Ahmad Bachir, 08/03/2022

Feng, Liang & Qiu, Yunyan & Guo, Qing-Hui & Chen, Zhijie & Seale, James & He, Kun & Wu, Huang & Feng, Yuanning & Farha, Omar & Astumian, Raymond & Stoddart, J.. **(2021)**. *Active mechanisorption driven by pumping cassettes. Science. 374 (6572), 1215-1221. DOI: 10.1126/science.abk1391.*

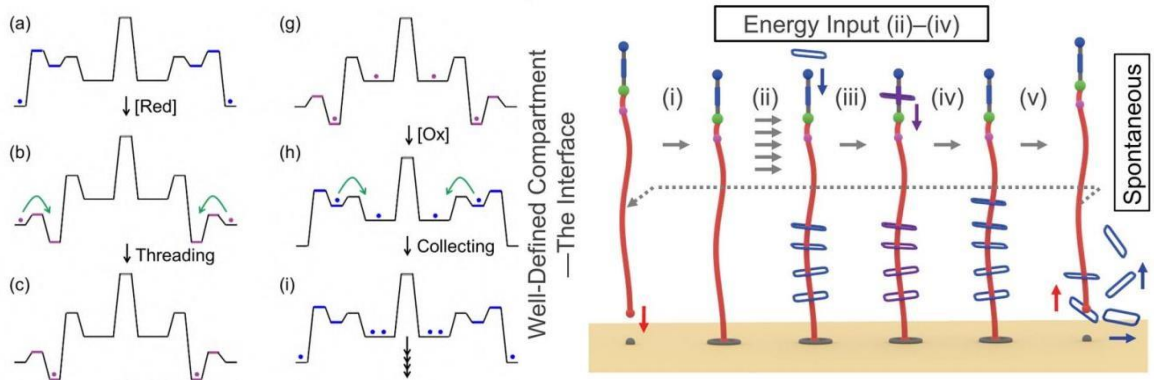

Figure 1: *A) Read on right figure, **i**=grafting, **ii, iii** and **iv**= repeated oxidative-reductive induced threading of bluebox macrocycle and **v**= acid triggering induced tail detachment.*

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

J. Fraser Stoddart, his most notable research area leverages the mechanical bond, which led him to share the Noblel Prize 2016 for Molecular Machines. He has pioneered the development of the use of molecular recognition and self-assembly processes in template-directed protocols for the syntheses of two-state mechanically interlocked molecules. A very well-known molecule synthesized and handled intensively by his work, is the "Blue Box" a redox-active macrocycle that becomes blue upon reduction, and was often colored in blue in talks and papers, to illustrate the strongly electron deficient properties.

What is the main claim of the article?

A demonstration of an out of equilibrium mechanical adsorption driven by redox switching, where a direct contribution from physical or chemical interaction does not play a major role to induce this phenomenon.

How is it demonstrated?

Mainly ^{1}H NMR 600 and ^{13}C MAS (solid state) NMR analysis were used to prove the mechanical adsorption concept. IR is used to verify the success of a click reaction during the attachment of the tail on the metal organic framework MOF.

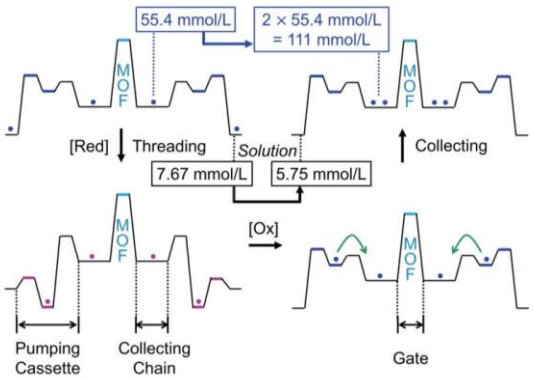

Figure 2: Scheme illustrate how the concentration of rings increased from 55.4 mmol/L to 111 mmol/L at the surface after the second redox cycle of threading mechanism.

What are the typical experimental conditions?

The mechanical absorption has been detected at room temperature in deuterated solvent composed of completely deuterated sulfuric acid and dimethyl sulfoxide. The chemical system was subjected recursively for five times to oxidative (Ferrocenium hexafluorophosphate) – reductive (bis(cyclopentadienyl)cobalt(II) (Cp2Co) solution (13 mg/mL)) medium, affording a 90% threading efficiency after the second cycle into highly energetic kinetic trapped state.

Which are the key related papers?

Odell, B., Reddington, M. V., Slawin, A. M. Z., Spencer, N., Stoddart, J. F., & Williams, D. J. (1988). Cyclobis(paraquat-p-phenylene). A Tetracationic Multipurpose Receptor. *Angewandte Chemie International Edition in English*, *27*(11), 1547-1550.

C. J. Bruns and J. F. Stoddart, The Nature of the Mechanical Bond: From Molecules to Machines, Wiley, New Jersey, 2016.

C. Pezzato, C. Cheng, J. F. Stoddart, R. D. Astumian, Chem. Soc. Rev. 46, 5491–5507 (2017). (review discussing also the exploited pump module)

Additional comments, including additional elements of interest

Conceptual: Richard Feynman said once a day during his talk, there is a lot to investigate at the nanoscale. Indeed, nanoscale chemical system always draws attention of scientist on what can be realized inside, this work has two brilliant advantages in my opinion, one is related to the fact that such proof seeks to reveal more insights about the fundamental concept of mechanical adsorption in a controlled way, and the other is dedicated more to many candidates applications related to energy and chemical storage, smart and controlled chemical system.

Experimental: Solid MOF (Solid where the blue macrocycle was threading on the surface) has been digested by mixture of sulfuric acid and dimethyl sulfoxide. However, the desorption was accomplished by adding hydrochloric acid solution. The axle attached to the MOF is stable in sulfuric acid but not in hydrochloric acid!

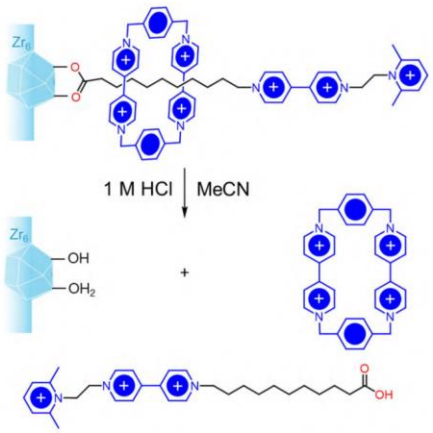

Figure 3: Desorption mechanism with 1M HCl in MeCN.