Supporting Information

Factor Analysis of Conformations and NMR Signals of Rotaxanes:

AIMD and Polarizable MD Simulations

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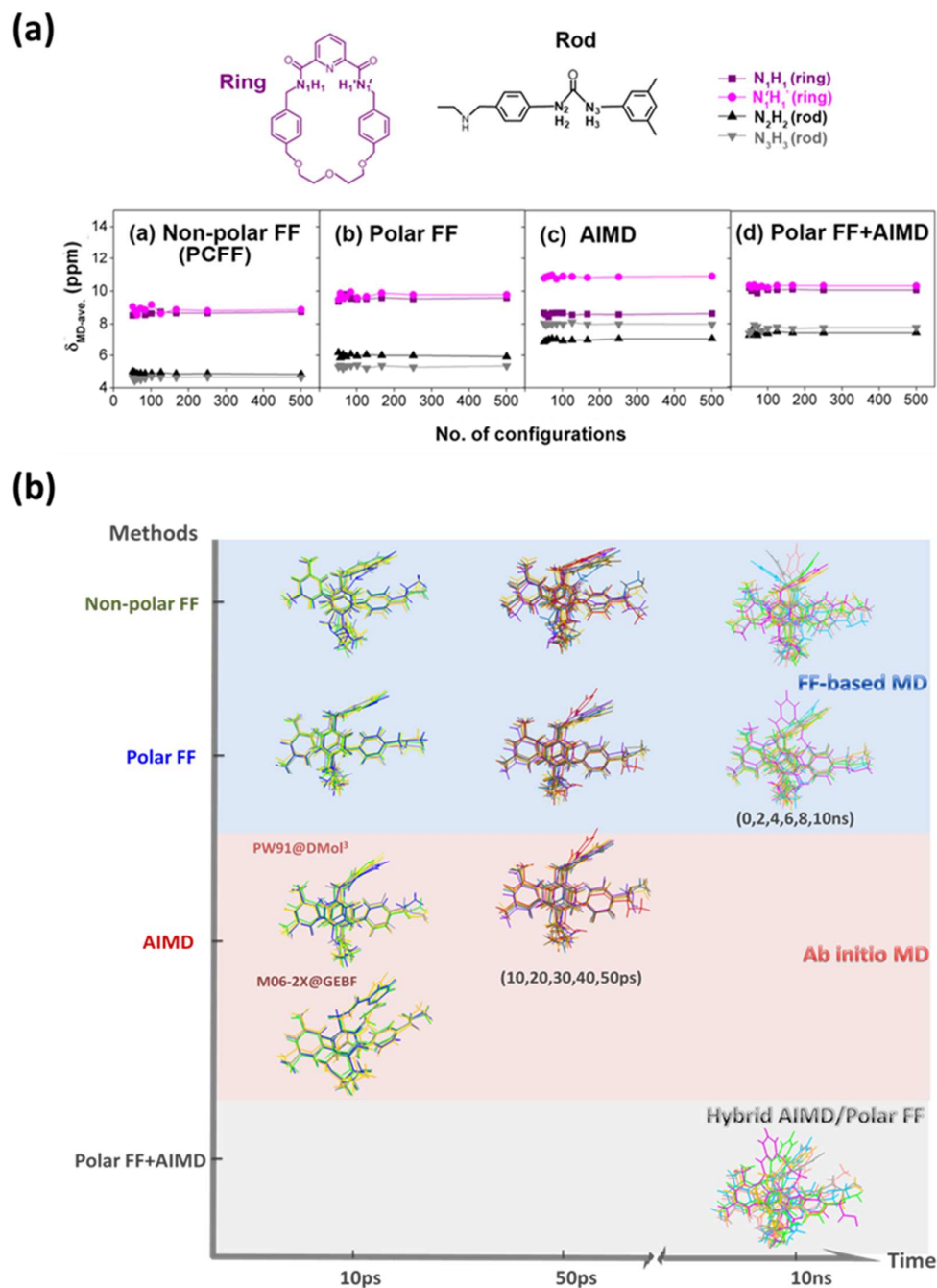*Corresponding author: wli@nju.edu.cn, Tel: 86-25-89687052

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Figure S1. (a) Convergence behaviors of calculated ^{1}H chemical shifts of amide protons for the pseudorotaxane in vacuum. (b) Structural variations with the time evolutions.
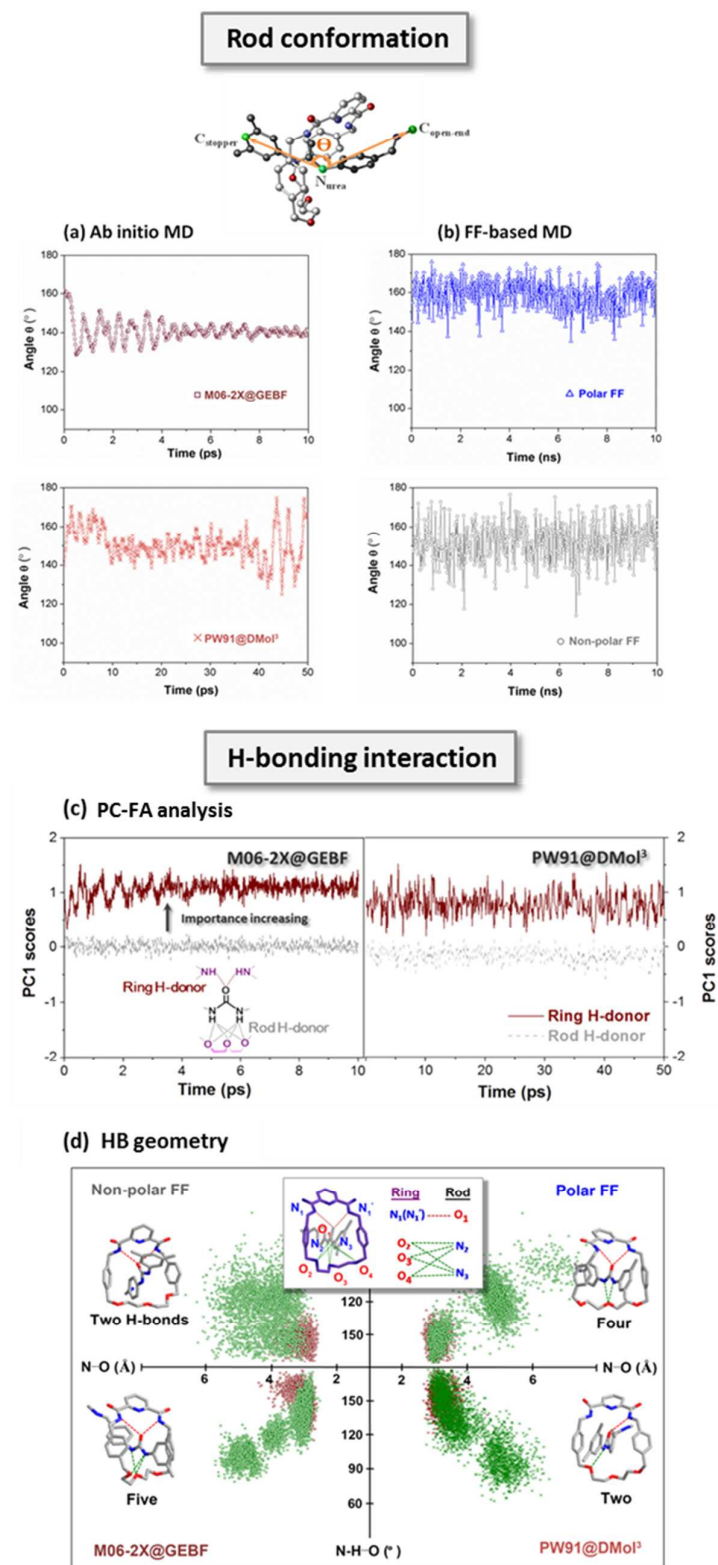
Figure S2. The comparison of PW91-based AIMD with the GEBF-M06-2X AIMD and the force field based MD simulations.
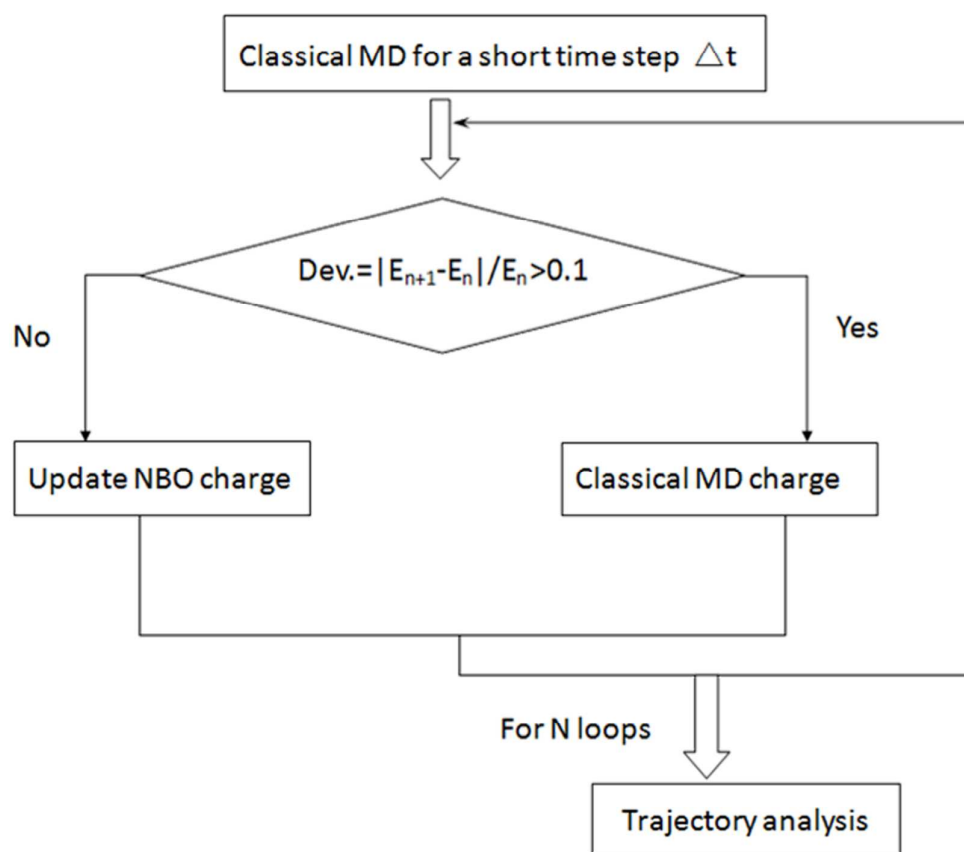
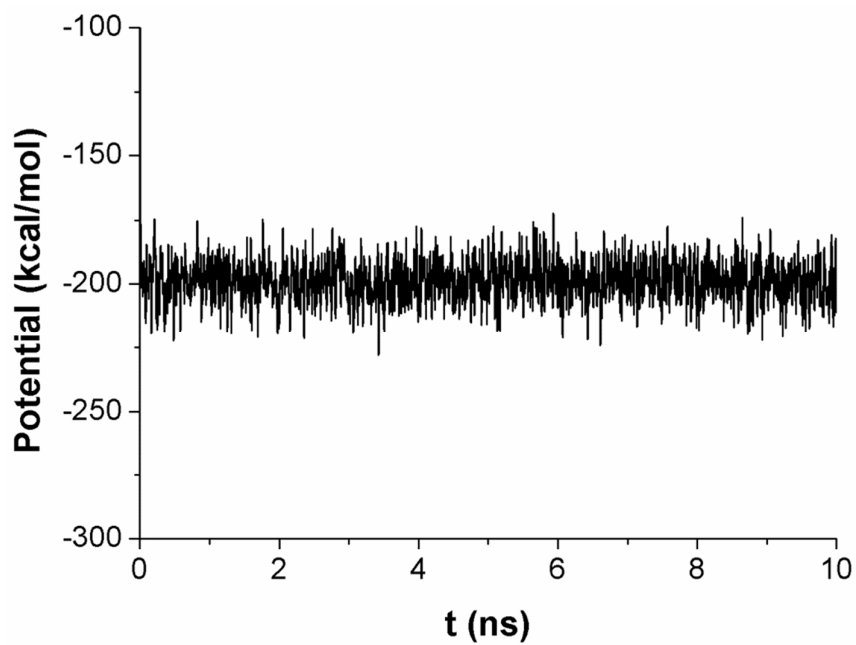**Figure S3**. Flow chart of polar-FF MD simulations.

Figure S4. Potential energies (kcal/mol) varied as a function of time for the pseudorotaxane. The molecular dynamics simulation are carried out at 298.15K by using PCFF with NBO charges, updated every 5ps.

Table S1. Correlation matrix of factor analysis using principal component method.

	∠N-H⋯O	$r_{N⋯O}$	$r_{N-H\ stretch}$	$r_{H⋯O}$	r_{N-H} / $r_{H⋯O}$
∠N-H⋯O	1.000	-0.656	0.037	-0.752	0.711
$r_{N⋯O}$	-0.656	1.000	-0.170	0.971	-0.930
$r_{N-H\ stretch}$	0.037	-0.170	1.000	-0.172	0.291
$r_{H⋯O}$	-0.752	0.971	-0.172	1.000	-0.948
r_{N-H} / $r_{H⋯O}$	0.711	-0.930	0.291	-0.948	1.000

Table S2. Total variance explained result of factor analysis using principal component method.

Component	Intial eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.546	70.916	70.916	3.546	70.916	70.916
2	0.991	7.700	90.735			
3	0.385	1.191	98.434			
4	0.060	0.375	9.625			
5	0.019	0.018	100.000			

Table S3. Component score coefficient matrix of factor analysis using principal component method.

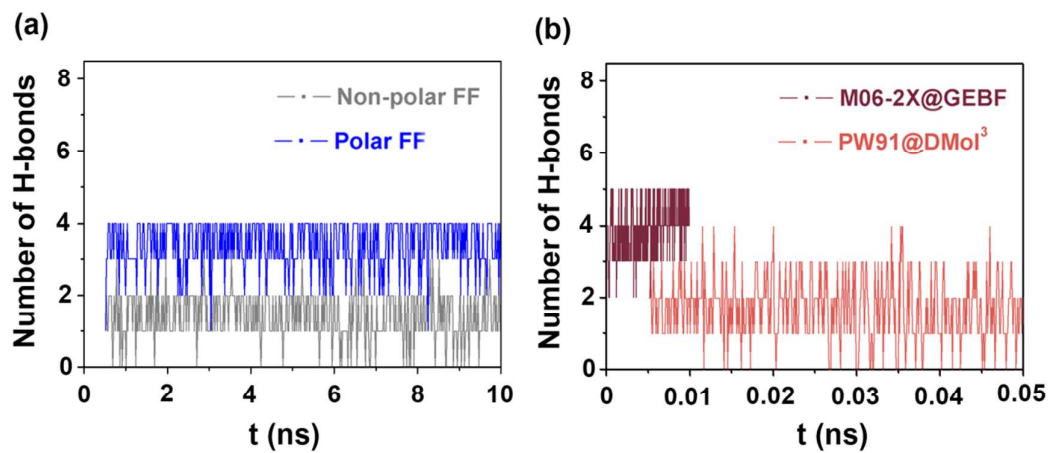|	Pincipal Componet 1
∠N-H⋯O	0.229
$r_{N⋯O}$	-0.270
$r_{N-H\ stretch}$	0.071
$r_{H⋯O}$	-0.277
r_{N-H} / $r_{H⋯O}$	0.274

Figure S5. Comparison of the number of H-bonds as a function of MD simulation time using four different molecular dynamics methods for pseudorotaxane in vacuum.
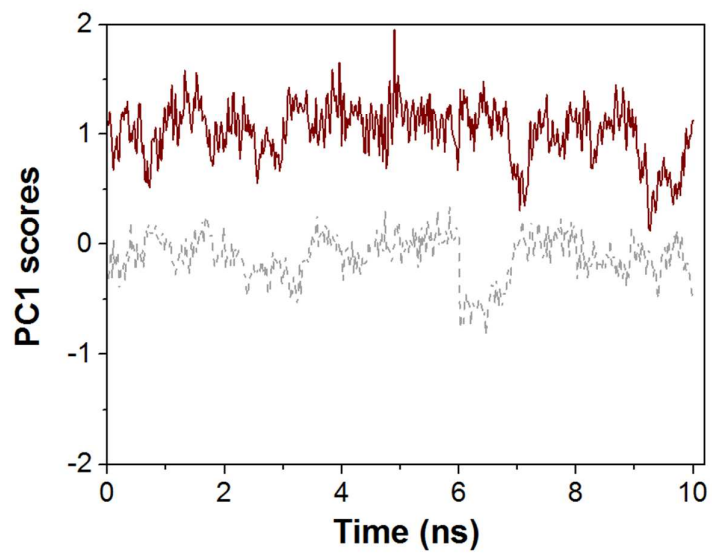
Figure S6. The first principle component scores of ring-rod contacting geometries for pseudorotaxane in vacuum using polar FF+AIMD method.
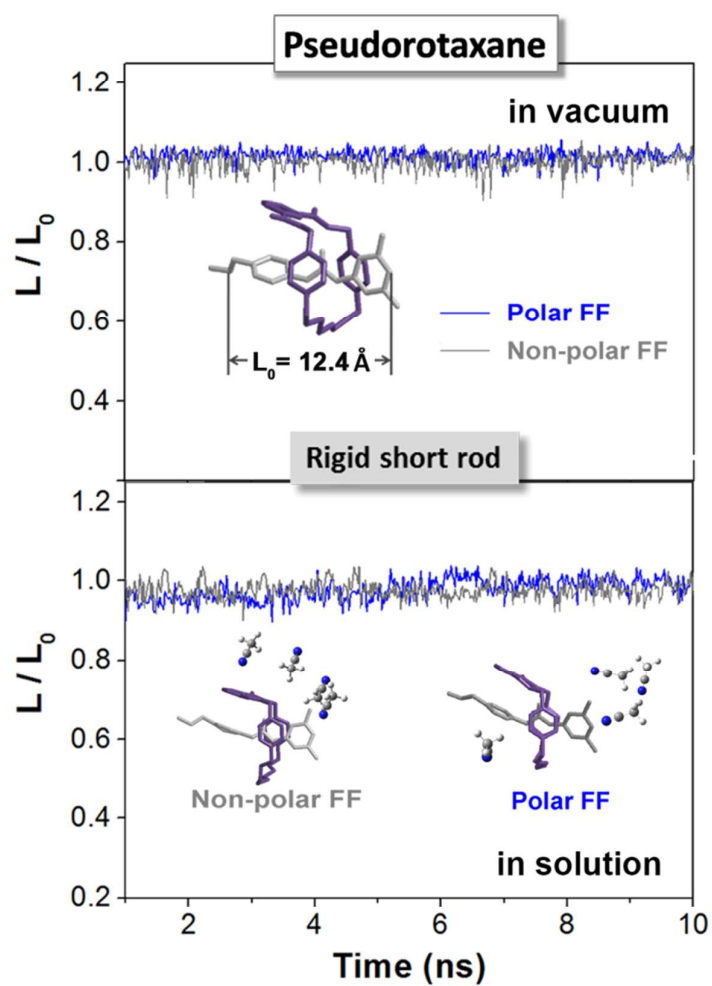
Figure S7. Fluctuations of end-to-end lengths of rod for pseudorotaxane using non-polar and polar FF MD simulations in vacuum and in solution.
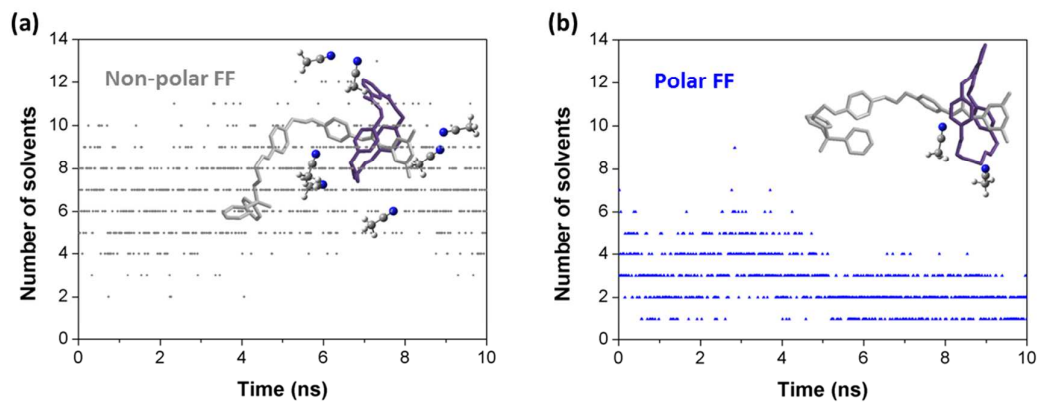
Figure S8. Variation of number of solvents around the solute with the distance cutoff (< 9 Å) using (a) non-polar FF and (b) polar FF-based MD simulations in solution for [2]rotaxane.

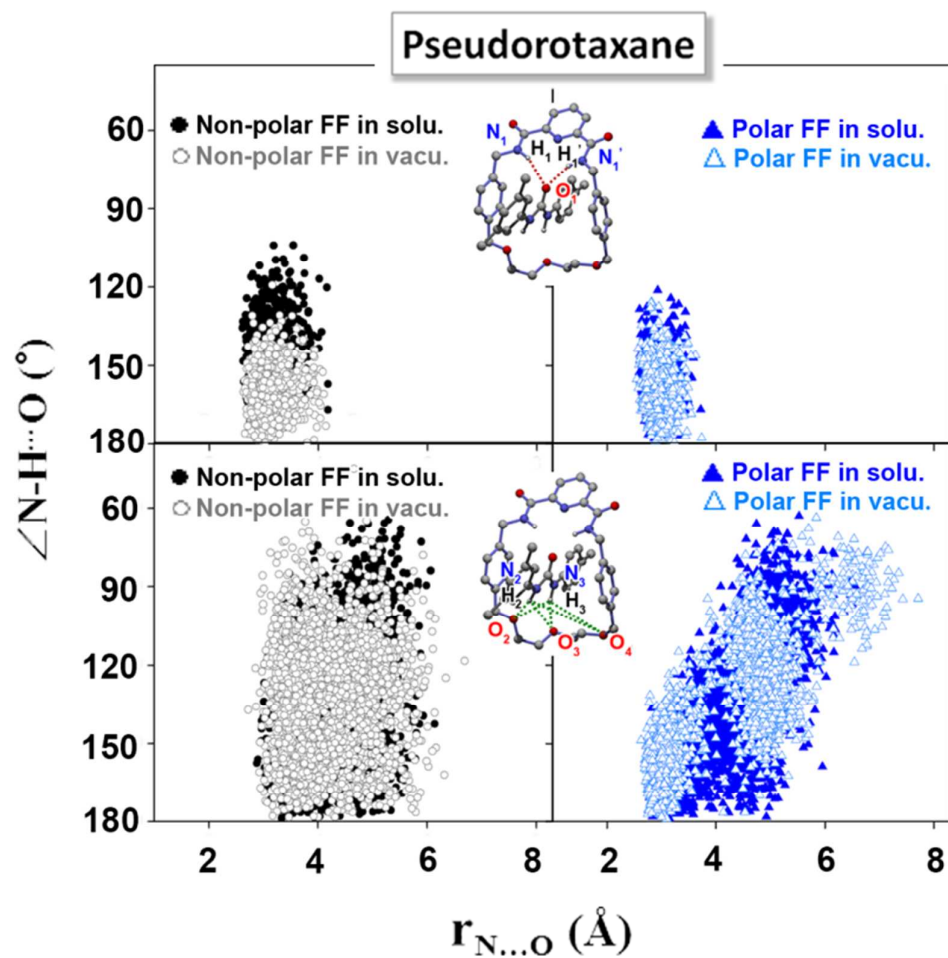**Figure S9.** Distributions of N···O lengths and N-H···O angles for pseudorotaxane in vacuum and in solution.
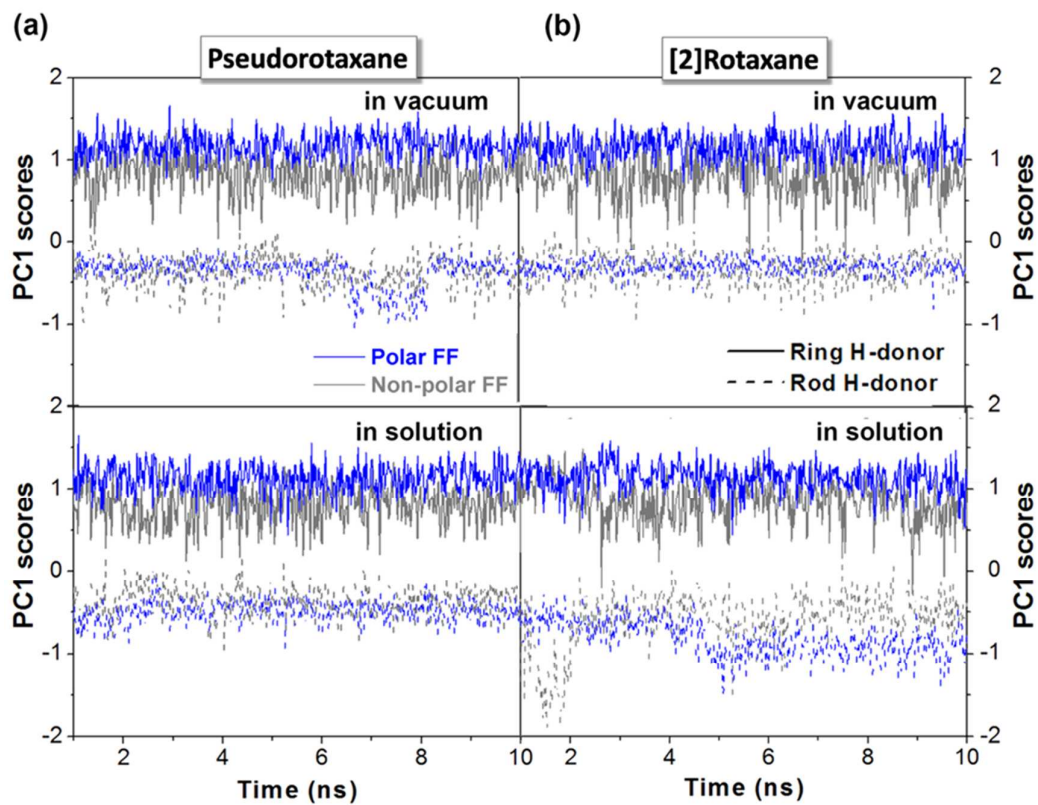
Figure S10. PC1 score plots for (a) pseudorotaxane, and (b) [2]rotaxane using non-polar and polar FF MD simulations in vacuum and in solution.