Mechanistic investigation of flame retardant coatings made by Layer-by-Layer

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SUPPORTING INFORMATION

Content **Page**

1. Mass Spectrometry (LDI-MS and MALDI-MS) 2
1.1. MALDI-MS of MMT 2
1.2. LDI-MS of PAH and PA6-(PAH-MMT)$_{40}$ 3

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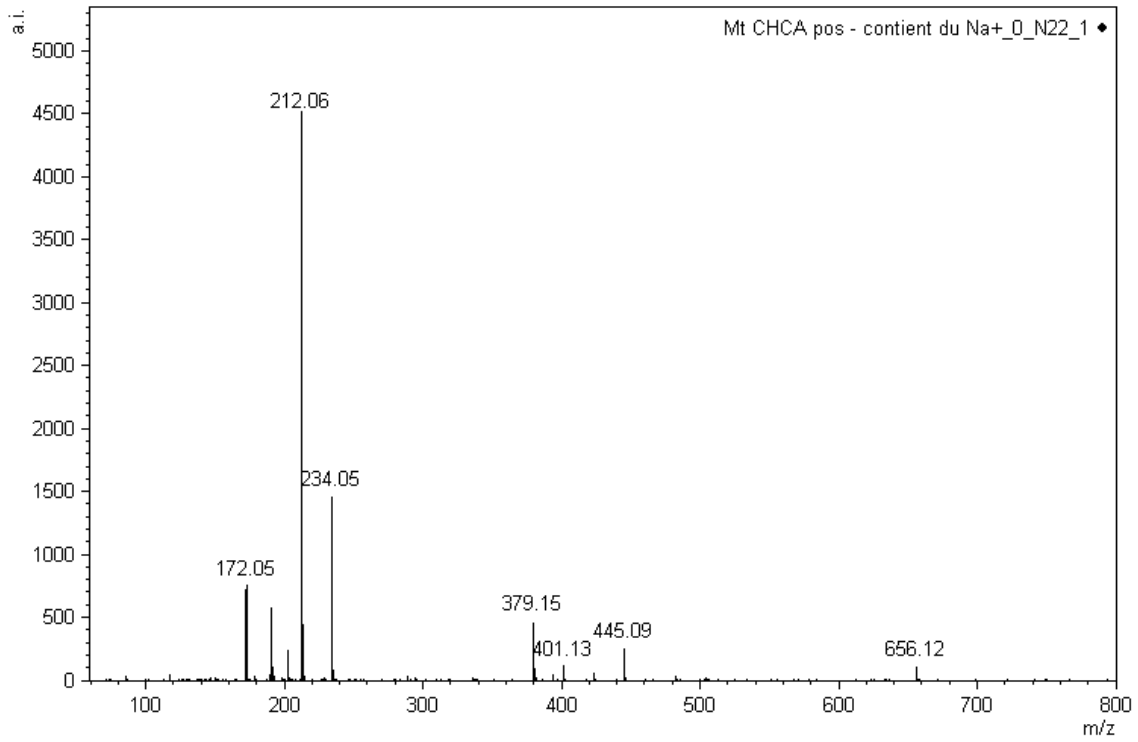
1. Mass Spectrometry (LDI-MS and MALDI-MS)

1.1. MALDI-MS of MMT



Suppl. Fig. S1. MALDI mass spectrum of the MMT clay sample, ground in large excess with CHCA and deposited on a MALDI target.

Suppl. Table S1. Mass measurements of ions detected in the MALDI mass spectrum of MMT (**Suppl. Fig. S1**).

Elemental composition	$(m/z)_{exp}$	Assignment
$C_{10}H_6NO_2^+$	172.1	$[CHCA + H - H_2O]^+$
$C_{10}H_8NO_3^+$	190.1	$[CHCA + H]^+$
$C_{10}H_7NO_3Na^+$	212.1	$[CHCA + Na]^+$
$C_{10}H_6NO_3Na_2^+$	234.1	$[CHCA - H + 2*Na]^+$
$C_{20}H_{15}N_2O_6^+$	379.2	$[2*CHCA + H]^+$
$C_{20}H_{14}N_2O_6Na^+$	401.1	$[2*CHCA + Na]^+$
$C_{20}H_{13}N_2O_6Na_2^+$	423.1	$[2*CHCA - H + 2*Na]^+$
$C_{20}H_{12}N_2O_6Na_3^+$	445.1	$[2*CHCA - 2*H + 3*Na]^+$
$C_{30}H_{18}N_3O_9Na_4^+$	656.1	$[3*CHCA - 3*H + 4*Na]^+$

MALDI-MS was already found to be a relevant technique for the analysis of intercalated species in clay samples [1]. If surfactants are large enough, they could be detected as intact species. On the contrary for native clays which contains alkali ions such as sodium, their indirect detection is based on the observation of a matrix peak adducted with the alkali ion of interest.

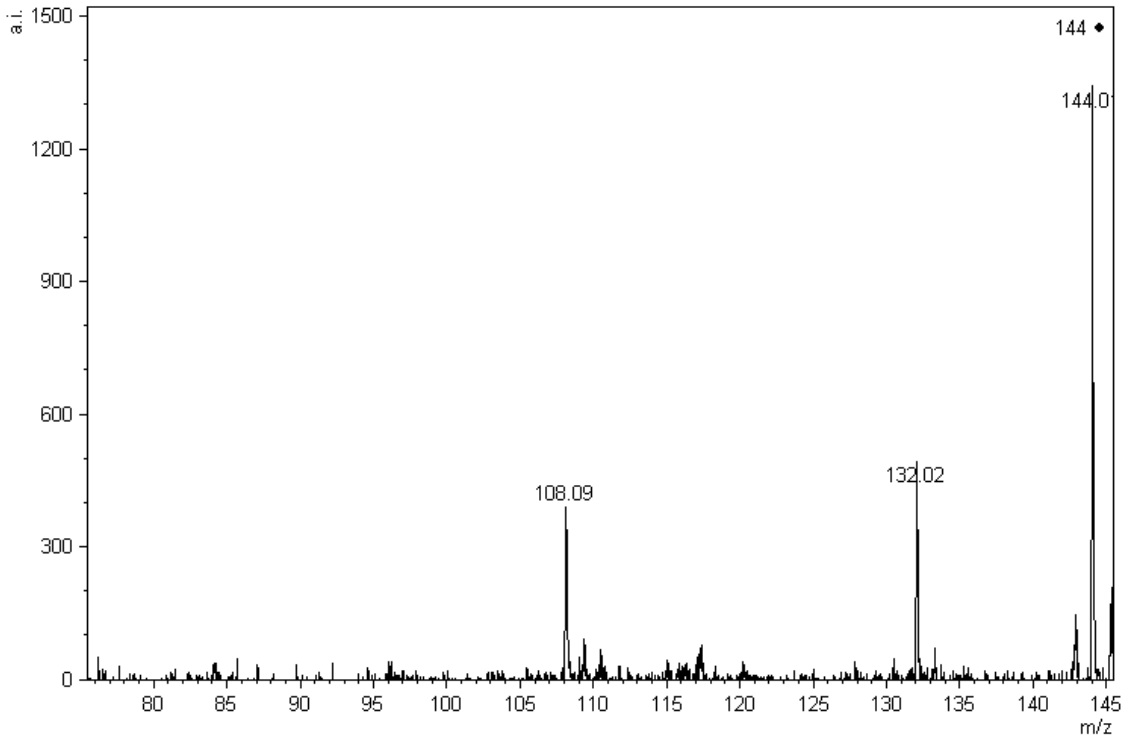
Here is detected with a huge and unusual abundance the $[CHCA+ Na]^+$ adduct, as well as many other sodium adducts of CHCA (gaining sodium adduction and losing hydride), highlighting the sodium intercalation between the clay platelets.

1.2. LDI-MS of PAH and PA6-(PAH-MMT)$_{40}$

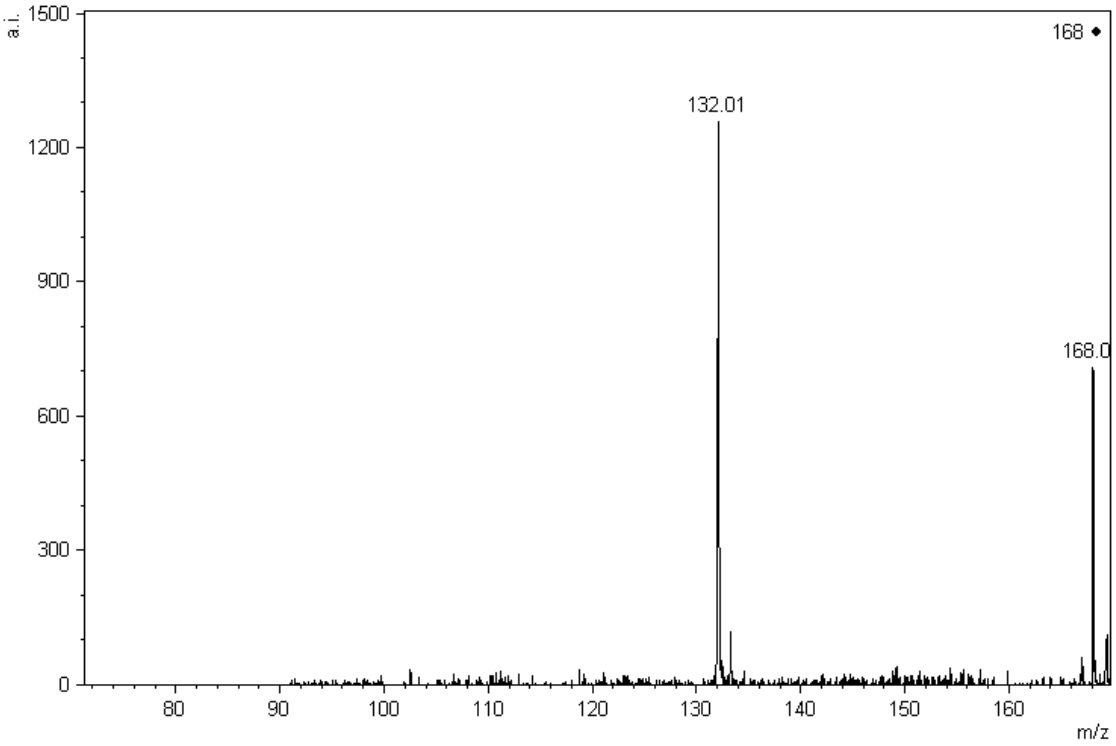
Suppl. Table S2 – Detected ions from a) **Fig. 8 PAH** and $\mathbf{t_{25s}}$ and b) **Fig. 8** $\mathbf{t_{TTI}}$, $\mathbf{t_{pHRR}}$ and $\mathbf{t_{TOF}}$.

Spectrum	$(m/z)_{exp}$	Assignment
PAH and t25s	83.92	ISD / PSD fragment from PAH
	95.94	
	107.96	
	119.97	
	131.99	
	144.00	
	156.01	
	168.03	
	180.03	
	192.04	
	216.06	
	228.08	
t_{TTI}, t_{pHRR} and t_{TOF}	108.13	ISD / PSD fragment from degraded PAH
	122.16	
	134.17	
	136.20	
	148.21	
	161.22	
	173.24	
	175.26	
	187.27	

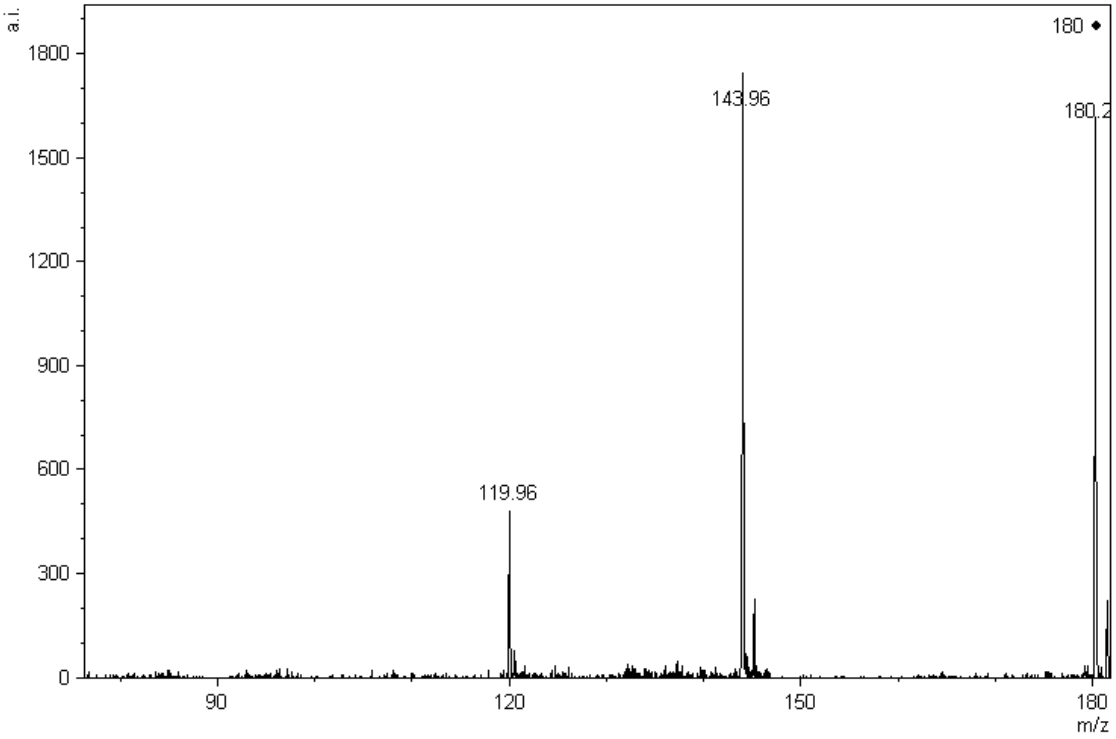
PSD experiments were then conducted on some of the above-listed peaks from native PAH.



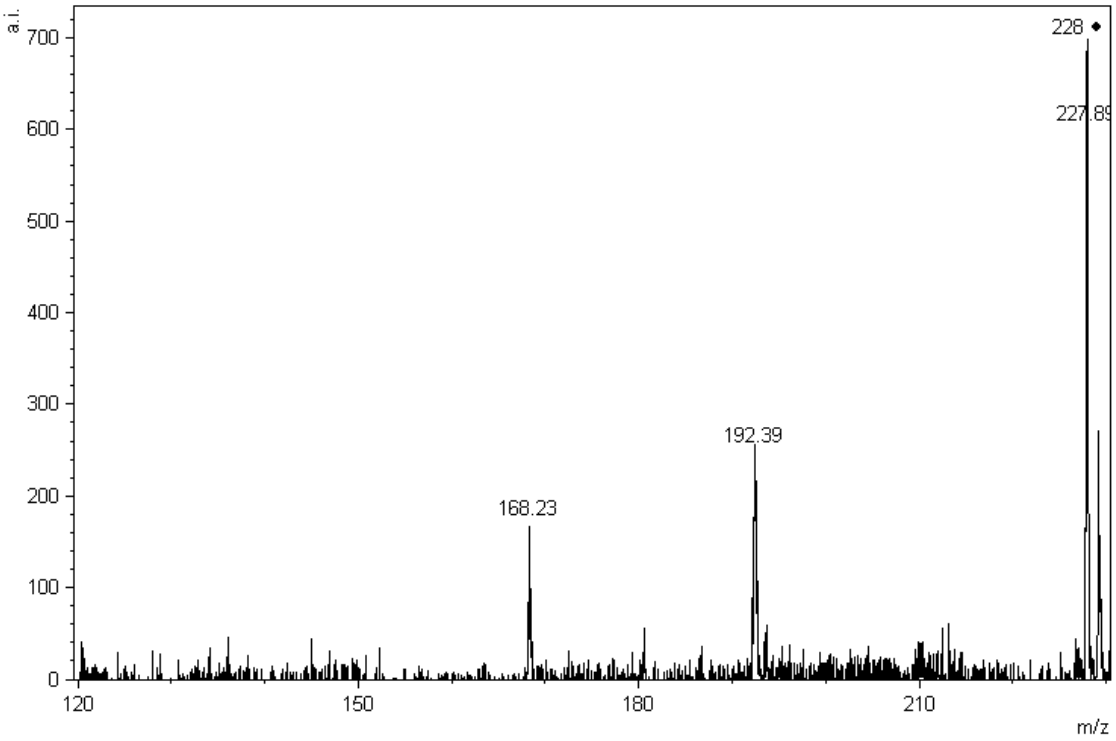
Suppl. Fig. S2a. PSD-LDI mass spectrum of m/z 144 from Fig. 8 (t_{25s})



Suppl. Fig. S2b. PSD-LDI mass spectrum of m/z 168 from Fig. 8 (t_{25s})



Suppl. Fig. S2c. PSD-LDI mass spectrum of m/z 180 from Fig. 8 (t_{25s})



Suppl. Fig. S2d. PSD-LDI mass spectrum of m/z 228 from Fig. 8 (t_{25s})

Reference:

1. P. Verge, T. Fouquet, C. Barrère, V. Toniazzo, D. Ruch and J. A. S. Bomfim, *Composites Science and Technology*, 2013, **79**, 126-132.