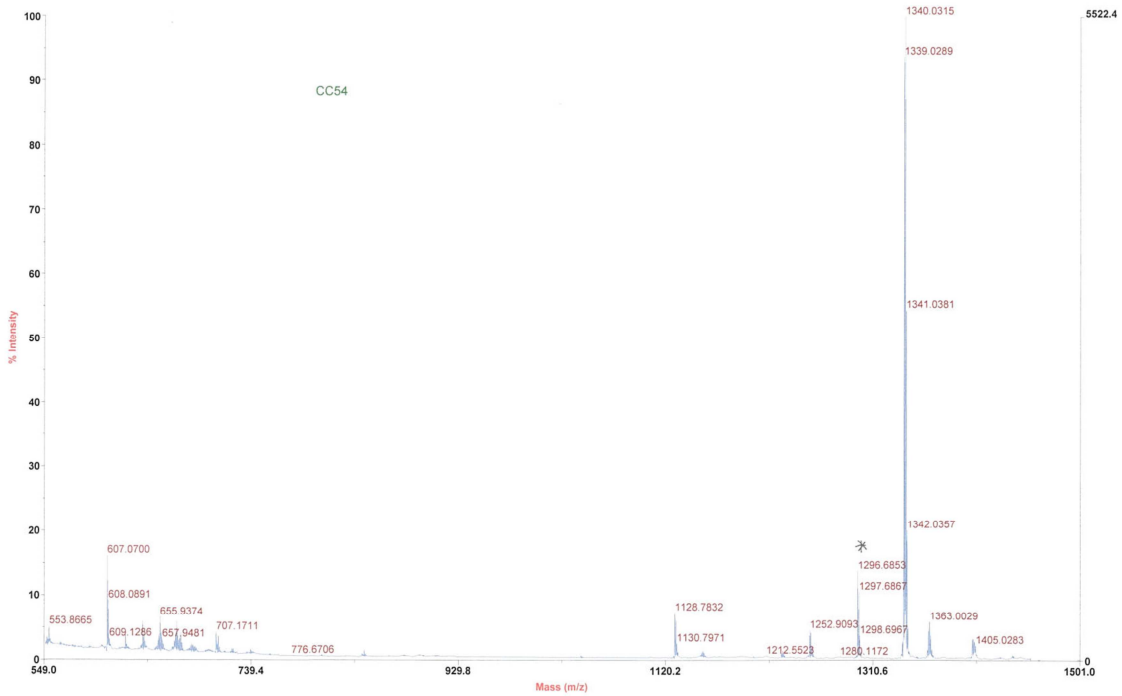
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

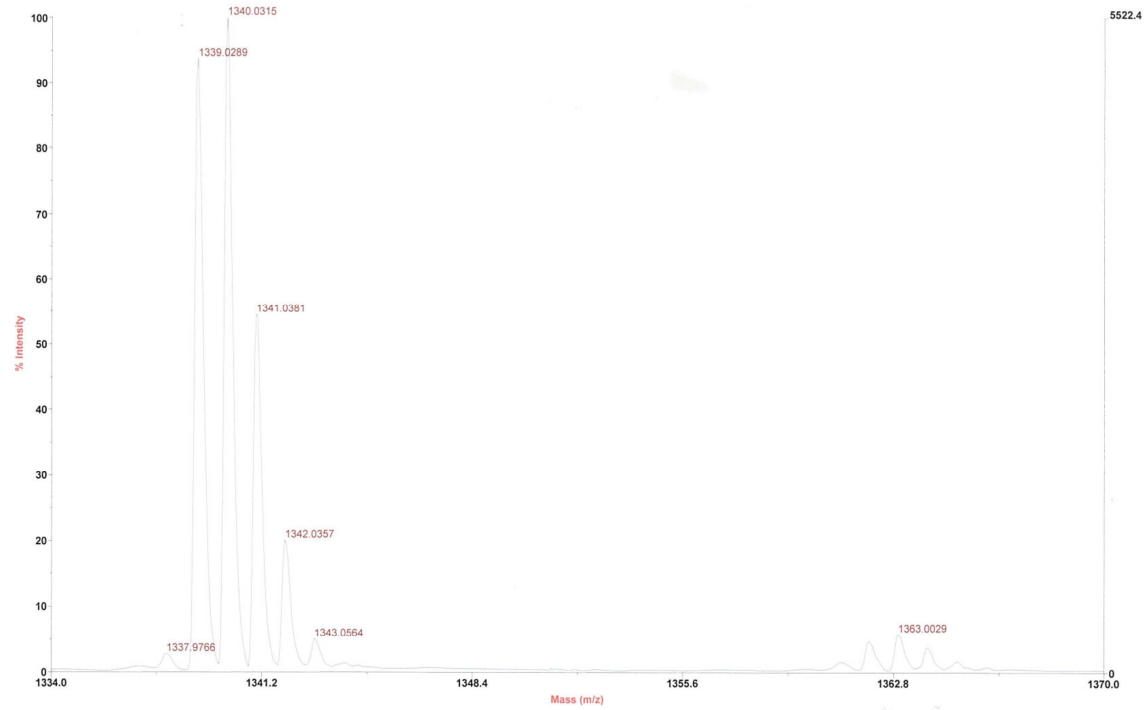
Supplementary materials

Characterization of compounds Ad_6-HPB and Ad_6-HBC

Useful information about the success of the cobalt-catalyzed cyclization (to produce Ad_6-HPB) and Scholl oxidation (yielding Ad_6-HBC) are obtained by mass spectrometry using techniques adapted to carbon-rich hydrocarbon compounds. Thus, the spectrum of the soluble compound Ad_6-HPB was recorded using MALDI-TOF technique with dithranol as matrix.

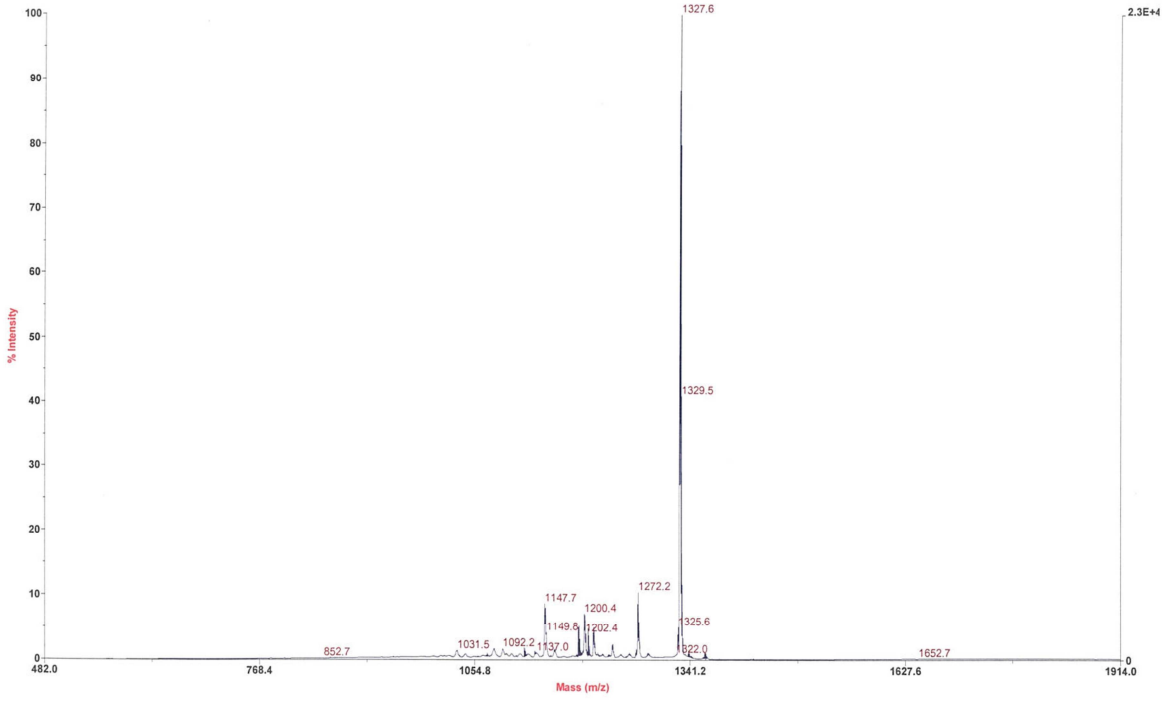


Ad_6-HPB

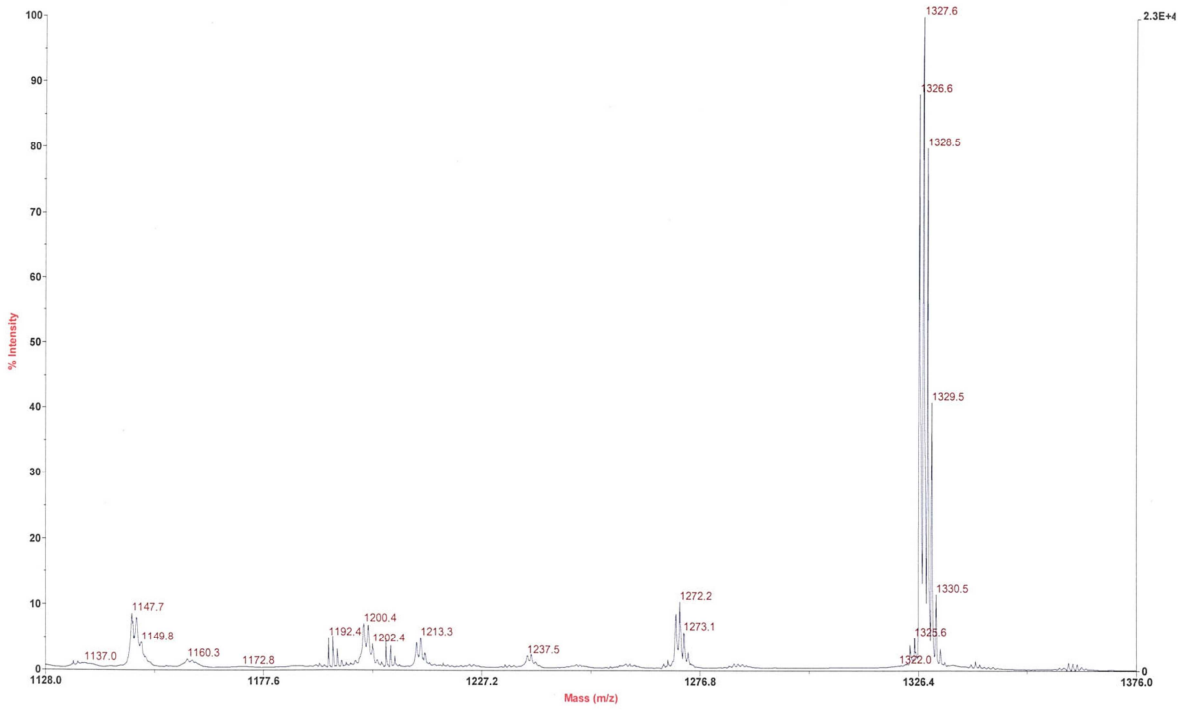


Ad_6-HPB

The molecular peak is clearly identified and corresponds to the simulated isotopic profile. Similarly, the very insoluble Ad_6-HBC was submitted to MALDI-TOF analysis with DDQ matrix. The spectrum shows the desired molecular peak and the absence of the Ad_6-HPB precursor (atom loss between both compounds: 12 hydrogen atoms).



Ad_6-HBC



Ad_6-HBC

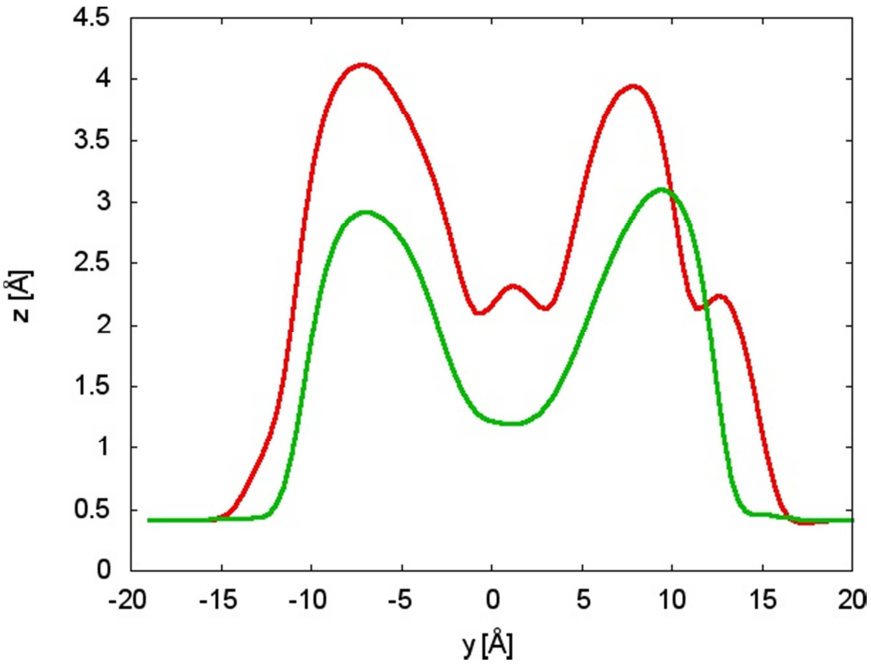
Notably, for both compounds, no peak corresponding to ions lacking of an adamantyl moiety (m/z: 135) is observed under these conditions, confirming that the adamantyl substituent persists throughout the synthetic schemes, and is not fragmented during the ionization process.

References

MALDI-TOF mass spectrometry: Obtaining reliable mass spectra for insoluble carbonaceous pitches W. F. Edwards, L. Jin, M. C. Thies *Carbon* **2003**, *41*, 2761–2768.

MALDI-TOF mass spectrometry of insoluble giant polycyclic aromatic hydrocarbons by a new method of sample preparation, L. Przybilla, J.-D. Brand, K. Yoshimura, H. J. Räder, K. Müllen, *Anal. Chem.* **2000**, *72*, 4591-4597.

Calculated corrugation on a single molecule



The two scan lines present the calculated corrugation on the ESQC-STM images: the green curve crosses the middle of the molecule and the red one is slightly off-center above maximum signal (see Fig. 14).