$$

A represents the monomer pair that gives rise to the detected fluorescence, B is the non-emissive photodimer, and C_0 is the total concentration of anthracene pairs. k_1 and φ_1 reflect reactions occurring in majority A regions and k_2 and φ_2 reflect the changed reaction rates in the presence of the photodimer B. For example, if $k_1 > k_2$, then the presence of dimer inhibits the dissociation. This reaction scheme leads to the nonlinear differential equation for $[A]$:

$$\frac{d[A]}{dt} = -\sigma I \phi_1 [A]^2 - \sigma I \phi_2 [A][B] + k_1 [A][B] + k_2 [B]^2$$

$$[B] = C_0 - [A]$$

We collect terms and then rearrange:

$$\frac{d[A]}{dt} = \left(\sigma I \phi_2 + k_2 - k_1 - \sigma I \phi_1\right)[A]^2 + \left(k_1 C_0 - \sigma I \phi_2 N_0 - 2k_2 N_0\right)[A] + k_2 N_0^2$$

$$\frac{d[A]}{c[A]^2 + b[A] + a} = dt$$

$$c = \sigma I \phi_2 + k_2 - k_1 - \sigma I \phi_1$$
$$b = k_1 C_0 - \sigma I \phi_2 N_0 - 2k_2 N_0$$
$$a = k_2 N_0^2$$
$$q = b^2 - 4ac$$

If q>0, the left side of this equation can be integrated (for example, using the table of integrals in the Handbook of Chemistry and Physics) and the right side is trivial. We obtain

$$\frac{1}{\sqrt{q}} \log\left[\frac{2c[A] + b - \sqrt{q}}{2c[A] + b + \sqrt{q}}\right] = t + K$$

Where K is again a constant of integration. K can be evaluated using the initial condition at t=0 $[A]=[A]_0$,

$$K = \frac{1}{\sqrt{q}} \log\left[\frac{2c[A]_0 + b - \sqrt{q}}{2c[A]_0 + b + \sqrt{q}}\right]$$

We can then rearrange the full solution to isolate $[A]$ on the left side:

$$[A](t) = \frac{b\left(e^{\sqrt{q}(t+K)} - 1\right) + \sqrt{q}\left(e^{\sqrt{q}(t+K)} + 1\right)}{2c\left(1 - e^{\sqrt{q}(t+K)}\right)}$$

9. Probe power holding

The amount of dimer that can be prevented from recovering can be controlled by the power of the probe beam. Each of the samples was bleached with the same intensity pump but had a different intensity probe beam. The Hold can be described by the following equation, where $F(0)$ is the initial fluorescence, which has been normalized to one, BD is the maximum bleach depth, and F is the final value at which the recovery stops.

$$Hold = \frac{F(0) - F(\tau_{end})}{1 - BD}$$

Using this equation to determine the Hold, this was then plotted against the probe power. There is a linear relationship between the Hold and probe power.

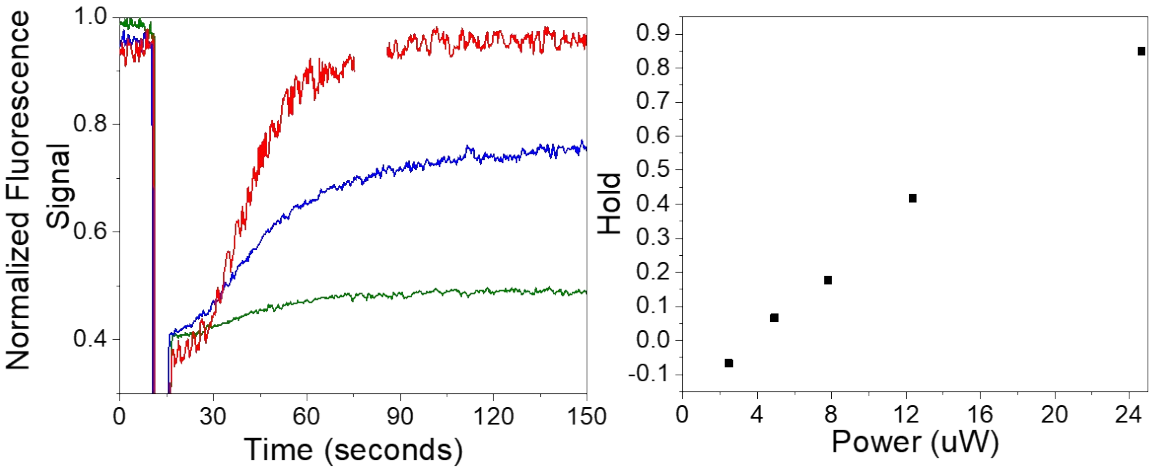

Figure S8. Three sample curves are shown for different probe powers, 2.4 µW (red), 7.8 µW (blue), 24.7 µW (green), and with the same deep bleach. The Hold values calculated from this data, along with two others at different probe powers, are plotted on the right.