

A molecular shuttle that operates inside a metal–organic framework

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Nat. Chem. **2015**, DOI: 10.1038/NCHEM.2258

1. Introduction

- Molecular Shuttle: An interlocked molecular assembly in which a macrocyclic ring is able to move back and forth between two recognition sites.¹
- Mechanically Interlocked Molecules (MIMs): Mimic the motion of macroscopic switches and machines and prototype for the construction of a variety of more sophisticated molecular assemblies.

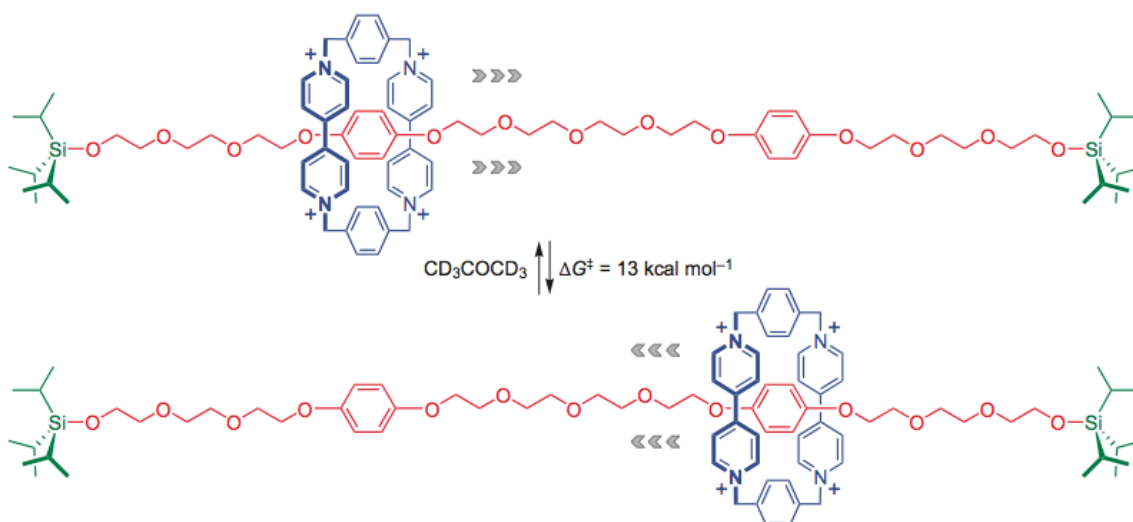


Fig. 1. Molecular shuttle operating in acetone solution. The electron-poor cyclophane macrocycle (blue) moves to and fro (shuttles) between the two electron-rich hydroquinol rings (red), but is prevented from sliding off the polyether chain because of the large size of the trisopropylsilyl groups (green) that act as stoppers.

- Problem:

No method to arrange ‘smart’ molecules in patterns or in solid phases

=> Difficult to organize and monitor the movement.²

- This work:

A new Metal-Organic Frameworks (MOFs): **UWDM-4**, which contains a shuttle between two linking struts, is designed to study the dynamic behavior of shuttle.

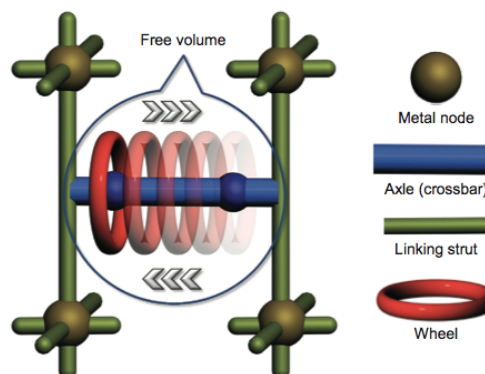
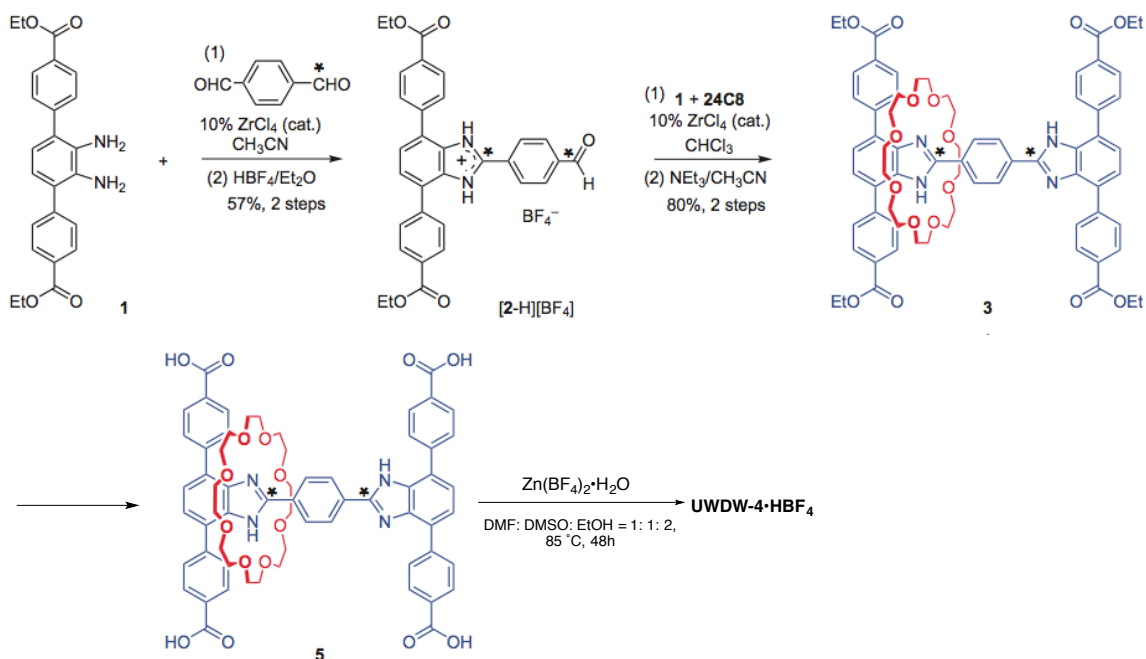


Fig. 2. Design of MOF.

2. Results and Discussion

2.1 Designing of MOFs

Scheme 1. Synthetic route of MOFs.



- Key of the design is the cross-bar, which separate the carboxylate struts from axel and wheel.
- **24C8** interacts with benzimidazole groups by O-H hydrogen-bond.
- Four carboxylate groups is coordinated to a Zn_4O cluster. The triphenyl struts form the sides of a cube, and the benzimidazole containing crossbars connect the cubes at the benzimidazole phenyl rings.
- Two tri-phenyl groups share one linker are perpendicular to each other in MOF structure (Fig. 3a) and form two non-covalently-connected cages separately. (Fig. 3b)
- The carbon atoms at the 2-positions of the benzimidazole rings of **5** were enriched to

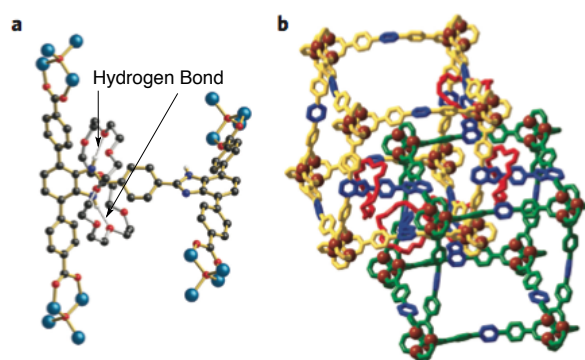


Fig. 3. Structure of UWDW-4·HBF₄ unit.

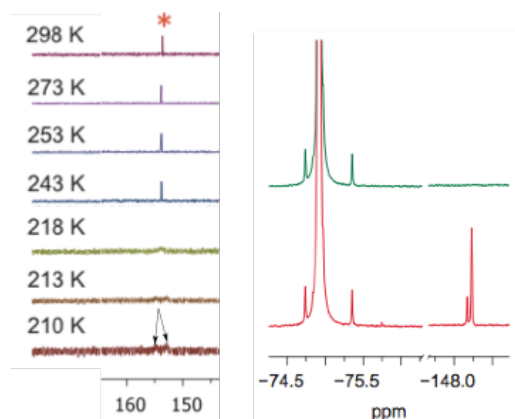


Fig. 4. ¹³C NMR spectra of **3*** in toluene-d₈ (* = ¹³C-enriched atoms).

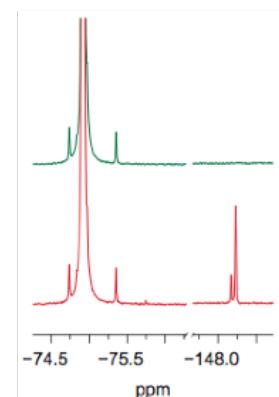


Fig. 5. ¹⁹F solution NMR spectra of UWDW-4 (top) and UWDW-4·HBF₄ (bottom).

50% ^{13}C by using ^{13}C -labelled 1,4-benzenedialdehyde.

- ^{13}C (mark as * in **2**, **3**, **5**) is used to identify the shuttling motion in the MOF by ^{13}C Solid-State NMR.
- A single resonance (*) was observed for both the 'occupied' and 'empty' sites at room temperature in ^{13}C -NMR spectroscopy. (Fig. 4)
- At lower temperature, two separate resonances for the occupied and empty recognition sites become visible. (Fig 4, indicates by arrows)
- **24C8** macrocycle undergoes rapid molecular shuttling between two benzimidazole recognition sites.
- N,N,N',N'-tetramethylnaphthalene-1,8-diamine (proton-sponge) in ethanol is added to neutralize the charge in benzimidazolium group. It is monitored by solid-state ^{19}F NMR spectroscopy until no BF_4^- is observed (Fig. 5). Therefore, the **24C8** will not be fixed in charged place and will shuttle inside lattice.
- Structures do not change so much after removing the HBF_4 molecule from the MOF structure and confirmed by XRD, IR and SEM.

2.2 Molecular Shuttle Study

- At high temperatures, only a single peak (154.0 ppm) in ^{13}C Solid-State NMR is observed.
- When the temperature is lowered this peak broadens, coalesces and then splits into two distinct resonances (152.7 and 155.2 ppm) at the lowest temperature.
- Averaging of the signals from the two recognition sites: one that is open and another that is occupied by a **24C8** macrocycle.
- Rapid molecular shuttling of the macrocyclic ring between the two

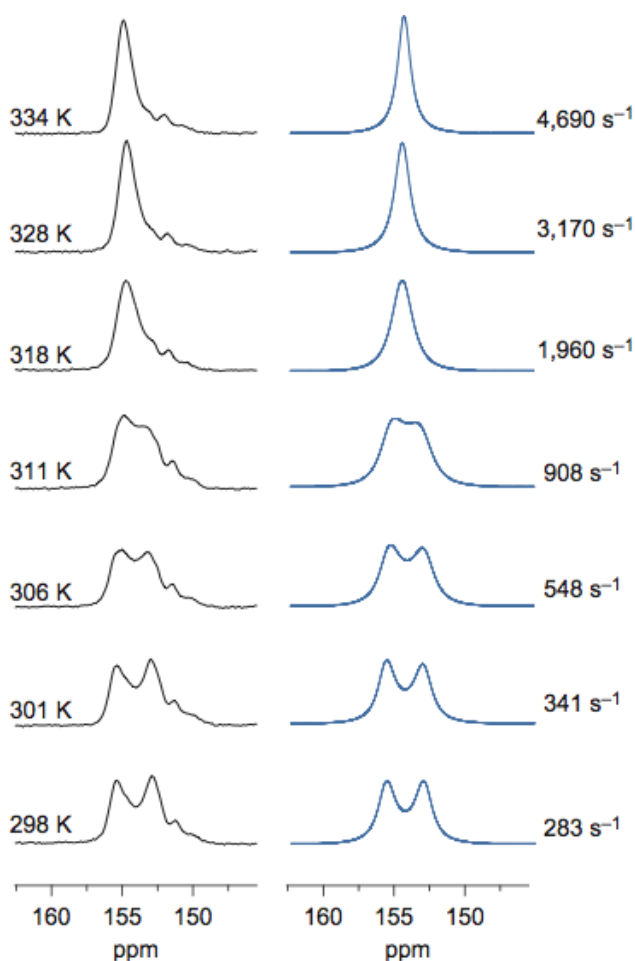


Fig. 6. ^{13}C -NMR spectra (left, experimental; right, simulation) of a ^{13}C -enriched sample of UWDM-4

recognition sites is occurring inside the MOF

- When the sample is cooled, the rate of this translational motion slows and both occupied and unoccupied sites are observed.
- An Eyring plot of $\ln(k/T)$ versus $1/T$ indicates the rate of shuttling inside the MOF lattice is 283 s^{-1} at 298 K with an activation barrier (ΔG^\ddagger) to this translational motion of $14.1 \text{ kcal mol}^{-1}$.
- Comparing the energy barrier and rate of shuttling in the solid state with that in solution ($7.7 \text{ kcal mol}^{-1}$ and $1.4 \times 10^7 \text{ s}^{-1}$), the solid one is much higher.
- Both enthalpic (ΔH^\ddagger) and entropic (ΔS^\ddagger) contributes to the high activation barrier.
- ΔH^\ddagger : surrounding framework will induce steric and electrostatic hindrances to the motion.
- ΔS^\ddagger : faster collisions in solution is to induce a wider range of ring conformations and increased relative shuttling motions of the rings and axes

3. Conclusion

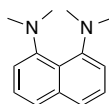
- UWDM-4, a MOF material with a molecular shuttle as part of its internal structure is synthesized.
- Solid-State NMR experiments demonstrate that the macrocyclic ring can undergo large-amplitude translational motion along the rigid skeleton of the MOF to which it is interlocked.

4. References

- (1) Anelli, P. L.; Spencer, N.; Stoddart, J. F. *J. Am. Chem. Soc.* **1991**, *113*, 5131–5133.
- (2) Deng, H.; Olson, M. A.; Stoddart, J. F.; Yaghi, O. M. *Nat. Chem.* **2010**, *2*, 439–443.

5. Appendix

N,N,N',N',-tetramethylnaphthalene-1,8-diamine



^{13}C -labelled 1,4-benzenedialdehyde

