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
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)

**Maitotoxin**

\[ C_{164}H_{256}O_{68}S_2Na_2; \text{ MW 3626} \]

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 (~$6.2 \times 10^{13}$) isomers
- 35 fused-benzene rings has 60 sextillion (~$5.8 \times 10^{21}$) isomers

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

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

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

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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

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<th>Stable molecule</th>
<th>Reactive intermediate</th>
<th>Molecular property</th>
<th>On-Surface Reaction</th>
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Imaging of Petroleum Asphaltenes with nc-AFM

IBM-Schlumberger Study, 2015

Nc-AFM Imaging of Petroleum Asphaltenes and Heavy Oils

IBM (STM / nc-AFM)

**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

C7 asphaltenes from crude oil

C7 Asphaltenes from deposit
C7 asphaltenes (feed)  

C7 Asphaltenes after Hydroconversion (product)
Steam cracked tar C7 asphaltenes

Non-asphaltenes (Aromatic 4R+ fraction)
Molecular Structures from AFM

Representativeness of Images

Image Nonplanar Molecular Conformations

Differentiate Heteroatoms

Detection of $\beta$-H in Petroporphyrins

- Petroporphyrins have different structures
- Etio are formed from DPEP
- Presence $\beta$-H in etio indicates dealkylation

Free Radical in Asphaltene Aggregation

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


Pancake Bonding in Asphaltene Aggregation

... 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

A-240 (Ashland Oil, 1974-1998)

- Dickinson (1980)
- Seshadri (1982)
- Dickinson (1985)

M-50 (Marathon Oil, 1998 -)

- Kershaw (1993)
- Thies (91-now)

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

Understanding the Role of Methyl Groups During the Polymerization of PAHs

(a) DMPY

(b) Pyrene

(c) Vaporization curves for DMPY and DMPY (6 h)

(d) Chemical shift (ppm) for DMPY and DMPY 6 h

(e) Nuclear magnetic resonance (NMR) spectra for DMPY and DMPY 6 h

(f) Mass spectra showing monomer, dimer, and trimer products
AFM images of the product mixture

Chemical Structures from nc-AFM

(1) methyl transfer

(2) direct coupling

(3) coupling via carbon addition

(4) coupling via carbon deletion
Mechanism of Polymerization via $\pi$-radicals
## AFM and GC-MS

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Average C_{12}H_{24} 34 21 0.68 424.4 24 2.5 31.0 0.92 7.5 13.6 0.65
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
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- Brookhaven National Lab: Percy Zahl

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