

Supplementary Material (ESI) for Chemical Communications

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Supporting Information

Current-less Photoreactivity Catalyzed by Functionalized AFM Tips

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Experimental Methods

To generate the appropriate substrate chemistry, Procion Red MX-5B (Aldrich) was deposited onto a glass substrate using a layer-by-layer adsorption technique for up to 10 consecutive layers. In effect, each layer consisting of 100 μl of a 0.65 mM Procion Red MX-5B in aqueous solution (with 1 mM H_2O_2) was deposited and then correspondingly oven dried at 45 $^\circ\text{C}$ until a uniform, homogeneous surface was formed. The thicknesses of the dye films were found to be in the range of 190 ± 30 nm. It should be noted that the dye concentration used in these films was identical to that of the dye concentration used in the bulk solution experiment. The substrate was then mounted onto a 300 mesh, lacey carbon-coated copper TEM grid (Ted Pella), which itself was glued onto a metal AFM sample puck. The purpose of the grid was to facilitate spatial localization of the reaction region in both AFM as well as for subsequent optical microscopy and spectroscopy studies.

The photochemical oxidation reaction was performed under ambient conditions using a Multimode Nanoscope IIIa scanning probe microscope (Digital Instruments, Inc., Santa Barbara, CA) operated in TappingModeTM. Scans were run for varying time intervals from 1 to 8 h with resonant frequencies in the range of 25-30 kHz for TiO_2 -functionalized tips and 60-80 kHz for control unfunctionalized tips. Scan sizes analyzed ranged from 30×30 μm with applied tapping forces in the range of 10-100 nN. Scan rates utilized were generally 1.74 Hz. We found that factors such as tip speed and dwell time did not substantially alter the degree of photodegradation. A handheld UV lamp (Ultra Violet Products, Model UVG-11) was positioned ~ 5 cm from the AFM head at an optimized angle to maximize the amount of light striking the sample surface. As control experiments, an uncoated conventional silicon tip was scanned over a dye surface under the presence of UV radiation and in addition, a TiO_2 -coated tip without the presence of UV radiation was scanned over a separate dye surface. All other experimental conditions were maintained.

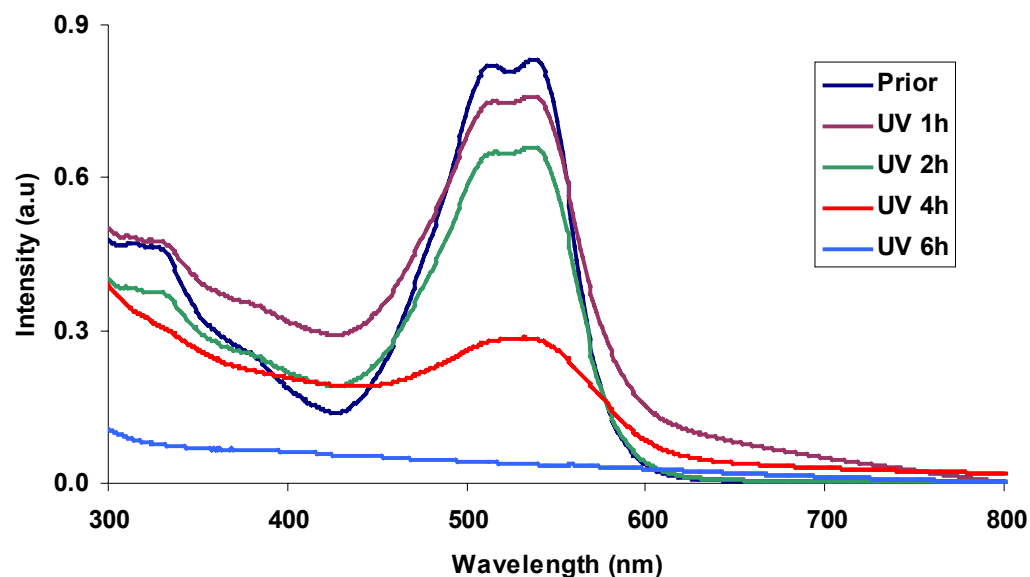


Figure S1. UV-Visible spectral absorption measurement changes, in bulk, of Procion Red MX-5B absorbance in aqueous TiO₂ dispersions with increasing irradiation time. Data traces from top to bottom: increasing times of irradiation up to 6 h. Reaction conditions: Procion Red MX-5B, 40 mg l⁻¹; TiO₂, 100 mg l⁻¹; H₂O₂, 1 mM; UV, 4 W at a ~5 cm separation distance. UV-Visible spectra were taken with a Beckman Coulter DU 640 spectrophotometer.

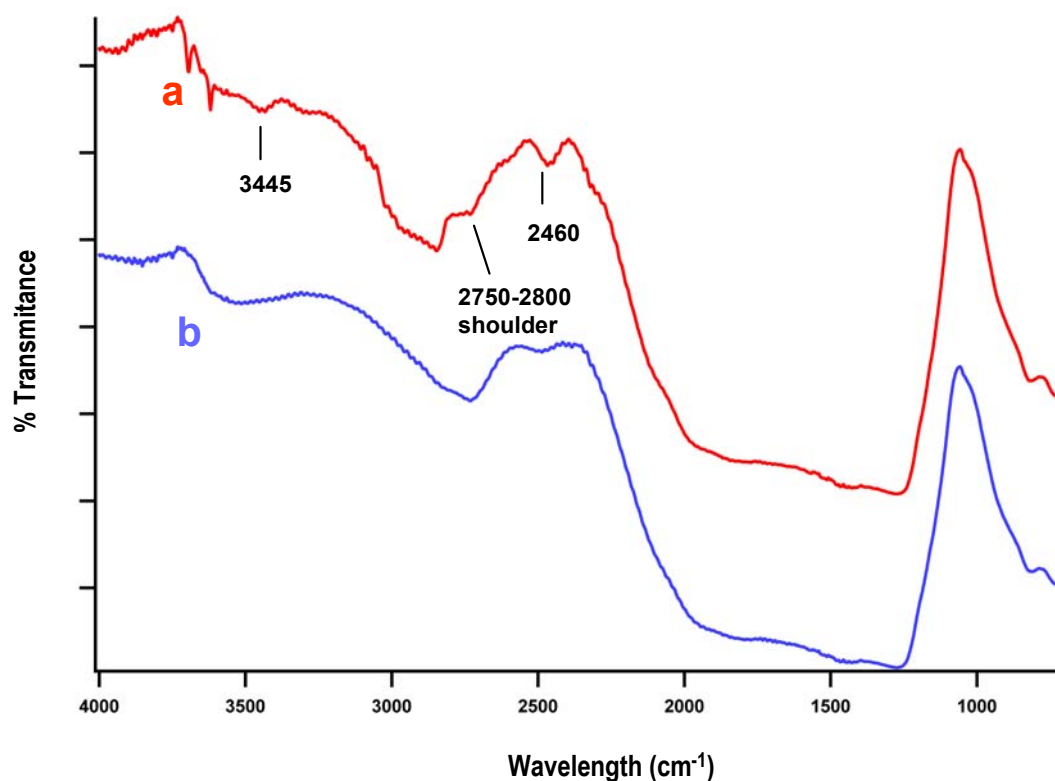


Figure S2. FT-mid-IR spectra of Procion Red MX-5B deposited on a glass surface. (a) unreacted and (b) reacted areas shown in Figure 2 of main text. Spectra were acquired with a Perkin Elmer Spectrum Spotlight FTIR Imaging System equipped with a Spectrum One Spectrometer and Spectrum Spotlight software. While the spectral features from 2000-1000 cm^{-1} are masked by the intense band interference of the glass substrate, spectral changes in the 3500–2000 cm^{-1} region are evident. Specifically, a weak shoulder located at 2800-2750 cm^{-1} , attributable to an asymmetrical aromatic C-H stretching vibration of the conjugated moiety attached to the N=N group, the medium band at 2460 cm^{-1} ascribed to a $\text{N}^+=\text{C}$ stretch, and finally, the significant band in the region of 3445 cm^{-1} , which is typical of an aromatic N-H stretch, significantly diminish or disappear in the analogous spectrum of the reacted region.

Additionally, a new absorption band in trace (b) appeared in 2900-2650 cm^{-1} region, originating from CH_3 stretching vibrations or from OH stretching vibrations of carboxylic acids, consistent with the expected formation of aliphatic carboxylic acid degradation intermediates, such as oxalic acid and malic

acid. These spectroscopic results are suggestive of site-selective degradation (and chemical change) of the initial dye composition.

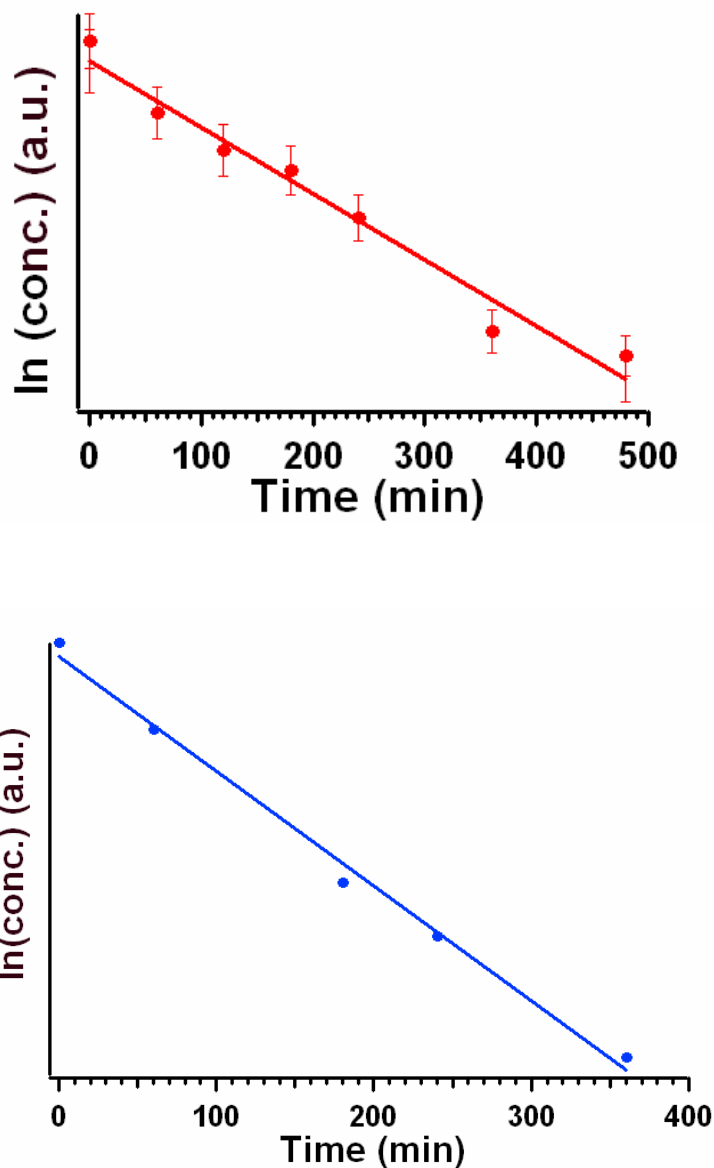


Figure S3. (a) Plot of concentration of the dye at varying reaction times on the glass substrate. The surface reaction was carried out with a TiO₂ coated AFM tip under UV irradiation. The decrease in the surface roughness was assumed to be directly proportional to the accompanying decrease in the dye concentration. (b) Plot of concentration, obtained from the absorbance of the dye solution at 539 nm and assuming Beer's Law validity, of the dye vs. varying reaction times in bulk solution.