Supporting Information For:

How Does the Solvent Modulate Shuttling in a Pillararene/Imidazolium [2]Rotaxane? Insights from Free Energy Calculations

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Discussion on the compatibility of the Force Fields. The parameters representing dichloromethane, benzene, diethyl ether, acetone, isobutanol and 2-butanol were taken from CGenFF.[1,2] DMSO was described by means of the all-atom model proposed by Strader and Feller[3], which has been incorporated in CGenFF.[4] The rigid model of chloroform developed by Dietz and Heinzinger (DH model)[5] was used by Yu et al.[4] in their contribution to simulate a sulfonamide-based peptide in chloroform, offering a reasonable reproduction of the available experimental liquid properties. Put together, we feel that the different force fields used here are suitable to model the supramolecular assemblies examined in the present work.

Comparison of the free energy profiles in acetone and DMSO. The experimental observations in the DMSO/chloroform binary solvent with different ratios shows that the P[5] binds the imidazolium moiety in chloroform, gradually moving away to include the methylene groups with an increasing DMSO ratio in the binary solvent.[6] This dependence of the molecular motion of the P[5] to the solvent polarity is also reflected in our calculations. As can be observed in Figure S1, the propensity of the P[5] in DMSO to bind the alkyl groups close to the carbamic stopper (around +4 Å) is more pronounced, compared to that in acetone with lower polarity.

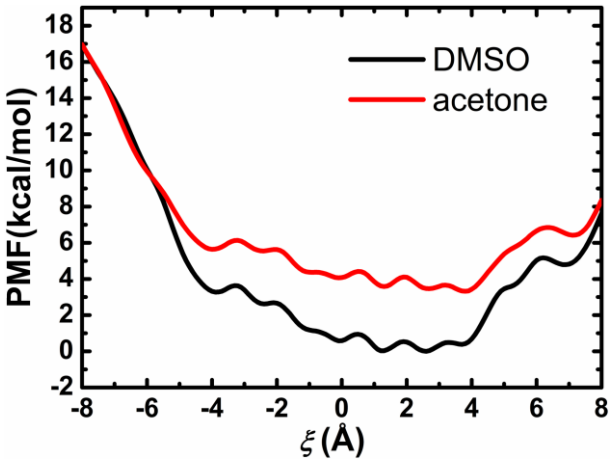

Figure S1. Comparison of the free energy profiles delineating the shuttling in acetone and DMSO.

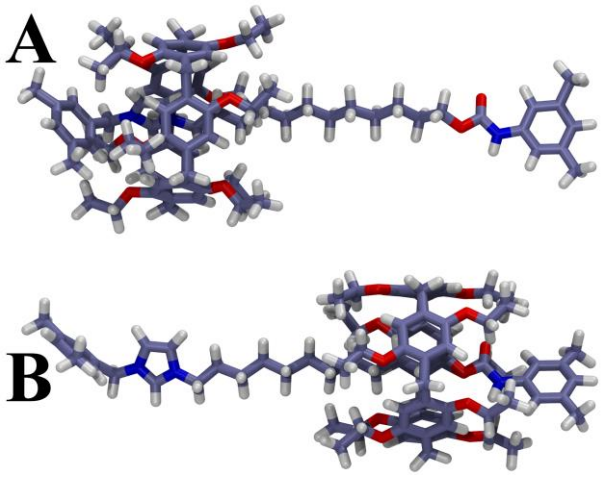

Figure S2. Snapshots of the [2]rotaxane. (A) ξ = −8.0 Å, (B) ξ = +6.5 Å. For clarity, the counterion and solvent molecules are not shown.

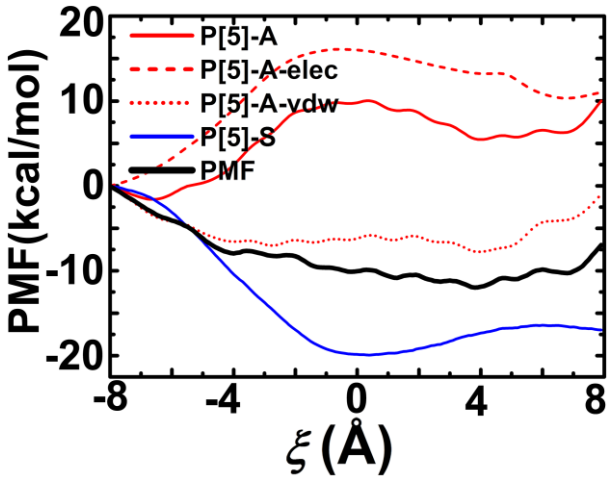

Figure S3. Decomposition of the total free energy profile into van der Waals P[5]−axle, electrostatic P[5]−axle, and P[5]−solvent contributions for the shuttling in isobutanol.

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