**Supporting Information**

# Theoretical Study on Conformation Dynamics of Three-Station Molecular Shuttle in Different Environments and its Influence on NMR Chemical Shifts and Binding Interactions

Pingying Liu[a,b], Wei Li[a], Li Liu[a], Leyong Wang[a] and Jing Ma[a,]*

[a]School of Chemistry and Chemical Engineering, Key Laboratory of Mesoscopic Chemistry of MOE, Nanjing University, Nanjing 210093, People's Republic of China
[b]School of Materials Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen 333403, China
*Corresponding author: majing@nju.edu.cn, Fax: 86-25-83596131, Tel: 86-25-83597408

## Contents

## 1. DFT functionals

All the structures were optimized using the density functional theory (DFT)[1] method with 6-31G(d,p)[2] basis sets. The B3LYP functional includes Becke's three-parameter-exchange functional and Lee-Young-Parr correlation functional[3], CAM-B3LYP[4] is the long range corrected version of B3LYP using the Coulomb-attenuating method, PBEPBE[5], uses 25% exchange and 75% correlation weighting. mPW1PW91[6] uses Perdew-Wang exchange as modified by Adamo and Barone combined with PW91 correlation. M06-2X[7] is a hybrid meta-functional that contains 27% HF exchange, parameterized using delocalized system, and WB97X-D[8] includes empirical dispersion and long range corrections.

**reference:**

1. P. Hohenberg, W. Kohn, Phys. Rev. **1964**, 136B, 864-871.

2. M.M.Francl, W.J.Pietro, W.J.Hehre, J.S.Binkley, M.S.Gordon, D.J.DeFrees, J.A.Pople J.Chem.Phys. 77, 3654-3665(1982).

3. a) A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652. b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B **1988**, 37, 785-789. c) R.G,. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford, New York, **1989**.

4. T. Yanai, D. Tew, and N. Handy, "A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP)," *Chem. Phys. Lett.*, **393** (2004) 51-57.

5. (a)C. Adamo and V. Barone, "Toward reliable density functional methods without adjustable parameters: The PBE0 model," *J. Chem. Phys.*, **110** (1999) 6158-69 (b) J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.*, **77** (1996) 3865-68. (c) J. P. Perdew, K. Burke, and M. Ernzerhof, "Errata: Generalized gradient approximation made simple," *Phys. Rev. Lett.*, **78** (1997) 1396.

6. C. Adamo and V. Barone, "Exchange functionals with improved long-range behavior and adiabatic connection methods without adjustable parameters: The mPW and mPW1PW models," *J. Chem. Phys.*, **108** (1998) 664-75.

7. Y. Zhao and D. G. Truhlar, "The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals," *Theor. Chem. Acc.*, **120** (2008) 215-41.

8. J.-D. Chai and M. Head-Gordon, "Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections," *Phys. Chem. Chem. Phys.*, **10** (2008) 6615-20.

Table S1. The details for the solvent models used in molecular dynamics simulations.

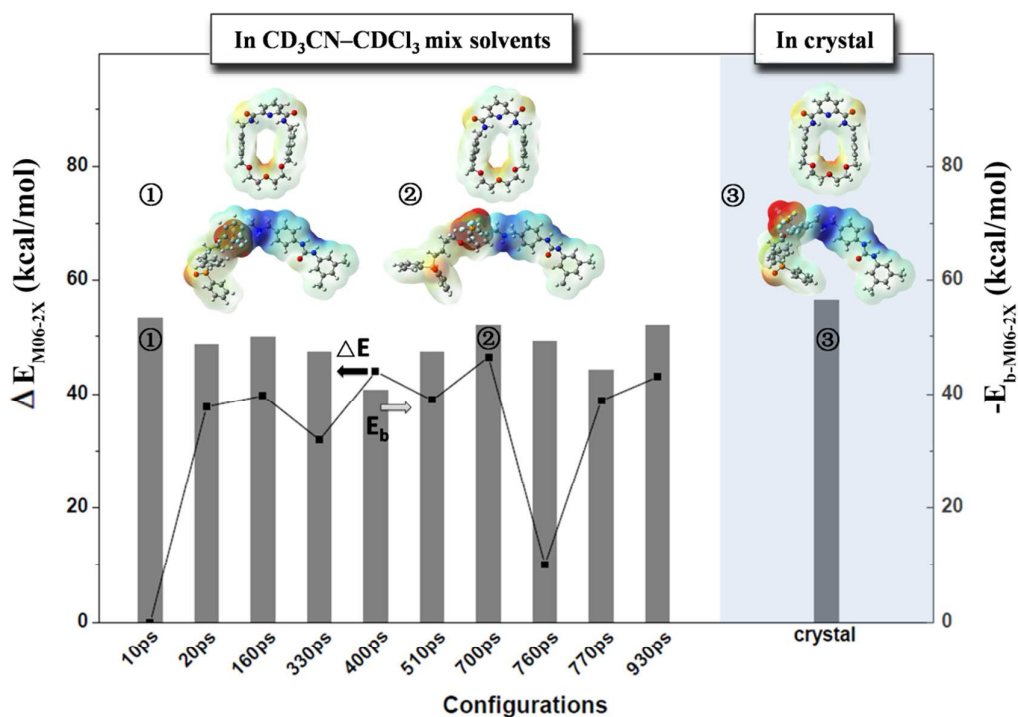| | MD averaged @solution | MD@CD$_3$CN-CDCl$_3$ solvents | MD@CDCl$_3$ solvents | MD@ vacuum | MD@mix solvents |
|---|---|---|---|---|---|
| Solute | 1 | 1 | 1 | 1 | 1 |
| Solvents | | | | | |
| CD$_3$CN | 1777 | 1777 | 0 | 0 | 1777 |
| CDCl$_3$ | 1223 | 1223 | 3000 | 0 | 1223 |

Figure S1. The relative energy, $\triangle E_{M06-2X}$, and BSSE-binding energies, $-E_{b-M06-2X}$, and electrostatic potential maps of macrocycles and threads at M06-2X/6-31G(d, p) level based on the ten energetically low-lying conformations extracted from MD simulation of interlocked [2]rotaxane at Station **I**. The 10ps structure has the lowest energy with $\triangle E_{M06-2X}=0$. Computational results using the crystal structure were also given for comparison.
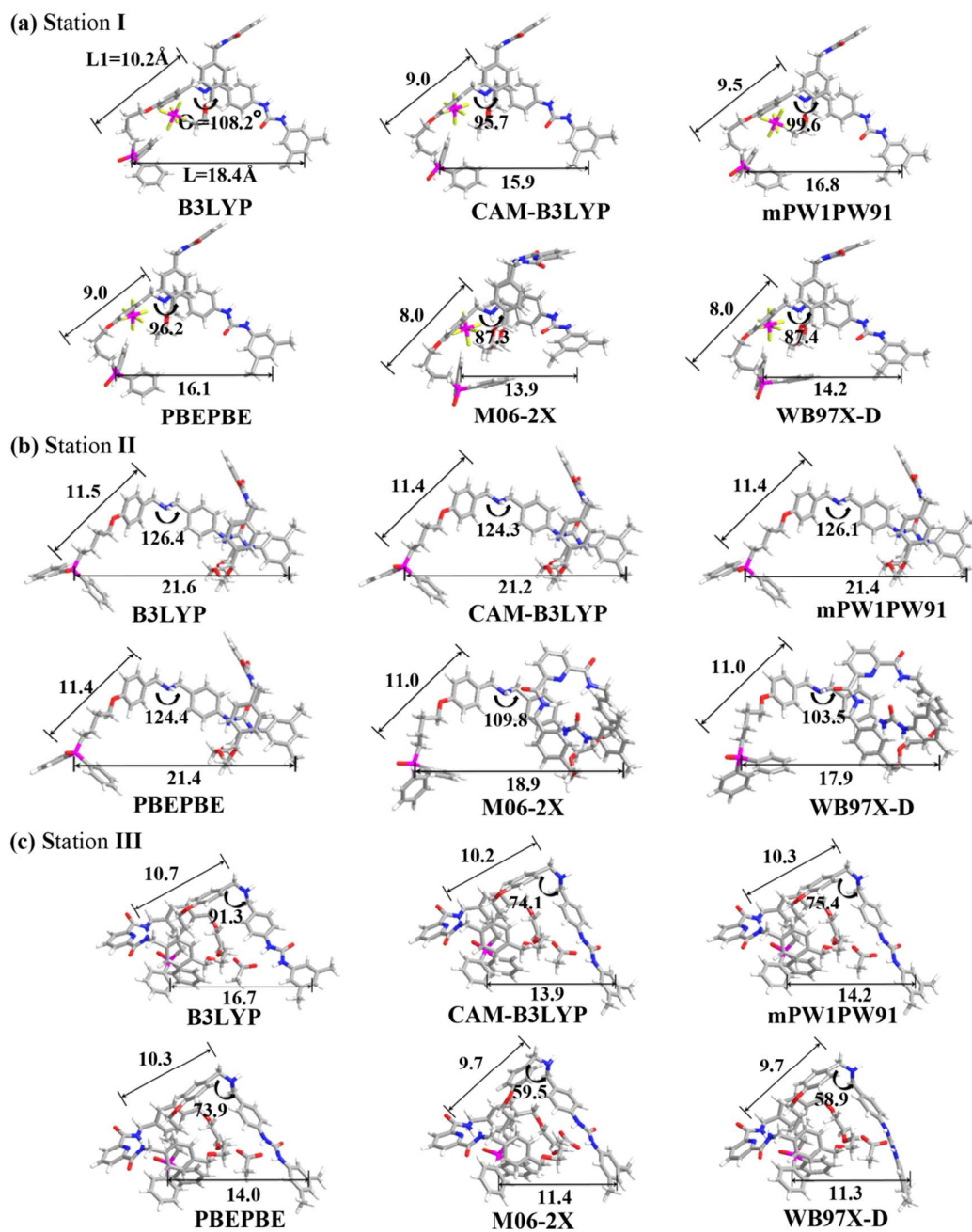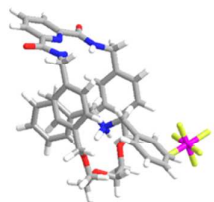
**(a) Station I**

L1=10.2Å
G=108.2°
L=18.4Å
**B3LYP**

9.0
95.7
15.9
**CAM-B3LYP**

9.5
99.6
16.8
**mPW1PW91**

9.0
96.2
16.1
**PBEPBE**

8.0
87.3
13.9
**M06-2X**

8.0
87.4
14.2
**WB97X-D**

**(b) Station II**

11.5
126.4
21.6
**B3LYP**

11.4
124.3
21.2
**CAM-B3LYP**

11.4
126.1
21.4
**mPW1PW91**

11.4
124.4
21.4
**PBEPBE**

11.0
109.8
18.9
**M06-2X**

11.0
103.5
17.9
**WB97X-D**

**(c) Station III**

10.7
91.3
16.7
**B3LYP**

10.2
74.1
13.9
**CAM-B3LYP**

10.3
75.4
14.2
**mPW1PW91**

10.3
73.9
14.0
**PBEPBE**

9.7
59.5
11.4
**M06-2X**

9.7
58.9
11.3
**WB97X-D**
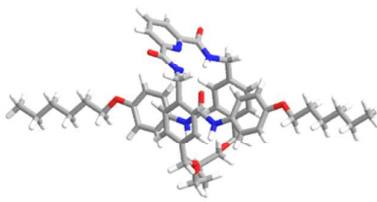
Figure S2. The optimized geometries and geometrical parameters of thread for three stations with six different functionals.
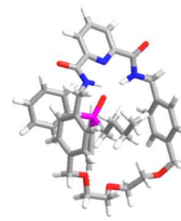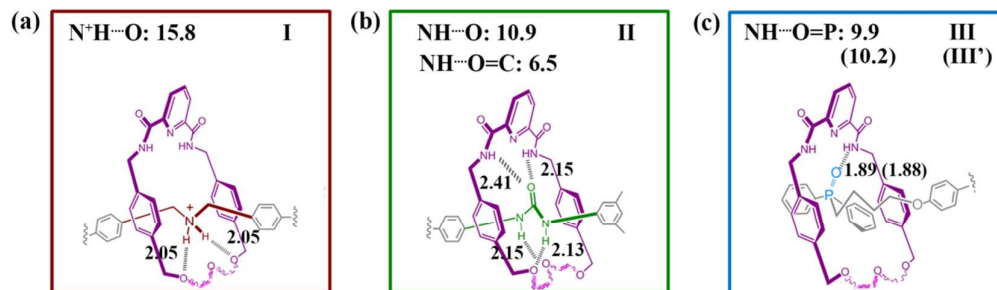
Figure S3. The optimized geometries for pseudorotaxanes at M062X/6-31G (d, p) level.

Table S2. Hydrogen bond lengths, $d_{O\cdots H}$, and stabilization energies obtained from second order perturbation, $E^{(2)}$, for H-bonding interactions of [2]rotaxane interlocking at different stations based on the NBO analysis.



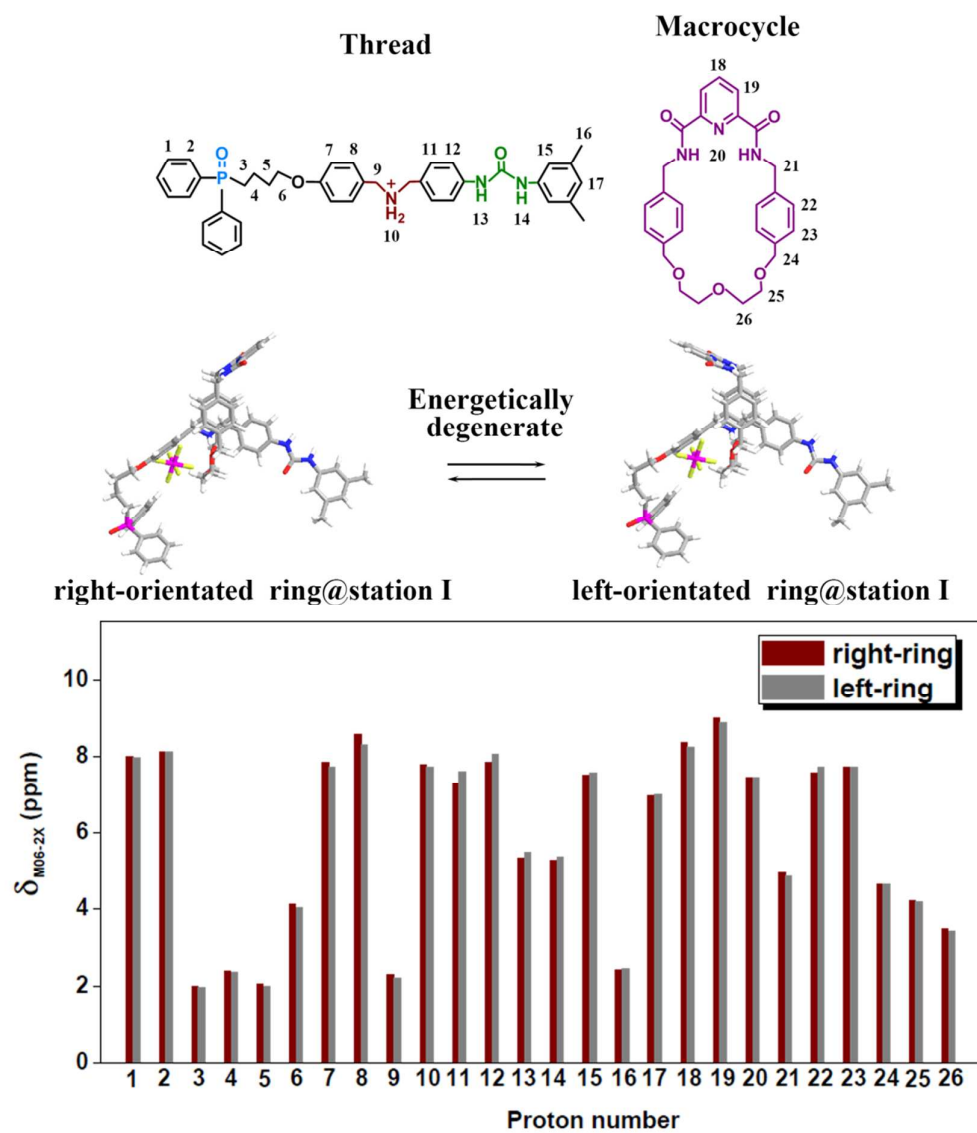| | Donor | Type | Acceptor | Type | $d_{O\cdots H}$ (Å) | Interaction | $E^{(2)}$ (kcal/mol) |
|---|---|---|---|---|---|---|---|
| **I**-HB1 | O 151 | LP (2) | N83 – H85 | BD*(1) | 2.05 | $n_O \rightarrow \sigma_{N-H}^*$ | 7.58 |
| **I**-HB2 | O 153 | LP (2) | N83– H84 | BD*(1) | 2.05 | $n_O \rightarrow \sigma_{N-H}^*$ | 7.80 |
| **I**-HB3 | O 152 | LP (2) | C22– H23 | BD*(1) | 2.32 | $n_O \rightarrow \sigma_{CH}^*$ | 1.08 |
| **II**-HB1 | O50 | LP (1) | N130-H131 | BD*(1) | 2.13 | $n_O \rightarrow \sigma_{N-H}^*$ | 7.19 |
| **II**-HB2 | O57 | LP (2) | N126-H127 | BD*(1) | 2.15 | $n_O \rightarrow \sigma_{N-H}^*$ | 3.73 |
| **II**-HB3 | O129 | LP (2) | N14-H150 | BD*(1) | 2.15 | $n_O \rightarrow \sigma_{N-H}^*$ | 5.08 |
| **II**-HB4 | O129 | LP (2) | N15-H16 | BD*(1) | 2.41 | $n_O \rightarrow \sigma_{N-H}^*$ | 1.43 |
| **III**-HB1 | O90 | LP (1) | N14-H150 | BD*(1) | 1.89 | $n_O \rightarrow \sigma_{N-H}^*$ | 9.88 |

Figure S4. The calculated $^1$H NMR chemical shifts for two degenerate molecular shuttle conformations (binding at Station **I**).
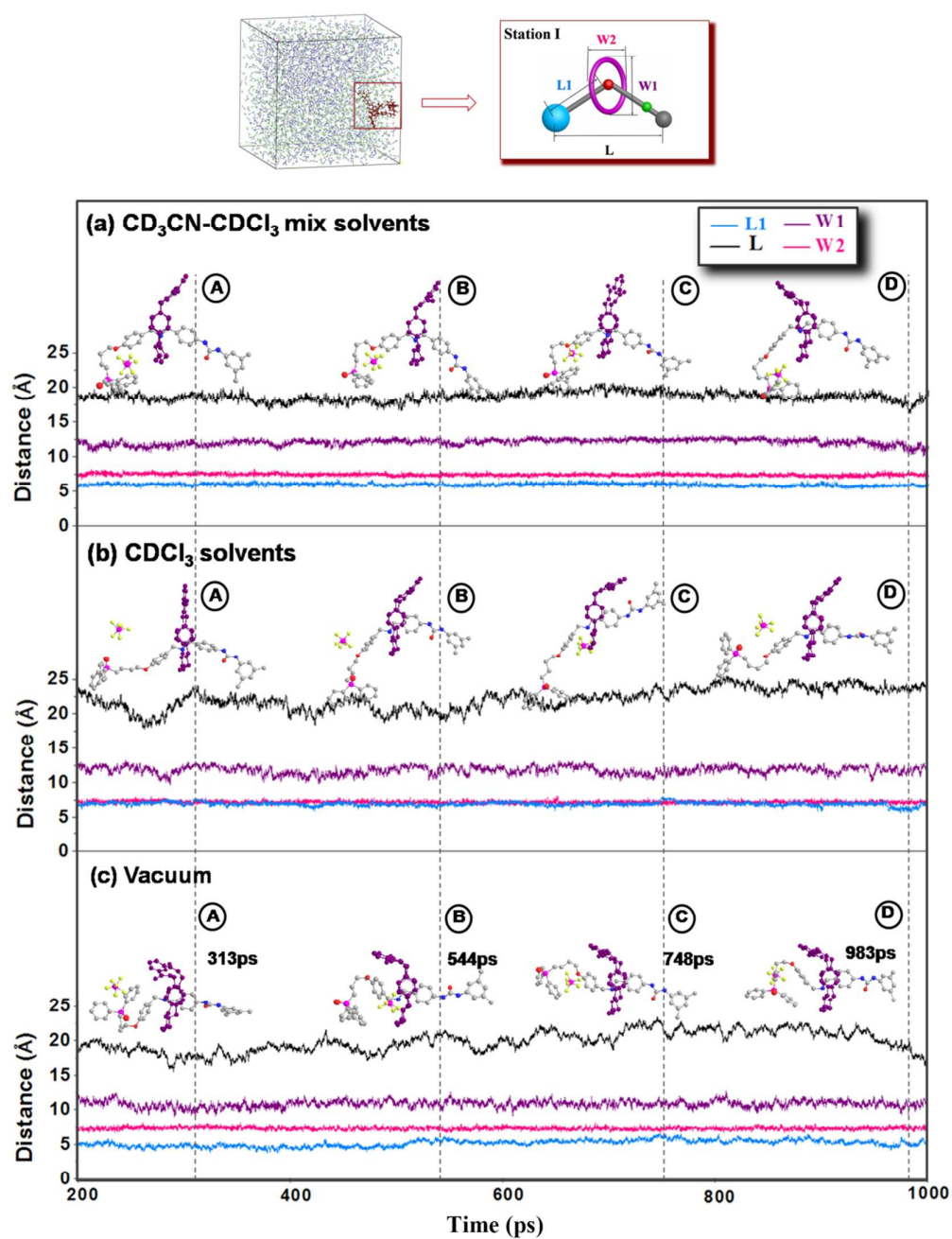
Figure S5. MD trajectories of molecular shuttle binding at Station **I** in (a) CD₃CN-CDCl₃ mix solvents (b) nonpolar CDCl₃ solvents (c) vacuum without any solvents.
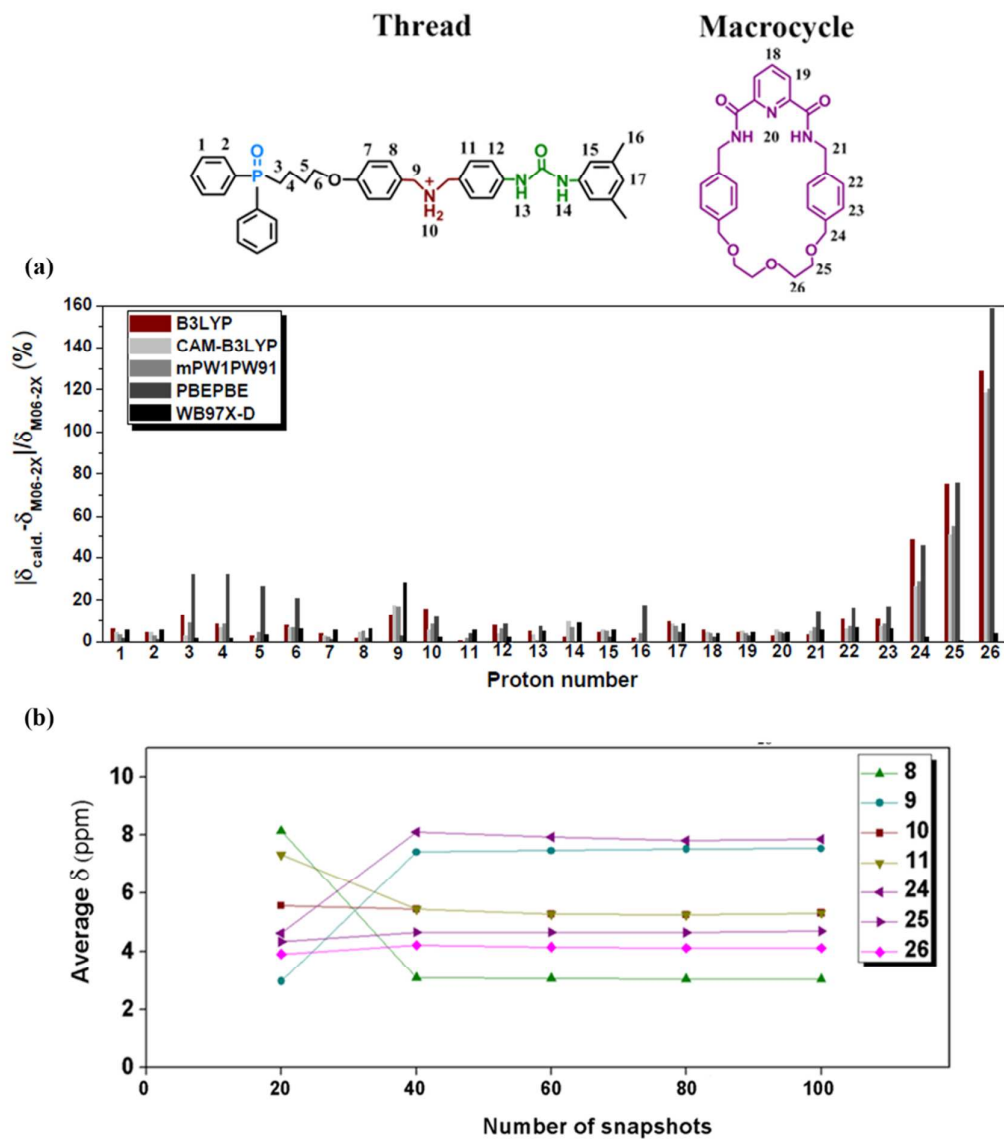
Figure S6. For the molecular shuttle binding at Station **I**: (a) comparison of the differences of computed ${}^1$H NMR chemical shifts using different DFT functionals with 6-31G (d, p) basis set with respect to the M06-2X functional results; (b) convergence test (along MD trajectory) of the calculated NMR chemical shifts of the protons attaching at Station **I**.

Table S3. The calculated ^{1}H NMR chemical shifts with PCM model and explicit solvent model (MD ensemble-average) for molecular shuttle binding at Station **I** at M06-2X/6-31G(d, p) level.

| NO.H | PCM solvent=$CH_3CN$ | PCM solvent=$CHCl_3$ | Solu.[MD] | Exp. |
|---|---|---|---|---|
| 1 | 8.82 | 8.70 | 8.70 | 7.54 |
| 2 | 8.90 | 8.86 | 9.07 | 7.76 |
| 3 | 3.97 | 3.85 | 2.47 | 2.37 |
| 4 | 3.03 | 3.20 | 2.47 | 1.78 |
| 5 | 2.78 | 2.71 | 2.49 | 1.85 |
| 6 | 5.14 | 5.19 | 4.54 | 3.91 |
| 7 | 8.52 | 8.50 | 8.53 | 6.65 |
| 8 | 9.28 | 9.16 | 8.44 | 6.95 |
| 9 | 3.98 | 3.87 | 2.95 | 2.50 |
| 10 | 6.46 | 6.50 | 5.24 | 7.20 |
| 11 | 8.50 | 8.42 | 8.10 | 6.96 |
| 12 | 8.54 | 8.52 | 8.46 | 7.36 |
| 13 | 4.91 | 4.69 | 5.20 | 7.51 |
| 14 | 6.03 | 5.76 | 5.03 | 7.27 |
| 15 | 8.16 | 8.12 | 7.87 | 7.03 |
| 16 | 2.5 | 2.49 | 2.72 | 2.25 |
| 17 | 8.37 | 8.34 | 7.75 | 6.66 |
| 18 | 9.44 | 9.42 | 9.30 | 8.17 |
| 19 | 9.34 | 9.38 | 9.43 | 8.43 |
| 20 | 9.29 | 9.04 | 7.73 | 9.01 |
| 21 | 4.95 | 4.93 | 5.16 | 4.65 |
| 22 | 8.57 | 8.52 | 8.51 | 7.08 |
| 23 | 8.26 | 8.26 | 8.56 | 6.83 |
| 24 | 4.99 | 4.96 | 4.62 | 4.21 |
| 25 | 3.92 | 3.89 | 4.04 | 3.59 |
| 26 | 4.65 | 4.71 | 4.02 | 3.25 |
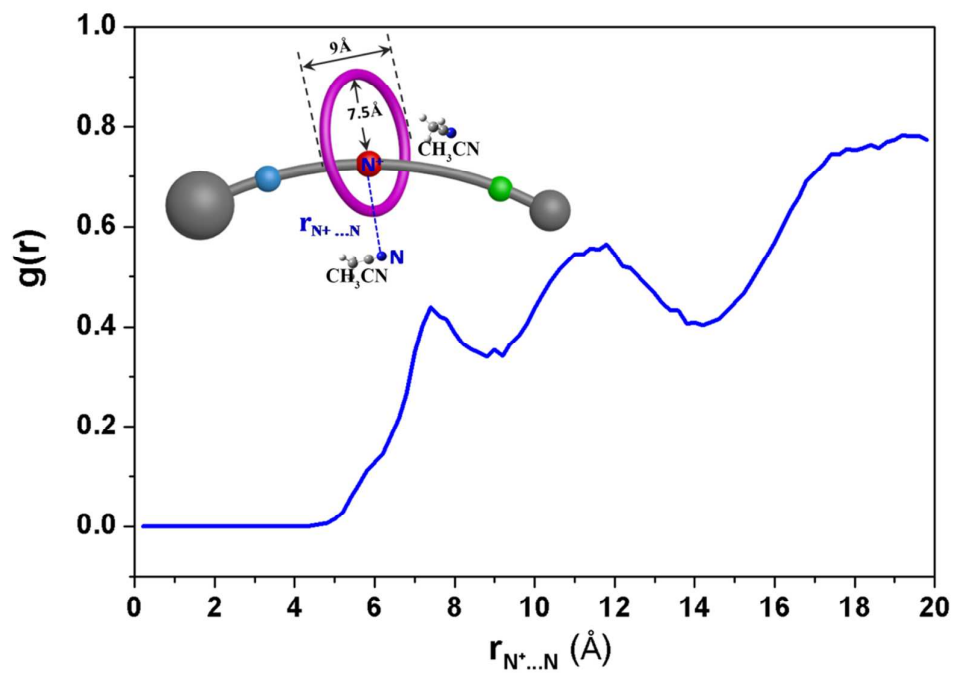
Figure S7. The radial distribution function of 1ns snapshot of MD simulation of

Station **I**.