

Supporting Information:

Unraveling the molecular structures of asphaltenes by atomic force microscopy

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This supplemental material presents complementary atomic force microscopy (AFM) and scanning tunneling microscopy (STM) images of different coal-derived asphaltene (CA) and petroleum asphaltene (PA) molecules. It is also discussed how representative the measured molecules are for the complete sample. For two CAs, molecular orbitals are calculated based on the structure proposals from AFM. In addition, AFM and STM measurements of a control compounds is used to support the assignment of common side-groups observed for CAs and PAs.

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I. REPRESENTATIVENESS OF MEASURED MOLECULES

To draw conclusions about the entire mixture from individual specimens, one has to discuss their representativeness. Like counting organisms in ecology, it is not feasible with our technique to count all molecules in the mixture. Instead, one is forced to investigate a small representative part of the ‘population’. Similar to ecology, we use a sampling square, a quadrat, defined by our overview scan area at random positions (macroscopic placement of the sensor tip). Within this area, we look at each molecule (see Figure S1). To give the reader the best possible impression, we include a comprehensive set of AFM and STM images of asphaltene molecules measured in such quadrats below (in addition to the measurements already shown in the main text). In

contrast to other techniques that examined asphaltenes, we can prove the existence of certain molecule structures and their properties within the mixture, but cannot directly determine the average characteristics of the mixture.

Despite the possible selectivity during the measurement procedure itself, the sample preparation might affect the representativeness of the sample. This potential issue has been described in the main text at the end of the Results and Discussion section.

II. COAL-DERIVED ASPHALTENES (CAs)

A. Additional AFM and STM measurements

In this section, we present the AFM raw data of Figure 3 and complementary STM orbital images of some CA molecules of the same figure. In addition, AFM and STM measurements of other CA molecules are provided to evidence the immense structural diversity observed. In Figure S2, AFM raw data of Figure 3 is provided. In the main text, the Laplace-filtered version has been chosen for better accessibility for non-specialists and printer-friendliness. A collection of different CA molecules and their corresponding orbitals are shown in Figure S3 and Figure S4. AFM images of the CA molecules displayed in Figure S3a-e are already presented in Figure S2. For many specimen, the lowest unoccupied (LUMO) and highest occupied molecular orbital (HOMO) were accessible and could be stably imaged.

Note that because of the CO functionalization, the tip comprises *s*– and *p*–wave contributions. However, for the tip and voltages used here, the *s*–wave character of the tip predominates [1, 2].

Interestingly, also radicals were observed, which feature a half-filled (singly occupied) HOMO, a so-called SOMO (e.g. Figure S3c). Organic free radicals are known to be present in asphaltenes, but at small

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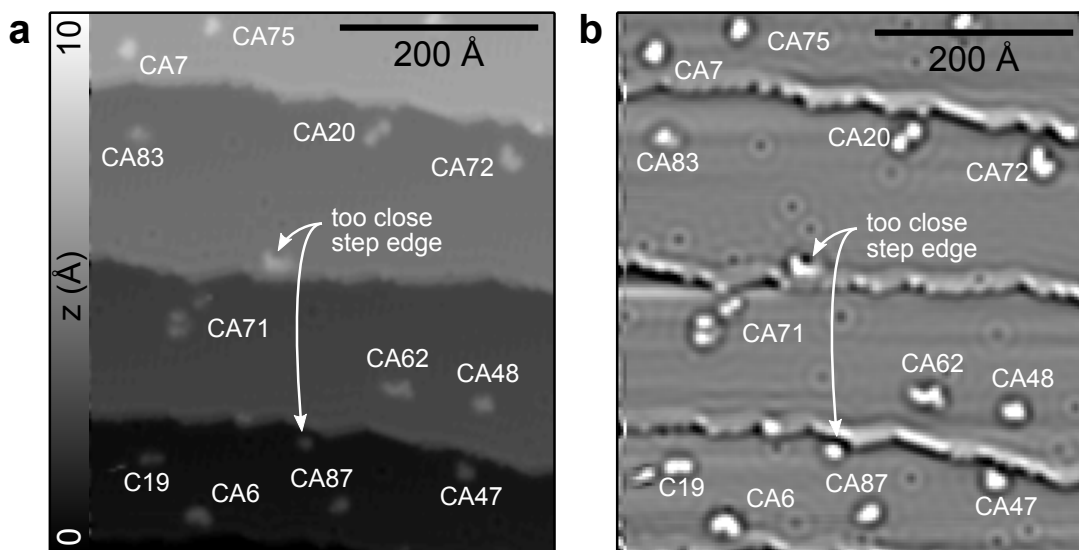


Figure S1. **STM overview image.** **a** STM overview image ($I = 2$ pA, $V = 0.2$ V) of the CA sample on Cu(111). **b** Laplace-filtered image in **a**. The individual molecules are labeled by their given identifier. The overview defines our sampling square.

molecular fractions [3]. It is not clear whether possible free radicals detected here occur naturally (for example as heterodimers [4] that might be cleaved during the sublimation process) or whether they form during post-treatment after extraction or sublimation from the wafer. In particular, the molecule shown in Figure S3c is assigned to the structure **CA12** (see Figure 4), a phenalenyl radical derivative, which can be considered as an open-shell graphene fragment with interest in the field of organic spintronics [4]. In other images, one can also observe that flexible parts of the molecules or parts that are oriented upright can disturb the imaging process. For example, in the bottom right part of Figure S3g, the disc-like contrast presumably stems from a molecule moiety pointing upright and therefore tilting the CO molecule at the tip away from it. Often, parts of the molecular structure can be obscured by the non-planar adsorption geometry. This is a consequence of the high sensitivity of Δf to changes in the tip-sample distance in the regime where short-ranged forces dominate (which holds in our case) [5, 6]. The contrast on the two hexagonal rings in the bottom part of Figure S4b, for example, diminishes towards the left side because of their downwards bending.

These difficulties certainly constitute a challenge for molecular structure identification by atomic-resolution AFM imaging. However, an experienced experimenter can gain intuition for certain recurring patterns. The development of a comprehensive database of high-resolution AFM images of synthetic model compounds using well-defined tips might enable the development of a systematic interpretation scheme.

In Figure S5, additional AFM measurements of CA molecules on Cu(111) are presented. As already stated in the main paper, the CA molecules are usually composed of a single polycyclic aromatic hydrocarbon (PAH) core to which one or several small side-groups are attached. Partially, PAH islands (sometimes made up of just a single ring) are connected by a single bond.

The characterization of the mean structural parameters of asphaltene molecules and nanocolloidal particles has been very useful, for example, in development of bulk and surface asphaltene thermodynamics. Moreover, the distribution breadth of asphaltene structures is known to be substantial. For example, molecular weight determinations of asphaltenes find broad distributions with high mass tails. However, there exists almost no structural information in these distributions. With the images acquired herein, it is now possible to characterize structural parameters in these distributions. A key conclusion is that the predominant molecular motif of a single PAH per molecule evidently extends into the high mass tail. The existence of corresponding large PAHs will likely figure prominently in particular asphaltene properties.

B. Molecular orbital calculations for CA2, CA3 and CA12

In this section, we present molecular orbital (MO) calculations for **CA2**, **CA3** and **CA12**. The proposed structures are based on the measured AFM images of the respective molecule. The MOs are calculated using density functional theory (DFT) implemented by the highly optimized plane-wave code CPMD [7]. We used the Perdew–Burke–Ernzerhof (PBE) exchange-correlation

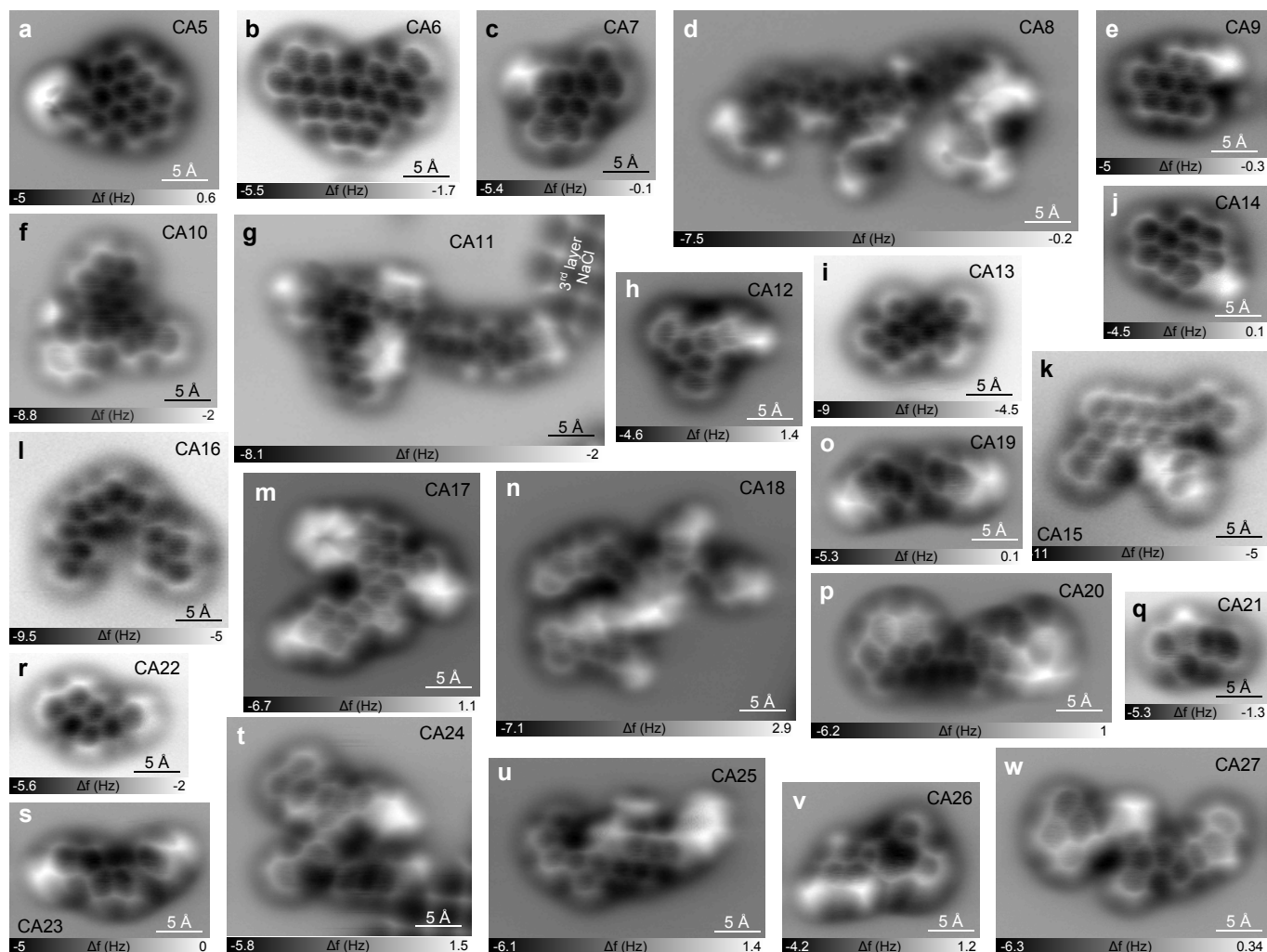


Figure S2. **Coal-derived asphaltenes CA5-CA27.** a-w AFM images of different CAs on Cu(111) or NaCl(2ML)/Cu(111). For some molecules, orbital images are available in Figure S3.

functional [8], *ab initio* norm-conserving pseudopotentials and added semiempirical van der Waals (vdW) corrections.

For **CA2**, the molecular structure of the entire molecule could be readily identified from the AFM measurement (cf. Figure S6a and Figure S6d). The calculated HOMO (Figure S6e) and LUMO (Figure S6f) are in good agreement with the measured orbitals (Figure S6b,c). The deviations in the LUMO can be explained by the small energy difference between LUMO and LUMO+1 ($\Delta E = 0.25$ eV). As the MOs are significantly vibrationally broadened on the NaCl film [9], both levels contribute to the measured STM orbital image [10].

The situation is less clear for **CA3**. Here, the molecular structure could only be partially resolved by AFM owing to the reduced contrast in certain parts of the molecule. Consequently, various structure proposals are legitimate. Some structure guesses are shown in Figure S7a. The unknowns here are the moieties at

the five-membered rings. Possible are CH, CH₂ or CO moieties or ring substitutions by N, NH or S. However, the heteroatom content in CA is relatively low, which renders the heteroatom substitution of the pentagonal rings less likely. In Figure S7d-o MO calculations are shown for the different structure hypotheses sketched in Figure S7a. Apparently, many orbitals share common motifs. However, only for a small number of structures are both the HOMO and the LUMO in reasonable agreement with the measured orbitals shown in Figure S7b,c. The best match is achieved for the structures shown in Figure S7f and Figure S7n. Note that both structures have a singly occupied HOMO in the neutral state. However, we observe a distinctively different positive (PIR) and negative ion resonance (NIR) for **CA3**, which excludes the possibility of a radical. Possibly, the molecule could be charged by one electron[11] (see Figure 4), which would fill up the semi-occupied HOMO. In addition, we performed further MO calculations using other molecule hypothesis (especially different PAH ring geometries) that showed less agreement with the

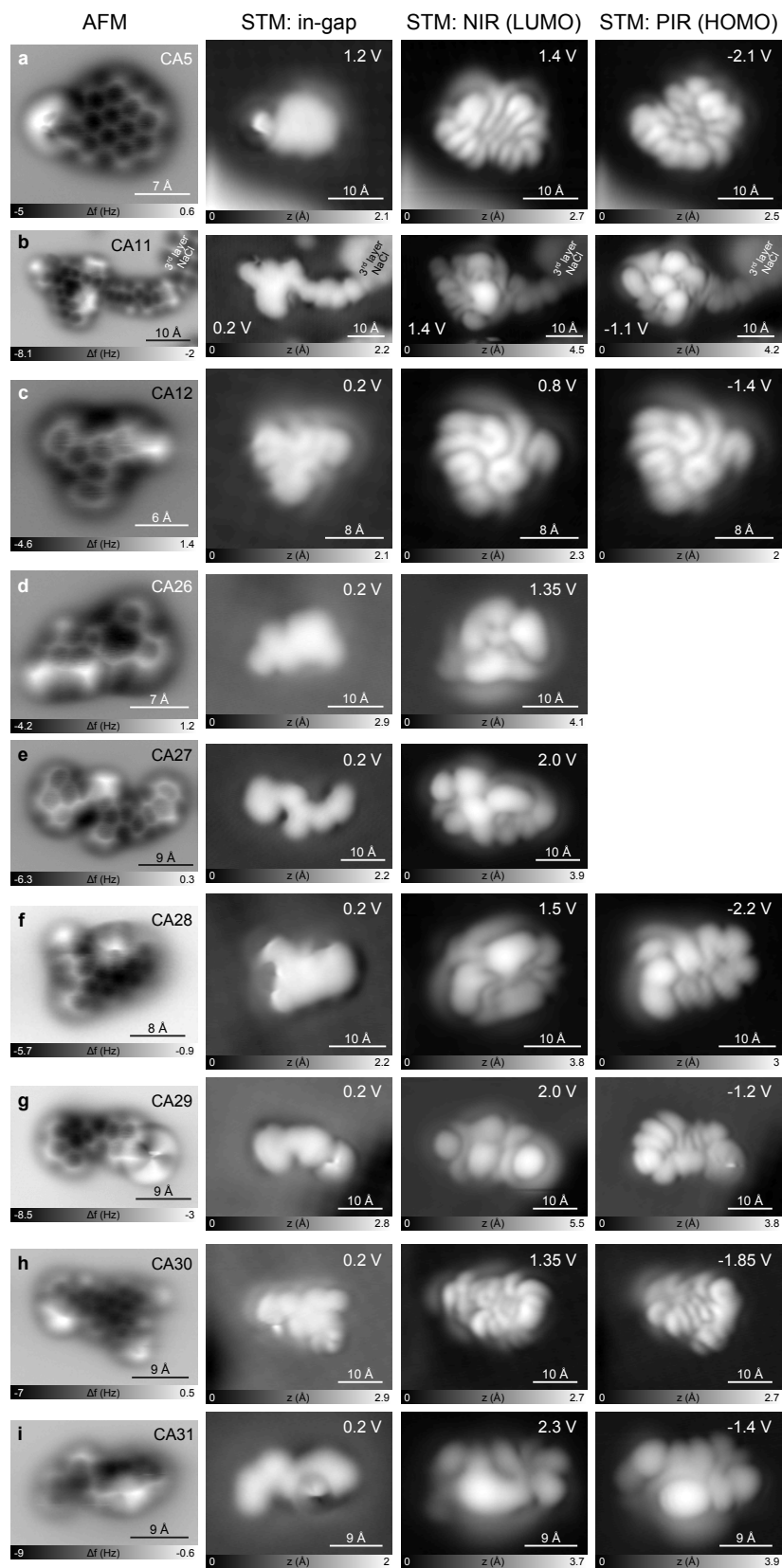


Figure S3. **CAs on NaCl(2ML)/Cu(111).** **a-i** Each row shows AFM and STM measurements of one CA molecule. The first column corresponds to AFM images. In the second column, STM images at lower voltages (in-gap) are shown. The third and fourth column display STM images recorded at the negative (NIR) and positive ion resonance (PIR), corresponding to the LUMO and HOMO orbital, respectively, if the molecule is not charged and has an even number of electrons. The PIR and NIR of the molecule in **c** look identical, which is indicative of a semi-occupied orbital. Therefore, the molecule is either a radical or it is singly charged. All measurements were performed with a CO tip.

measured orbitals.

As argued in section II A, molecule **CA12** is a radical, as NIR and PIR have the same spatial appearance (see Figure S3c). Absence of interface state scattering indicates a neutral molecule [9]. From the AFM image we could directly propose the molecular structure as depicted in Figure S8a. The calculated SOMO of the molecule is shown in Figure S8b. The symmetry and the weight of the different orbital lobes are in good agreement with the measured orbitals Figure S8c,d. Certain deviations in the measurements (such as apparent nodal planes on the lobe maximum) can be ascribed to the p -wave character of the CO tip [1].

III. PETROLEUM ASPHALTENES (PAs)

A. Additional AFM and STM measurements

In Figure S9, AFM and STM data of two additional PA molecules are shown. By comparing Figure S9a and Figure S9e, one can get an idea about the size span, ranging from a few rings (five in Figure S9e) up to about 23 rings in Figure S9a. Also for PAs we occasionally observed some radicals. In this case, the LUMO and the HOMO resonance look identical (as seen in Figure S9g,h).

In Figure S10, AFM measurements of some other PA molecules are shown. As PAs generally have more side-groups than CAs, the constant-height measurement of PAs is more challenging. During the scan at close distance, rearrangements of the molecule can occur, as seen in Figure S10e. Partially, this problem can be accounted for by a three-dimensional force mapping technique to adapt the scan height to the molecule geometry [12].

IV. PROPOSED CHEMICAL STRUCTURES FOR SOME CAs AND PAs MOLECULES

In the following, we propose chemical structures for certain CA and PA molecules measured that we could assign with high fidelity by means of the measured AFM and STM orbital images. In Figure S11 molecule models for some CA molecules presented in Figure S4 and Figure S5 are shown. In general, the aromatic core of asphaltenes can be well resolved by high-resolution AFM with CO terminated tips. The non-planar side-groups are usually difficult to assign.

V. CONTROL COMPOUND

We also analyzed, a synthetic control molecule to assign its side-groups to the observed AFM contrast. This assignment of the side-groups is then compared with the AFM contrast observed at side-groups of the asphaltenes. Because of the influence of the micro- and macroscopic shape of the tip, the comparison between the control molecules and asphaltenes remains, however, qualitative.

A. 1-Methylpyrene (MP)

In Figure S12a, a model of 1-Methylpyrene (**MP**) is depicted. **MP** features four fused benzene rings, to which a CH_3 substituent is attached. In AFM images [13] (Figure S12b,c) this CH_3 substituent appears as a single bright spot that turns out to be slightly elongated perpendicularly to its bonding direction at close distance. A very similar behaviour is also observed for the molecules **CA1-4**, **CA7**, **CA9**, **CA12**, **CA14**, **CA19**, **CA23**, **CA24**, **CA26**, **PA1**, **PA3** and others. Therefore, we assign the most frequently observed side-group present in the above-mentioned molecules to CH_3 .

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- [1] Leo Gross, Nikolaj Moll, Fabian Mohn, Alessandro Curioni, Gerhard Meyer, Felix Hanke, and Mats Persson, *Phys. Rev. Lett.*, **2011**, 107, 086101.
 - [2] Niko Pavliček, Ingmar Swart, Judith Nidenführ, Gerhard Meyer, and Jascha Repp, *Phys. Rev. Lett.*, **2013**, 110(13), 136101.
 - [3] J Uebbersfeld, A Etienne, and J Combrisson, *Nature*, **1954**, 174, 614.
 - [4] Yasushi Morita, Shuichi Suzuki, Kazunobu Sato, and Takeji Takui, *Nature Chem.*, **2011**, 3(3), 197–204.
 - [5] Niko Pavliček, Benoit Fleury, Mathias Neu, Judith Nidenführ, Coral Herranz-Lancho, Mario Ruben, and Jascha Repp, *Phys. Rev. Lett.*, **2012**, 108(8), 086101.
 - [6] Bruno Schuler, Wei Liu, Alexandre Tkatchenko, Nikolaj Moll, Gerhard Meyer, Anish Mistry, David Fox, and Leo Gross, *Phys. Rev. Lett.*, **2013**, 111, 106103.
 - [7] CPMD, IBM Corporation and MPI für Festkörperforschung Stuttgart, www.cpmd.org/.
 - [8] J.P. Perdew, K Burke, and M Ernzerhof, *Phys. Rev. Lett.*, **1996**, 77(18), 3865–3868.
 - [9] Jascha Repp, Gerhard Meyer, Sami Paavilainen, Fredrik Olsson, and Mats Persson, *Phys. Rev. Lett.*, **2005**, 95(22), 225503.
 - [10] Christof Uhlmann, Ingmar Swart, and Jascha Repp, *Nano Lett.*, **2013**, 13(2), 777–780.
 - [11] Molecules can be charged depending on the level alignment of their states with the Fermi energy of the surface.
 - [12] Fabian Mohn, Leo Gross, and Gerhard Meyer, *Appl. Phys. Lett.*, **2011**, 99(5), 053106.
 - [13] The stripes in the AFM images stem from vibrational instabilities of the setup.

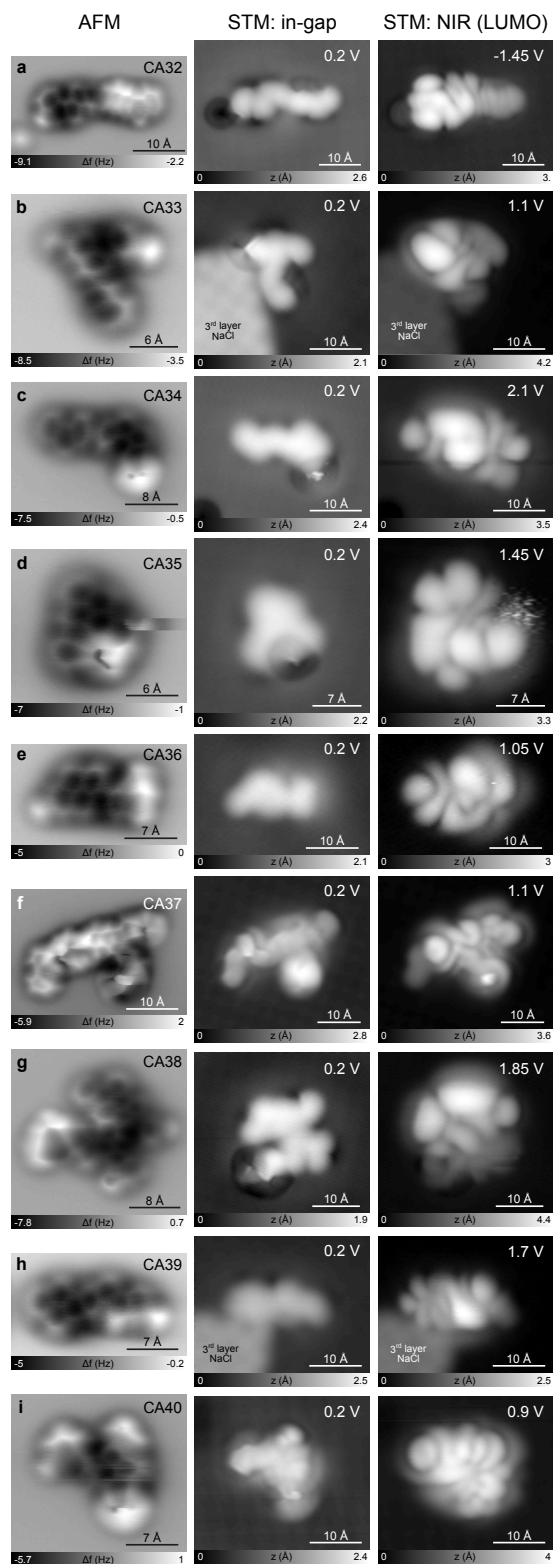


Figure S4. **CA32-CA40 on NaCl(2ML)/Cu(111)**. **a-i** Each row shows AFM and STM measurements of one CA molecule. The first column shows the AFM images. In the second column, in-gap STM images are shown. In the third column, STM LUMO orbital images are shown. In these cases, the HOMO orbital was either out of our bias range ($[-2.5\text{ V}, 2.5\text{ V}]$) or the molecule was displaced by inelastic excitations when imaged at its resonance.

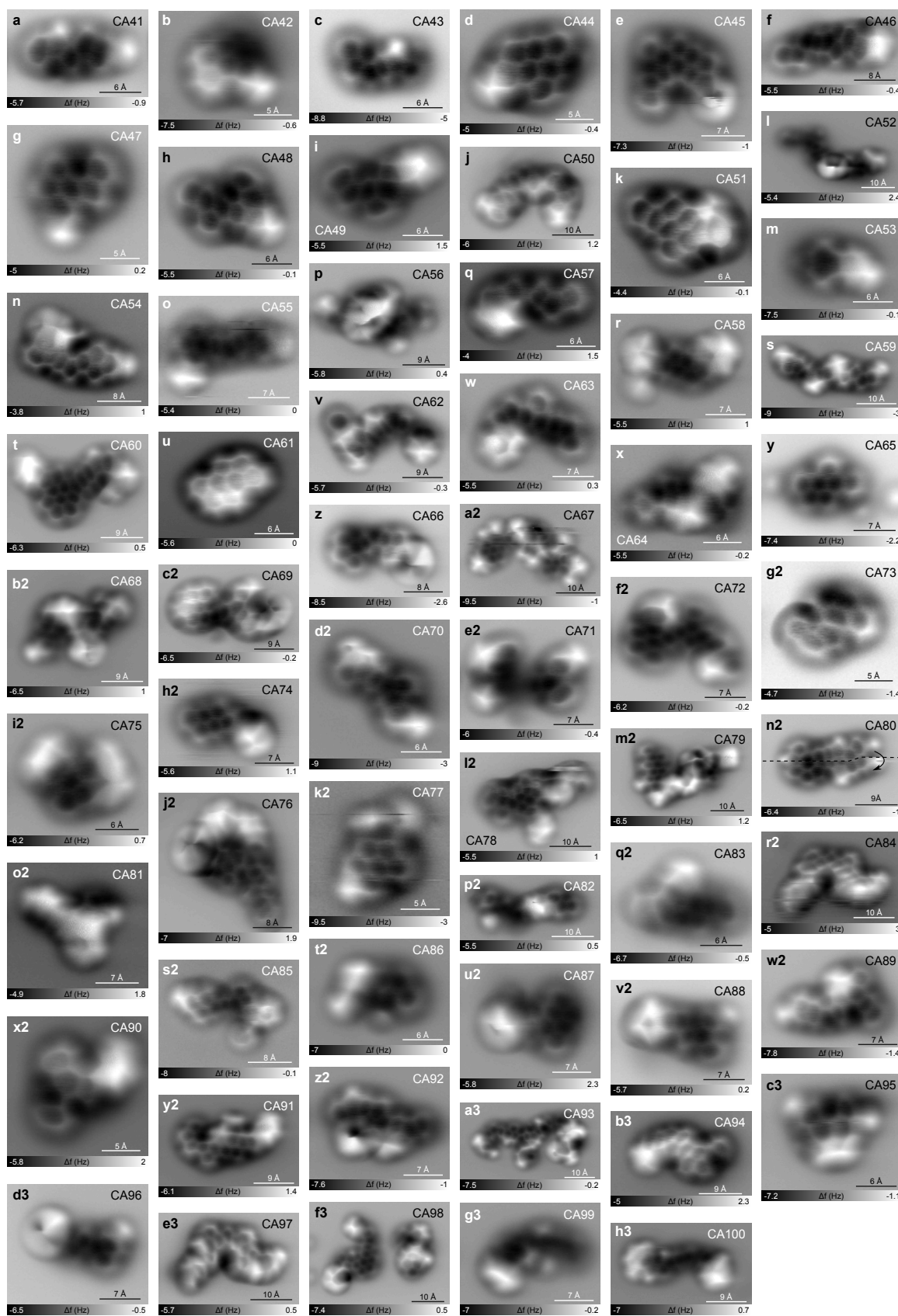


Figure S5. CA41-CA100 on Cu(111). a-h3 AFM images of other CA molecules on Cu(111). In panel n2, the molecule rotated slightly during the scan, indicated by the black arrow.

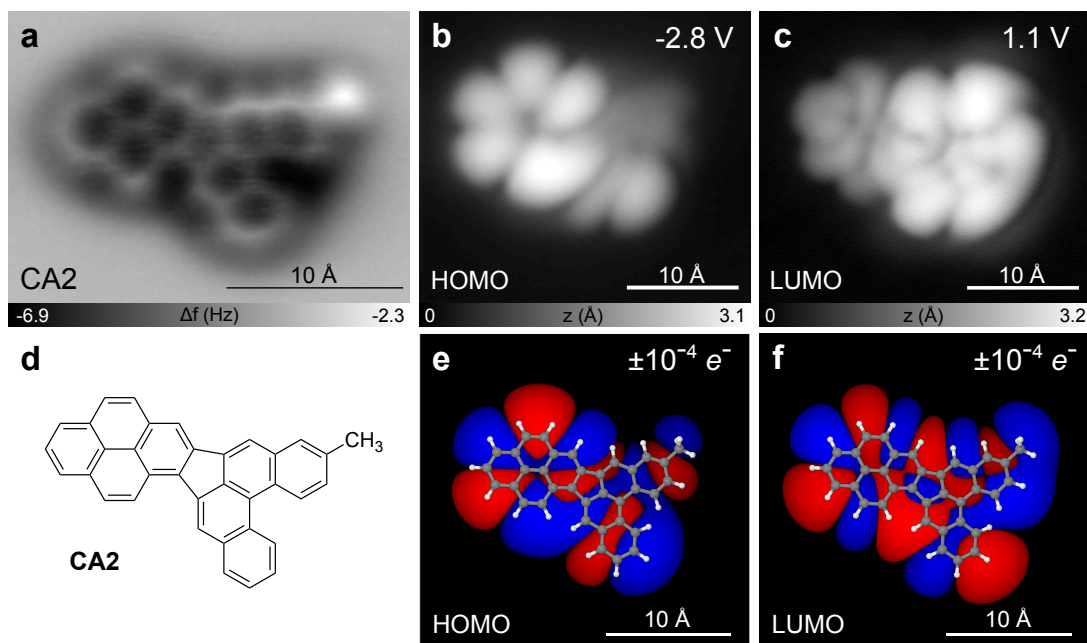


Figure S6. **CA2** calculated orbitals. **a** AFM image of **CA2** on NaCl(2ML)/Cu(111). **b,c** STM orbital images of **CA2** of the PIR (**b**) and the NIR (**c**). **d** Structural model of **CA2**. **e,f** HOMO (**e**) and LUMO (**f**) orbital of the structure in **d**.

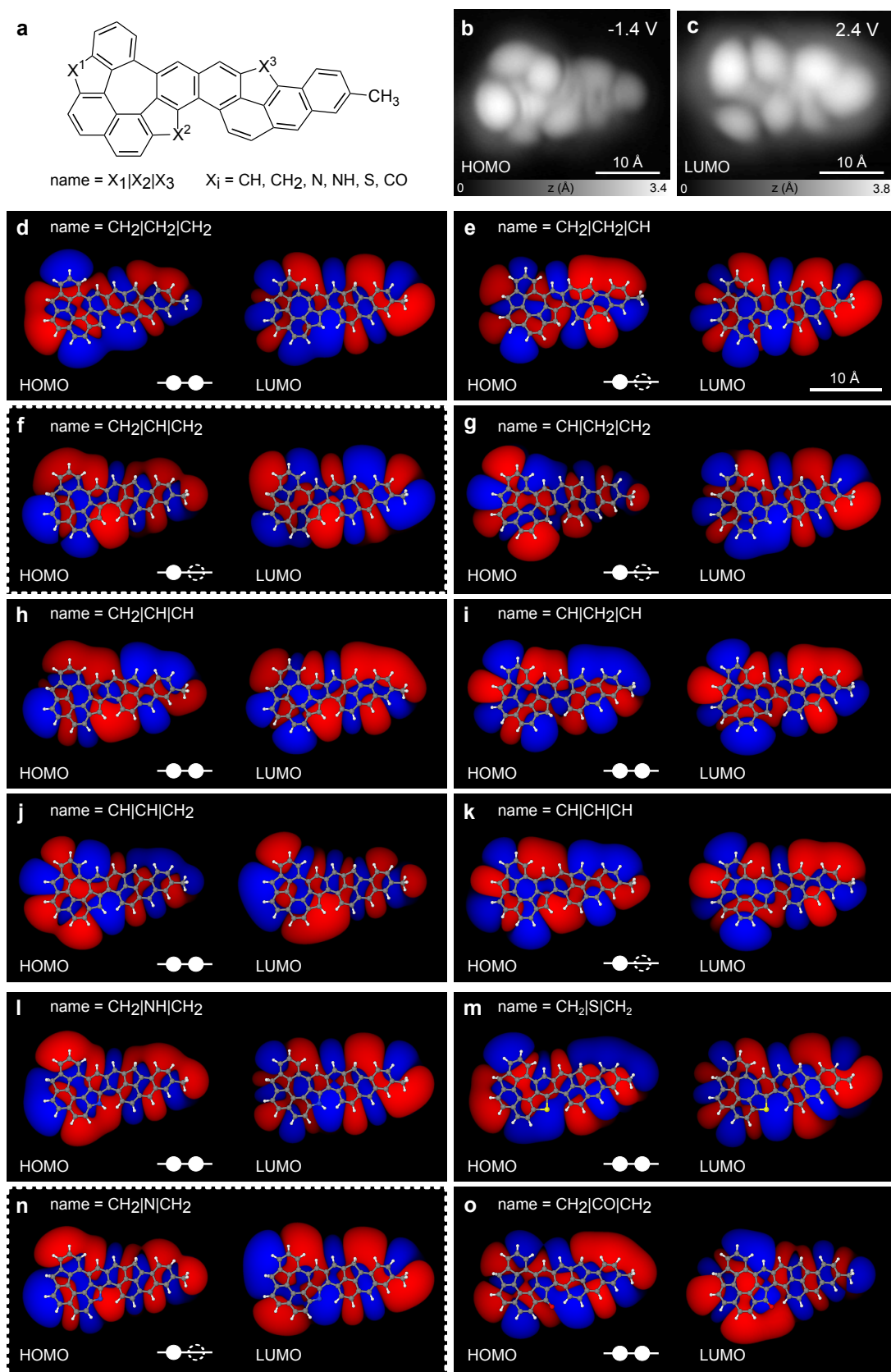


Figure S7. **CA3** calculated orbitals. **a** Different possible structures of **CA3**. **b,c** STM orbital images of **CA3** of the PIR (**b**) and the NIR (**c**). **d-o** HOMO and LUMO orbital isosurfaces (at $\pm 10^{-4} e^-$) using the different structure hypotheses shown in **a**. The structures in **f** and **n** (dashed white box) show the best agreement with the measured orbitals. The two white circles indicate whether the molecule has a singly (filled and empty circle) or a doubly (two filled circles) occupied HOMO in the neutral state.

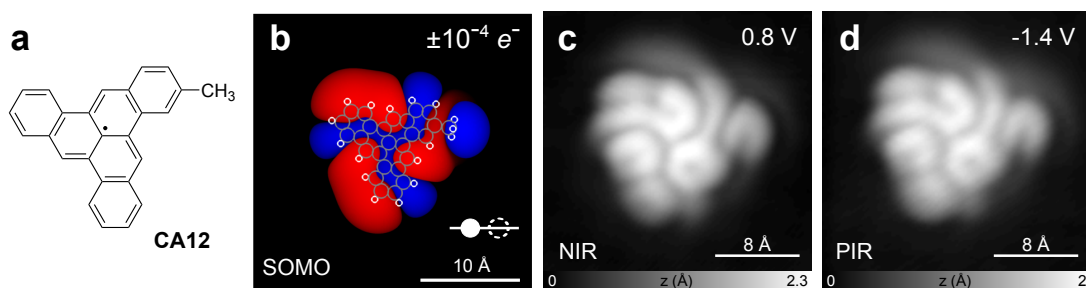


Figure S8. **CA12** calculated orbital. **a** Proposed chemical structure of **CA12** on the basis of the AFM image in Figure S3c. **b** Calculated SOMO orbital of the structure in **a**. **c,d** Measured NIR and PIR of **CA12**, respectively.

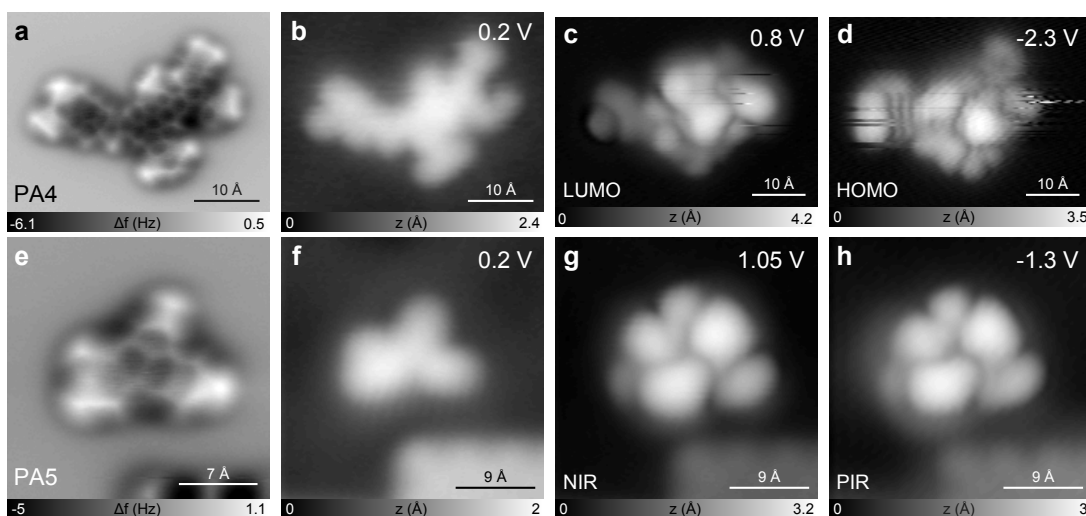


Figure S9. **Petroleum asphaltenes PA4 and PA5 on NaCl(2ML)/Cu(111)**. **a-d** AFM and STM images of **P4**. **e-h** AFM and STM images of **P5**. As in Figure S3c, NIR and PIR are essentially identical. Again, this is due to the molecule being a radical or singly charged.

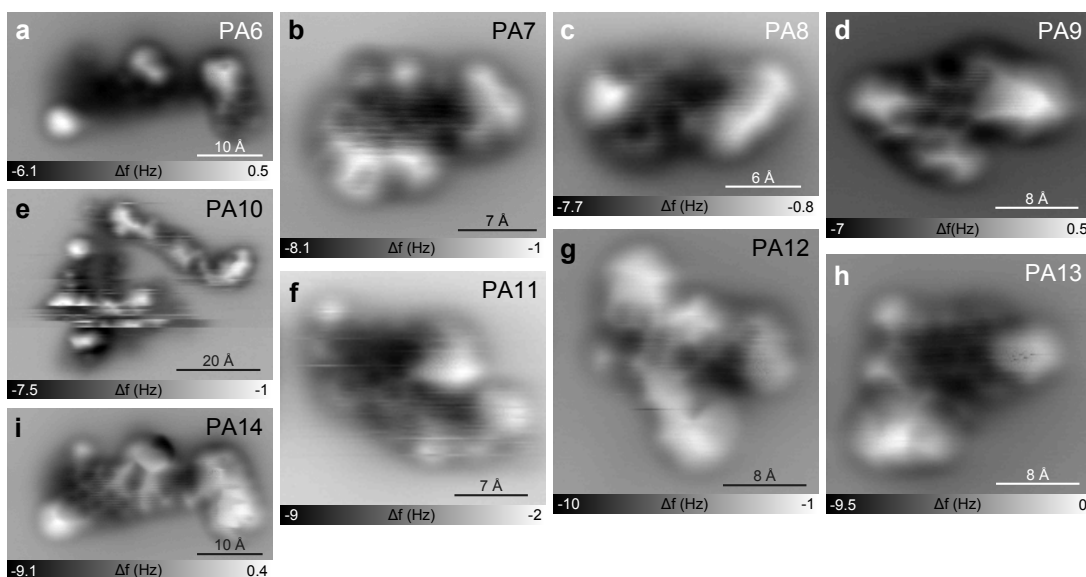


Figure S10. **PA6-PA14 on Cu(111)**. **a-i** AFM images of different PAs on Cu(111).

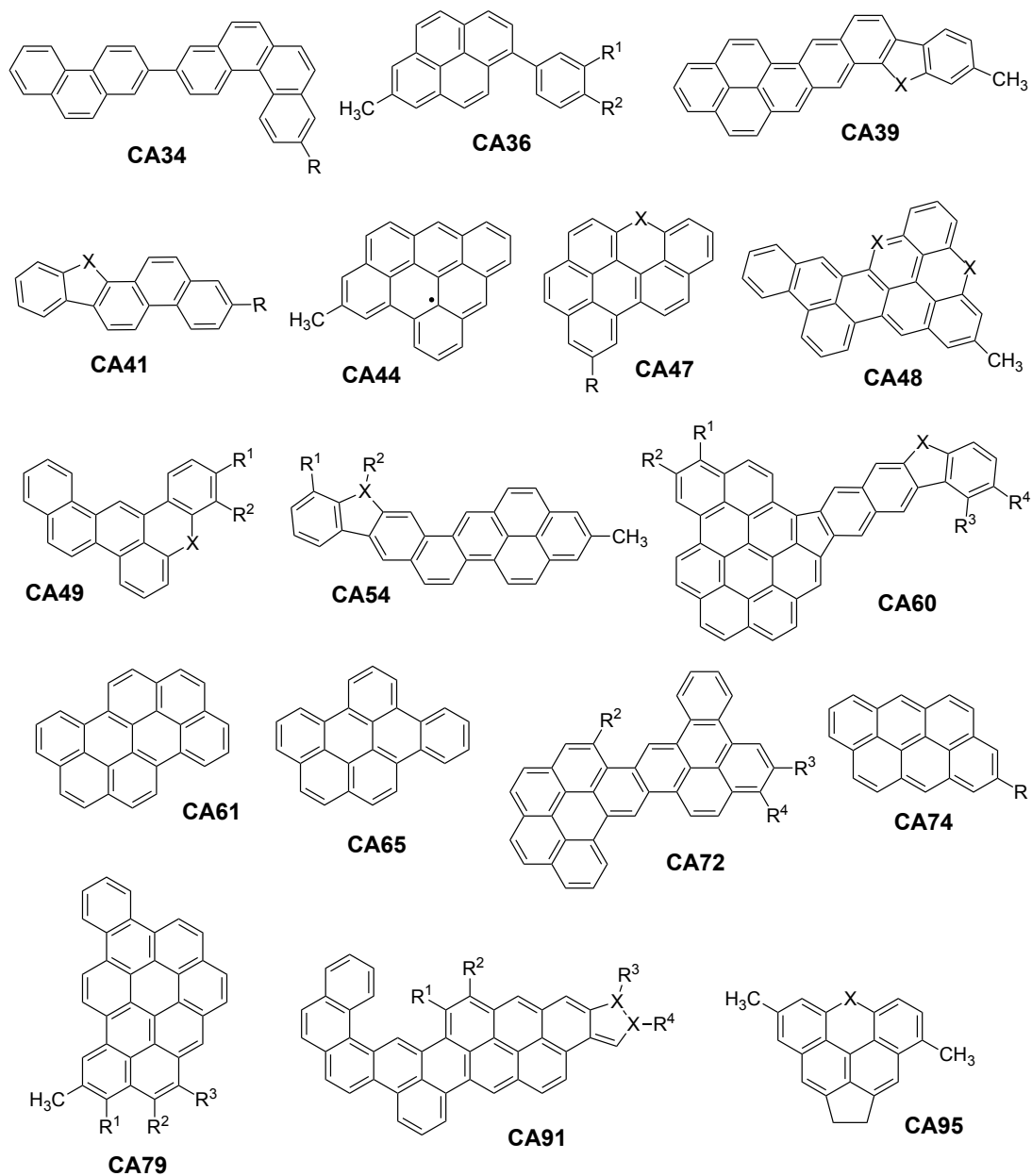


Figure S11. **Proposed chemical structures for molecules shown in the SI only.** The proposed structures are based on AFM measurements and STM orbitals images. *X* denotes unknown moieties within the carbon framework (likely CH, CH₂, N, NH, CO or S and in some cases CHCH or CH₂CH₂) and *R* denotes unknown side-groups.

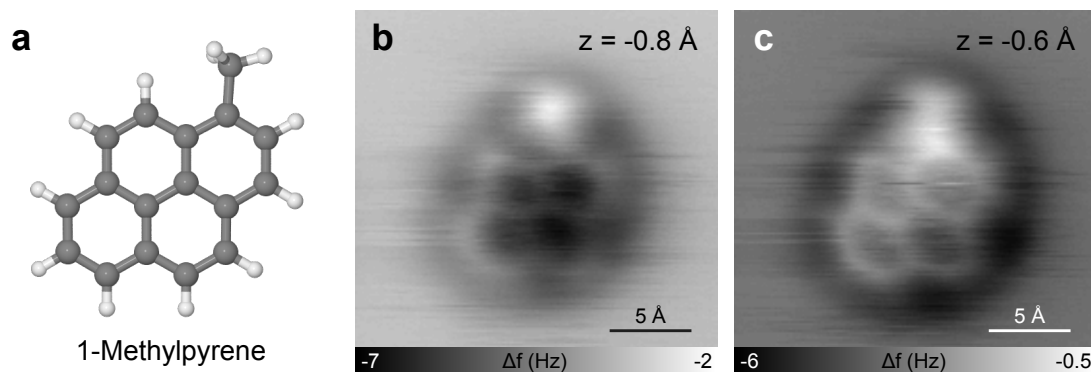


Figure S12. **1-Methylpyrene (MP) on NaCl(2ML)/Cu(111).** **a** Model of 1-Methylpyrene. **b,c** AFM images of **MP** on NaCl(2ML)/Cu(111) at different set-points z from ($I = 1.4 \text{ pA}$, $V = 0.2 \text{ V}$).