Have Questions?

Type them into questions box!

“Why am I muted?”
Don’t worry. Everyone is muted except the presenter and host. Thank you and enjoy the show.

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- View the Collection
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- College to Career
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**ACS Committee on Science (COMSCI)**

“The ACS Committee on Science aims to engage the global chemistry enterprise to build a better tomorrow by identifying new frontiers of chemistry, examining the scientific basis of, and formulate public policies related to, the chemical sciences, and recognizing outstanding chemical scientists.”

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Artificial Molecular Machines: Going from Solution to Surfaces

Presentation slides are available now! The edited recording will be made available as soon as possible.  
www.acs.org/acswebinars

This ACS Webinar is co-produced with the ACS Committee on Science.

Presidential Theme – Growth, Collaboration and Advocacy

- **Chemistry is a central science.** A strong and growing global chemistry enterprise is good for the profession and its members

- **Some possible actions:**
  - Innovation, new frontiers, new applications
    - Entrepreneurship, industrial engagement
  - Sustainability and green chemistry
  - International partnership and mutual assistance
  - Collaboration

- **Need continued public and government support**
New Frontiers and Opportunities for Chemistry

- Chemistry continues to be a productive field, with new or expanded areas where future chemists and chemical engineers can find exciting opportunities
- Chemistry is also becoming multidisciplinary, and many innovations are found at the interfaces of two or more disciplines
- The goal of the Presidential – Committee on Science Webinar Series and Symposium is to highlight some of the major growth and emerging areas of chemistry, to provide the opportunity to meet the foremost leaders in these areas, and to inform our members and students as to the future directions of chemistry
- Thanks are due to Sir Fraser Stoddart, ACS Committee on Science (particularly Young-Shin Jun, Michael Morello, Martin Kociolek, and Mary Kirchhoff) and the ACS webinar team for their critical role in making these webinars possible.

ACS New Frontiers Symposium at ACS National Meeting on August 22-24

35 speakers in 9 sessions (all virtual) covering advanced materials, catalysis, nanotechnology, biotechnology, biomedical, electronics, environmental chemistry, advanced food technology, and sustainability.

The first session will start on Sunday, August 22, at 2:00pm EDT, and will run continuously until Tuesday, August 24 at 6:30pm EDT.
New Frontiers and Opportunities for Chemistry

ACS “Frontier Friday” Webinars in May and June

5/28/2021: Dr. Zhenan Bao, Stanford University, “Skin-Inspired Organic Electronics”

6/11/2021: Dr. Amy Prieto, Colorado State University, “Lithium-ion Batteries: The Road to Sustainable Energy Storage”

6/25/2021: Sir Fraser Stoddart, Northwestern University, “Artificial Molecular Machines: Going from Solution to Surfaces”

Sir Fraser Stoddart, Featured Speaker

• B.Sc. (1964) and Ph.D. (1967) Univ. of Edinburgh; NRCC postdoc at Queen’s Univ. (1967-1970)
• University of Sheffield and ICI Corporate Lab, 1970 – 1990.
• Univ. of Birmingham (1990-1997); UCLA (1997-2008) Saul Winstein Professor of Chemistry; Director of California NanoSystems Institute (2002-2008), Kavli Chair of NanoSystems Sciences; Northwestern Univ (since 2008), Board of Trustees Professor of Chemistry
• In 35 years, nearly 300 PhD students and postdocs have been trained in his labs. He has published over 1000 papers; h-index of 130. He is ranked as one of the world’s most cited chemists
• Recipients of numerous awards and recognition, including Nobel Prize in Chemistry (2016), member of NAS (2014), Fellow, American Academy of Arts and Sciences (2012), Honorary Fellow of RSC (2011), Knight Bachelor by HM Queen Elizabeth II (2006), ACS Cope Award (2008), and many others
Artificial Molecular Machines
Going from Solution to Surfaces
Featuring 2016 Nobel Laureate in Chemistry Sir Fraser Stoddart

PUMPS THROUGH THE AGES

Nanoscopic Molecular Pumps
Macroscopic Pumps
Microscopic Biomolecular Pumps

Pumps Through the Ages / Chem 2020, 6, 1954–1979
Molecular Pumps and Motors / J. Am. Chem. Soc. 2021, 143, 5569–5591
ACS FRONTIERS FRIDAY ROADMAP

Radical Chemistry | Flashing Energy Ratchets | Away-From-Equilibrium | Mechanisorption

Molecular Pumps
Mark I & II

[3]Catenane
Electric Motor

Molecular Dual & Duet
Pumps

Physisorption
Chemisorption
Molecular
Molecules
Mechanisorption

Chemisorption
Robust Dynamics
MIMs on MOFs

Precise Polyrotaxane
Synthesizer

Outlook for Molecular Nanotechnology

The Rise and Promise of Molecular Nanotopology


GETTING TO KNOW ARTIFICIAL MOLECULAR MACHINES

Big Machines  “It’s Night and Day”  Small Machines

Mechanical Approach

Hard to achieve...
...in a top-down manner...
...by mimicking...
...macroscopic machines

Chemical Approach

More likely to happen...
...in a bottom-up approach...
...by controlling...
...the free energy states...
...of collections of molecules

“Great Expectations: Can Artificial Molecular Machines Deliver on Their Promise?”
Insofar as it becomes possible to control the movement of one molecular component with respect to the other in a [2]rotaxane, the technology for building molecular machines will emerge.
UNIDIRECTIONAL THREADING AND DETHREADING OF A PSEUDOROTAXANE

Flashing Energy Ratchet  Molecular Pump Prototype

---

INTRODUCING RADICALS

---

\[
K_a = 50400 \text{ M}^{-1} \\
\Delta G = -6.4 \text{ kcal mol}^{-1}
\]

Attraction under reduced conditions
Repulsion under oxidized conditions

---

Nature Chem. 2010, 2, 42–49

J. Am. Chem. Soc. 2013, 135, 18609–18620

Nature Chem. 2010, 2, 42–49

Highly STABILIZING Radical-Radical Interactions
BIPY\(^{2+}\) Units \(\text{CBPQT}^{4+}\) Rings

REDUCTION \(\uparrow\) \(\Downarrow\) OXIDATION

BIPY\(^{2+}\) Units \(\text{CBPQT}^{4+}\) Rings
Strongly DESTABILIZING Coulombic Repulsions

Kinetics of Association and Dissociation
Can be Modulated

MOLECULAR PUMP DESIGN BLUEPRINT

SYSTEM MOVES AWAY FROM EQUILIBRIUM

Xyl

Dumbbell

First redox cycle
10 min

120 min

second redox cycle
10 min

120 min

δ / ppm

8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0

Nature Nanotechnol. 2015, 10, 547–553
PUMPING ONE FOLLOWED BY TWO RINGS

First Redox Cycle

\[
\Delta G^1 = 23.0 \text{ kcal mol}^{-1}
\]

Second Redox Cycle

\[
\Delta G^2 = 23.1 \text{ kcal mol}^{-1}
\]

Nature Nanotechnol. 2015, 10, 547–553

NEW DESIGN | EFFICIENT OPERATION

The pump’s stroke is completed within 1 h at RT and within minutes at 42 °C!!

\[ \text{CH}_2 \]

DB\(^{3+}\) + CBPQT\(^{4+}\)

Redox Cycle (Zn / NO\(^+\))

10 min

130 min

\[ \delta / \text{ppm} \]

\[ 6.0 \ 5.8 \ 5.6 \ 5.4 \ 5.2 \ 5.0 \ 1.0 \ 0.4 \ \cdots \ -1.4 \ -2.0 \]
ACS FRONTIERS FRIDAY ROADMAP

Radical Chemistry | Feashing Energy Ratchets | Away-From-Equilibrium | Mechanisorption

Molecular Pumps Mark I & II  [3]Catenane Electric Motor  Molecular Dual & Duet Pumps

MOLECULAR DUAL PUMP DESIGN

[Diagram of molecular dual pump design]

CBPQT$^{4+}$  MDP$^{8+}$

III  IPP

 PY$^+$ BIPY$^{2+}$

T

PY$^+$ BIPY$^{2+}$
CONTROLLED CAPTURE AND RELEASE PROCESS

CBPQT$^{4+}$ + NOPF$_6^-$ → [2]Rotaxane

I

Zn or
+1.4 V

NOPF$_6^-$ or
+1.4 V

Zn or
-0.7 V

IV

III

MDP$^{6+}$

2019 MOLECULAR DUAL PUMP 2019

Yunyan Qiu


Yunyan Qiu
The operation of the pump is promoted by alternating the redox potential in situ.

Bulk Electrolysis Setup & Conditions

- DP$^{18+}$/CBPQT$^{4+}$
- 50 : 1000 μM
- 0.1 M TBAPF$_6$
- Dry MeCN
- 313 K
AFTER ONE CYCLE / [3]ROTAXANE

Efficiency of conversion is 85% after one cycle!

DP1\textsuperscript{8+}\textlangle (CBPQT\textsuperscript{4+})\textrangle\textsubscript{2}

PUMP OPERATION AND COULOMETRY / 2

The operation of the pump is promoted by alternating the redox potential in situ...Coulombs Consumed / Released upon two consecutive cycles...

Oxidized State

Reduced State


AFTER TWO CYCLES / [5]ROTAXANE

Efficiency of conversion is 50% after two cycles!


ACS FRONTIERS FRIDAY ROADMAP

Radical Chemistry | Feashing Energy Ratchets | Away-From-Equilibrium | Mechanisorption

Molecular Pumps Mark I & II

[3]Catenane Electric Motor

Molecular Dual & Duet Pumps

Precise Polyrotaxane Synthesizer
TOWARD POLYCATIONIC POLYROTAXANES

Mark II Design
...a model polymeric duet pump...

\[
\begin{align*}
M_n & 2,000 \\
\text{Cu(MeCN)}_4\text{PF}_6 & > 50\% \\
\text{TBTA} / \text{Me}_2\text{CO} &
\end{align*}
\]

\[n = 50\]

\[\text{H NMR} \quad 500 \text{ MHz} \quad \text{CD}_3\text{COCD}_3 \quad 298 \text{ K}\]

Duet Pump DP2\textsuperscript{6+}

SEQUENTIAL CHEMICAL SYNTHESIS OF POLYROTAXANES

Integration
2 Rings : 1 DB [3]Rotaxane

Integration
4 Rings : 1 DB [5]Rotaxane

Integration
6 Rings : 1 DB [7]Rotaxane

Upfield Shift
WHAT MIGHT BE POSSIBLE?

Rings  2  4  6  8  10  12
+ve Charge  8  16  24  32  40  48

Stationary  48 Movable Charges  Stationary Charges

52 Overall

HAVE WE A NEW WAY TO MAKE ALL-ORGANIC BATTERIES?

PEG 5000 / TWO REDOX CYCLES

Repeating Controlled Potential Coulometry

PolyDB6+/ CBPQT1+
1 eq : 10 eq
0.05 M TBAPF₆
dry MeCN
Room Temp.

Reduction (-0.7 V)
Oxidation (+0.7 V)
2 Redox Cycles

[5]Rotaxane DB + 4 Rings

1H NMR
500 MHz
CD₃CN
298 K
PEG 5000 / FOUR AND SIX REDOX CYCLES

[9] Rotaxane DB + 8 Rings

\[ \text{PEG 5000 / FOUR AND SIX REDOX CYCLES} \]

\[ \text{[9] Rotaxane DB + 8 Rings} \]

\[ \text{PEG 5000 / FOUR AND SIX REDOX CYCLES} \]

[13] Rotaxane DB + 12 Rings

\[ \text{[13] Rotaxane DB + 12 Rings} \]

\[ \text{PEG 5000 / EIGHT AND TEN REDOX CYCLES} \]

[17] Rotaxane DB + 16 Rings

\[ \text{[17] Rotaxane DB + 16 Rings} \]

\[ \text{PEG 5000 / EIGHT AND TEN REDOX CYCLES} \]

[21] Rotaxane DB + 20 Rings

\[ \text{[21] Rotaxane DB + 20 Rings} \]
Repeating Controlled Potential Coulometry

PolyDB^{2+} / CBPQT^{4+}

1 eq : 72 eq
0.05 M TBAPF_6
dry MeCN
Room Temp.

[49] Rotaxane DB + 48 Rings

6 Redox Cycles

\[ \text{CH}_2' / 10' \]

\( \alpha'6'/9' \beta'7'/8' \)

(52) (52)

\( \delta / ppm \)

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5 10.0

1H NMR
500 MHz
CD_3CN
298 K

TAKE HOME MESSAGES SO FAR

The controlled synthesis of polyrotaxanes through an autonomous electrochemical approach using artificial molecular pumps

The installment of up to 20 rings onto a linear PEG polymer (MW 5000) with a total of 86 positive charges!!!

The installment of up to 80 rings onto a star PEG polymer (MW 20000) with a total of 344 positive charges!!!

HAVE WE A NEW WAY TO MAKE ALL-ORGANIC BATTERIES?
MECHANICAL BONDING-INDUCED SITE-SELECTIVE FUNCTIONALIZATION

Radical Chemistry | Flashing Energy Ratchets | Away-From-Equilibrium | Mechanisorption

Molecular Pumps Mark I & II → [3]Catenane Electric Motor → Molecular Dual & Duet Pumps

Physisorption Chemisorption Mechanisorption

Robust Dynamics MIMs on MOFs → Precise Polyrotaxane Synthesizer

Outlook for Molecular Nanotechnology
Kinetics control AMMs | AMPs

- Kinetics provide the foundation for developing AMMs | AMPs.
- Kinetics are important in creating and maintaining non-equilibrium states.
- Kinetics have led to the development of pumping cassettes in AMPs.

Radicals provide the Driving Force

- Radical-pairing is a powerful way of driving molecular assembly and motion.
- Radical-pairing provides us with powerful forces to module energy barriers.
- Radical-pairing has led to the design and use of pumping cassettes.

Pumping Cassettes create Far-From-Equilibrium System

- Externally driven AMMs | AMPs operate by using energy ratchets.
- Energy ratchets produce away-from-equilibrium AMMs | AMPs.
- AMPs when attached to surfaces can produce non-equilibrium systems.

THE RADICAL CHEMISTS

Albert Fahrenbach

Cristian Pezzato

Hao Li

Chuyang Cheng

Jonathan Barnes

Paul McGonigal

Marco Frasconi

Ali Trabolsi

Minh Nguyen

Yuping Wang

Melissa Dumartin

Kang Cai

Mark Lipke

Mechanisorption

AMMs ≡ Artificial Molecular Machines  AMPs ≡ Artificial Molecular Pumps

Radical-Pairing-Induced Molecular Assembly and Motion  A Radical Departure For Supramolecular Chemistry

THE RADICAL SCIENTISTS

Bo Song
Yunyan Qiu
Damien Sluysmans
Ommid Anamimoghadam
Jim Seale
Qinghui Guo
Hongliang Chen
Yang Jiao
Liang Feng
Yuanning Feng
Long Zhang

Radical-Pairing-Induced Molecular Assembly and Motion

A Radical Departure For Supramolecular Chemistry

ACS FRONTIERS FRIDAY ROADMAP

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Robust Dynamics
MIMs on MOFs
Precise Polyrotaxane Synthesizer

Outlook for Molecular Nanotechnology
The Rise and Promise of Molecular Nanotopology


CROP OF LOCKDOWN REVIEWS

Pumps through the Ages
Chem 2020, 6, 1952–1977

Dawning of the Age of Molecular Nanotopology
Nano Lett. 2020, 20, 5597–5600

Cyclodextrin Metal-Organic Frameworks and Their Applications

Emergent Behavior in Nanoconfined Molecular Containers
Chem 2021, 7, 919–947

Molecular Triangles: A New Class of Macroycles

Molecular Pumps and Motors
J. Am. Chem. Soc. 2021, 143, 5569–5591

Aromatic Hydrocarbon Belts
Nat. Chem. 2021, 13, 402–419

The Rise and Promise of Molecular Nanotopology
CCS Chem. 2021, 3, 1542–1572

Radical-Pairing-Induced Molecular Assembly and Motion

From Molecular to Supramolecular Electronics

Coming Soon

Chiroptical Properties of Mechanically Interlocked Molecules
Israel J. Chem.

Whither Second-Sphere Coordination?
CCS Chem.
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Artificial Molecular Machines: Going from Solution to Surfaces

Featuring 2016 Nobel Laureate in Chemistry Sir Fraser Stoddart

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