REVERSIBLE SWITCHING FROM A THREE- TO A NINE-FOLD DEGENERATE DYNAMIC SLIDER-ON-DECK THROUGH CATENATION

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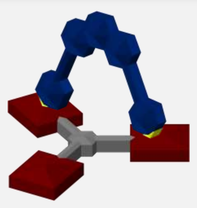
- Assembling heteromultimeric proteins has evolved as a powerful strategy of nature for increasing diversity and complexity. Analogously in artificial self-assembly, multicomponent self-sorting provides a promising and potent approach to generate wide-ranging structures with emergent functions. Herein, we reveal an authoritative example of self-assembled multicomponent devices and machines.

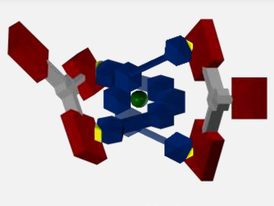
- Two dynamic slider-on-deck assemblies, i.e., a two-component threefold degenerate (k_{298} = 34.9 kHz) and a catenated three-component ninefold degenerate (k_{298} = 27.9 kHz) system, were quantitatively interconverted. Inspection of their computed structures revealed an allosteric effect on the sliding rates due to the spatial interaction between the components.

Reversible interconversion between two-component slider-on-deck DS1 and three-component catenate slider-on-deck DS2



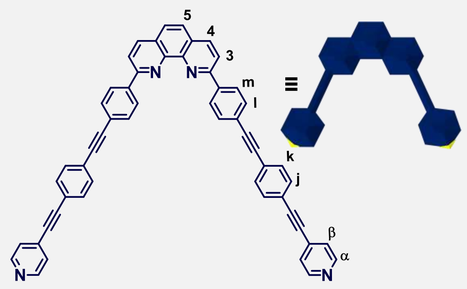
Slider on Deck **DS1**

$[Cu(CH_3CN)_4]PF_6$ ⇌ Cyclam

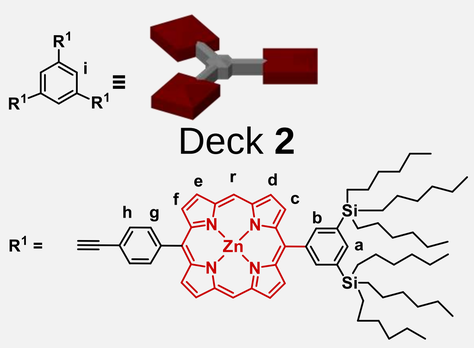


Catenate Slider on Deck **DS2**

Schematic representation of slider-on-deck systems (DS1 and DS2) self-assembled in this study. Simple inputs (Cu^+ and cyclam) were used to reversibly catenate and decatenate the slider.



Slider **1**

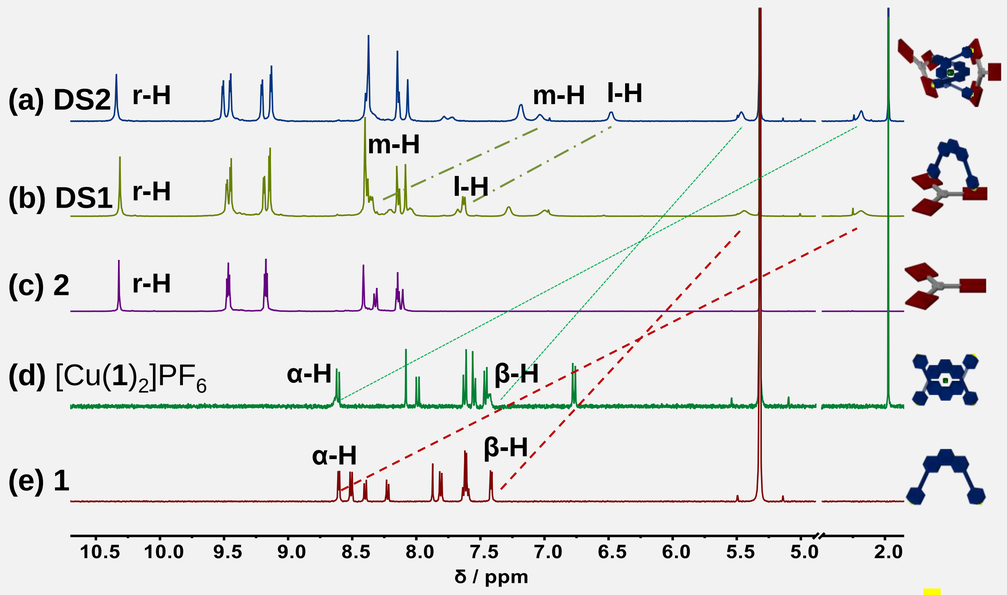


Deck **2**

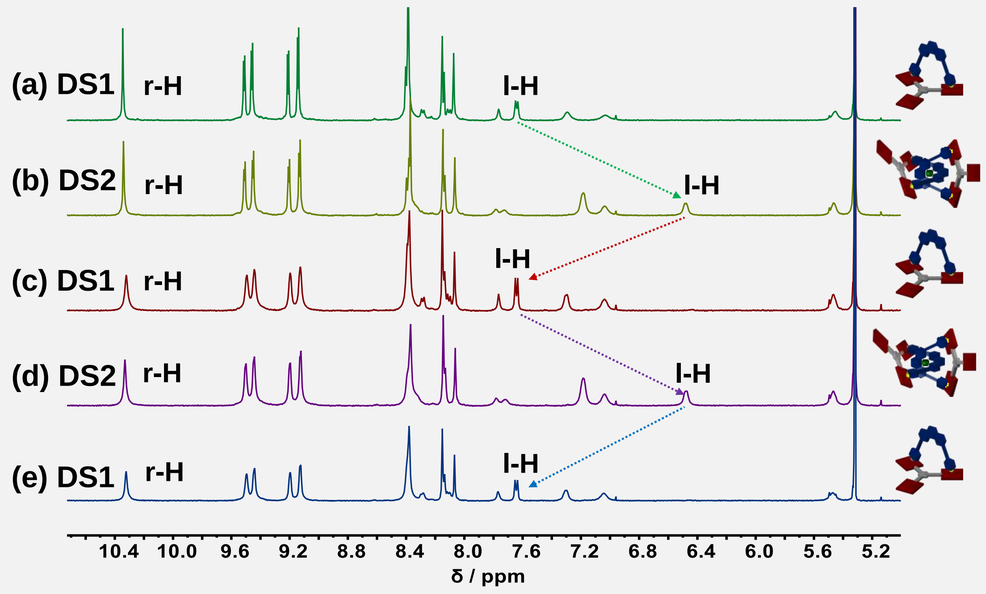
Synthesis of Deck 2

(a) High-dilution acid-catalyzed porphyrin synthesis using condensation and subsequent oxidation
(b) Deprotection of the acetone-protected acetylene group using NaOH/toluene
(c) Copper-free Pd(0)-catalyzed Sono-gashira coupling of terminal acety-lene and triiodobenzene

Monitoring Catenation/Decatenation using ^{1}H-NMR spectroscopy



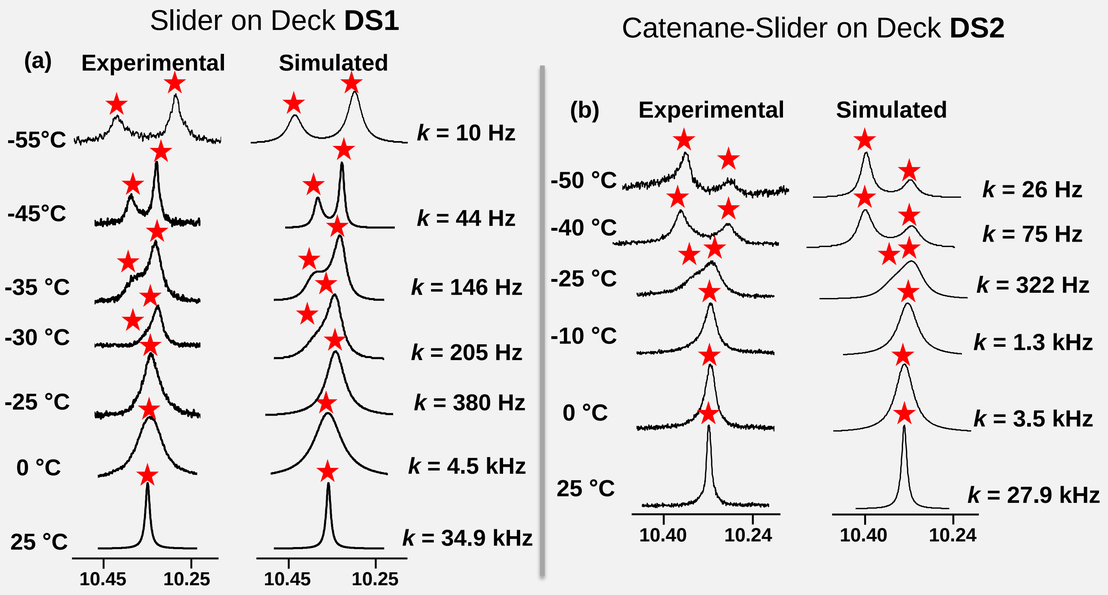
^{1}H-NMR stack of all the components in this report show a clean quantitative assembly due to the orthogonal self-sorting motifs in (a) and (b) : Homoleptic phenanthroline Cu^+ and N_{py}→ZnPor interactions



^{1}H-NMR stack of the clean, quantitative interconversion between assemblies DS1 and DS2 by adding stochiometric inputs of Cu^+ and cyclam with high reproducibility over 2.5 cycles.

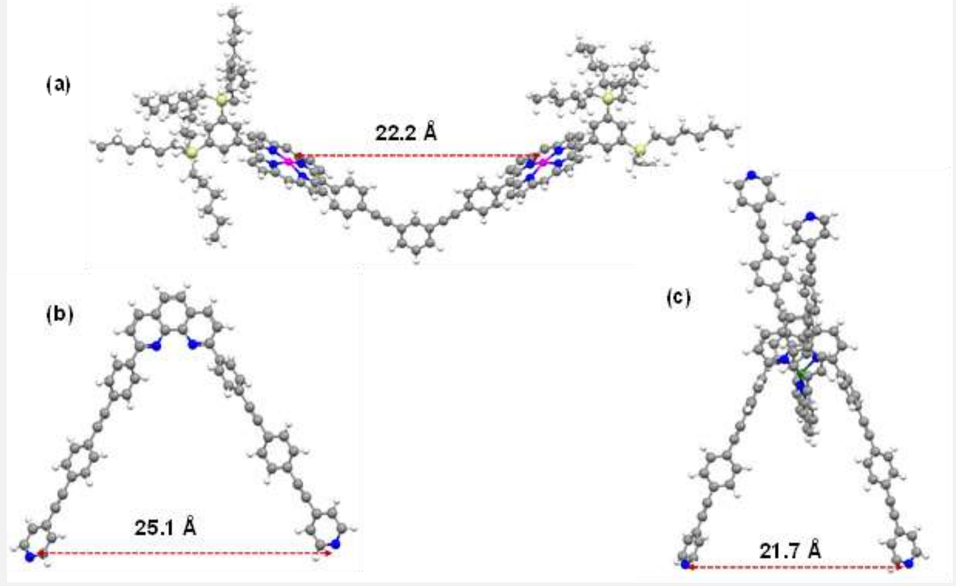
Measuring and rationalizing the kinetics in the catenate slider DS2 and the slider-on-deck DS1. Can allosteric changes improve intercomponent fitness in multicomponent machines ?

Kinetic analysis of variable temperature ^{1}H-NMR studies



Kinetic analysis using VT ^{1}H-NMR for the two sliders (DS1 and DS2) provide evidence of allosteric modification of rotational dynamics. Eyring analysis yielded $\Delta G^{\#}_{298}$(DS1) = 47.1 ± 0.1 kJ mol^{-1} and $\Delta G^{\#}_{298}$(DS2) = 47.9 ± 0.1 kJ mol^{-1} thus confirming an allosteric effect on the exchange.

Allosteric effects guide geometric changes !



DFT-optimized structures show the geometric fit of the slider and the deck components. Figure (c) illustrates how allosteric geometry modification guides a geometry change in the slider component of DS2. Allosteric modification leads to better intercomponent fitness.

References

[1] Rajasekaran, V. V.; Paul, I.; Schmittel, M. Reversible Switching from a Three- to a Nine-Fold Degenerate Dynamic Slider-on-Deck through Catenation. *Chem. Commun.* **2020**, *56*, 12821–12824