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

Fei Tong\(^{(1)}\), Mervin P. Hanson\(^{(2)}\), and Christopher J. Bardeen\(^{(1)}\)*

\(^{(1)}\)Department of Chemistry  
University of California, Riverside  
501 Big Springs Road  
Riverside, CA 92521 (USA)

\(^{(2)}\)Department of Chemistry  
Humboldt State University  
1 Harpst Street  
Arcata, CA 95521

*E-mail: christopher.bardeen@ucr.edu

**Table of Contents**

*Page 2.* **Figure S-1.** \(^{1}\)H-NMR of 9MA monomer, dimer and mixed solutions, showing methyl peak in CDCl\(_3\) that indicates the monomer concentration

*Page 3.* **Figure S-2.** UV-Vis absorption spectra of 9MA in THF solution irradiated by 365 nm light for different exposure times

*Page 3.* **Figure S-3.** Plot of the UV-Vis absorption decay of 9MA versus exposure time in THF solution

*Page 4.* Description of fluorescence lifetime analysis using FAST Software

*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:

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

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.