

Strained Surface Siloxanes as Source of Synthetically Important Radicals

Antony J. Ward,^a Rebecca A. Lesic,^a Nicholas Proschogo^b Anthony F. Masters^a and Thomas Maschmeyer^{a,*}

^a *Laboratory of Advanced Catalysis for Sustainability, School of Chemistry, The University of Sydney, 2006, Australia.*

^b Mass Spectrometry Unit, School of Chemistry, The University of Sydney, 2006, Australia.

SUPPLEMENTARY INFORMATION

Experimental

The following chemicals were used without further purification: anthracene (Merck), methyl acrylate (99% stabilised with 100 ppm hydroquinone; Merck), 2,6-di-*tert*-butylphenol (Aldrich), 5,5-dimethyl-1-pyrroline-1-oxide (Aldrich), cyclohexyltrichlorosilane (Lancaster), tetraethoxysilane (Alfa Aesar), triethanolamine (Alfa Aesar), cetyltrimethylammonium bromide (Aldrich). Carbon dioxide (99.9%) was obtained from BOC. Hexanes were purified using an apparatus similar to that described in the literature.^[1] The amorphous silicas TUD-1,^[2] MCM-41^[3] and the silsesquioxanes (*a6b0* and *a7b3*)^[4] were prepared according to published literature methods. Flash chromatography silica (flash chromatography grade, 230–400 mesh, Ajax) was pre-treated at 120, 300, 600 or 850 °C (ramp rate: 2 °C / min) for 10 h under a stream of air to remove physisorbed and chemisorbed water. The calcined silica was stored in a desiccator or under a nitrogen atmosphere to prevent re-absorption of water.

Solid-state and solution EPR spectra (X-band) were acquired on a Bruker Eleksys E500 spectrometer, using quartz capillaries (solid state) and a Wilmad quartz flat cell (solutions); calibrations of the magnetic field and the microwave frequency were performed with an EMX 035 NMR gaussmeter and an EMX 048T microwave bridge controller, respectively. Low-temperature (77 K) EPR spectra were recorded using a “coldfinger” liquid N₂ dewar. Typical instrumental settings were as follows: center field, 3480 G; sweep width, 6900 G (solids) or 200 G (solutions); resolution, 1024 points; microwave power, 2.0 mW; microwave frequency, ~9.27 GHz (solids at 77 K), ~9.78 GHz (solids at 295 K), or ~9.67 GHz (solutions); modulation frequency, 100 kHz; modulation amplitude, 5.0 G (solids) or 0.40–1.0 G (solutions); time constant, 20.48 ms; receiver gain, 10²–10⁵; and number of scans, 5. The EPR spectra were processed with WinEPR.

¹H NMR (300.13 MHz) and ¹³C NMR (75.48 MHz) spectra were recorded on a Bruker Advance DPX300 spectrometer at 300 K using XWIN NMR software. ²⁹Si{¹H} NMR (79.48 MHz) spectra were recorded on a Bruker DRX400 spectrometer. NMR spectra were referenced internally, either to TMS (δ 0.00 ppm) or to the residual solvent resonances (CDCl₃; δ 7.26 ppm).

Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy (SEM-EDX) were conducted using a Philips Scanning Electron Microscope (SEM) 505. All samples were

mounted on aluminium plates using graphite tape, and lightly coated with gold prior to analysis.

A Waters Gel Permeation Chromatograph (GPC) was used to investigate the change in polymer size for the various samples of PMA produced under different conditions. Samples were dissolved in THF and passed through four Waters Styragel columns (HR1, 2, 3, 4) connected in series at 313 K, using THF as the eluent with a flow rate of 1 mL/min. A refractive index detector was used and all samples were calibrated against polystyrene standards with molecular weights ranging from 162–54000 amu.

High-resolution mass spectra were recorded using a Bruker Daltonics Apex-Qe 7T Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FTICR). The Atmospheric Pressure Chemical Ionisation (APCI) source was used in this study. The following settings were applied: corona needle 800 nA; capillary voltage 2000 V; spray shield 1500 V; APCI temperature 350 °C; capillary voltage: 310 V; deflection plate 295 V; TOF 0.0008 sec.

EPR Studies

To ascertain whether the observations of Hall,^[5] of the generation of anthracene radicals on silica alumina, freshly calcined at 750 °C, also applied to silica, calcined at 600 °C, we used anthracene as an EPR probe on SiO₂₍₆₀₀₎. This resulted in the observation of a strong signal at 3339 G ($g = 2.0037$) in the EPR spectrum recorded at 77 K (Figure S1(a)). Such a signal correlates well with literature and theoretical values for aromatic CH-based cationic radicals,^[6] however no hyperfine splitting was observed. When anthracene was loaded onto uncalcined silica, no signal was observed (Figure S1(b)). This shows that for radical formation to occur on silica no heteroatoms, such as aluminium, are necessary and that silica surface species on their own are sufficient. Furthermore, these surface species appear sensitive to atmospheric water.

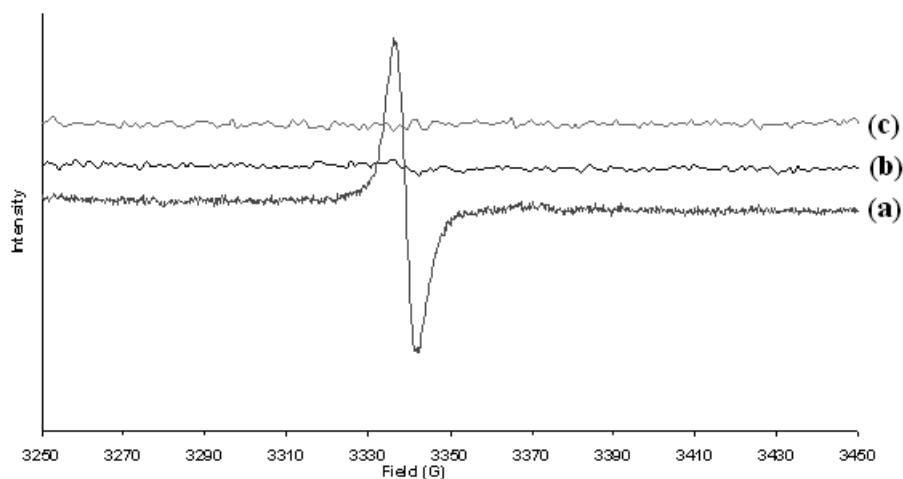


Figure S1. EPR spectra of (a) $\text{SiO}_{2(600)}$ -anthracene, (b) uncalcined silica-anthracene, and (c) an empty EPR tube. All samples were prepared as neat solids and the spectra were recorded at 77 K.

When frozen chloroform solutions of the silsesquioxanes and anthracene were analysed using EPR spectroscopy there was a signal for both the anthracene (Figure S2(b)) and the *a6b0*-anthracene (Figure S2(a)) samples. In both cases, the signal was located at 3339 G ($g = 2.0037$). The observance of the EPR signal for the anthracene sample in CHCl_3 is attributable to solvent-substrate interactions. In the case of the anthracene-*a6b0* sample, the EPR signal has lost the fine structure that is apparent for the anthracene sample and is indicative that there is an interaction between the radical cation and the strained Si_3O_3 rings (and closely resembles the signal observed for the $\text{SiO}_{2(600)}$ sample in Figure S1). The lack of an EPR signal for the anthracene-*a7b3* sample (Figure S1(c)) shows that this species is able to quench the anthracenyl radical cation (presumably as a consequence of the presence of the hydroxyl groups) that was observed for the anthracene- CHCl_3 sample.

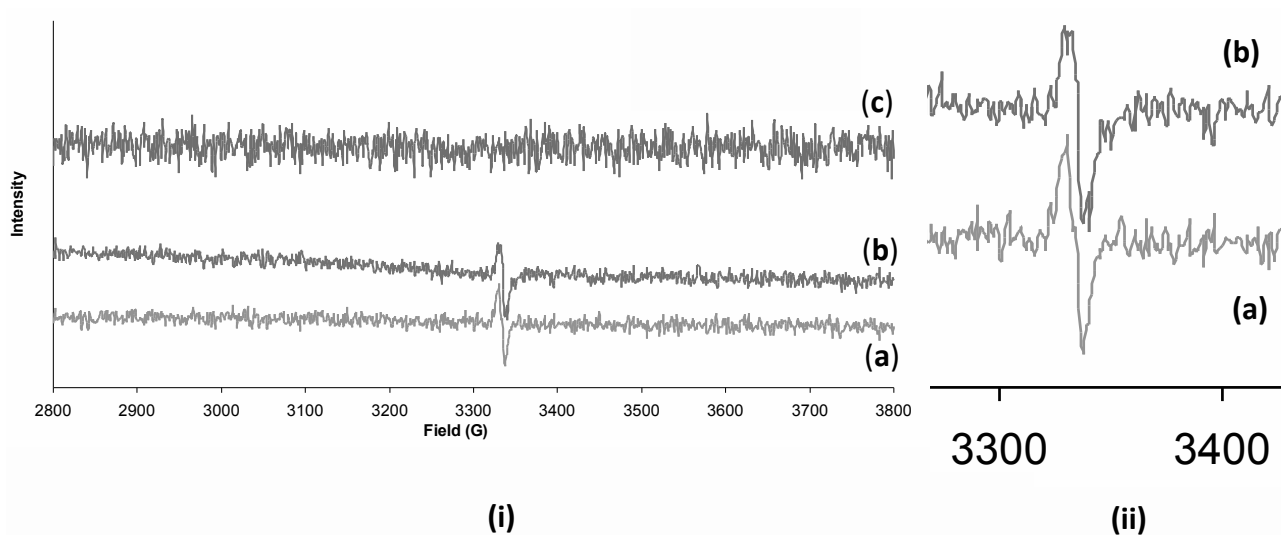
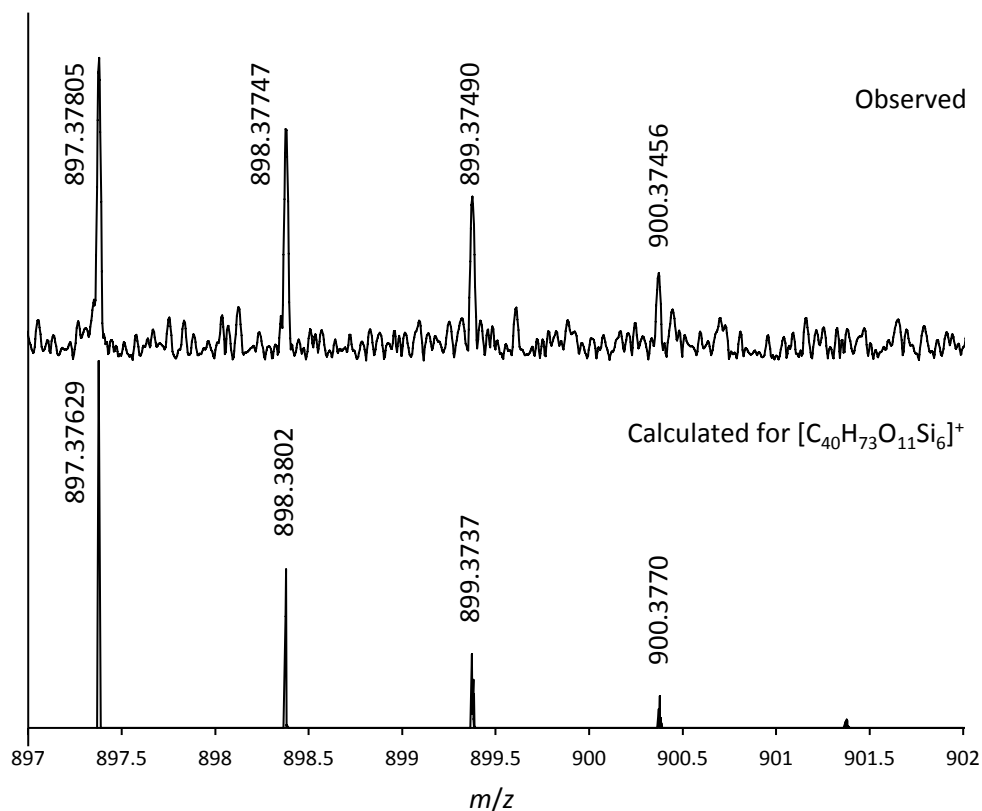


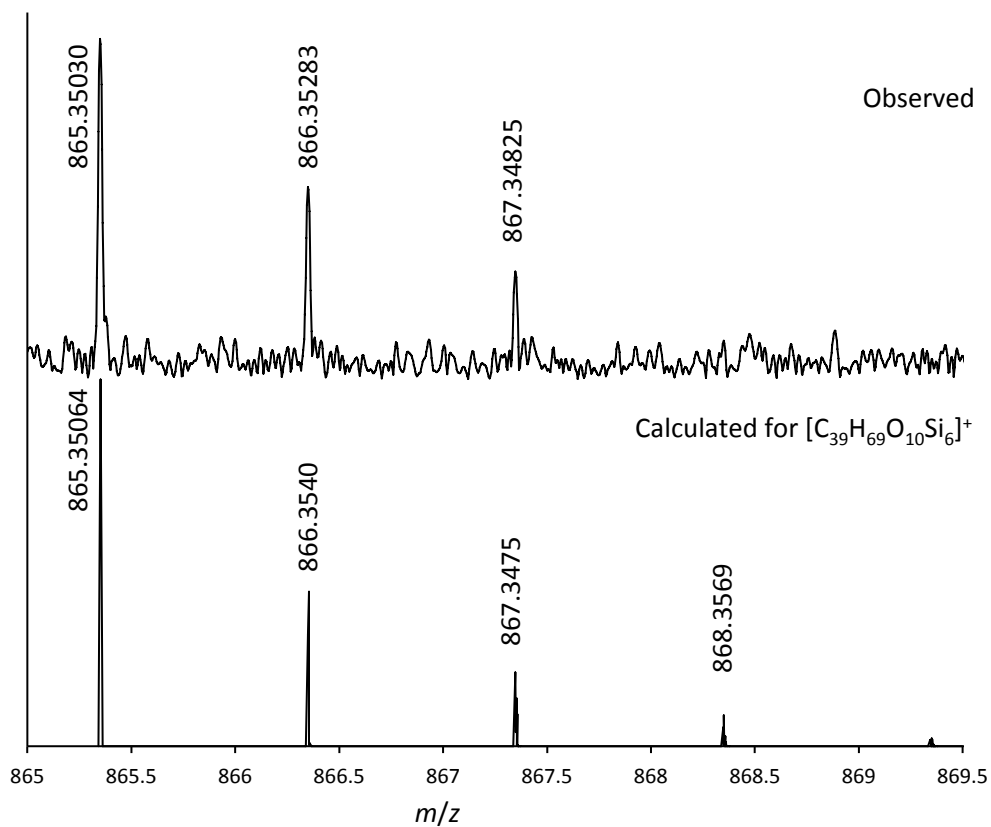
Figure S2. EPR spectra of: (i)(a) *a6b0* and anthracene; (b) anthracene; and (c) *a7b3* and anthracene. (ii) Expansion of (a) *a6b0* and anthracene; (b) anthracene. All samples were prepared as frozen solutions in chloroform and the spectra were recorded at 77 K.

Modelling of high-resolution mass spectrum peaks

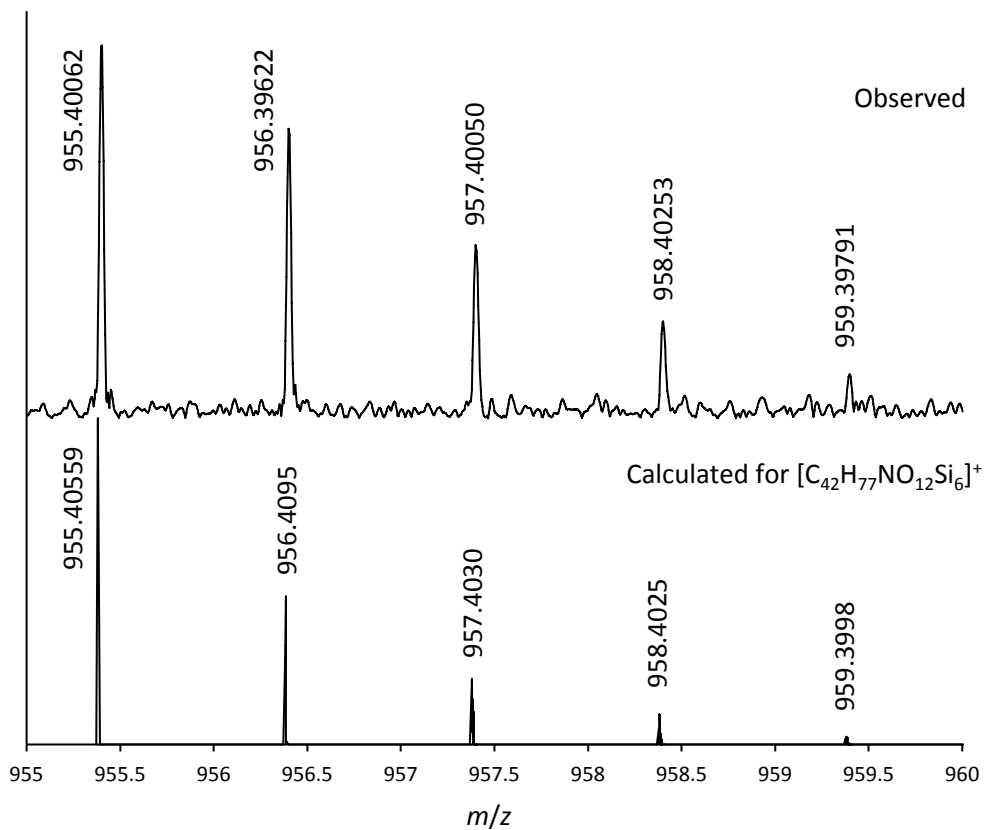
Species 3 ($m/z = 897.37805$):



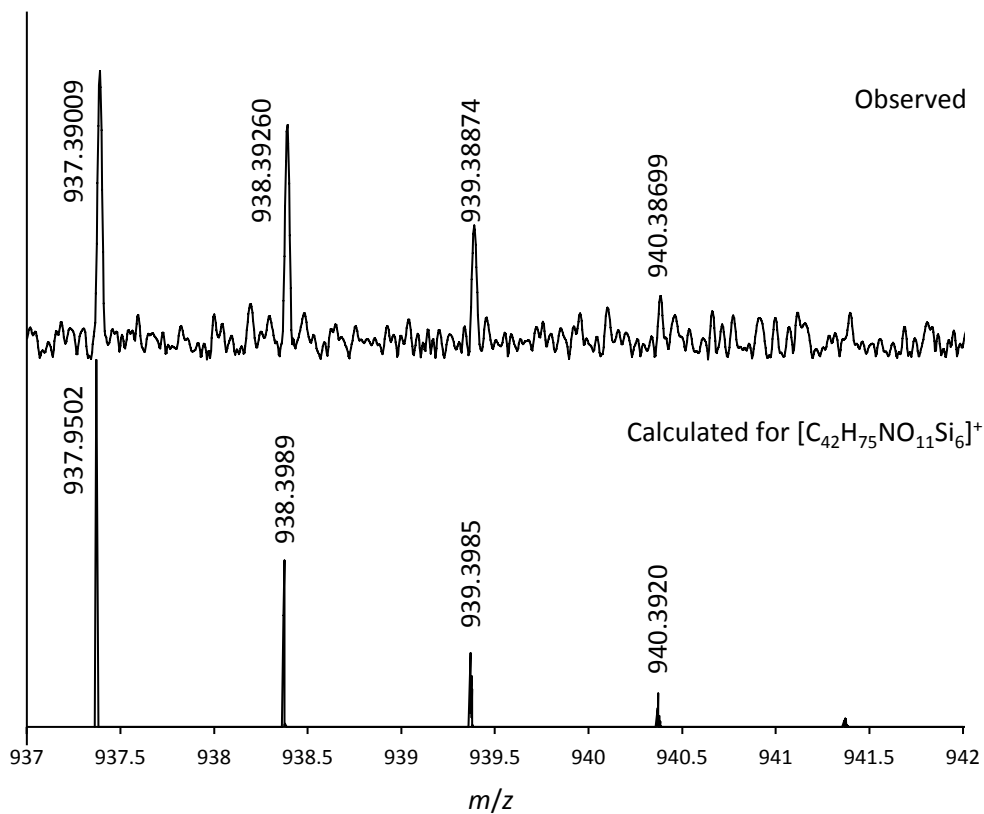
Species 4 ($m/z = 865.35030$):



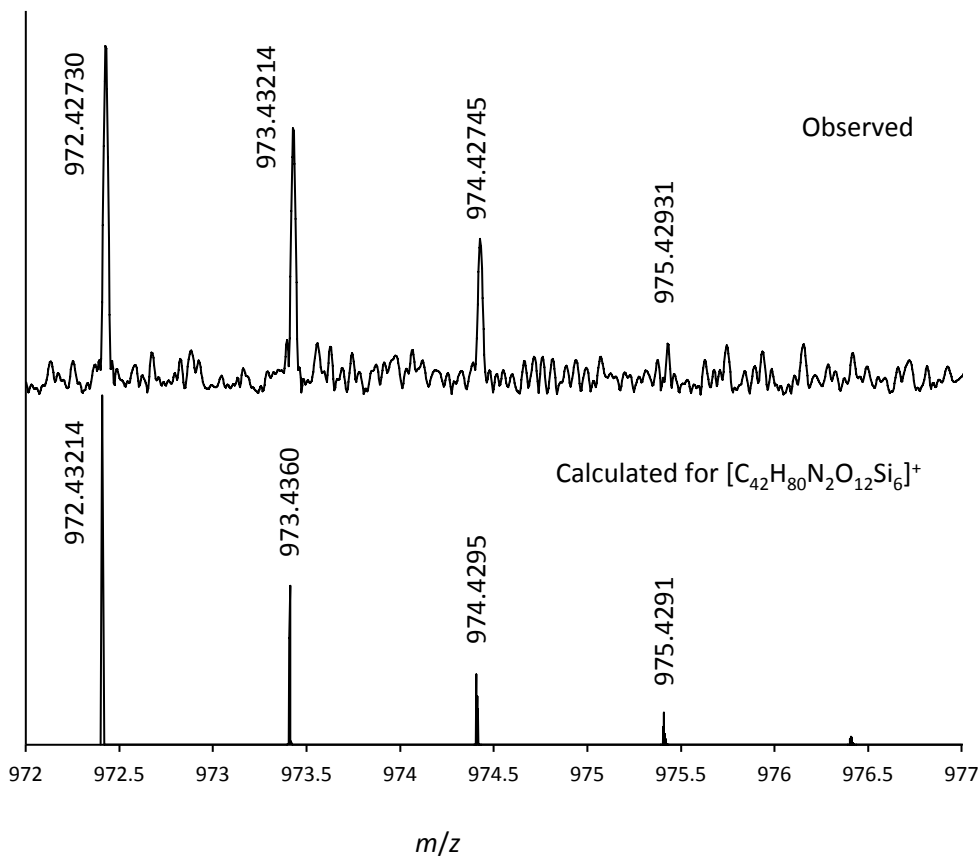
Species 5 ($m/z = 955.40062$):



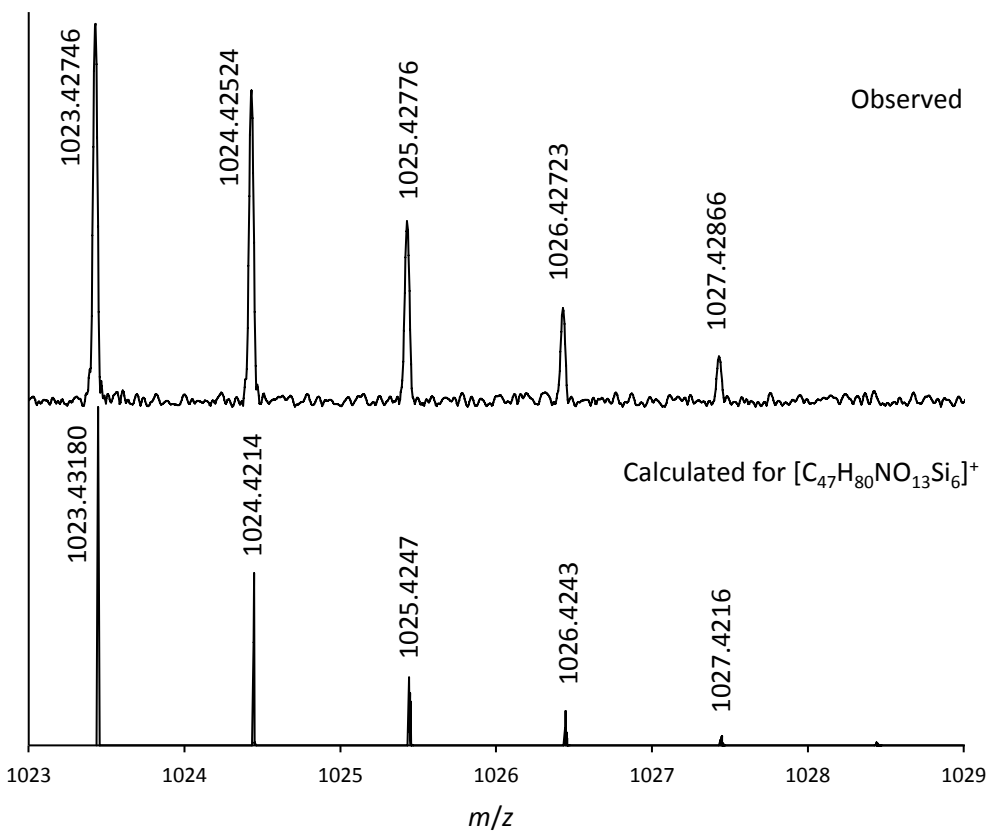
Species 6 ($m/z = 937.39009$):



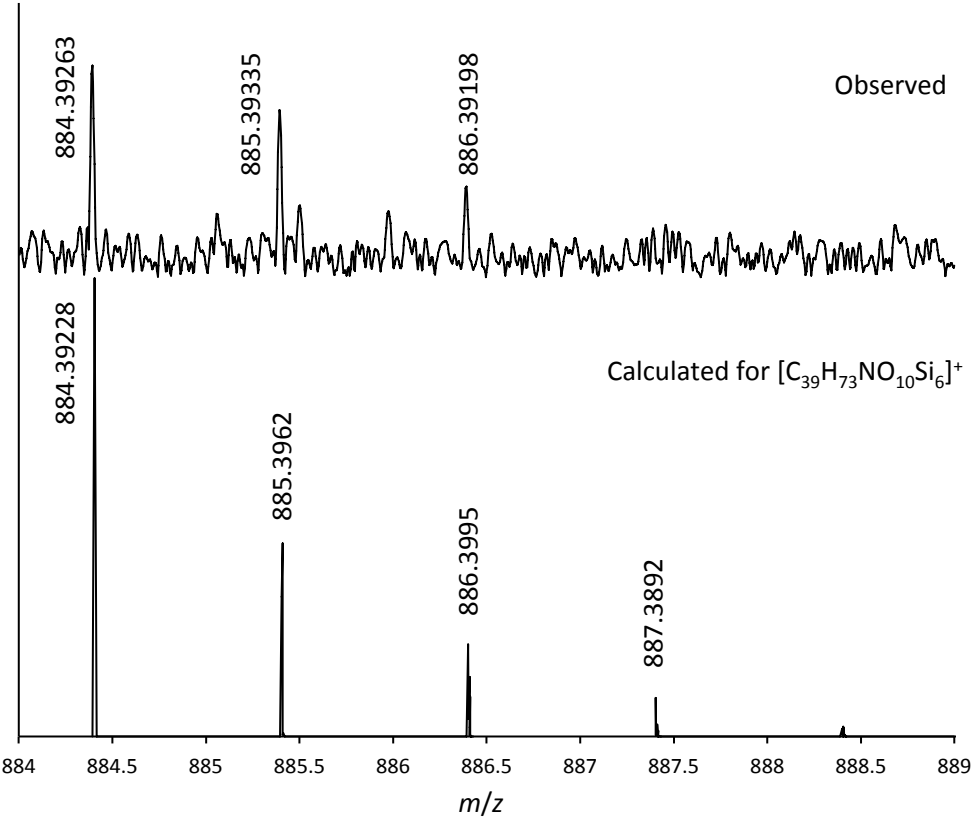
Species 7 ($m/z = 972.42730$):



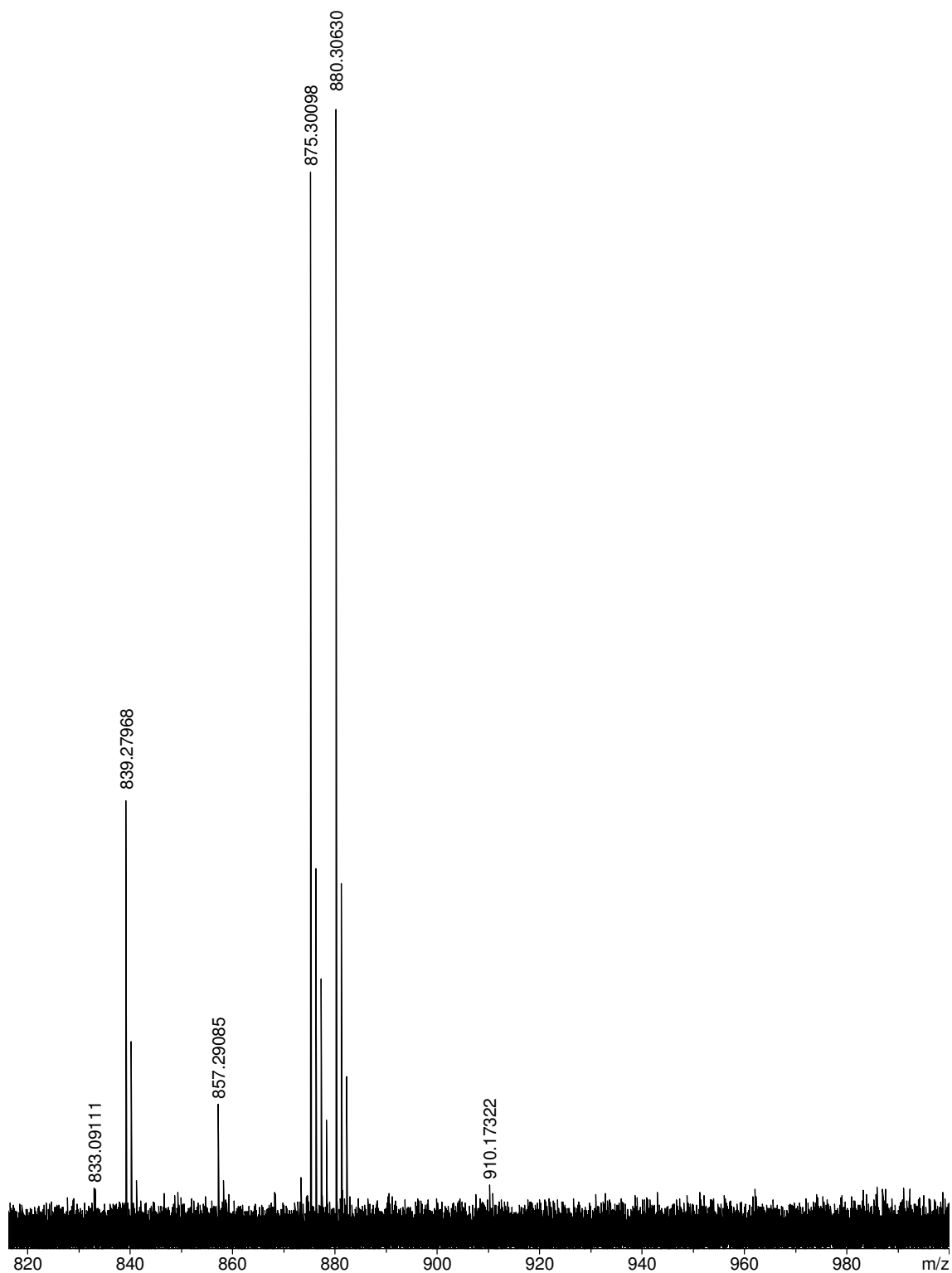
Species 8 ($m/z = 1023.42746$):



Species 9 ($m/z = 884.39263$):



High-resolution mass spectrum of the silsesquioxane *a7b3* in CH₃CN with methyl acrylate



The peak at $m/z = 875.30098$ represents the molecular ion $[\text{MH}]^+$ ($[\text{C}_{35}\text{H}_{66}\text{O}_{12}\text{Si}_7]^+$; calculated $m/z = 875.30119$). The peak at $m/z = 857.29085$ results from loss of one H_2O molecule from $[\text{MH}]^+$ to afford $[\text{C}_{35}\text{H}_{65}\text{O}_{11}\text{Si}_7]^+$ (calculated $m/z = 857.29117$), whilst the peak at $m/z = 839.27968$ results

from the loss of two H₂O molecules from [MH]⁺ to afford [C₃₅H₆₃O₁₀Si₇]⁺ (calculated *m/z* = 839.28061). The species at *m/z* = 880.30653 results from the addition of CH₃CN to the species with *m/z* = 839.27968 to afford [C₃₇H₆₆NO₁₀Si₇]⁺ (calculated *m/z* = 880.30716).

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