The Switch That Wants To Be a Machine

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- Dendrimers
- Si Quantum Dots
- Water Splitting
- Molecular Logic
- CdSe Quantum Dots
- Molecular Machines and Devices
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- Molecular Machines and Devices

- IMM: Vittorio Morandi, Luca Ortolani (QDs)
- ISOF: Giovanna Barbarella, Francesca Di Maria (Supramolecular Systems)
Rotaxanes: “Molecules in which a ring encloses another, rod-like molecule having end groups too large to pass through the ring opening, and thus holds the rod-like molecule in position without covalent bonding.”

IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book").
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Pseudorotaxanes: Rotaxane-like molecular assembly in which the threading component(s) has(have) ends small enough to permit threading or dethreading of the macrocyclic molecule(s).

Andrey Yerin, Edward S. Wilks, Gerard P. Moss and Akira Harada Nomenclature for rotaxanes and pseudorotaxanes (IUPAC Recommendations 2008)
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The Axle \((E,E\text{-}1\text{H}\cdot\text{PF}_6)\)

Made of two terminal azobenzene units and a central ammonium station, which is a recognition site for DB24C8.
The Beginnings…

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Made of two terminal azobenzene units and a central ammonium station, which is a recognition site for DB24C8.

The Ring \((DB24C8)\)

Dibenzo[24]crown-8
The Pseudorotaxane

\[ \text{H NMR (400 MHz, CD}_3\text{CN, 304 K)} \]

5mM in both components.

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Dibenzo[24]crown-8

The Pseudorotaxane

\[ {^1}\text{H NMR (400 MHz, CD}_3\text{CN, 304 K)} \]

5mM in both components.
The azobenzene units of the axle-molecule can be almost quantitatively photoisomerized from trans to cis by means of UV-light irradiation. The complete cis > trans thermal conversion takes place in ca. 4 weeks at 20°C.
Slow down
Slow down
Slow down

$400 \text{ MHz, CD}_3\text{CN, 304 K}$

\[ k(\text{in})_{zz} = 2.9 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1} \]

\[ k(\text{out})_{zz} = 7.2 \times 10^{-5} \text{ s}^{-1} \]
Slow down

\[ \text{Concentration (mM)} \]

\[ 400 \text{ MHz, CD}_3\text{CN, 304 K} \]

\[ k(\text{in})_{ZZ} = 2.9 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1} \]

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Pseudorotaxane and Rotaxane

\[ k(\text{in})_{EE} = 37 \text{ M}^{-1}\text{s}^{-1} \]

\[ K_{EE} = 820 \text{ M}^{-1} \]

\[ k(\text{out})_{EE} = 4.5 \times 10^{-2} \text{ s}^{-1} \]
Pseudorotaxane and Rotaxane

$k_{\text{in}}^{\text{EE}}$ 37 M$^{-1}$s$^{-1}$

$K_{\text{EE}}$ 820 M$^{-1}$

$k_{\text{out}}^{\text{EE}}$ 4.5 x 10$^{-2}$ s$^{-1}$

$h_\nu$ or $\Delta$

$k_{\text{in}}^{\text{ZZ}}$ 2.9 x 10$^{-3}$ M$^{-1}$s$^{-1}$

$K_{\text{ZZ}}$ 400 M$^{-1}$

$k_{\text{out}}^{\text{ZZ}}$ 7.2 x 10$^{-5}$ s$^{-1}$

$h_\nu$ or $\Delta$
Photoisomerization of the azobenzene ends of the axle destabilizes the complex and slows down the threading/dethreading processes: both the energy minimum and the energy barriers are raised.
The opera-

We have designed, synthe-

Qualitative observations indicate

Moreover, we show that a change in

The structural formulas of the molecular components,

Keywords:

Figure 1: Schematic representation of the pseudorotaxane system. The energy barriers associated with the threading–dethreading process are shown. The transition states and ground states are indicated by dashed and solid lines, respectively. The energy barriers are given by $\Delta G^\#(\text{in})_{EE}$ and $\Delta G^\#(\text{out})_{EE}$ for the EE isomer, and $\Delta G^\#(\text{in})_{ZZ}$ and $\Delta G^\#(\text{out})_{ZZ}$ for the ZZ isomer. The equilibrium constants are $K_{eq}^\#(\text{in})_{EE}$ and $K_{eq}^\#(\text{out})_{EE}$ for the EE isomer, and $K_{eq}^\#(\text{in})_{ZZ}$ and $K_{eq}^\#(\text{out})_{ZZ}$ for the ZZ isomer. The process occurs within seconds in acetoni-

dedicated to Professor Luigi Fabbrizzi, recipient of the 2010 International Izatt–Christensen Award in Macrocyclic Chemistry

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The End
A New Beginning

\[ \Delta G^\ddagger \text{threading EE} \]

\[ \Delta G_{EE} \]

\[ \Delta G^\ddagger \text{threading ZZ} \]

\[ \Delta G_{ZZ} \]

\[ h\nu \]

\[ h\nu' \text{ or } \Delta \]
Directionally Controlled Threading/Dethreading

Gate unlocking
Reset

Fast
Slow

\[ \Delta G^\ddagger_{E-azo} \]

\[ \Delta G^\ddagger_P \]

\[ h\nu' \text{ or } \Delta \]

Photochemical gate locking

\[ h\nu \]

Fast
Slow

\[ \Delta G^\ddagger_{Z-azo} \]

\[ \Delta G^\ddagger_P \]
Directionally Controlled Threading/Dethreading

**Gate unlocking**
- **Reset**
- $h\nu'$ or $\Delta$

**Photochemical gate locking**
- $h\nu$

**Directionally controlled threading**

**Directionally controlled dethreading**
- Fast
- Slow

$$\Delta G^\ddagger_{E-azo}$$

$$\Delta G^\ddagger_P$$

$$\Delta G^\ddagger_{Z-azo}$$
Standing On The Shoulders of Giants


\[
\text{Rate} = 1.3 \times 10^{-1} \text{ M}^{-1}\text{s}^{-1}
\]
Standing On The Shoulders of Giants

Kinetic and thermodynamic data for the self-assembly of the investigated complexes in CD$_3$CN at 298 K.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$K$ (M$^{-1}$)</th>
<th>$-\Delta G^\circ$ (kcal mol$^{-1}$)</th>
<th>$k_{\text{in}}$ (M$^{-1}$s$^{-1}$)</th>
<th>$-\Delta G^#_{\text{in}}$ (kcal mol$^{-1}$)</th>
<th>$k_{\text{out}}$ (s$^{-1}$)</th>
<th>$-\Delta G^#_{\text{out}}$ (kcal mol$^{-1}$)</th>
<th>$t_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[EE-1H\subset R][PF_6]$</td>
<td>820</td>
<td>3.9</td>
<td>37</td>
<td>15</td>
<td>4.5 x 10$^{-2}$</td>
<td>19.3</td>
<td>15.4 s</td>
</tr>
<tr>
<td>$[ZZ-1H\subset R][PF_6]$</td>
<td>400</td>
<td>3.5</td>
<td>2.9 x 10$^{-3}$</td>
<td>20.9</td>
<td>7.2 x 10$^{-6}$</td>
<td>24.5</td>
<td>27 h</td>
</tr>
<tr>
<td>$[2H\subset R][PF_6]$</td>
<td>~30</td>
<td>2</td>
<td>1.3 x 10$^{-1}$</td>
<td>18.6</td>
<td>4.4 x 10$^{-3}$</td>
<td>20.7</td>
<td>2.6 min</td>
</tr>
<tr>
<td>$[E-3H\subset R][PF_6]$</td>
<td>225</td>
<td>3.2</td>
<td>22</td>
<td>15.6</td>
<td>0.1</td>
<td>18.8</td>
<td>6.3 s</td>
</tr>
<tr>
<td>$[Z-3H\subset R][PF_6]$</td>
<td>230</td>
<td>3.2</td>
<td>5.1 x 10$^{-2}$</td>
<td>19.2</td>
<td>2.6 x 10$^{-4}$</td>
<td>22.3</td>
<td>46 min</td>
</tr>
</tbody>
</table>
Directionally Controlled Transit

Toward a Molecular Pump

Directionally controlled threading

Gate unlocking
Reset

hν' or Δ

Photochemical gate locking

hν

Directionally controlled dethreading

ΔG‡

E

E

E

E

IN
Toward a Molecular Pump

Gate unlocking

Reset

$\nu$ or $\Delta$

Directionally controlled threading

Photochemical gate locking

hv

Directionally controlled dethreading

Slow

Fast

$\Delta G^+$

Z-azo

$\Delta G^+$

P
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