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Understanding the Structure of Petroleum Asphaltenes and the Mechanism of Molecular Weight Growth with nc-AFM Molecular Imaging

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Outline

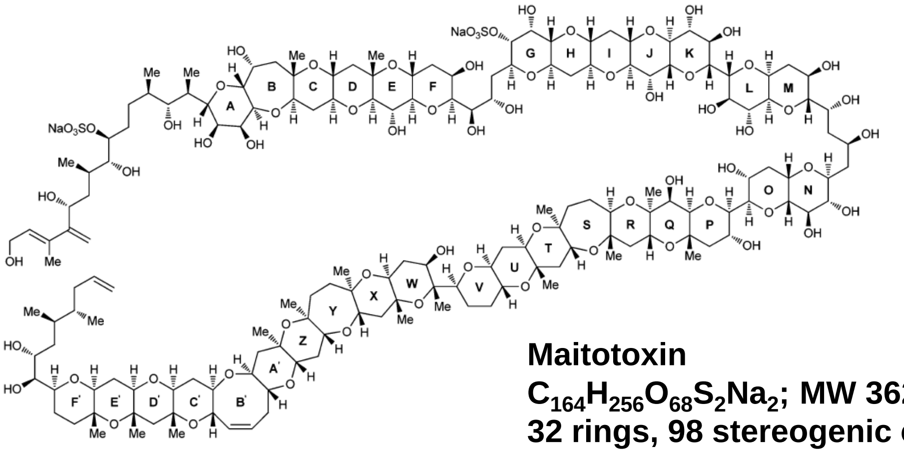
- Challenges of characterizing complex molecular mixtures
- Introduction to molecular imaging with nc-AFM/STM
- Imaging of molecular structure of petroleum asphaltenes
- Characterization of carbon materials
- Summary

Structure Function Relationship

There is **no more basic enterprise in chemistry than the determination of the geometrical structure of a molecule**. Such a determination, when it is well done, ends all speculation as to the structure, and provides us with the starting point for the understanding of every physical, chemical and biological property of the molecule.

Roald Hoffman (1981)

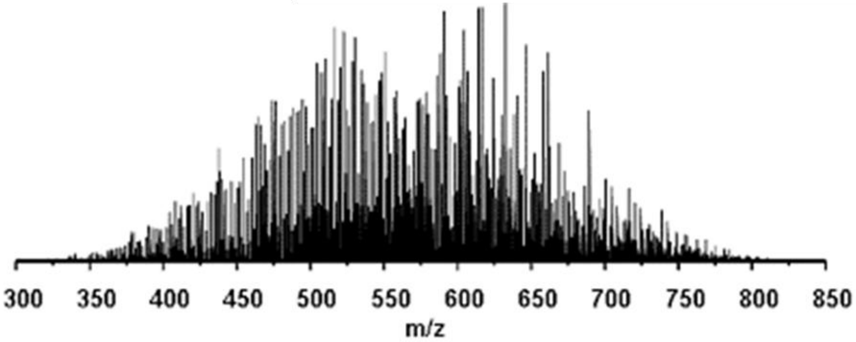
State of the art in modern structure determination for pure compounds



Maitotoxin
$C_{164}H_{256}O_{68}S_2Na_2$; MW 3626
32 rings, 98 stereogenic centers

Petroleum is a Complex Molecular Mixture

up to 10^{16} molecules in total in one oil droplet



- ~10^5 peaks identified can be identified by FT-ICR MS
- A 40-carbon alkane is estimated to have 60 trillion (~ 6.2×10^{13}) isomers
- 35 fused-benzene rings has 60 sextillion (~ 5.8×10^{21}) isomers

Marshall, A. G.; Rodgers, R. P., Petroleomics: chemistry of the underworld. *Proc. Natl. Acad. Sci.* **2008,** *105*, 18090-18095.

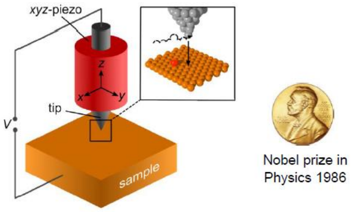
Take a Look and See Where the Atoms Are

If you have a strange substance and you want to know what it is, you go through a long and complicated process of chemical analysis. [...] It would be very easy to make an analysis of any complicated chemical substance; all one would have to do would be to **look at it and see where the atoms are**.

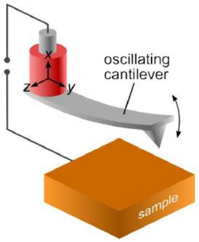
There's Plenty of Room at the Bottom
Richard P. Feynman (1959)

A Brief Introduction to STM/nc-AFM

- **Scanning Tunneling Microscopy (STM)**
  - STM topology reflects the local density of states

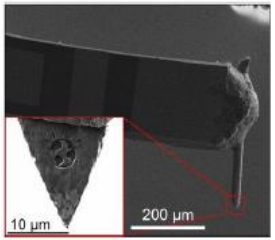


- **Atomic Force Microscopy (AFM)**
  - Frequency shift reflects the interaction force



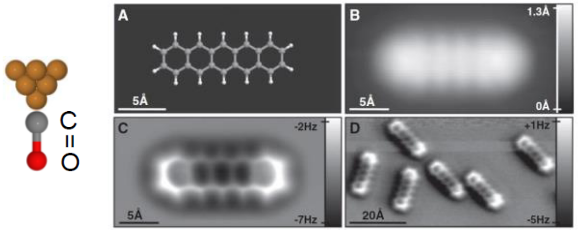
$$\Delta f \approx -\frac{f_0}{2k_0}\frac{\partial F_{ts}}{\partial z}$$

- **qPlus Sensor (1996) → Non-contact Mode**
  - Oscillation amplitudes down to 0.1 Å



F. Giessibl et al. *Appl. Phys. Lett. 73*, 3956 (**1998**)

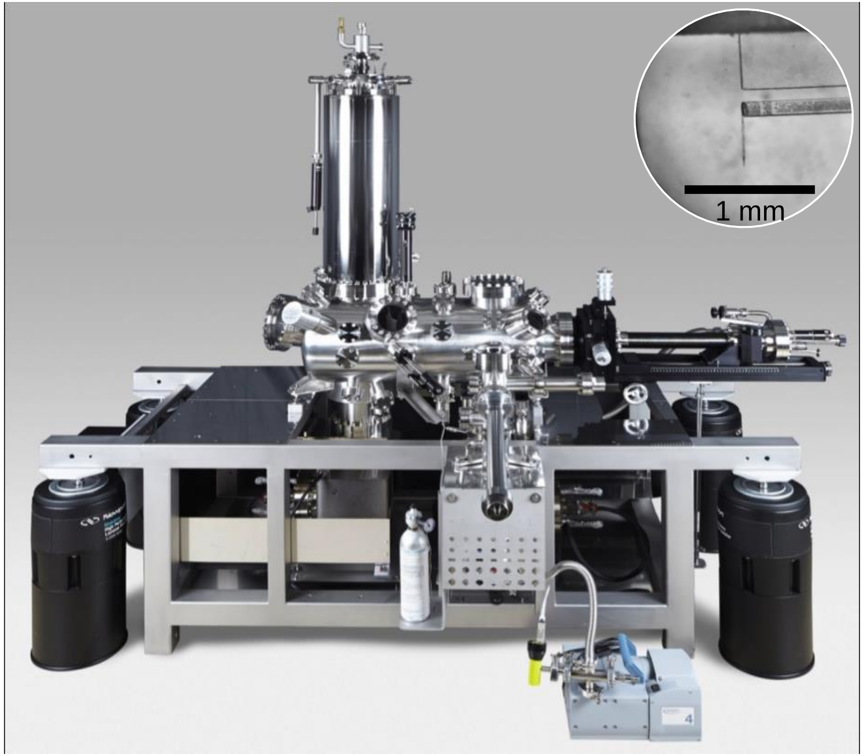
- **CO-functionalized Tip (2009)**
  - Resolution down to 0.02 Å



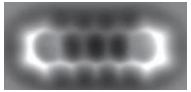
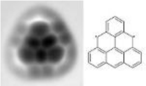
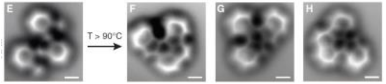
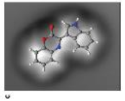
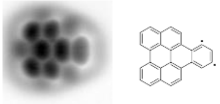
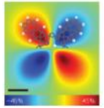
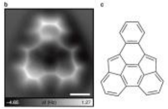
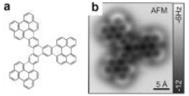
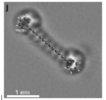
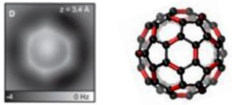
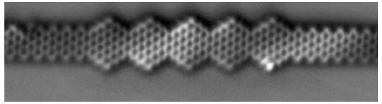
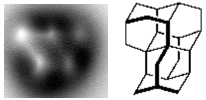
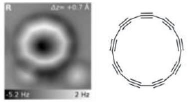
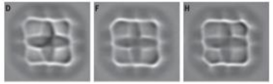
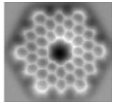
L. Gross et al. *Science 325*, 1110 (**2009**)

What it Takes to Image a Molecule?

- **Low temperature (4.7 K)**
  Limit thermal diffusion
- **Ultra high vacuum (10^{-10} mbar)**
  Atomically clean
- **Prepare the substrate and the CO tip**
  Single crystal Cu (111)
  Functionalized CO tip
- **Depositing samples**
  Flash heating on a silicon wafer



A Versatile Toolbox with nc-AFM/STM

Stable molecule	Reactive intermediate	Molecular property	On-Surface Reaction
			
Gross, L.; et al. The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy. *Science* **2009**	Pavlicek, N.; et al. Synthesis and characterization of triangulene. *Nat. Nanotechnol.* **2017**	Repp, J.; et al., Molecules on Insulating Films: Scanning-Tunneling Microscopy Imaging of Individual Molecular Orbitals. *Phys. Rev. Lett.* **2005,** *94*, 026803.	de Oteyza, D. G.; et al. Direct Imaging of Covalent Bond Structure in Single-Molecule Chemical Reactions. *Science* **2013**
			
Gross, L.; et al. Organic structure determination using atomic-resolution scanning probe microscopy. *Nat. Chem.* **2010**	Pavlicek, N.; et al. Generation and Characterization of a meta-Aryne on Cu and NaCl Surfaces. *ACS Nano* **2017**	Mohn, F.; et al. Imaging the charge distribution within a single molecule. *Nat. Nanotechnol.* **2012**	Kawai, S.; et al. Thermal control of sequential on-surface transformation of a hydrocarbon molecule on a copper surface. *Nat. Commun.* **2016**
			
Schuler, B.; et al. From perylene to a 22-ring aromatic hydrocarbon in one-pot. *Angew. Chem., Int. Ed.* **2014**	Pavliček, N.; et al. Polyyne formation via skeletal rearrangement induced by atomic manipulation. *Nat. Chem.* **2018**	Gross, L.; et al. Bond-Order Discrimination by Atomic Force Microscopy. *Science* **2012**	Gröning, O.; et al., Engineering of robust topological quantum phases in graphene nanoribbons. *Nature* **2018,** *560*, 209-213.
			
Ebeling, D.; et al. Assigning the absolute configuration of single aliphatic molecules by visual inspection. *Nat. Commun.* **2018,** *9*, 2420.	Kaiser, K.; et al. An sp-hybridized molecular carbon allotrope, cyclo[18]carbon. *Science* **2019**	Fatayer, S.; et al. Molecular structure elucidation with charge-state control. *Science* **2019**	Fan, Q.; et al. On-Surface Synthesis and Characterization of a Cycloarene: C108 Graphene Ring. *J. Am. Chem. Soc.* **2020,** *142*, 894-899.

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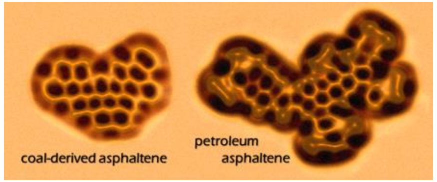
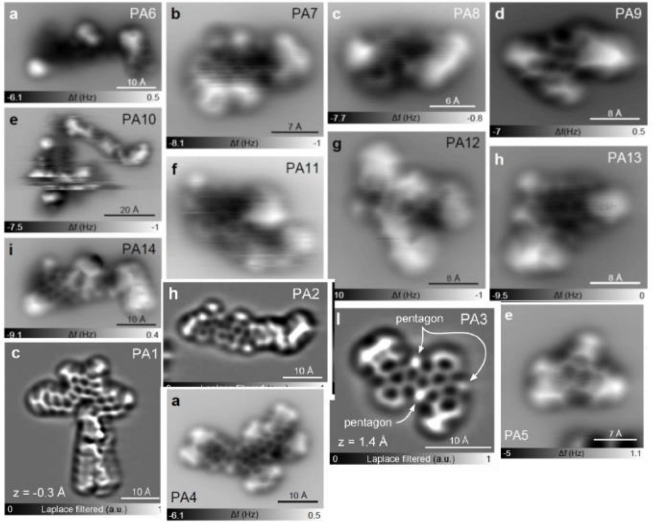
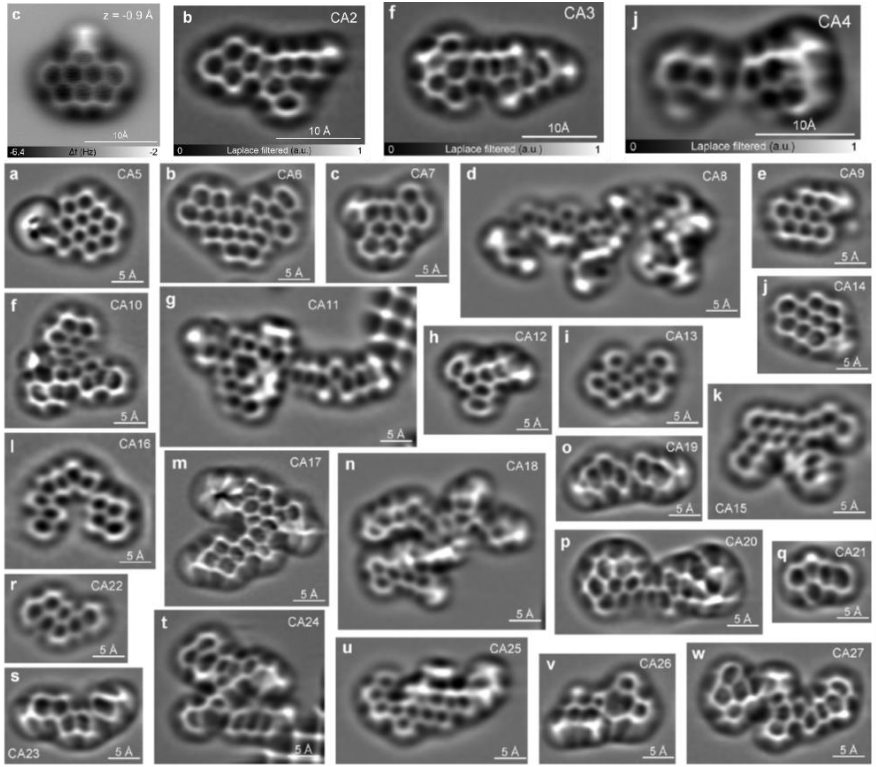
Imaging of Petroleum Asphaltenes with nc-AFM

IBM-Schlumberger Study, 2015





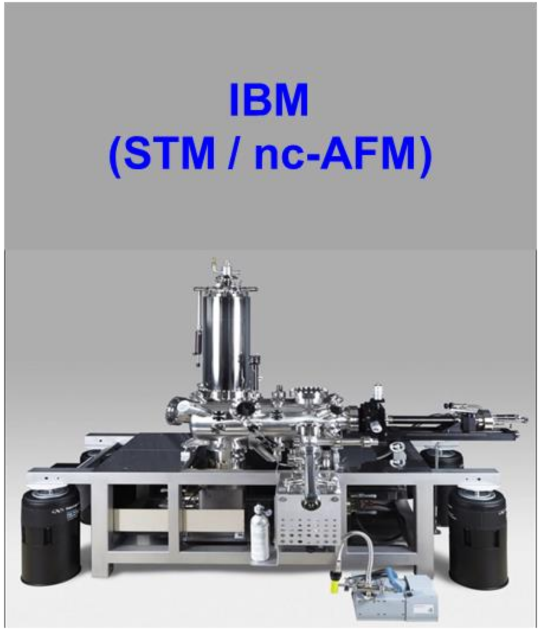
Petroleum-Derived Asphaltenes



Coal-Derived Asphaltenes

Schuler, B.; Meyer, G.; Pena, D.; Mullins, O. C.; Gross, L., Unraveling the Molecular Structures of Asphaltenes by Atomic Force Microscopy. *J. Am. Chem. Soc.* **2015,** *137*, 9870-9876.

Nc-AFM Imaging of Petroleum Asphaltenes and Heavy Oils



ExxonMobil:
a) De-asphalted aromatic fraction
b) Steam cracker tar asphaltenes

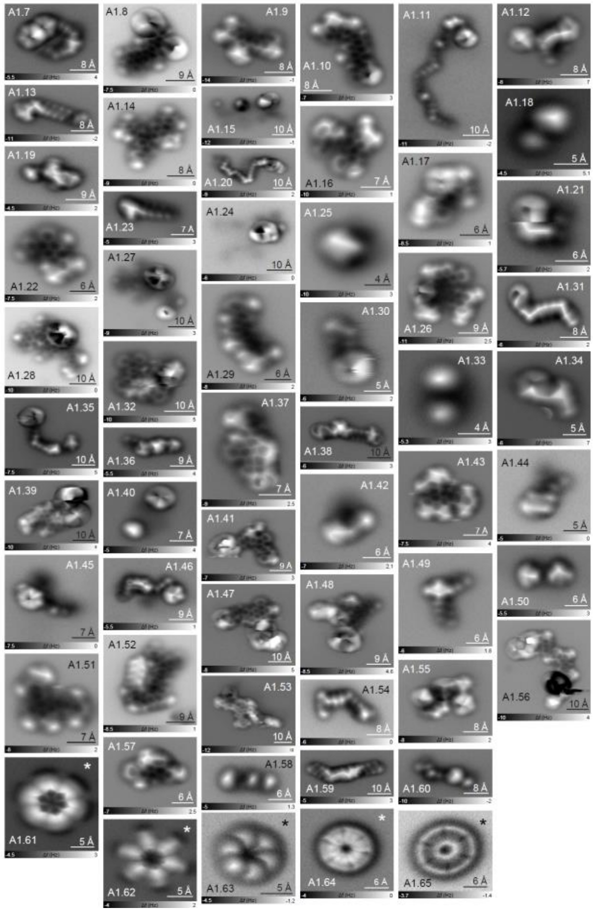
Shell: Asphaltenes
a) Before hydroconversion
b) After hydroconversion

Chevron: Asphaltenes
a) Isolated from crude
b) Deposited from crude

Schlumberger: Asphaltenes
a) High S shale crude
b) Low S shale crude

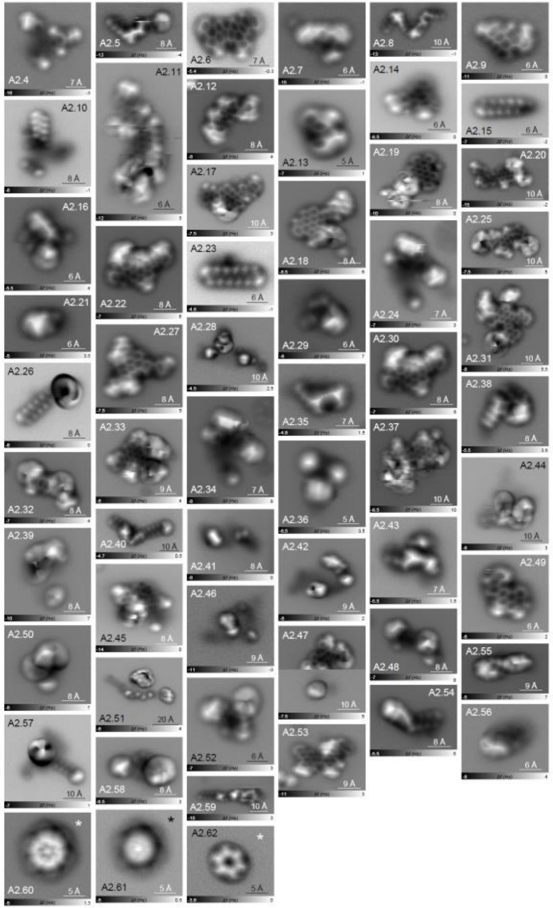
Schuler, B.; Fatayer, S.; Meyer, G.; Rogel, E.; Moir, M.; Zhang, Y.; Harper, M. R.; Pomerantz, A. E.; Bake, K. D.; Witt, M.; Pena, D.; Kushnerick, J. D.; Mullins, O. C.; Ovalles, C.; van den Berg, F. G. A.; Gross, L., Heavy Oil Based Mixtures of Different Origins and Treatments Studied by Atomic Force Microscopy. *Energy & Fuels* **2017,** *31*, 6856-6861. (**Most cited article in the last 5 years**)

A1



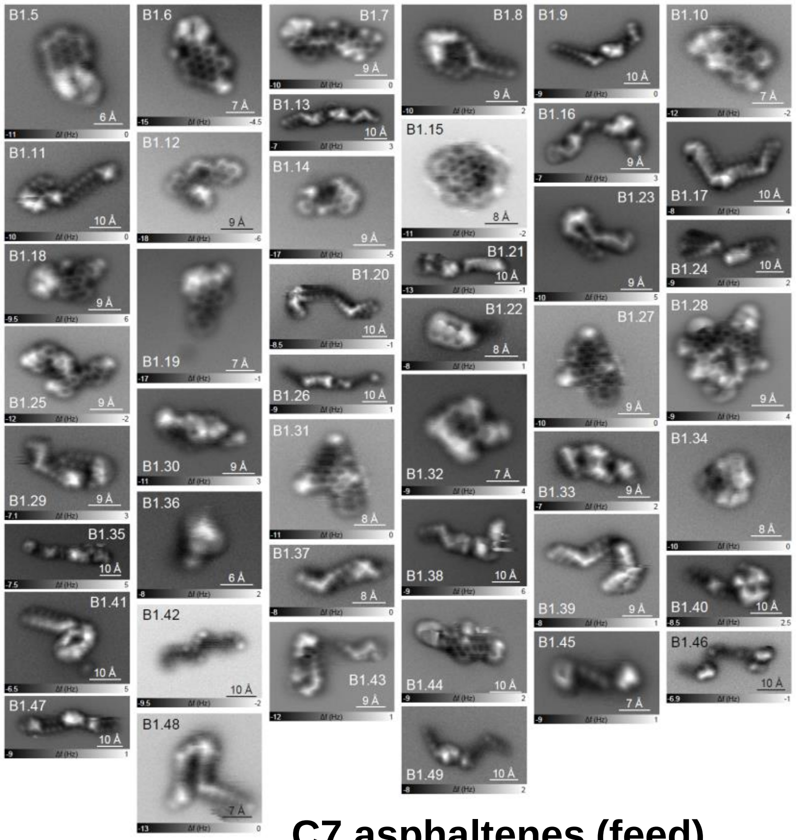
C7 asphaltenes from crude oil

A2



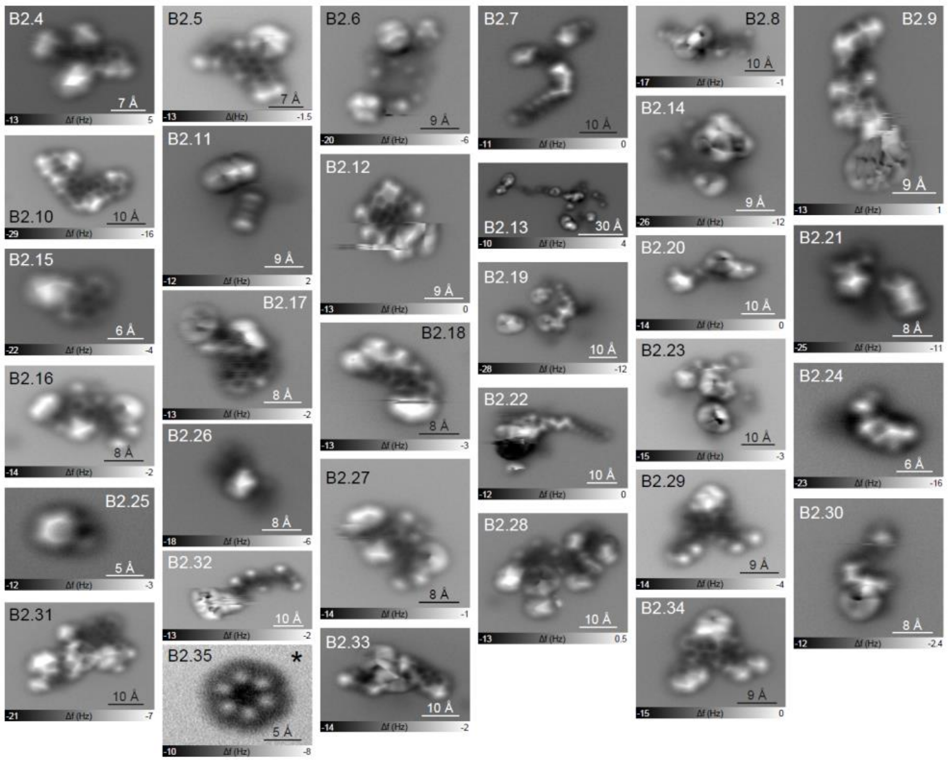
C7 Asphaltenes from deposit

B1



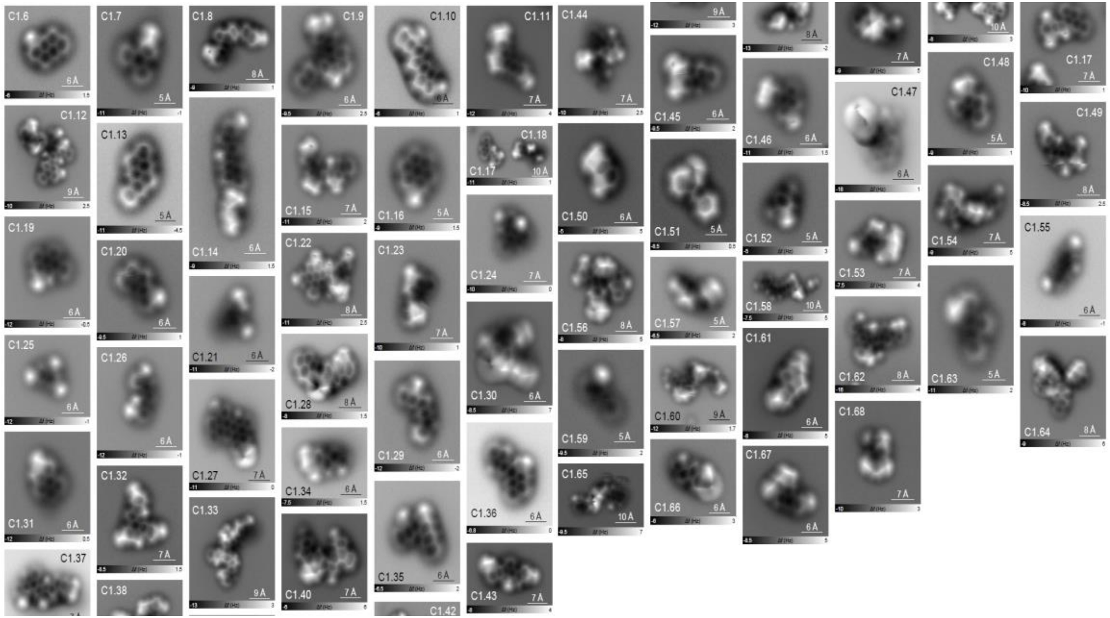
C7 asphaltenes (feed)

B2



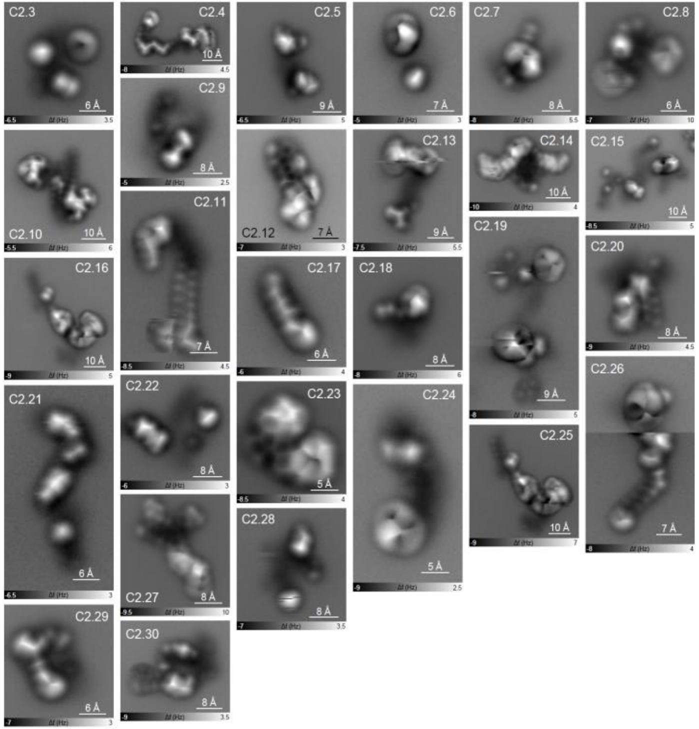
C7 Asphaltenes after Hydroconversion (product)

C1



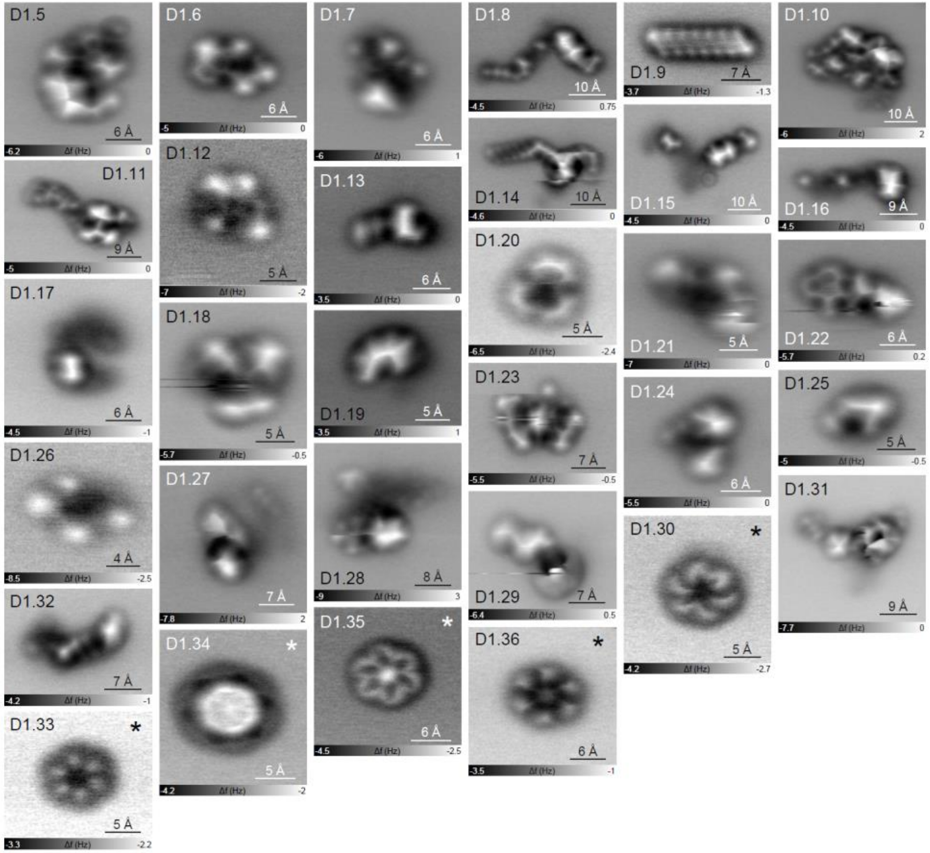
Steam cracked tar C7 asphaltenes

C2



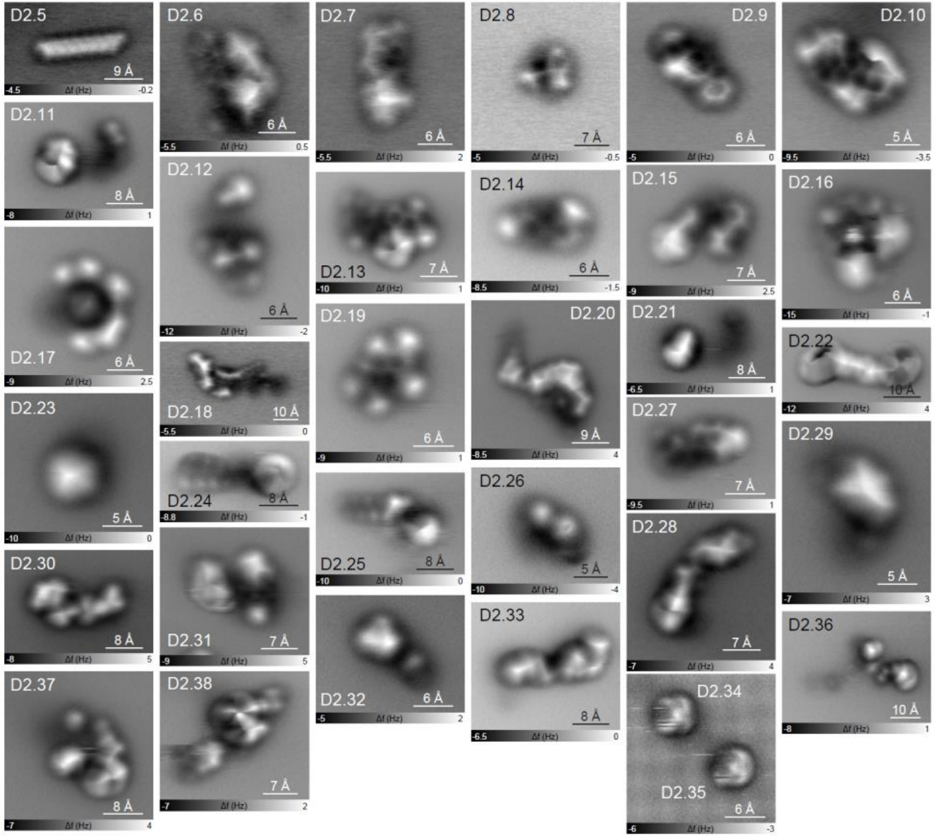
Non-asphaltenes (Aromatic 4R+ fraction)

D1



Green River Shale Asphaltenes

D2



Eagle Ford Shale Asphaltenes

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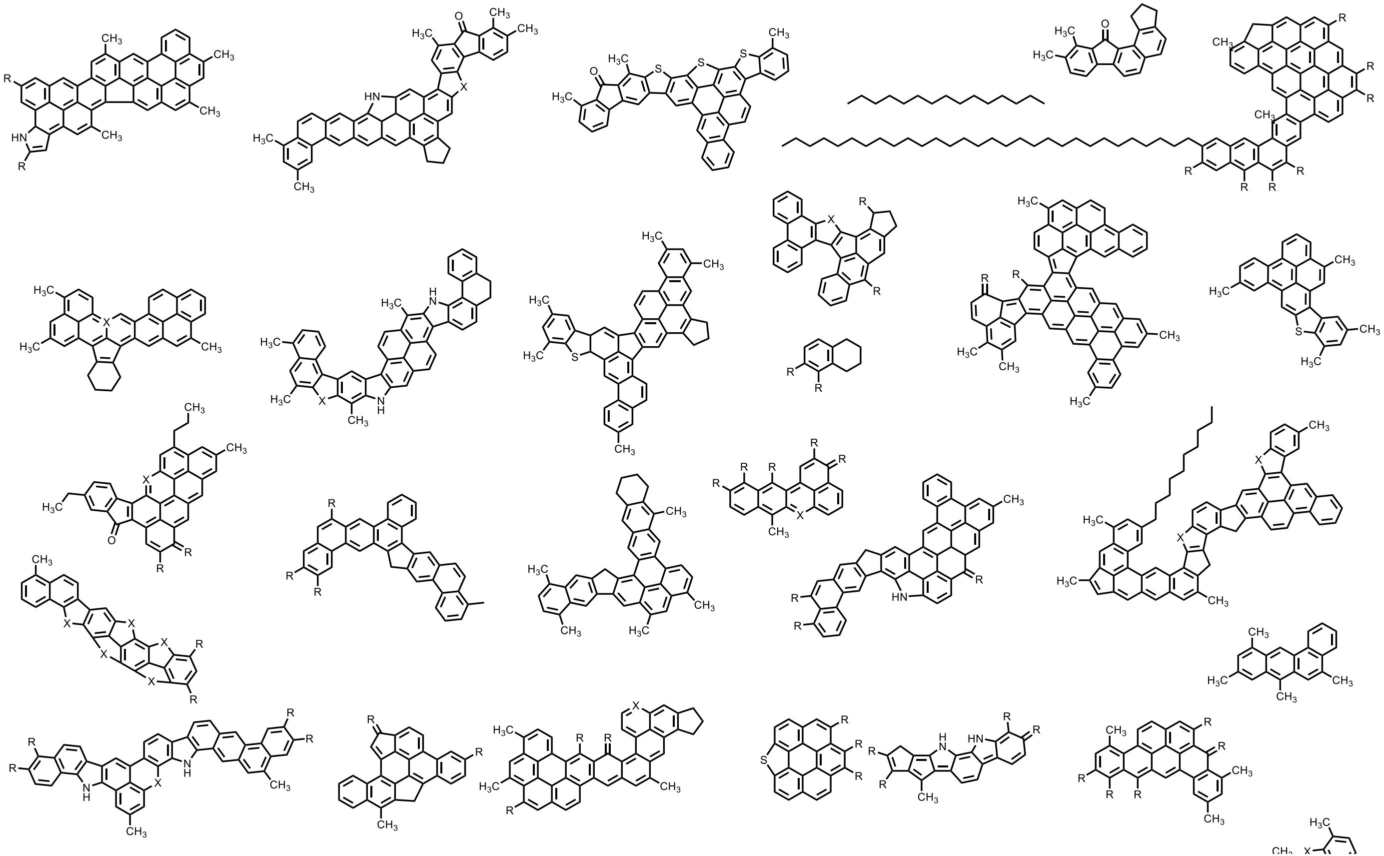
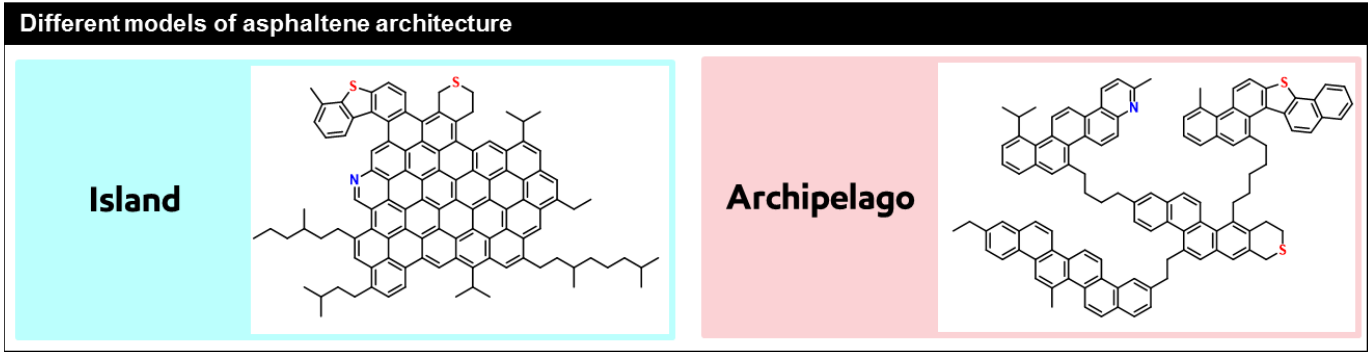
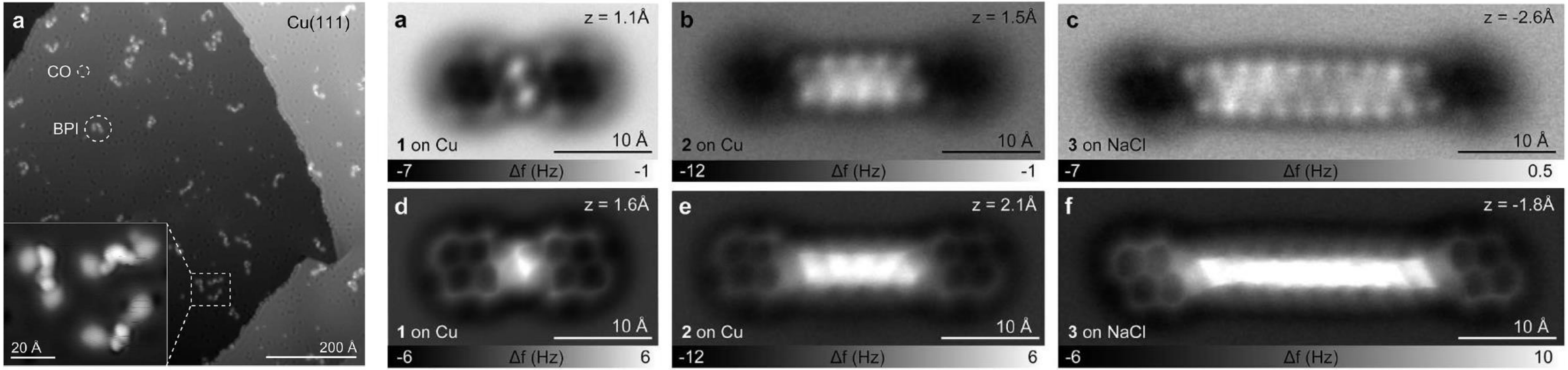
Molecular Structures from AFM



Book chapter: Zhang, Y., Identify Similarities in Diverse Polycyclic Aromatic Hydrocarbons of Asphaltenes and Heavy Oils Revealed by Noncontact Atomic Force Microscopy: Aromaticity, Bonding, and Implications in Reactivity.

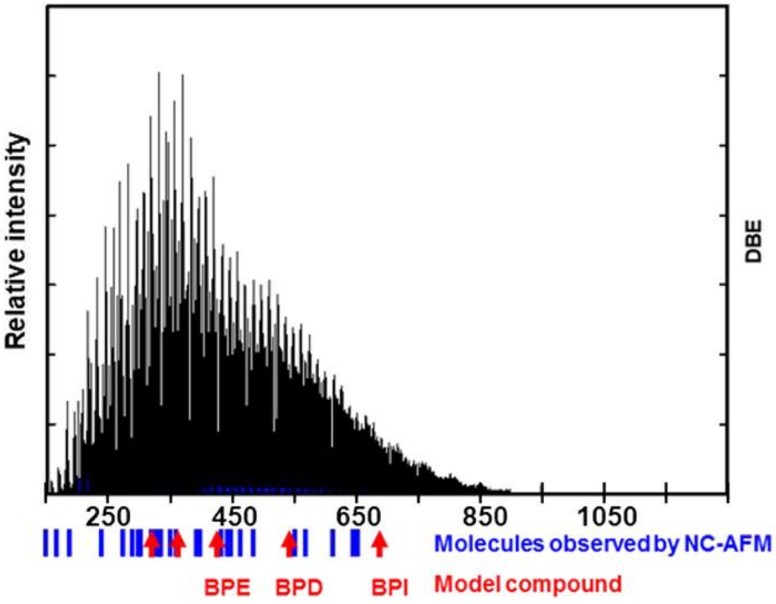
A Control Experiment of Archipelago Structures

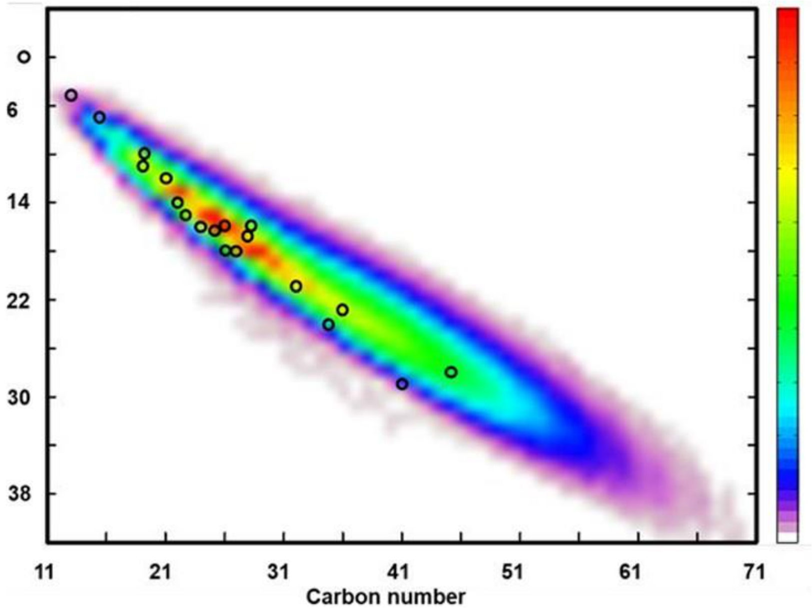




Schuler*, B.; Zhang*, Y.; Collazos, S.; Fatayer, S.; Meyer, G.; Perez, D.; Guitian, E.; Harper, M. R.; Kushnerick, J. D.; Pena, D.; Gross, L., Characterizing aliphatic moieties in hydrocarbons with atomic force microscopy. *Chem. Sci.* **2017,** *8*, 2315-2320

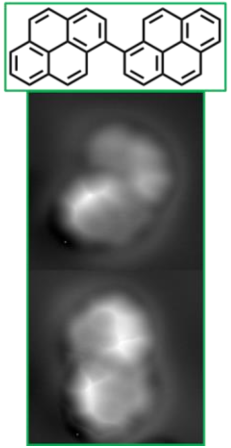
Representativeness of Images

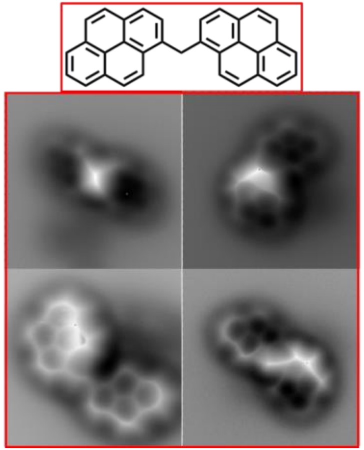


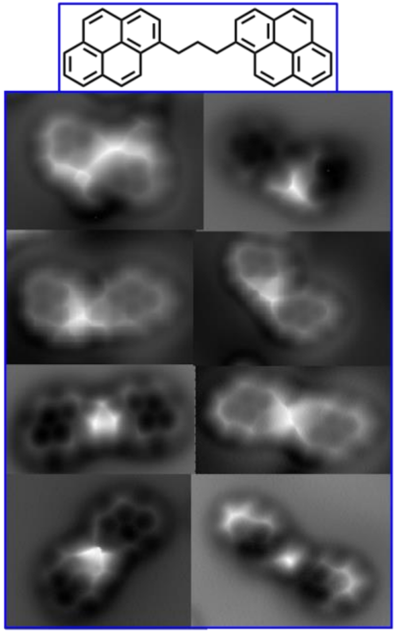


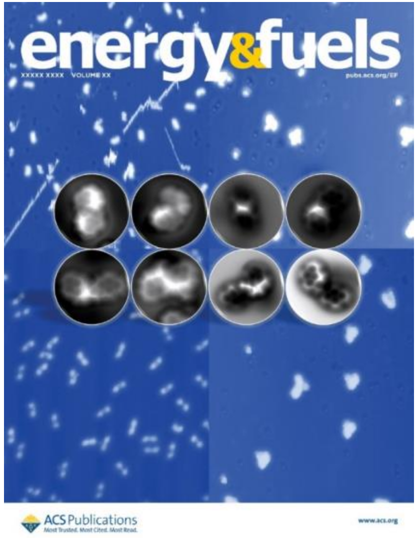
Zhang, Y.; Schuler, B.; Fatayer, S.; Gross, L.; Harper, M. R.; Kushnerick, J. D., Understanding the Effects of Sample Preparation on the Chemical Structures of Petroleum Imaged with Noncontact Atomic Force Microscopy. *Industrial & Engineering Chemistry Research* **2018,** *57*, 15935-15941.

Image Nonplanar Molecular Conformations



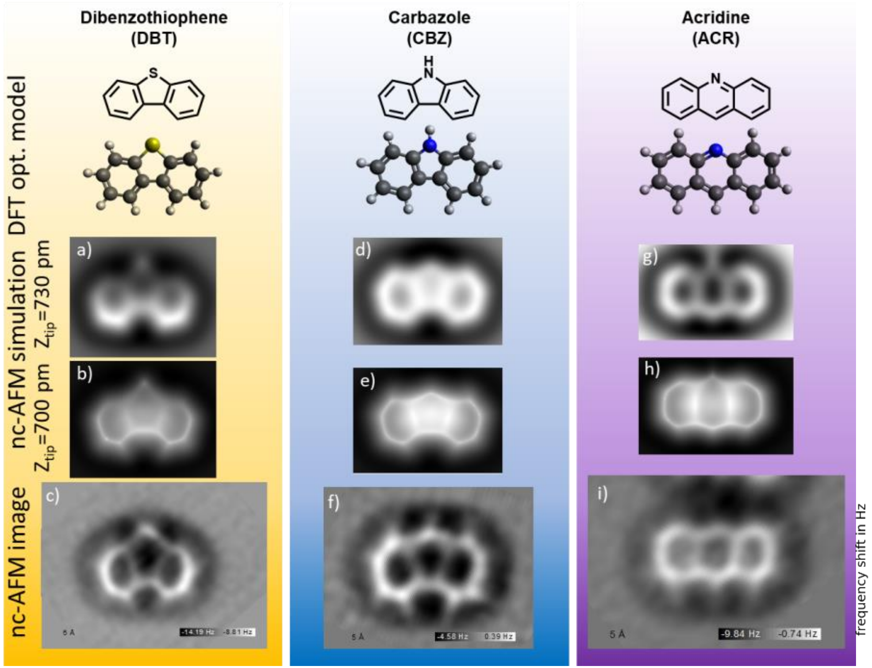


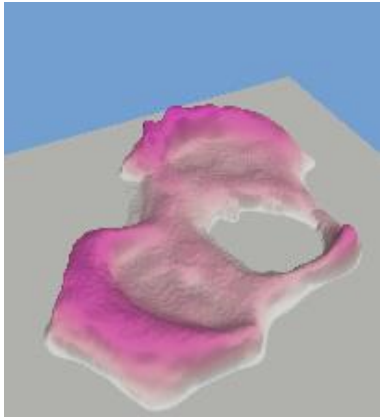


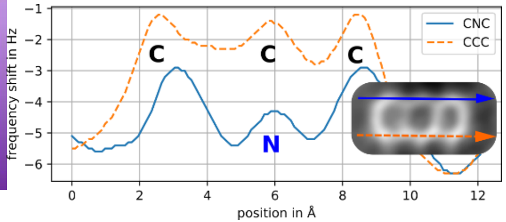


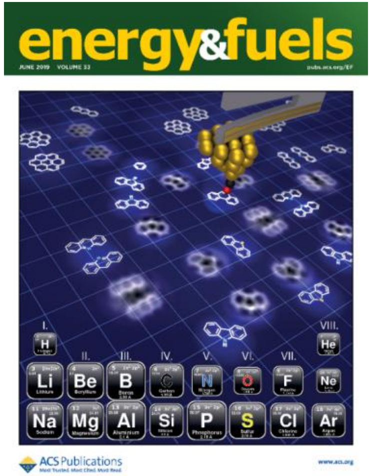
Chen, P.; Joshi, Y. V.; Metz, J. N.; Yao*, N.; Zhang*, Y., Conformational Analysis of Nonplanar Archipelago Structures on a Cu (111) Surface by Molecular Imaging. *Energy Fuels* **2020**, 10.1021/acs.energyfuels.0c01861.

Differentiate Heteroatoms



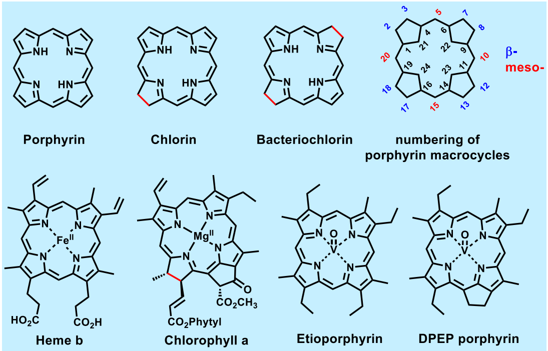


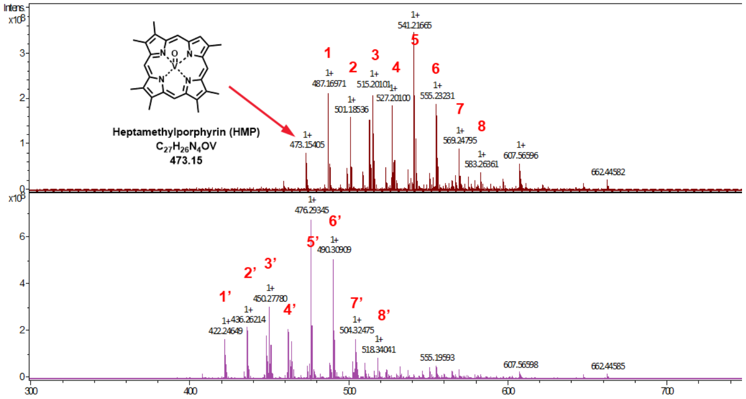


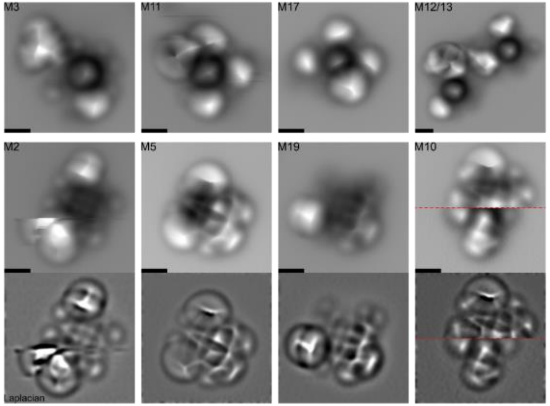


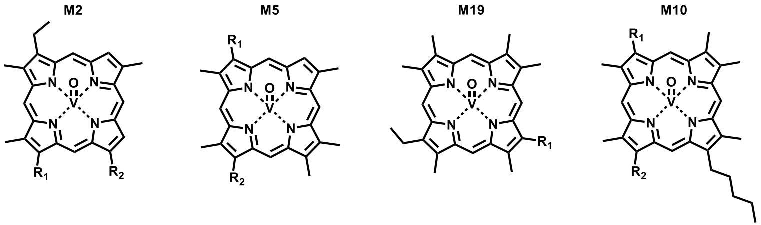
*Zahl, P.; *Zhang, Y., Guide for Atomic Force Microscopy Image Analysis To Discriminate Heteroatoms in Aromatic Molecules. *Energy Fuels* **2019**, doi.org/10.1021/acs.energyfuels.9b00165.

Detection of β-H in Petroporphyrins





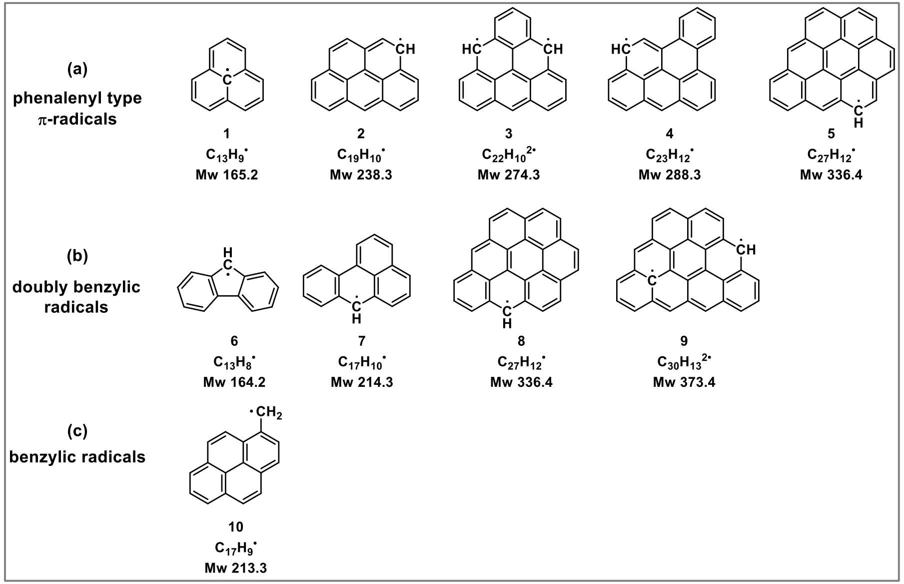


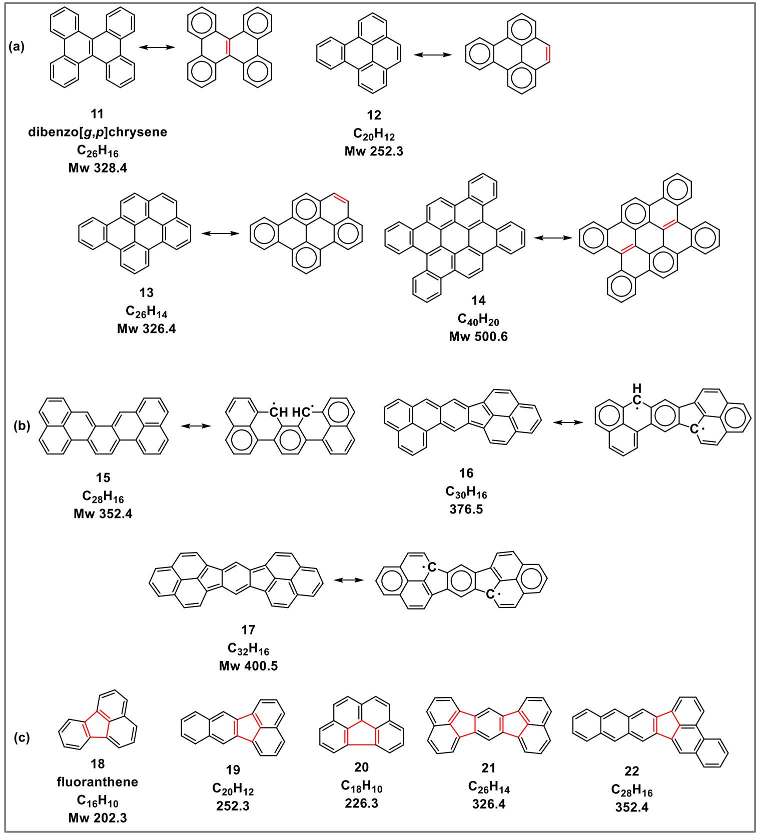


- **Petroporphyrins have different structures**
- **Etio are formed from DPEP**
- **Presence β-H in etio indicates dealkylation**

Zhang, Y.; Schulz, F.; Rytting, B.; Walters, C.; Kaiser, K.; Metz, J.; Harper, M.; Merchant, S.; Mennito, A.; Qian, K.; Kushnerick, J.; Kilpatrick, P.; Gross, L., Elucidating the Geometric Substitution of Petroporphyrins by Spectroscopic Analysis and AFM Molecular Imaging. *Energy Fuels* **2019,** *33* (7), 6088-6097.

Free Radical in Asphaltene Aggregation

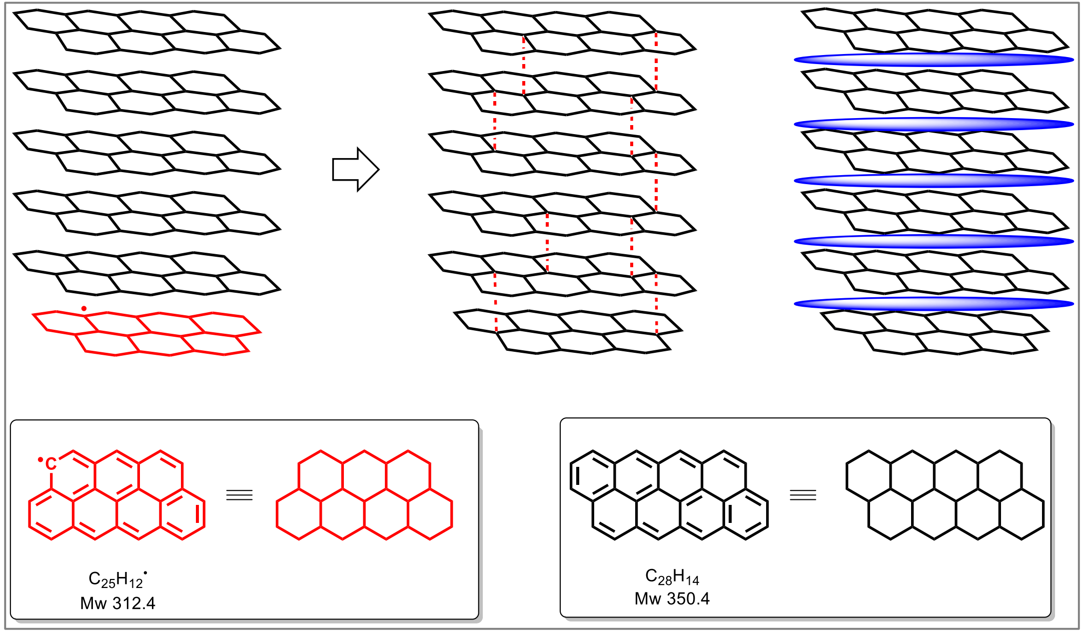




0.3-1.3 mol% (10^{18}-10^{19} spins/g)

1. Gutowsky, H. S.; Ray, B. R.; Rutledge, R. L.; Unterberger, R. R., Carbonaceous Free Radicals in Crude Petroleum. *J. Chem. Phys.* **1958,** *28*, 744-745.
2. Brown, T. H.; Gutowsky, H. S.; Van Holde, K. E., Electron Spin Resonance and Colloidal Properties of Crude Oil. *J. Chem. Eng. Data* **1960,** *5*, 181-182.

Pancake Bonding in Asphaltene Aggregation



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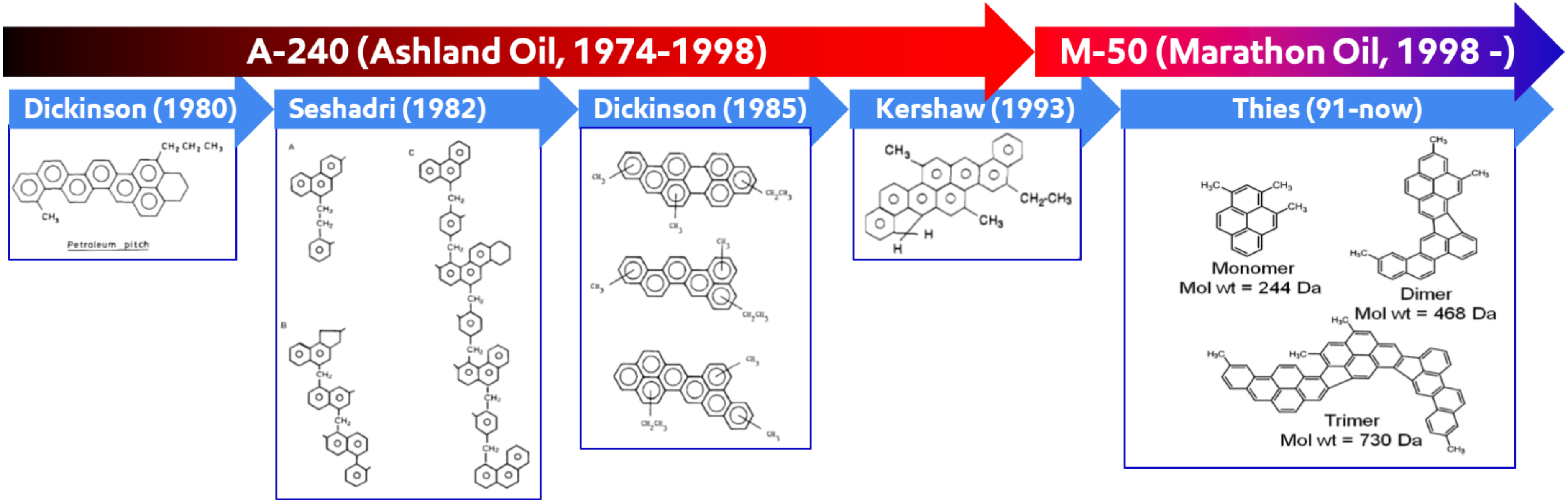
… ***Burning petroleum as a fuel would be akin to firing up a kitchen stove with bank notes.***

Dmitri Mendeleev (1834 - 1907)

Long History of M-50 Petroleum Pitch



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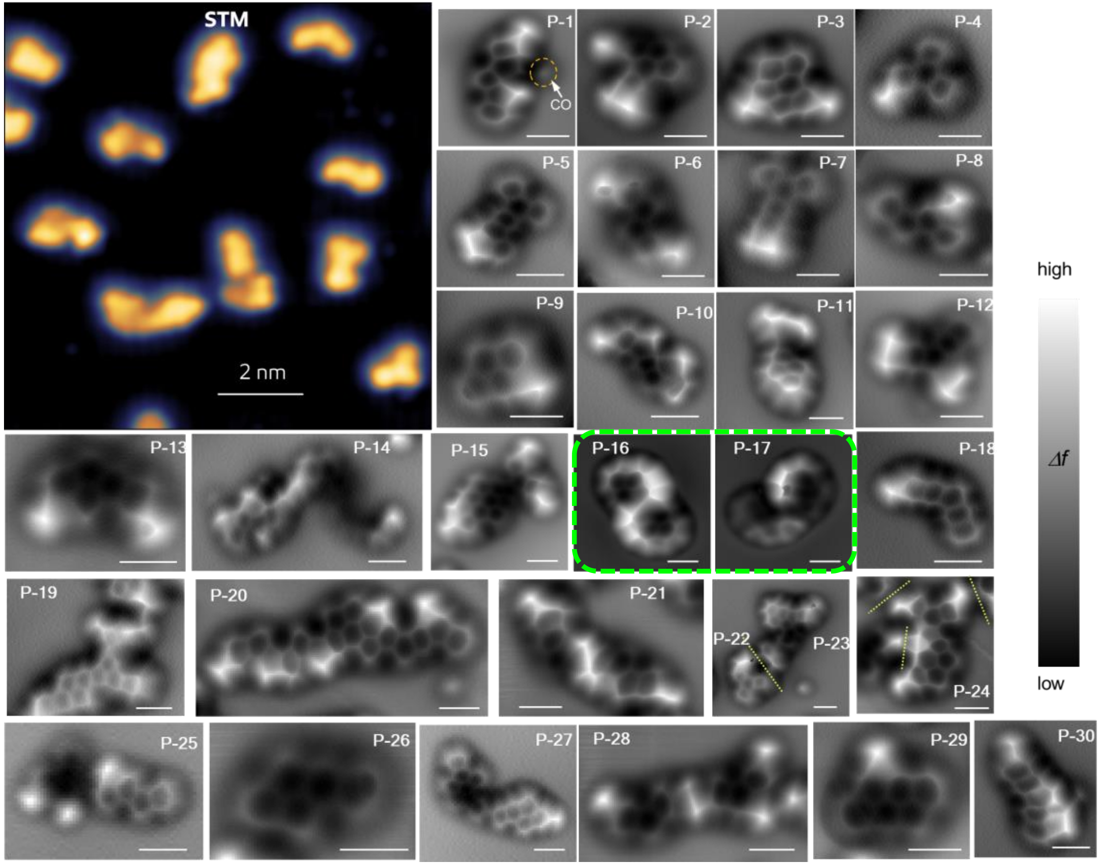
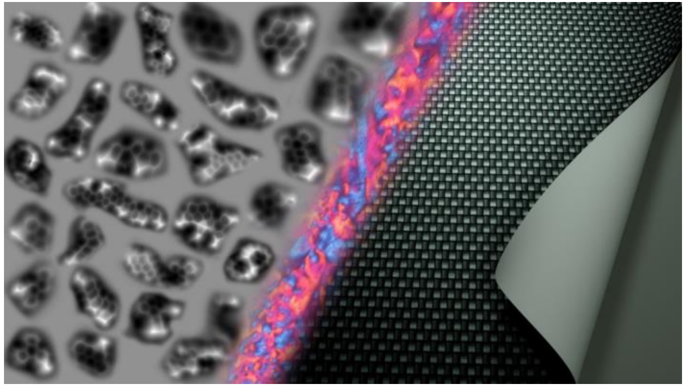
Molecular Structures of M-50 Pitch by AFM

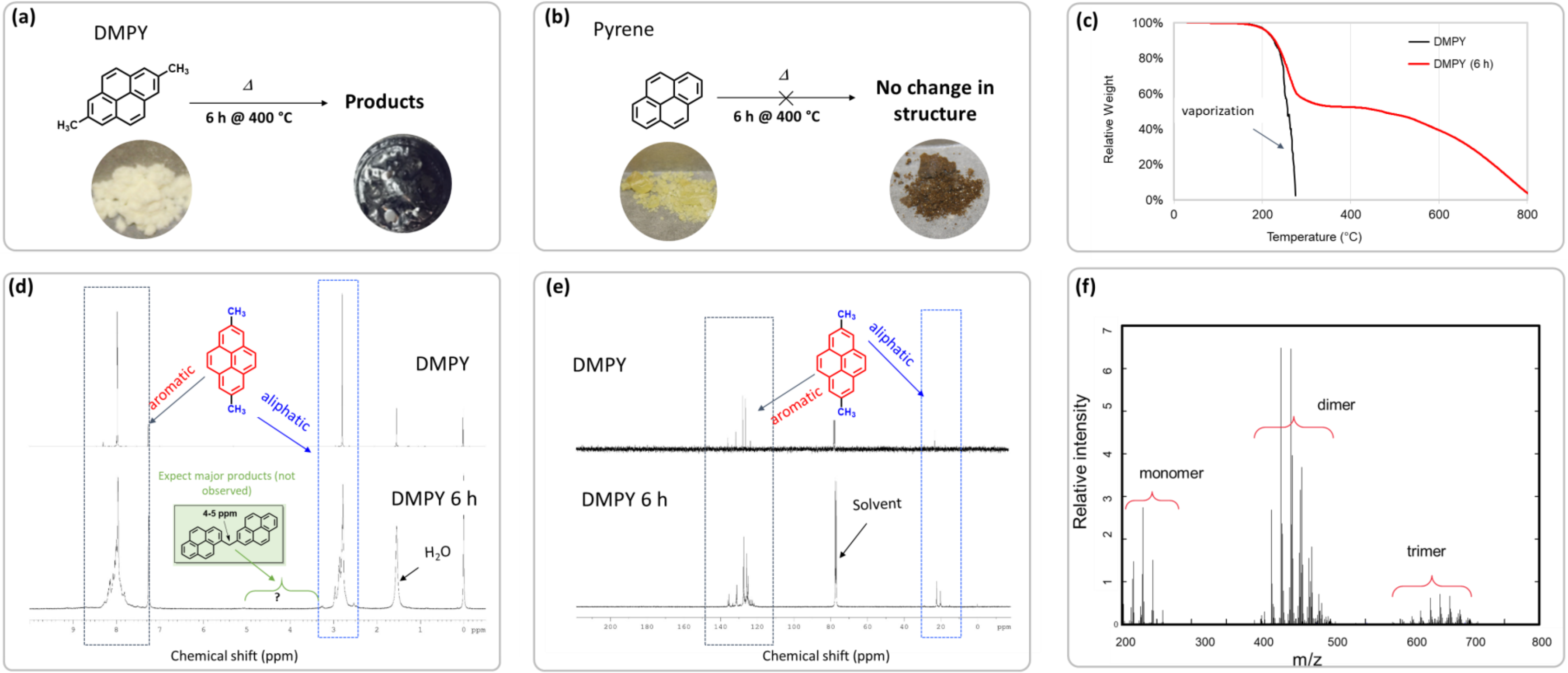


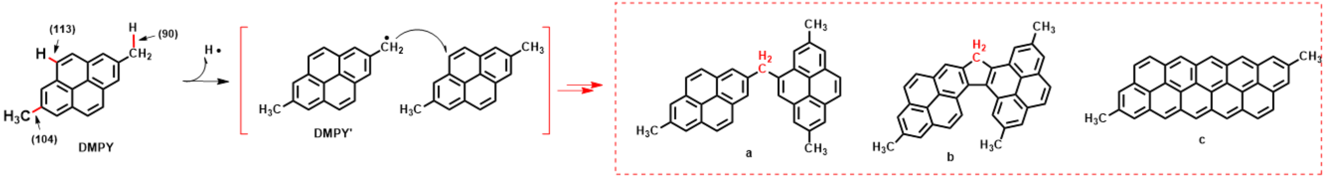


1. Consistent w/ historic data
2. Also with NMR and FTICR data
3. Dominant branches are methyls
4. Most cata-condensed, little peri-condensed
5. Two types of five-membered rings
6. Free radicals

Chen, P.; Metz, J. N.; Mennito, A. S.; Merchant, S.; Smith, S. E.; Siskin, M.; Rucker, S. P.; Dankworth, D. C.; Kushnerick, J. D.; Yao, N.; Zhang, Y., Petroleum pitch: Exploring a 50-year structure puzzle with real-space molecular imaging. Carbon 2020, 161, 456-465.

Understanding the Role of Methyl Groups During the Polymerization of PAHs





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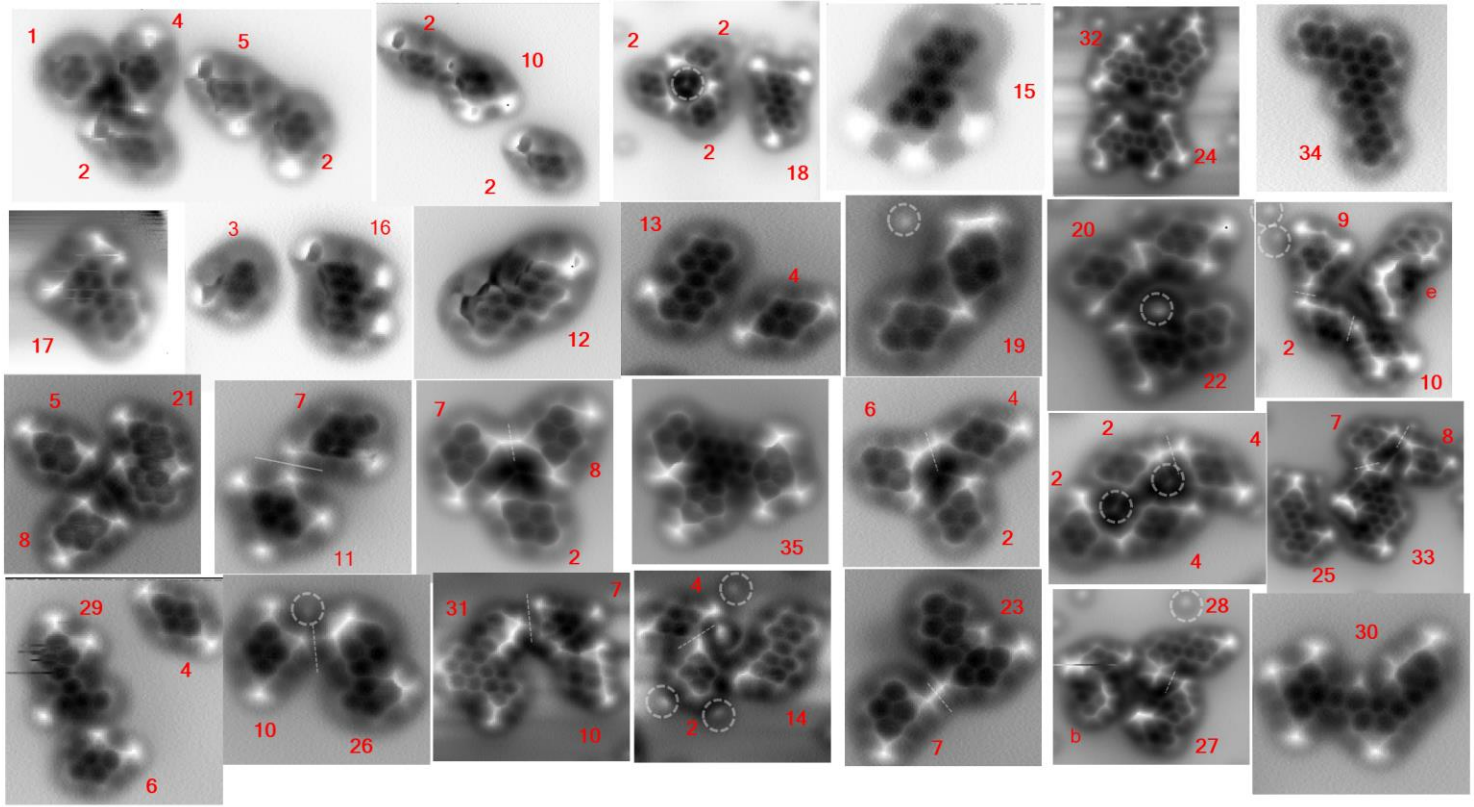
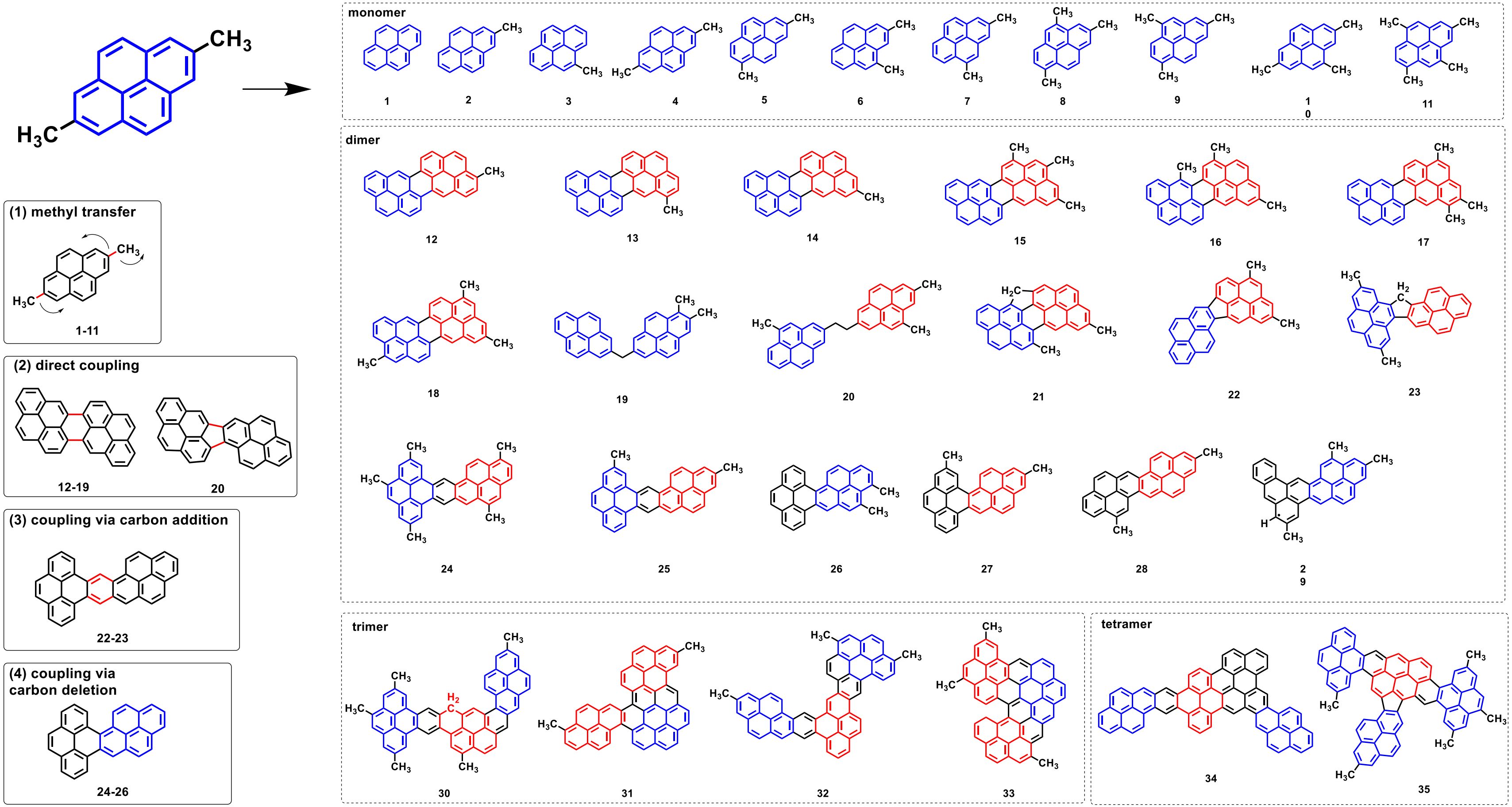
AFM images of the product mixture

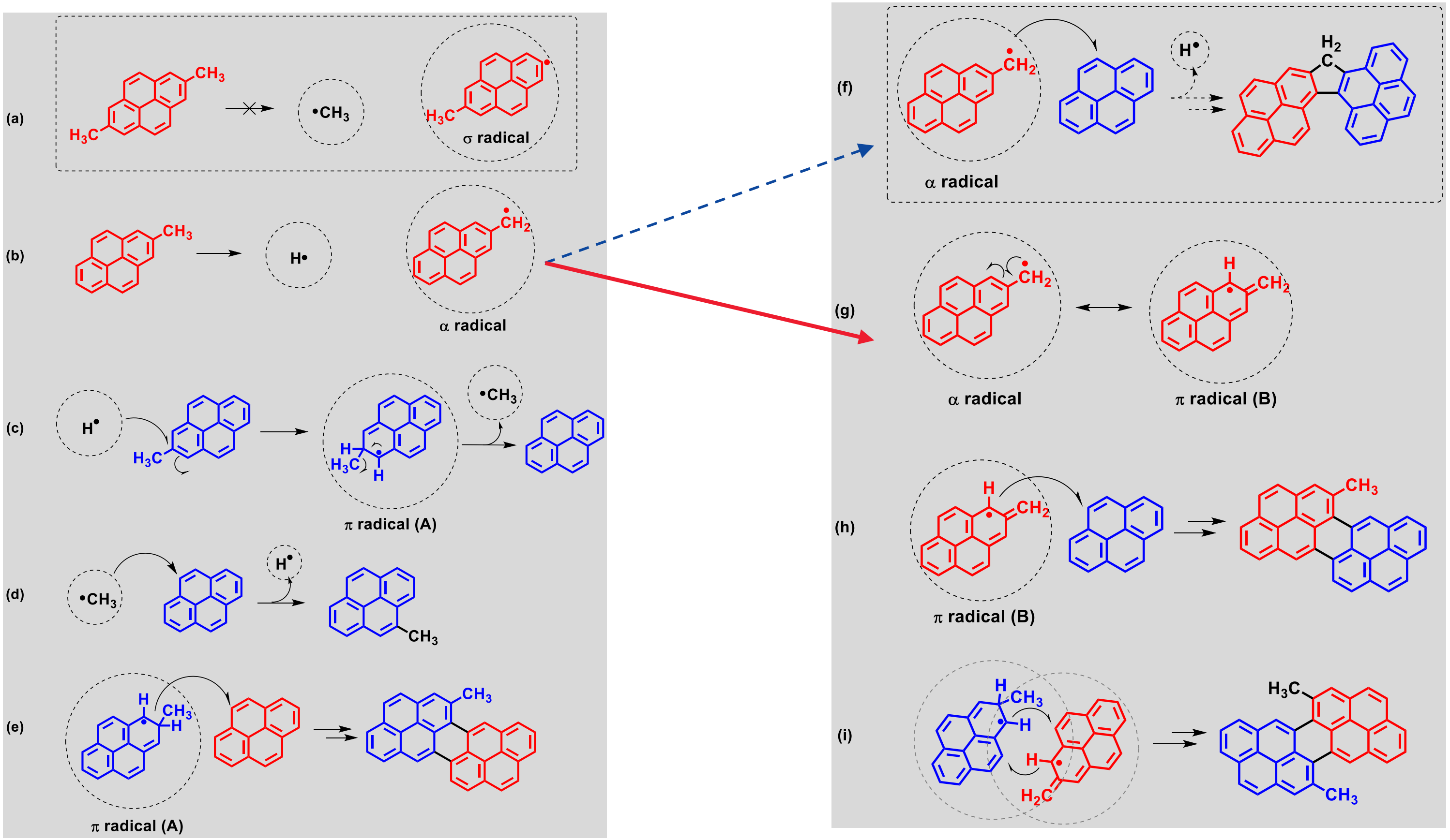


Chen, P.; Fatayer, S.; Schuler, B.; Gross, L.; Metz, J. N.; Yao, N.; Zhang, Y., The Role of Methyl in the Early Stage of Thermal Polymerization of Polycyclic Aromatic Hydrocarbons Revealed by Molecular Imaging. *Energy&Fuels* **2021,** *35*, 3, 2224–2233.

Chemical Structures from nc-AFM



Mechanism of Polymerization via π-radicals



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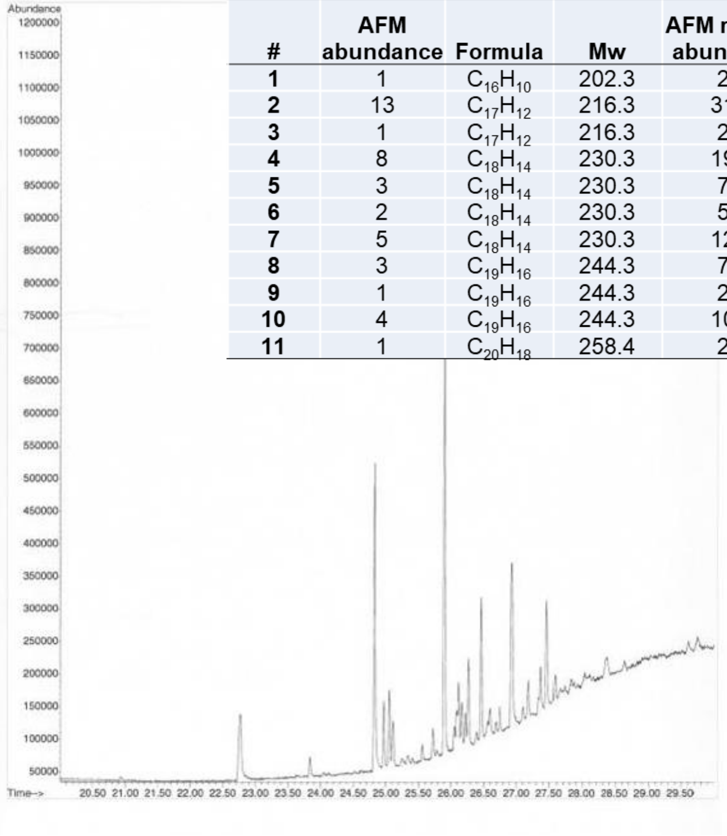
AFM and GC-MS

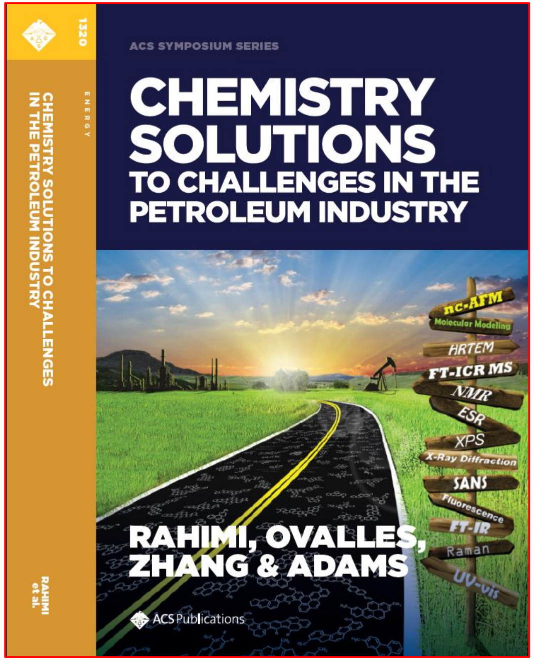
#	abundance	Formula	C	H	H/C	Mw	DBE	Aliphatic C	Aromatic C	fa	aliphatic H	Aromatic H	fa'
1	1	$C_{16}H_{10}$	16	10	0.63	202.3	12	0	16	1.00	0	10	1.00
2	13	$C_{17}H_{12}$	17	12	0.71	216.3	12	1	16	0.94	3	9	0.75
3	1	$C_{17}H_{12}$	17	12	0.71	216.3	12	1	16	0.94	3	9	0.75
4	8	$C_{18}H_{14}$	18	14	0.78	230.3	12	2	16	0.89	6	8	0.57
5	3	$C_{18}H_{14}$	18	14	0.78	230.3	12	2	16	0.89	6	8	0.57
6	2	$C_{18}H_{14}$	18	14	0.78	230.3	12	2	16	0.89	6	8	0.57
7	5	$C_{18}H_{14}$	18	14	0.78	230.3	12	2	16	0.89	6	8	0.57
8	3	$C_{19}H_{16}$	19	16	0.84	244.3	12	3	16	0.84	9	7	0.44
9	1	$C_{19}H_{16}$	19	16	0.84	244.3	12	3	16	0.84	9	7	0.44
10	4	$C_{19}H_{16}$	19	16	0.84	244.3	12	3	16	0.84	9	7	0.44
11	1	$C_{20}H_{18}$	20	18	0.90	258.4	12	4	16	0.80	12	6	0.33
12	1	$C_{33}H_{18}$	33	18	0.55	414.5	25	1	32	0.97	3	15	0.83
13	1	$C_{33}H_{18}$	33	18	0.55	414.5	25	1	32	0.97	3	15	0.83
14	1	$C_{33}H_{18}$	33	18	0.55	414.5	25	1	32	0.97	3	15	0.83
15	1	$C_{35}H_{22}$	35	22	0.63	442.6	25	3	32	0.91	9	13	0.59
16	1	$C_{35}H_{22}$	35	22	0.63	442.6	25	3	32	0.91	9	13	0.59
17	1	$C_{35}H_{22}$	35	22	0.63	442.6	25	3	32	0.91	9	13	0.59
18	1	$C_{35}H_{22}$	35	22	0.63	442.6	25	3	32	0.91	9	13	0.59
19	1	$C_{35}H_{24}$	35	24	0.69	444.6	24	3	32	0.91	8	16	0.67
20	1	$C_{37}H_{28}$	37	28	0.76	472.6	24	5	32	0.86	13	15	0.54
21	1	$C_{35}H_{20}$	35	20	0.57	440.5	26	3	32	0.91	8	12	0.60
22	1	$C_{34}H_{20}$	34	20	0.59	428.5	25	2	32	0.94	6	14	0.70
23	1	$C_{35}H_{22}$	35	22	0.63	442.6	25	3	32	0.91	8	14	0.64
24	1	$C_{39}H_{28}$	39	28	0.72	496.7	26	5	34	0.87	15	13	0.46
25	1	$C_{36}H_{22}$	36	22	0.61	454.6	26	2	34	0.94	6	16	0.73
26	1	$C_{32}H_{20}$	32	20	0.63	404.5	23	2	30	0.94	6	14	0.70
27	1	$C_{32}H_{20}$	32	20	0.63	404.5	23	2	30	0.94	6	14	0.70
28	1	$C_{32}H_{20}$	32	20	0.63	404.5	23	2	30	0.94	6	14	0.70
29	1	$C_{34}H_{23}^{*}$	34	23	0.68	431.6	24	3	31	0.91	9	14	0.61
30	1	$C_{56}H_{36}$	56	36	0.64	708.9	39	6	50	0.89	17	19	0.53
31	1	$C_{52}H_{26}$	52	26	0.50	650.8	40	2	50	0.96	6	20	0.77
32	1	$C_{57}H_{32}$	57	32	0.56	716.9	42	3	54	0.95	9	23	0.72
33	1	$C_{54}H_{27}^{*}$	54	27	0.50	675.8	42	3	51	0.94	9	18	0.67
34	1	$C_{66}H_{30}$	66	30	0.45	823.0	52	0	66	1.00	0	30	1.00
35	1	$C_{71}H_{40}$	71	40	0.56	893.1	52	5	66	0.93	15	25	0.63
Average		$C_{34}H_{21}$	34	21	0.66	424.4	24	2.5	31.0	0.92	7.5	13.6	0.65



#	AFM abundance	Formula	Mw	AFM relative abundance	GC-MS
1	1	$C_{16}H_{10}$	202.3	2%	-
2	13	$C_{17}H_{12}$	216.3	31%	22%
3	1	$C_{17}H_{12}$	216.3	2%	-
4	8	$C_{18}H_{14}$	230.3	19%	37%
5	3	$C_{18}H_{14}$	230.3	7%	5%
6	2	$C_{18}H_{14}$	230.3	5%	5%
7	5	$C_{18}H_{14}$	230.3	12%	7%
8	3	$C_{19}H_{16}$	244.3	7%	-
9	1	$C_{19}H_{16}$	244.3	2%	3%
10	4	$C_{19}H_{16}$	244.3	10%	16%
11	1	$C_{20}H_{18}$	258.4	2%	-

Summary

- **Advantages and disadvantages of nc-AFM Imaging**
  - Advantages
    - direct physical characterization (without deduction)
    - individual molecules in a mixture (without purification)
  - Challenges
    - Representativeness
    - Sample integrity
    - Nonplanar molecules
    - Classification of structures
- **New opportunities and future directions**
  - Reactivity
    - Advanced materials
  - Properties
    - Asphaltene aggregation
  - Origins
    - Geochemistry



Acknowledgements

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- **IBM Research (Zurich)**: Leo Gross, Bruno Schuler, Shadi Fatayer
- **Princeton University:** Nan Yao, Pengcheng Chen
- **Brookhaven National Lab**: Percy Zahl

Thank you!