Analysis of Reaction Kinetics in the Photomechanical Molecular Crystal 9-Methylanthracene Using an Extended Finke-Watzky Model

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Note: The Mathematica code used to fit the experimental [A](t) data using the FW-P0, FW-P1 and FW-P2 models can be found in the accompanying Mathematica workbook.

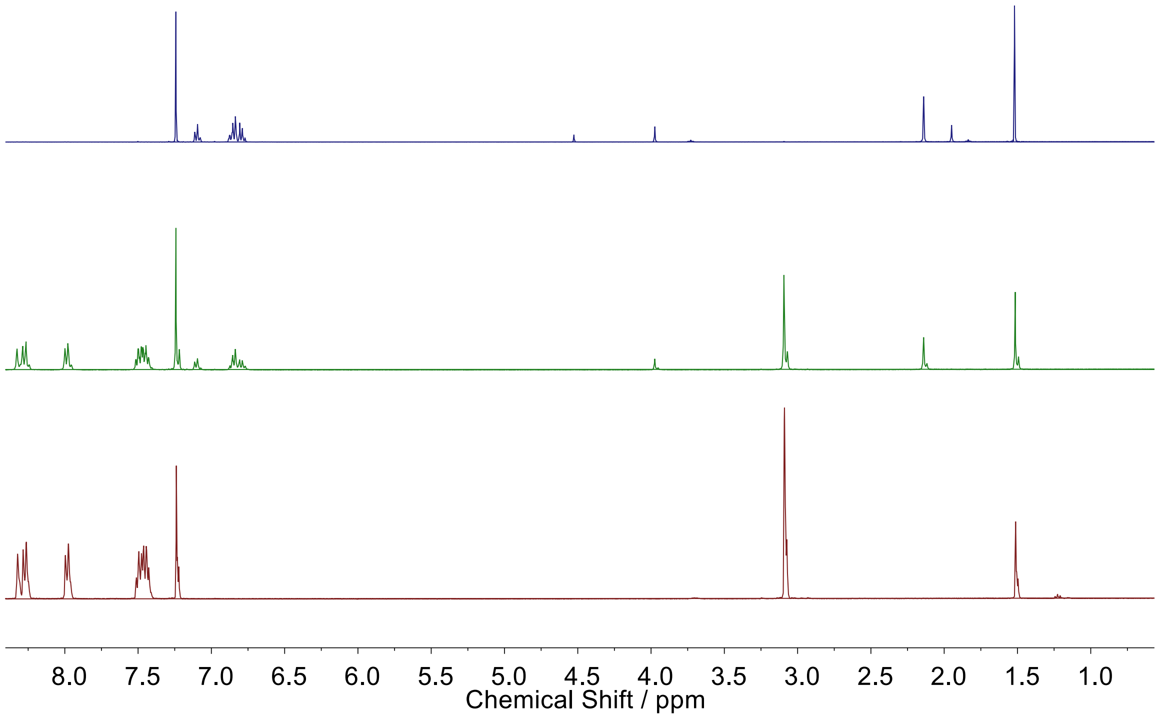

Figure S-1. The ^{1}HNMR data of pure **9MA** monomer (red), a mixture of **9MA** monomer and dimer after irradiation by 365 nm light (green), and pure dimer (blue, made by long time 365 nm irradiation in THF solution of **9MA** monomer). Deuterated chloroform was used as solvent and the CH_3 resonance at 3.1 ppm indicates the amount of monomeric **9MA**. This peak will decrease as the irradiation time increases.

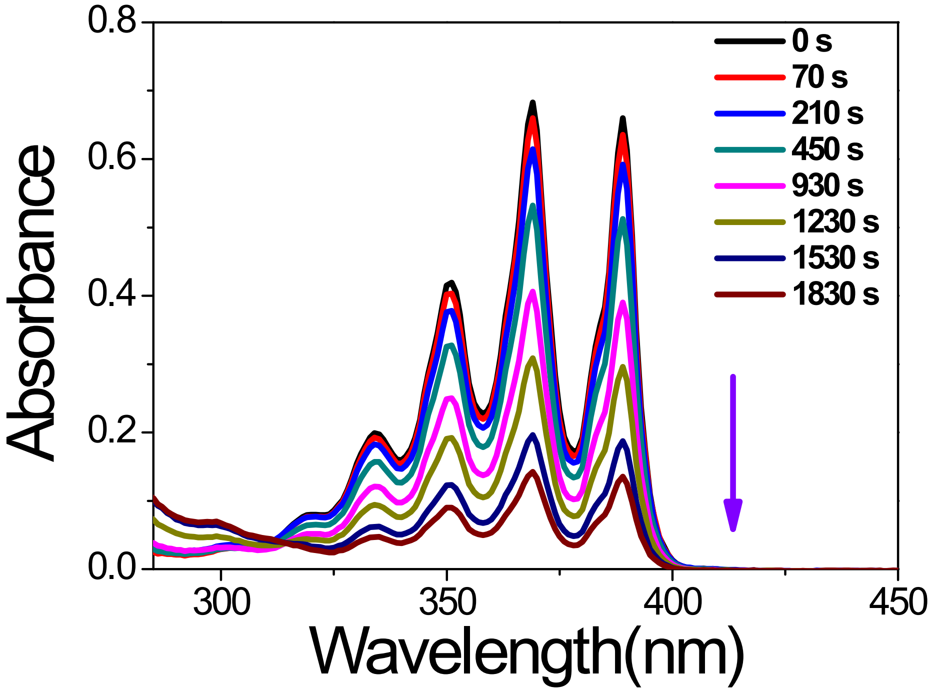

Figure S-2. Time-dependent spectral evolution of **9MA** (in THF, ~4.5×10^{-5} M) by 365 nm irradiation at ambient temperature. The black trace is the absorption spectrum of 9MA without any irradiation.

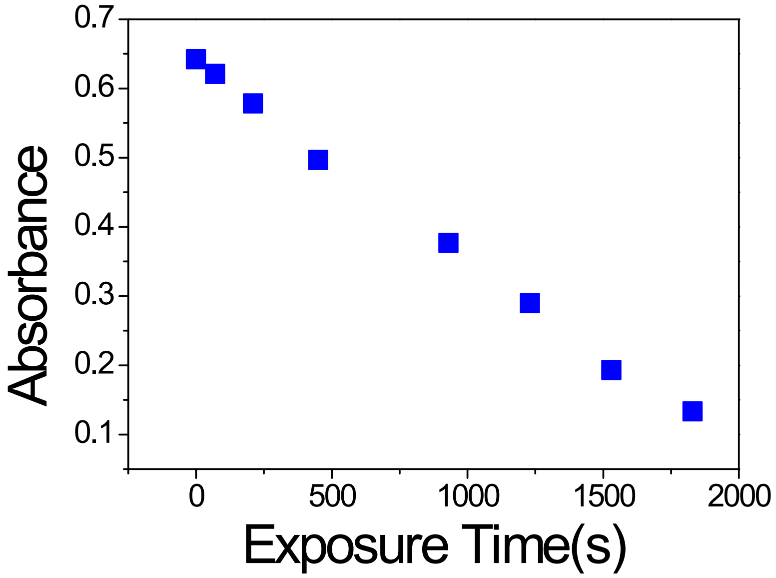

Figure S-3. UV-Vis absorption decay of **9MA** in THF solution with increasing UV exposure time. The experimental data points are based on the absorption intensity of peak around 370 nm. No induction time is observed for the photodimerization reaction in solution, in contrast to the solid-state data.

Description of Fluorescence Lifetime Analysis Using FAST Software

FAST Advanced Analysis of Fluorescence Kinetics software (Edinburgh Instruments Limited, 2010, version 3.0) was used to analyze the fluorescence lifetime decay data of solid-state crystalline film of **9MA**. The fluorescence lifetime decay of **9MA** at each irradiation time was divided into 20 nm wide spectral windows, from 400-420 nm, 420-440 nm, … 580-600 nm. Each window was integrated over wavelength to produce a single decay curve. These 10 decay curves were then fit using standard global exponential components analysis in the FAST software. All 10 curves were simultaneously fit using the biexponential decay given in Equation (16) in the text:

$$PL(\lambda,t) = A_1(\lambda)\exp\left[-k_{fl1}t\right] + A_2(\lambda)\exp\left[-k_{fl2}t\right]$$

The same rate constants k_{fl1} and k_{fl2} were used for each wavelength interval, but their respective amplitudes A_1 and A_2 were allowed to vary for different spectral regions. In this way we could obtain the spectra $A_1(\lambda)$ and $A_2(\lambda)$ associated with each decay rate k_{fl1} and k_{fl2}. For each irradiated sample, the rate constants k_{fl1} and k_{fl2} were allowed to vary. All data were corrected for background but the instrument response function was assumed to be faster than the decay dynamics and was not convolved with the fits. The measured width of the instrument response was 20-30 ps.