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Energetically Demanding Transport in a Supramolecular Assembly

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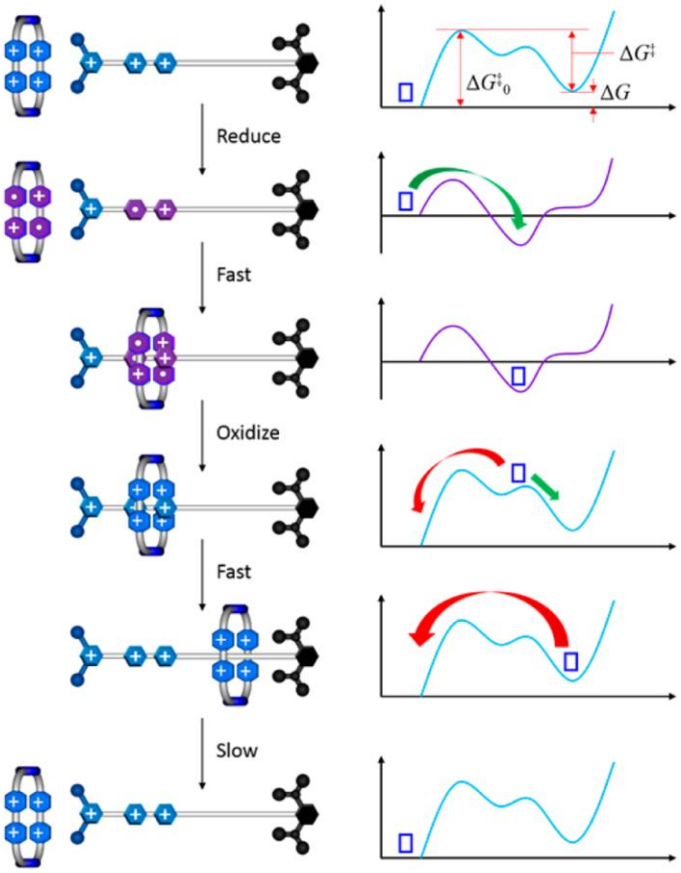


Figure 1. Graphical representation of redox-active pumping mechanism of [2]pseudorotaxane and corresponding energy profile.

Who are the corresponding authors and what are their research areas?

Stoddart's group is actively working on molecular recognition and self-assembly processes of functionalized and mechanized molecules. Their research interests spread over supramolecular chemistry, molecular machines, energy storage, etc.

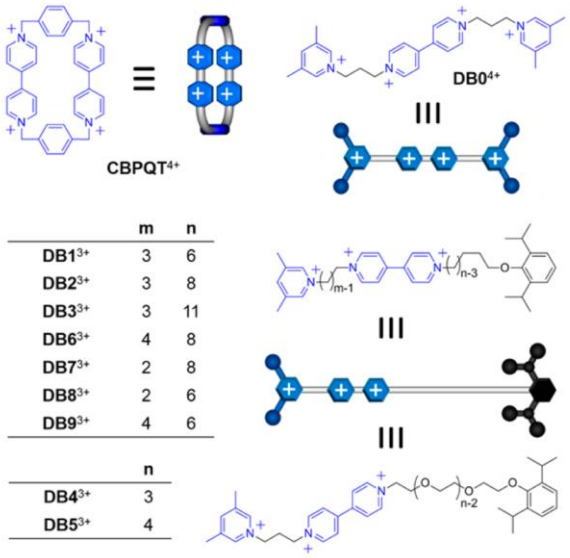
What is the main claim of the article?

Authors showed that they could design and synthesize artificial molecular pumps that are capable of generating high energy, metastable state under redox changes. They illustrated the kinetics and energy profiles that demonstrate the formation of [2]pseudorotaxane away from equilibrium. The fine-tuning of

chemical structure and energetics of supramolecular pumps allow them to drive a ring over the dumbbell in one direction. Interestingly, they generate [2]pseudorotaxane with a trapped ring over dumbbell without any stabilizing interaction.

How is it demonstrated?

Authors synthesized a homologous series of dumbbells with 4,4′-bipyridinium ($BIPY^{2+}$) units as radical recognition sites for cyclobis(paraquat-p-phenylene) ($CBPQT^{4+}$). A 3,5-dimethylpyridinium (PY^{+}) unit is attached to one side of the BIPY2+ unit by a short oligomethylene chain, while a bulky stopper is attached to the other side by a longer chain. DB1-9^{3+} are the series of dumbbells while $DB0^{4+}$ is symmetrical derivative act as a model compound to confirm the threading of ring over dumbbell under reduction by radical-radical interaction (Figure 2).



	m	n
$DB1^{3+}$	3	6
$DB2^{3+}$	3	8
$DB3^{3+}$	3	11
$DB6^{3+}$	4	8
$DB7^{3+}$	2	8
$DB8^{3+}$	2	6
$DB9^{3+}$	4	6

	n
$DB4^{3+}$	3
$DB5^{3+}$	4

Figure 2. Structural formulas and pictorial representations of components of artificial pumps.

The authors confirmed the formation of a ring-dumbbell complex with model compound $DB0^{4+}$ under the reducing condition using UV-vis spectroscopy and X-ray diffractometry. Further, they developed [2]pseudorataxane bearing $CBPQT^{4+}$ and DB1-9^{3+} under the cycle of reduction and oxidation using activated zinc and tris(4-bromophenyl)aminium hexachloridoantimonate respectively. The pumping and dethreading of ring over the dumbbell was monitored using 1H NMR spectroscopy. The dethreading follows first-order kinetics and determined the rate constant and activation energy based on NMR data. For instance, it is calculated as $k = (8.4 \pm 0.6) \times 10^{-5}\ s^{-1}$ and $\Delta G^{\ddagger} = 21.5$ kcal mol^{-1} for [2]pseudorotaxane with $DB1^{3+}$.

What are the typical experimental conditions?

The pumping and dethreading experiments are mainly monitored by 1H NMR. The equimolar concentration (~1.3mM) of the dumbbell and ring in CD_3CN (~0.75mL) and the Zn dust is added to the solution in an inert atmosphere. ~8mM of tris(4-bromophenyl)aminium hexachloridoantimonate is added

to the purple-colored solution at 0^0C after 5 min of stirring and filtration of Zn dust. The adduct is further characterized using 1H NMR.

Which are the key related papers?

1. Trabolsi, A., Khashab, N., Fahrenbach, A. *et al.* Radically enhanced molecular recognition. *Nature Chem* **2,** 42–49 (2010).
2. Cai, K., Zhang, L., Astumian, R.D. *et al.* Radical-pairing-induced molecular assembly and motion. *Nat Rev Chem* **5,** 447–465 (2021).

Additional comments, including additional elements of interest

The paper is very well-described and as a reader, it is easier to follow and understand even if you are new to this topic. Trapping a molecule at a high energy state without any stabilizing interaction is exciting. Moreover, the detailed DFT analysis by considering different interactions provided an insight into the energetics and mechanism of similar kinds of systems.