Electronic Supplementary Information

Insights into Directional Movement in Molecular Machines from Free-Energy Calculations

Heying Feng,[a] Haohao Fu,[a] Xueguang Shao,[*ab] and Wensheng Cai[*a]

[a] *Tianjin Key Laboratory of Biosensing and Molecular Recognition, Research Center for Analytical Sciences, College of Chemistry, Nankai University, Tianjin 300071, China. E-mail: xshao@nankai.edu.cn, wscai@nankai.edu.cn*

[b] *State Key Laboratory of Medicinal Chemical Biology, Tianjin 300071, China.*

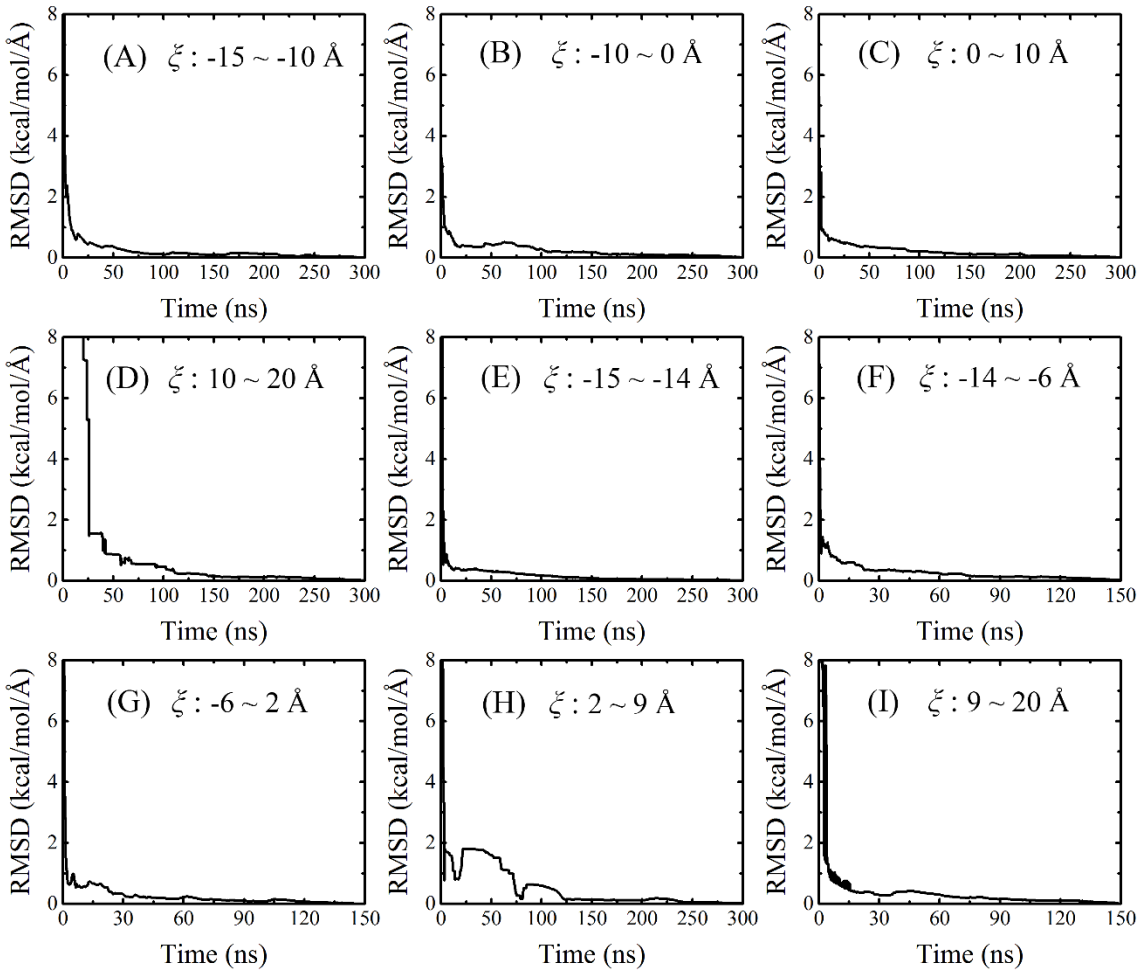

Fig. S1 Time evolution of the root-mean-square deviation (RMSD) over the gradients of the free-energy profiles depicted in Fig. 2A for the shuttling of the unprotonated (A-D) and protonated (E-I) rotaxanes in dichloromethane. Reaction coordinate ξ extends from −15 to +20 Å.

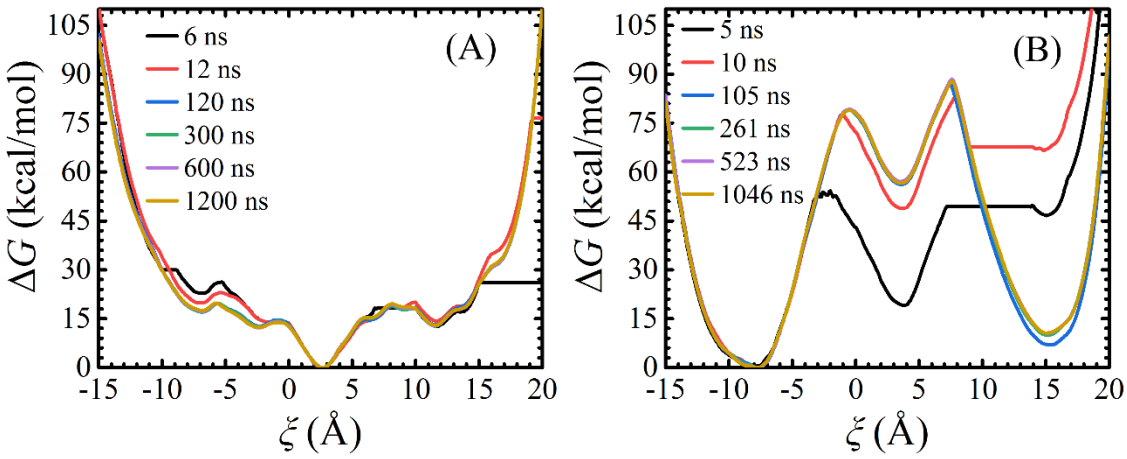

Fig. S2 Free-energy profiles characterizing the shuttling of the unprotonated (A) and protonated (B) rotaxanes in dichloromethane at different simulation times. The results show that the calculations have converged within 1200 ns (A) and 1046 ns (B), respectively.

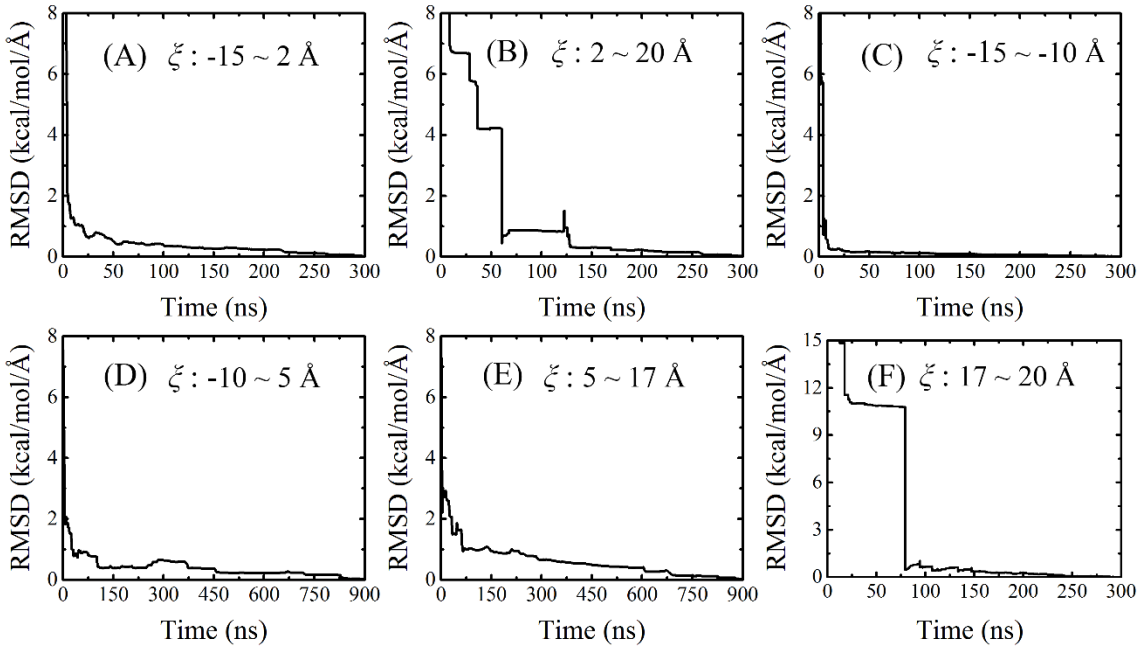

Fig. S3 Time evolution of the root-mean-square deviation (RMSD) over the gradients of the free-energy profiles depicted in Fig. 4A for the shuttling of the unprotonated (A, B) and protonated (C-F) rotaxanes in acetonitrile. Reaction coordinate ξ extends from −15 to +20 Å.

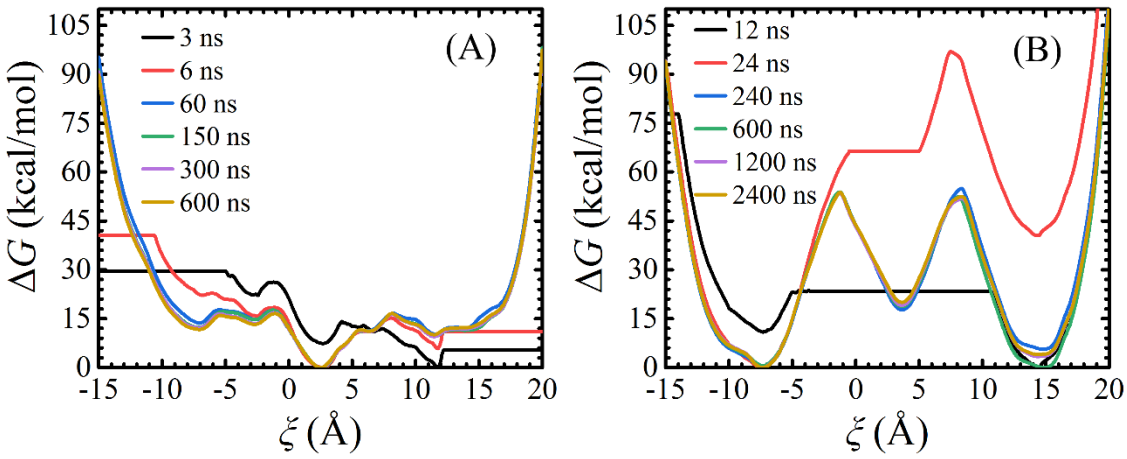

Fig. S4 Free-energy profiles characterizing the shuttling of the unprotonated (A) and protonated (B) rotaxanes in acetonitrile at different simulation times. The results show that the calculations have converged within 600 ns (A) and 2400 ns (B), respectively.

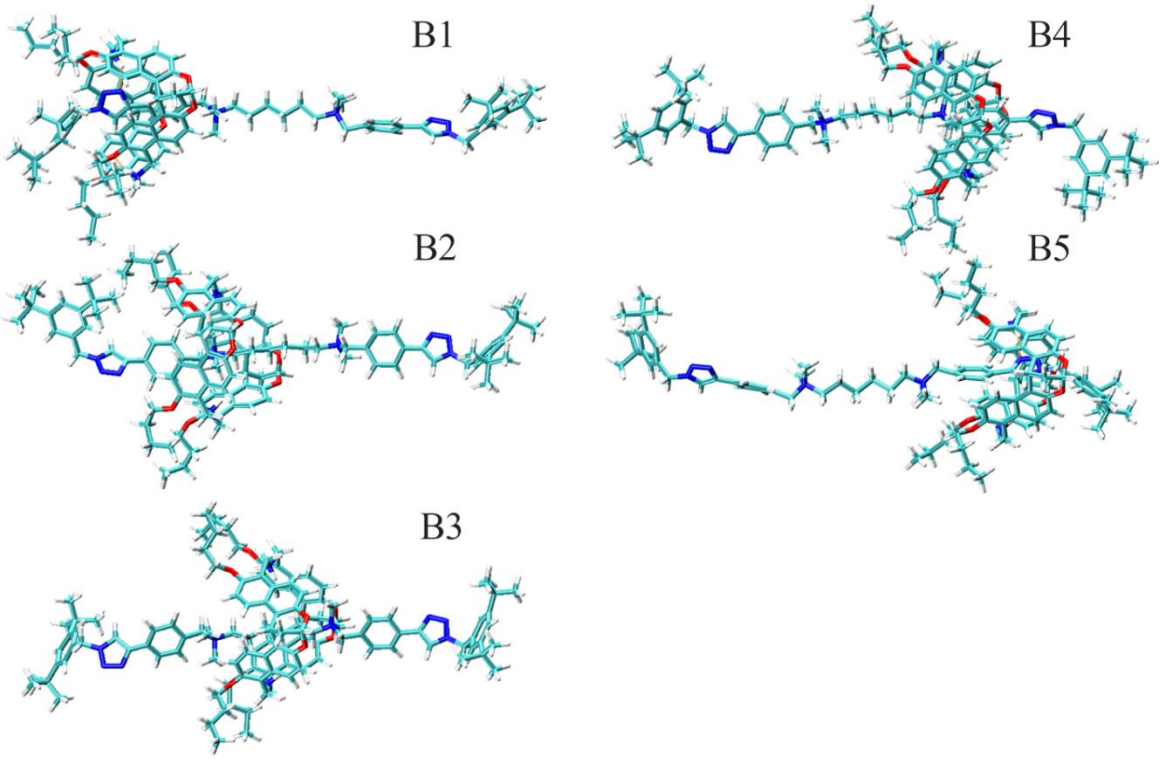

Fig. S5 Representative structures of the rotaxane at B1-B5 in acetonitrile at low pH.

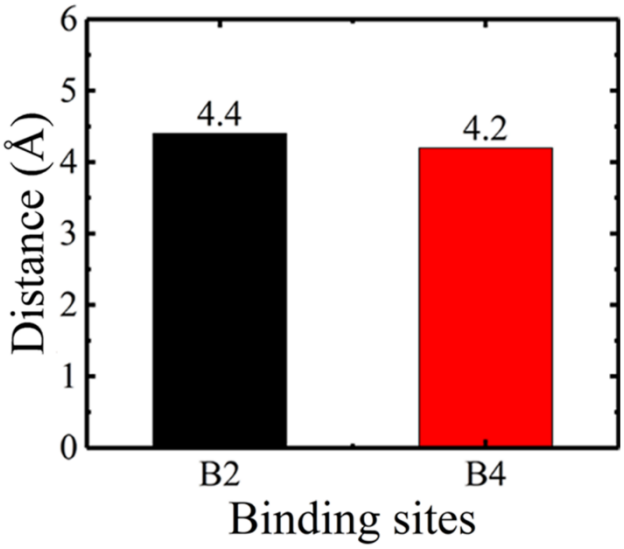

Fig. S6 The minimum distances between the nitrogen atoms of the quaternary ammonium moieties on the axle and nitrogen atoms of the ring at B2 and B4 in acetonitrile at low pH.