

Supporting Information

The Role of Surface Phenomena on the Reaction of Molecular Solids: the Diels-Alder Reaction on Pentacene

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General Procedures for Solution Phase Kinetic Measurements:

All reactions were performed in N₂ purged chloroform at room temperature (23 °C). Kinetics were measured under pseudo-first-order conditions with the dienophile/adsorbate concentration roughly 100-fold higher than that of pentacene (0.26 mM for pentacene, 44 mM for the enophile/adsorbate). At high concentrations, the dienophile/adsorbates have non-zero absorptions, especially at lower wavelengths, and thus the initial dienophile/adsorbate spectrum is subtracted from those shown in Figure S1. Concentration was monitored via the S₀-S₁ band at 576 nm.

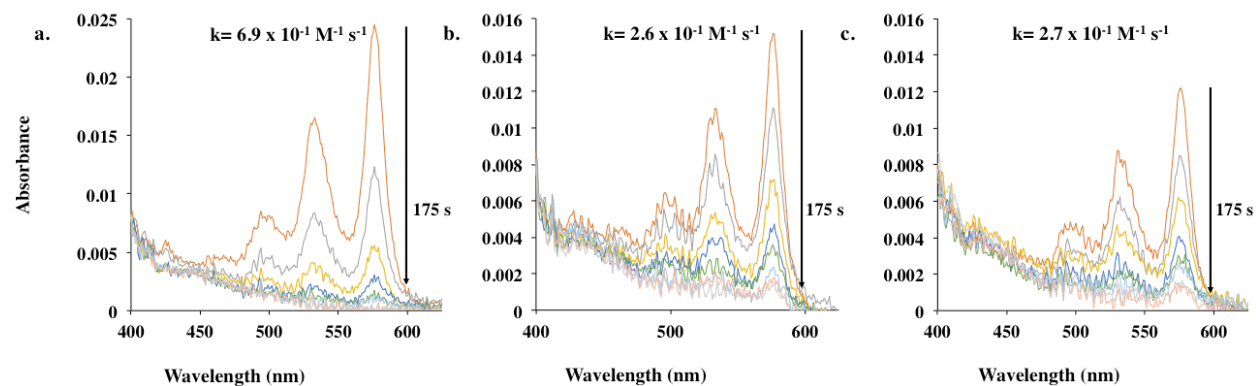
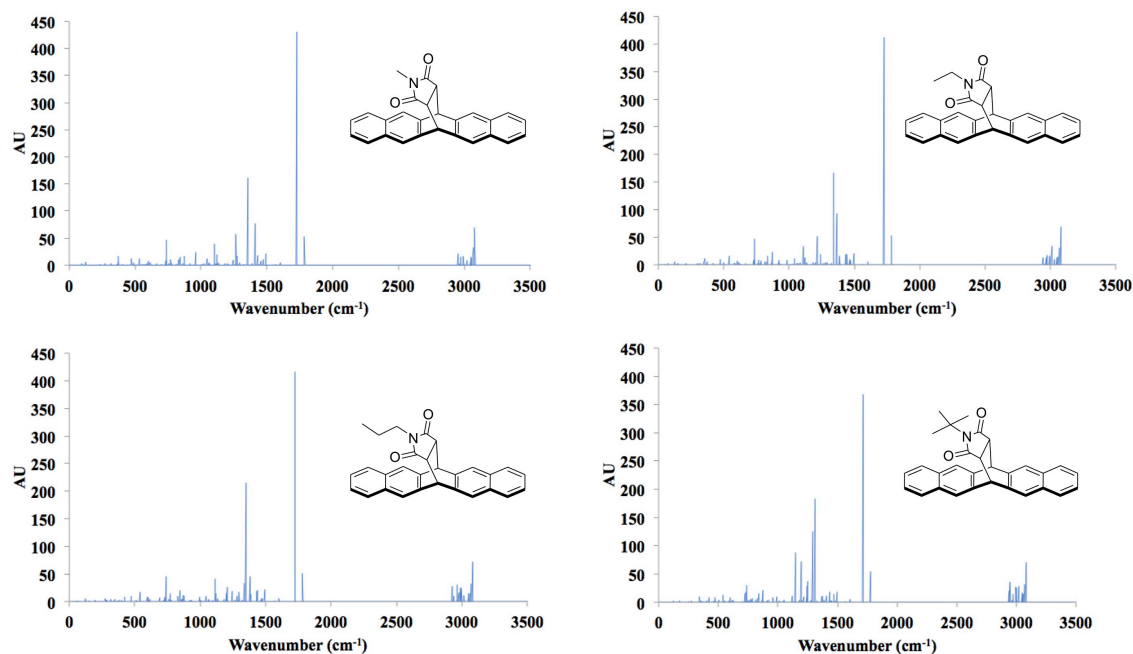


Figure S1. Solution phase kinetic data for *N*-methylmaleimide, *N*-ethylmaleimide, and *N*-propylmaleimide. The reaction between pentacene and adsorbate molecules *N*-methylmaleimide, **b)** *N*-ethylmaleimide, **c)** *N*-propylmaleimide at 23 °C. All spectra are after subtraction of the absorbance of the adsorbate/dienophiles.



Adduct	Carbonyl Stretching Intensity
<i>N</i> -methylmaleimide	411
<i>N</i> -ethylmaleimide	430
<i>N</i> -propylmaleimide	416
<i>N</i> -tert-butylmaleimide	368

Figure S2. Calculated IR spectra and carbonyl absorption intensity for *N*-methylmaleimide, *N*-ethylmaleimide, *N*-propylmaleimide, and *N*-tert-butylmaleimide. Spectra were calculated with a B3LYP hybrid functional and 6-31G* basis set. Frequencies have been scaled by the NIST CCCBDB precalculated vibrational scaling factor (0.96)

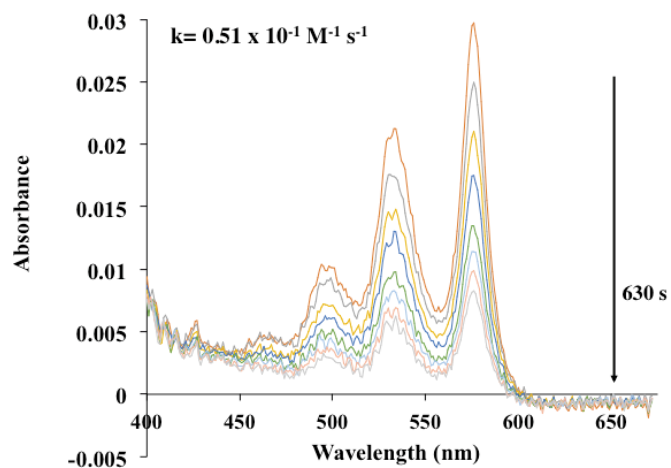


Figure S3. Reaction of Pentacene with *N*-*tert*-Butylmaleimide. Solution phase kinetic data for the reaction of pentacene with *N*-propylmaleimide at 23 °C. Spectrum is after subtraction of the absorbance of the adsorbate/dienophiles

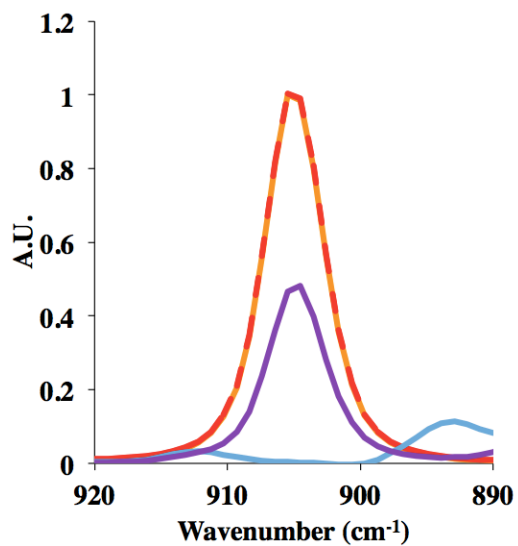


Figure S4. Reactions of thin-film tetracene (orange) with *N*-methylmaleimide (red), *N*-ethylmaleimide (blue), *N*-propylmaleimide (purple) showing thin film consumption.

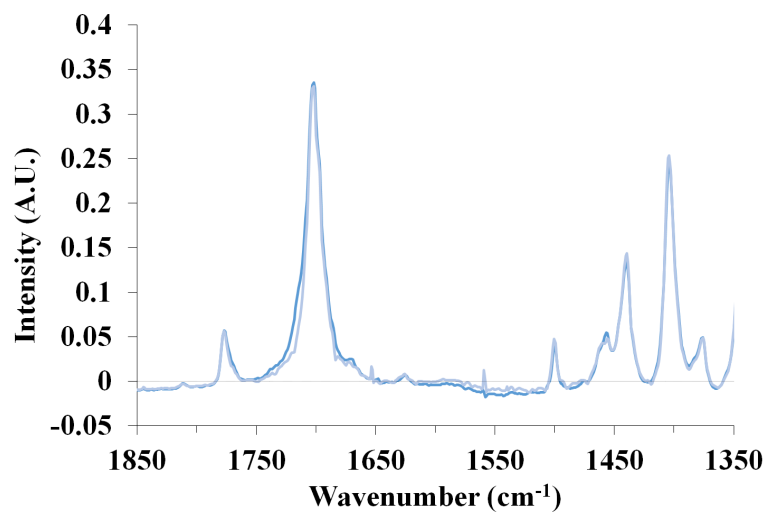
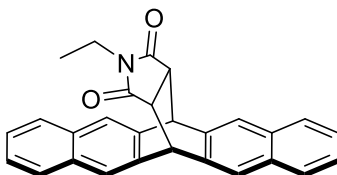


Figure S5. PM-IRRAS spectra of *N*-ethylmaleimide reacted with a pentacene thin film used for the subtraction of spectra in Figure 4b. Dark blue line is after 6 h of reaction at 50 °C while the light blue line is the same sample after 30 minutes of exposure to a N_2 purge.

Synthetic Methods

All materials were purchased from Sigma-Aldrich or TCI and were used without further purification. Reagent grade toluene was purged with nitrogen before use. Pentacene used in reactions was sublimed grade ($\geq 99.9\%$ pure). ^1H and ^{13}C NMR spectra were taken in CDCl_3 and recorded on a Varian 500 MHz spectrometer. All chemical shifts (δ) are reported in ppm and are referenced to tetramethylsilane. IR spectra were taken using a Shimadzu IRAffinity-1 with a Pike Technologies MIRacle single reflection ATR accessory.



6,13-dihydro-6,13-ethano-pentacene-16-N-ethylpyrrolidine-15,17-dione: Pentacene (0.0356 g, 0.128 mmol), *N*-ethylmaleimide (0.0222 g, 0.177 mmol), and toluene (1.4 mL) were placed in a sealed tube and was purged with nitrogen prior to the addition of solvent. Degassed toluene was then added via a syringe and the tube was sealed. The mixture was stirred for 29 h at 120 °C. After completion, the mixture was cooled to 4 °C and the precipitate was collected via vacuum filtration. The grey powder (0.0201 g, 0.0498 mmol) was then recrystallized from toluene to afford the adduct at 39% yield. ^1H NMR (500 MHz): δ 7.85 (s, 2H), 7.81 (dd, $J = 6.1, 3.2$, 2H), 7.76-7.73 (m, 4H), 7.45 (dd, $J = 6.3, 3.4$, 2H), 7.40 (dd, $J = 6.3, 2.9$, 2H), 5.02 (s, 2H), 3.33 (t, $J = 1.7$, 2H), 3.08 (q, $J = 7.3$, 2H), 0.09 (t, $J = 7.3$, 3H). ^{13}C NMR (125 MHz): δ 176.51, 138.25, 135.43, 132.39, 132.37, 127.52, 127.46, 125.95, 125.83, 123.53, 122.66, 46.63, 45.45, 33.14, 11.63. IR (cm^{-1}) 3055, 2961, 1776, 1697, 1609, 1499, 1439, 1402, 1339, 1225, 1130, 999, 895, 849, 752.

STANDARD PROTON PARAMETERS
Pulse Sequence: szpu1

