Supramolecular Chemistry of Nanomaterials

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Lecture 5 – Molecular Switches

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Synthesis of rotaxanes/catenanes

Pictorial representation of the self-assembly of pseudorotaxanes based on

- (a) CT and C-H⋯O hydrogen-bonding interactions and
- (b) N⁺-H⋯O hydrogen-bonding interactions. A possible route toward the synthesis of rotaxanes and catenanes is also indicated.

“Crossovers” - Interlocking

- (a) A simple cross-over gives (i) a catenane upon two ring closures or (ii) a rotaxane upon one ring closure and blocking
- (b) a fused turn can be used for macrobicycle syntheses
- (c) use of two anchors and ditopic turns to form a trefoil knot
- (d) a composite knot from two two-anchor templates
- (e) an oligocatenane resulting from multiple cross-overs on the same anchor.
Hydrogen Bonding in Catenane Formation

- Leigh's simple and flexible synthesis of amide [2]-catenanes.
Magic Rings

Thermodynamically controlled self-assembly / disassembly of benzylic amide macrocycles and [2]catenanes under RORCM (>95% yield).

*J. Am. Chem. Soc.*, 121 (7), 1599 -1600, 1999
Circumrotation

Solvent effects and structural modifications can induce large variations in the rate of circumrotation of benzylic amide catenanes (which can range from the submicro-second time scale (e.g., thiophene catenane 3 at elevated temperatures in polar solvents) to many hours to achieve a single circum-rotation (e.g., pyridine catenane 2 at low temperatures in nonpolar solvents)) allowing tremendous control over the kinetics of a mechanically interlocked molecular system.
**Template Directed Catenane Synthesis**

- Template-directed synthesis of the [2]catenane \(1 \cdot 4\text{PF}_6\). The key step is the spontaneous threading through BPP34C10 of the tricationic intermediate, formed when \(2 \cdot 2\text{PF}_6\) reacts with \(p\)-xylylene dibromide. This supramolecular assistance is followed by covalent modification and counterion exchange to give \(1 \cdot 4\text{PF}_6\).
Catenane Kinetics

Three different degenerate co-conformational processes observed in temperature-dependent $^1$H NMR spectra of the [2]catenane $1^{4+}$:

(a) circumrotation of CBPQT$^{4+}$ through BPP34C10;
(b) circumrotation of BPP34C10 through CBPQT$^{4+}$; and
(c) rocking of BPP34C10 within CBPQT$^{4+}$. The rates of these processes at room temperature are shown.

First Molecular Shuttle

• The first molecular shuttle

**Molecular Switches - Rotaxanes**

A chemically controllable molecular shuttle: the ring can be switched between the two "stations" of the dumbbell component by base/acid "inputs".

Logic Operations – Rotaxanes and Catenanes

Schematic representations of the mechanical movements relating two states (0 and 1) in
(a) pseudorotaxanes
(b) rotaxanes
(c) Catenanes
the stimulus ($S$) can be chemical or electro-chemical energy, or it can be light.

Molecular Switch - All Optical Processing

UV light, visible light, and $\text{H}^+$ induce the interconversion between the three states SP, ME, and MEH. Absorption spectra of SP recorded after (a in Lower) and before (b in Lower) irradiation at 254 nm for 5 min.

*PNAS* 2002, 99, 4941–4944
An optical signal (yellow arrows) travels from a light source to a detector after passing through a quartz cell containing a solution of SP. The intensity of the optical output ($O$) switches between low and high values as the optical input ($I$) is turned on and off. This signal transduction behavior is equivalent to a NOT operation.

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\[ \begin{array}{c|c} 
0 & 1 \\
1 & 0 \\
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PNAS 2002, 99, 4941–4944
An optical signal (yellow arrows) travels from a light source to a detector after passing through two quartz cells containing a solution of SP. The intensity of the optical output ($O$) switches between low and high values as the two optical inputs ($I_1$ and $I_2$) are turned on and off. This signal transduction behavior is equivalent to a two-input NOR operation.

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Logic Function - Pseudorotaxane

Schematic representation of the unthreading/rethreading pattern of pseudorotaxane 1, which corresponds to an XOR logic function.

\[ 1 + B \xrightarrow{\text{unthreading}} 1 \xrightarrow{\text{"locked" thread}} 3 \xrightarrow{\text{"locked" ring}} 2 - B_2 \xrightarrow{+ H^+} 1 + B\]

\[ \begin{align*}
B & \equiv (\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N} \\
H^+ & \equiv \text{CF}_3\text{SO}_3\text{H}
\end{align*} \]

Molecular Switch – AND Logic Gate

Switching processes of catenane $3H^{5+}$. Starting from catenane $3^{4+}$, the position of the macrocyclic polyether switches under acid/base and redox inputs (AND logic).

Light Driven Dethreading

Controllable dethreading/rethreading of a pseudorotaxane based on a trans-cis photoisomerization reaction (80% complexed species).

Light-driven dethreading of pseudorotaxanes by excitation of a photosensitizer P as (a) an external reactant, (b) a stopper in the wire-type component, and (c) a component of the macrocyclic ring.

Molecular Level Plug

A molecular-level plug/socket device: "plug in/plug out" is acid/base controlled, and photoinduced energy transfer takes place in the "plug in" state (CH₂Cl₂, room temperature).

**Photocontrollable Abacus**

Rotaxane \(7^{6+}\): photoinduced abacus-like movement of macrocycle \(R\) between the two stations \(A_1\) and \(A_2\).

Macrocycle \(R\)

Dumbbell component \((P, A_1, A_2, S, T)\):

(i) a photoactive Ru(II) polypyridine complex \((P)\) as a stopper
(ii) a 4,4\(^\prime\)-bipyridinium unit \((A_1)\) and a 3,3\(^\prime\)-dimethyl-4,4\(^\prime\)-bipyridinium unit \((A_2)\) as electron-accepting stations
(iii) a \(p\)-terphenyl-type ring system as a rigid spacer \((S)\)
(iv) a tetraarylmethane group as the second stopper \((T)\).

The stable translational isomer: \(R\) encircles the better electron-acceptor \(A_1\).

The intramolecular mechanism, which implies the conversion of light energy into mechanical energy without generating waste products, is based on the four operations

(a) **Destabilization of the stable translational isomer**: light excitation of \(P\) (step 1) is followed by the transfer of an electron to the \(A_1\) station (step 2), which is encircled by ring \(R\); such a photoinduced electron-transfer process, which competes with the intrinsic excited-state decay (step 3), "deactivates" the \(A_1\) station.

(b) **Ring displacement**: the ring movement from \(A_1^-\) to \(A_2\) (step 4) has to compete with the back-electron-transfer process from \(A_1^-\) (still encircled by \(R\)) to the oxidized photoactive unit \(P^+\) (step 5).

(c) **Electronic reset**: the back-electron-transfer process from the "free" reduced station \(A_1^-\) to \(P^+\) (step 6) restores the electron-acceptor power to the \(A_1\) station.

(d) **Nuclear reset**: as a consequence of the electronic reset, back movement of the ring from \(A_2\) to \(A_1\) occurs (step 7).

Directionality

A three-station rotaxane in which the direction of ring displacement is determined by the selected input.

The $A_1$ and $A_2$ stations can be a 4,4'-bipyridinium and a 3,3'-dimethyl-4,4'-bipyridinium unit, respectively. Depending on the sequence in which the three stations are assembled, a suitable macrocyclicpolyether component can be moved along the thread according to predetermined patterns.
A rotaxane carrier powered by electrochemical inputs designed to perform (a) transport of an amine, (b) formation of an exciplex, and (c) stretching of a molecular spring.
Rotaxane as Molecular Gears

A rotacatenane designed to couple linear and rotary motions under acid/base stimuli.

Device Architectures

Two possible device architectures that tile in two dimensions and so may potentially be fabricated through chemical techniques.

(a) Three-terminal devices (transistors) arranged in a hexagonal lattice

(b) two-terminal devices arranged in a square lattice or crossbar structure.

G, S, and D represent the gate, source, and drain terminals of a field effect transistor; M stands for a molecule.

Molecular Switches - Catenanes

Electrochemically controlled movements upon one-electron oxidation/reduction of a TTF unit in a catenane containing a nonsymmetric ring.

Mechanomechanical Mechanism

$[A^+] \rightarrow [B^+] \rightarrow [B^0] \rightarrow [AB^\#] \rightarrow [A^0] \rightarrow [A^+]$

$+2 \text{ V}$

Net Oxidizing

$0$

Net Reducing

$-2 \text{ V}$

**Electroswitchable Catenane**

(a) Structural formula of the [2]catenane $3^{4+}$.

(b) Ball-and-stick representation of the catenane's solid-state structure showing the TTF unit of the crown ether residing inside the CBPQT$^{4+}$ component.

(c) Space-filling representation of its solid-state superstructure.

UV-vis spectroscopic evidence for the redox switching of the [2]catenane $3^{4+}$. (a) Spectrum of the catenane prior to addition of (b) 1 equiv of Fe(ClO$_4$)$_3$ followed by (c) a second equivalent of Fe(ClO$_4$)$_3$. Oxidation is reversed on addition of 2 equiv of ascorbic acid.
Redox Switch Device Construction

Construction of a molecular-based device.

(a) A smooth silicon substrate.

(b) A series of parallel polysilicon wires etched onto the substrate photolithographically.

(c) Following deposition of the catenane monolayer onto the wafer by a LB procedure.

(d) The result when titanium vapor is condensed through a shadow mask, depositing a second layer of wires aligned perpendicularly with respect to the first.
Redox Switch SAM

Schematic representation of the monolayer of $1^{4+} \cdot 4\text{DMPA}$ at the air-water interface. Note the intermolecular $\pi-\pi$ stacking interactions between the catenane tetracations.

Redox Switch LB Behaviour

(a) \(\pi-A\) isotherms of monolayers of the [3]catenane \(3^{4+}\) and its oxidized derivative \(3^{6+}\) anchored with 4 and 6 equiv of DMPA\(^-\) anions, respectively.

(b) Schematic representation of the monolayer of \(3\cdot4\)DMPA stabilized by extensive \(\pi-\pi\) interactions.

(c) Schematic depiction of the first stable monolayer formed by \(3\cdot6\)DMPA. The dicationic TTF units show no affinity for the neighboring catenane hexacations, and so the six DMPA\(^-\) anions fill the voids in the monolayer.

**Redox Switch SAM - Hysteresis**

(a) Hysteresis curve associated with a conventional magnetic memory bit.
(b) Voltage profile used in the acquisition of
(c) the remnant molecular signature of a device incorporating the switchable [2]catenane 3^{4+}.

The device response was monitored at 0.1 V (b). Robust and significant hysteresis (c) was observed in the bistable [2]catenane, but not in the control devices, indicating that the bistable [2]catenane device is, in fact, a solid-state molecular switch. It exhibited a "read" current difference between the open and closed states of approximately a factor of 3, a "close" voltage of about 1.8 V, and an "open" voltage of about -1.0 V. The bistable [2]catenane device was fairly stable. It was intermittently cycled many times over a two-month period before it showed signs of failure.

Mechanochemical Mechanism

Proposed mechanochemical mechanism for the operation of the device fabricated from the bistable [2]catenane $3^{4+}$. Co-conformation $[A^0]$ is the "switch open" state and co-conformation $[B^0]$ the "switch closed" state of the device. When $3^{4+}$ is oxidized, the TTF unit is ionized in state $[A^+]$ and experiences a Coulomb repulsion inside the CBPQT$^{4+}$ component, resulting in circumrotation of the crown ether and formation of co-conformation $[B^+]$. When the voltage is reduced to near-zero bias, the TTF$^+$ unit is reduced to give co-conformation $[B^0]$, which does not return to co-conformation $[A^0]$ by further circumrotation of the crown ether ring via state $[AB^\#]$ until the cyclophane component is reduced.