Supporting Information

In order to aid in the assignment of the IR spectral features measured in this work, a series of calculations were performed using electronic structure calculations with the Gaussian09 code.

First, the geometry of nitrate-terminated linear alkanes in the gas phase with varying chain length was optimized using both B3LYP/6-31G* and MP2/6-31G* levels of theory, and harmonic vibrational mode analyses were performed on each molecule using both methods. Since addition of a nitrate radical to a ω-vinyl SAM results in the breakage of the vinyl pi bond, the molecules were constructed as R-CH-CH_2ONO_2 radicals. The calculated harmonic frequencies of the scissoring (δ), symmetric stretch (ν_s), and asymmetric stretch (ν_a) ONO_2 normal modes were found to converge to a constant value with increasing chain lengths. Fig. S1 shows the calculated vibrational frequencies of each vibrational mode as a function of chain length. All calculated vibrational frequencies reported in this work have been scaled by the recommended factors of 0.96 for B3LYP/6-31G* and 0.94 for MP2/6-31G*.[1]

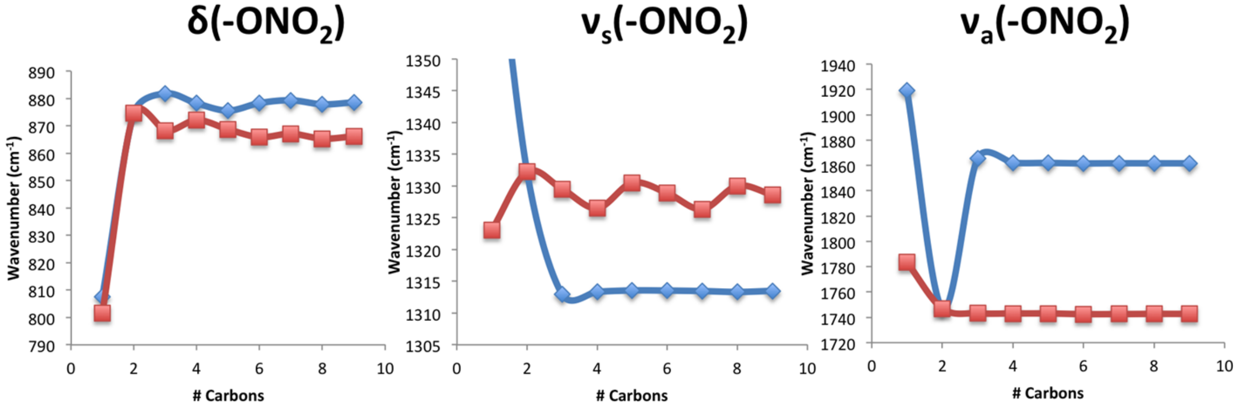

Figure S1. Vibrational frequencies calculated for gas-phase ω-ONO_2 alkyl chains with varying numbers of carbon atoms. B3LYP/6-31G* frequencies are shown in red, and MP2/6-31G* frequencies are shown in blue.

To test the reliability of the SAM model used in this work, all calculations involving the use of the universal force field (UFF)[2] were repeated using the Amber force field[3] for the MM region. Not all of the Amber force field parameters required for this system were available in the Gaussian09 implementation and had to be specified manually. Table 1 gives these specified input parameters.

Table 1. Auxiliary parameters for the AMBER forcefield used in this work.[a]

Bond Stretch	Stretching Force Constant (kcal mol^{-1} Å^{-2})	Equilibrium distance (Å)
O(nitrate)-N (in C-O-N)[4]	600.0	1.390
O(nitro)-N (in O-N-O)[4]	1530.0	1.200
Angle Bend	**Bending Force Constant (kcal mol^{-1} rad^{-2})**	**Equilibrium angle (°)**
C-O-N[4]	111.0	109.6
O-C-H[4]	210.0	106.7
O(nitrate)-N-O(nitro)[4]	210.0	115.0
C-C-C(=)[5]	63.0	111.0
C=C-H[5]	50.0	119.7
H-C(=)-H[6]	40.0	120.0
O(nitro)-N-O(nitro)[6]	210.0	130.0
C-C(=)-H[5]	50.0	120.0

[a] O(nitrate) indicates an oxygen bound to a carbon and a nitrogen. O(nitro) indicates an oxygen bound solely to a nitrogen. C(=) indicates a vinyl carbon.

Figure S2 shows the complete calculated vibrational spectra of $CH_3(CH_2)_5CHCH_2ONO_2$ both in the gas phase and in a SAM. Due to the heightened role of intermolecular interactions in the SAM, most of the vibrational modes have been blueshifted relative to those in the gas phase. To further quantify this shifting of frequencies, several analogous vibrational modes were compared for gas-phase and SAM-confined ω-ONO_2 octyl radical chains. The average of the absolute values of the shift was found to be 8.5 cm^{-1} with a maximum shift of 24.7 cm^{-1}, corresponding to a redshift in the SAM model of the R-CH-C out-of-plane bending mode in the R-CH-CH_2. Of the 16 modes used in this comparison, four of these modes were similarly redshifted (average redshift = 12.3 cm^{-1}), and the remaining 12, including those ω-ONO_2 modes presented in Table 1, were blueshifted (average blueshift = 7.2 cm^{-1}).

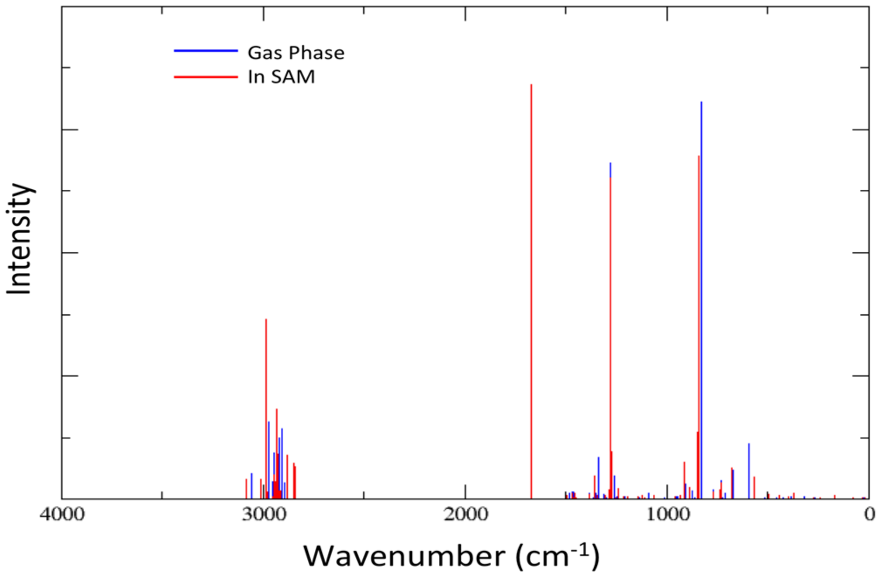

Figure S2. Theoretical vibrational frequencies for $CH_3(CH_2)_5CHCH_2ONO_2$ in the gas phase (blue) and as a central chain in a self-assembled monolayer (red). Note that the red peak at 1673 cm^{-1} overlaps a blue peak at the same frequency.

All the calculations mentioned above were performed on ω-ONO_2 and ω-vinyl alkyl chains. However, in an experimental SAM grown on a thin film of gold, the alkyl chains are anchored to the gold surface by an α-S atom. Thus, vibrational modes of α-S alkyl chains were compared to those of α-CH_3 alkyl chains to rule out any influence of a sulfur atom on the vibrational modes being examined in experimental spectra. The comparison of calculated frequency calculations of $CH_3(CH_2)_5CHCH_2$ and $SH(CH_2)_5CHCH_2$ is given in Table 2 for this purpose. The invariance of vibrational frequency (5 cm^{-1} maximum difference) of the modes at the chain terminus with respect to the anchor group demonstrates that the treatment of the anchor group has little influence on the calculations reported in this work.

Table 2. B3LYP/6-31G* Vibrational modes of $CH_3(CH_2)_5CHCH_2$ and $SH(CH_2)_5CHCH_2$.

Calculated Vibrational Mode	Vibrational Wavenumber (cm^{-1})	
	α-CH_3	α-SH
ω(=CH_2)	899	901
δ(CH_2)	1482	1480
ν(C=C)	1664	1664
$\nu_s(CH_2)$	2908	2908
$\nu_a(CH_2)$	2957	2962
$\nu_s(=CH_2)$	3028	3029
$\nu_a(=CH_2)$	3103	3105

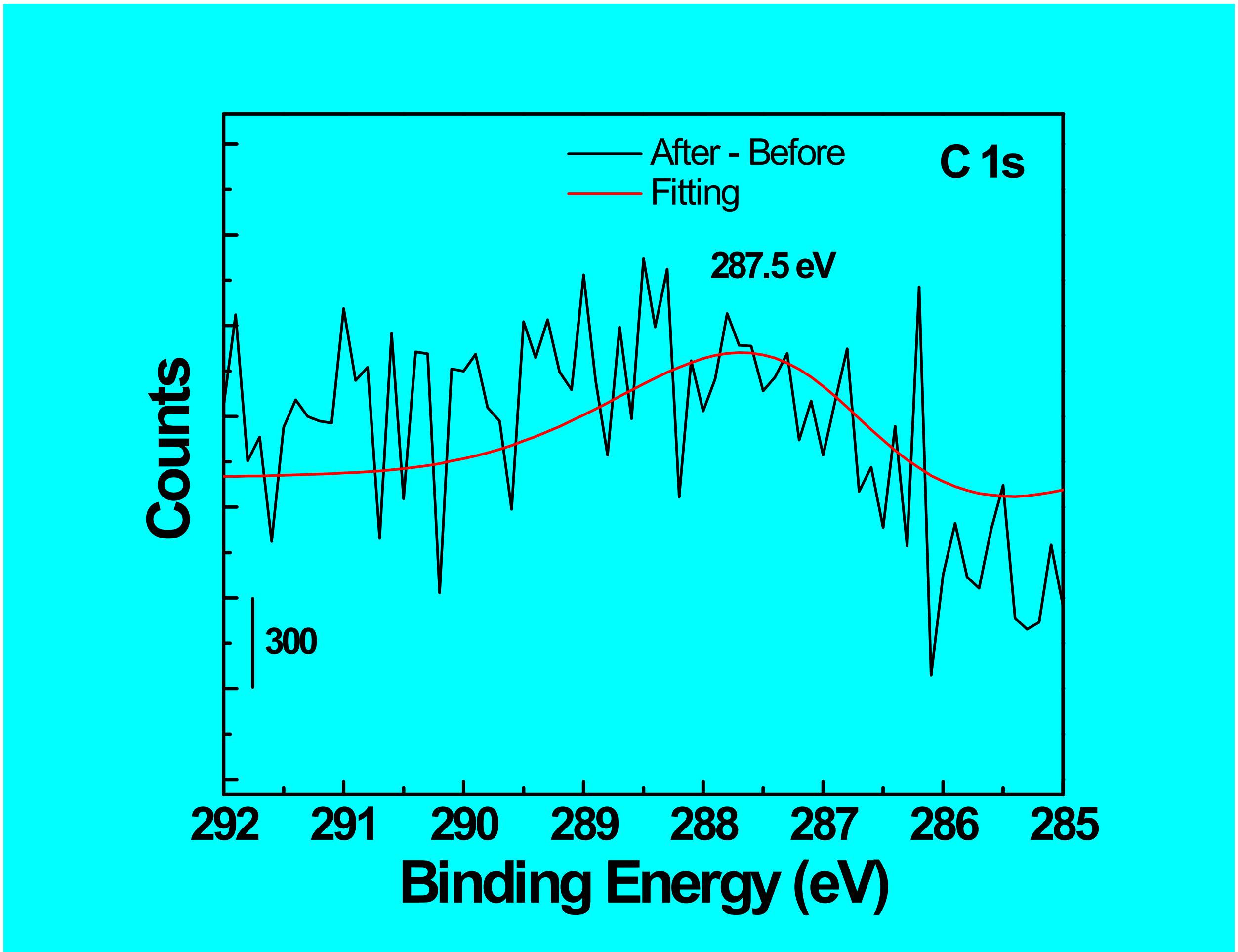

Figure S3. High resolution XPS in the C 1s region upon NO_3 exposure after subtracting the spectrum before reactions.

References

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