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Supporting Information

Synergistic Host-Guest Hydrophobic and Hydrogen Bonding Interactions in the Complexation Between Endo-Functionalized Molecular Tube and Strongly Hydrophilic Guest Molecules in Aqueous Solution

Rabindranath Paul and Sandip Paul*

Department of Chemistry, Indian Institute of Technology, Guwahati, Assam, India-781039

(Dated: May 23, 2018)

Here it is worth to mention that the geometry optimization of host-1b molecule was also performed using DFT method in which the same basis set as that for HF method was used (see main article text). It is observed that the configurations adopted by host-1b molecule for these two methods are very similar. Moreover, the orientation of both the $N-H$ groups of host-1b, as we move from gas phase to solution phase, is changed and this may be attributed due to the presence of solvent water molecules. Furthermore, following previous works[1,2], we have also calculated the binding free energies for guests dioxane and acetone from the respective estimated PMF values obtained from umbrella sampling method (discussed in the main text). We find that MM-PBSA method gives approximately five times more negative values of binding free energies for both the systems in comparison to that calculated using the PMF values. This is as per our expectation because, MM-PBSA method considers the contributions of all the atomic sites while calculating different interaction energies whereas, we calculated PMF by considering only the center of masses of host and guest molecules. Moreover, MM-PBSA method has some limitations. In brief, in MM-PBSA method, the electrostatic contribution to the solvation free energy is calculated by solving the linerarized Poisson-Boltzmann equation and then an empirical term is added for calculating the hydrophobic contributions. Nevertheless, the highly negative binding free energy values obtained from both the methods suggest favorable host-guest interactions.

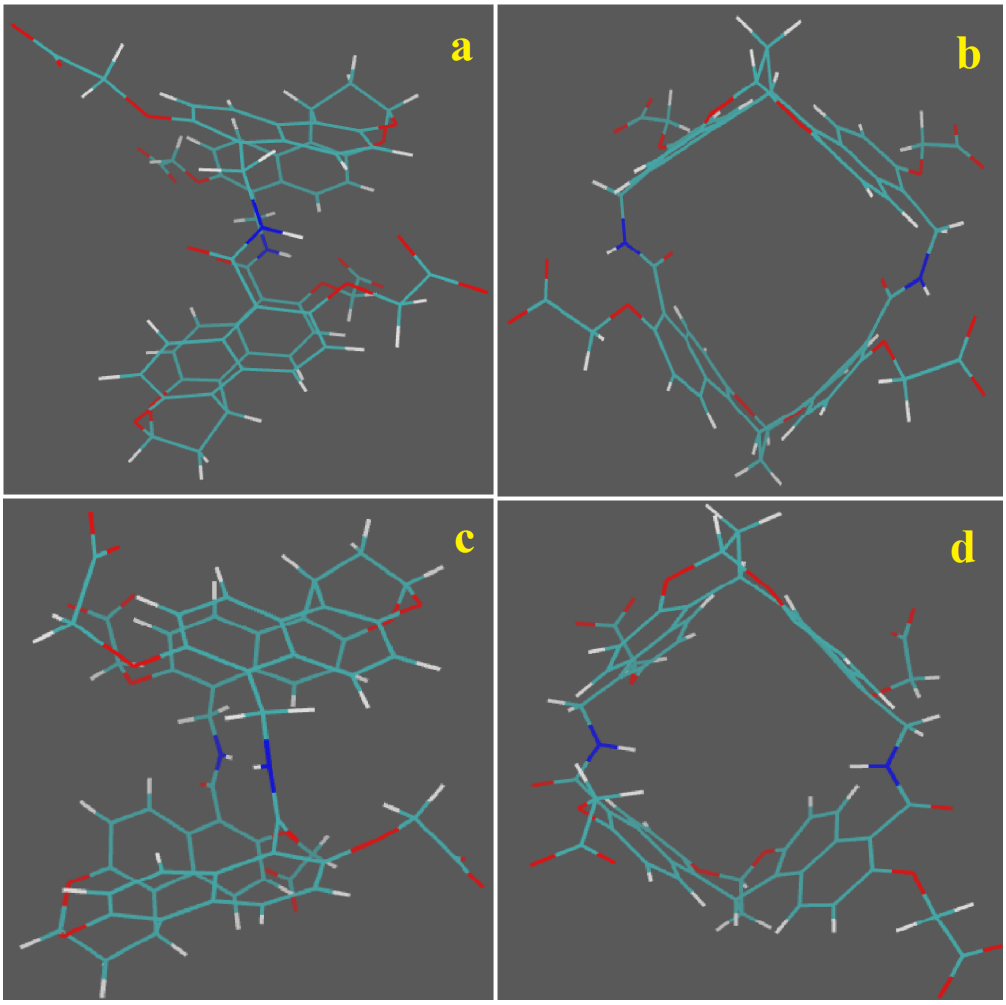

FIG. S1: (a) and (b) are the initial Hartree-Fock optimized configuration in gas phase and (c) and (d) are the configuration after MD run in pure water (without any guest molecules) of the host-1b. Left and right panels represent side and top view, respectively.

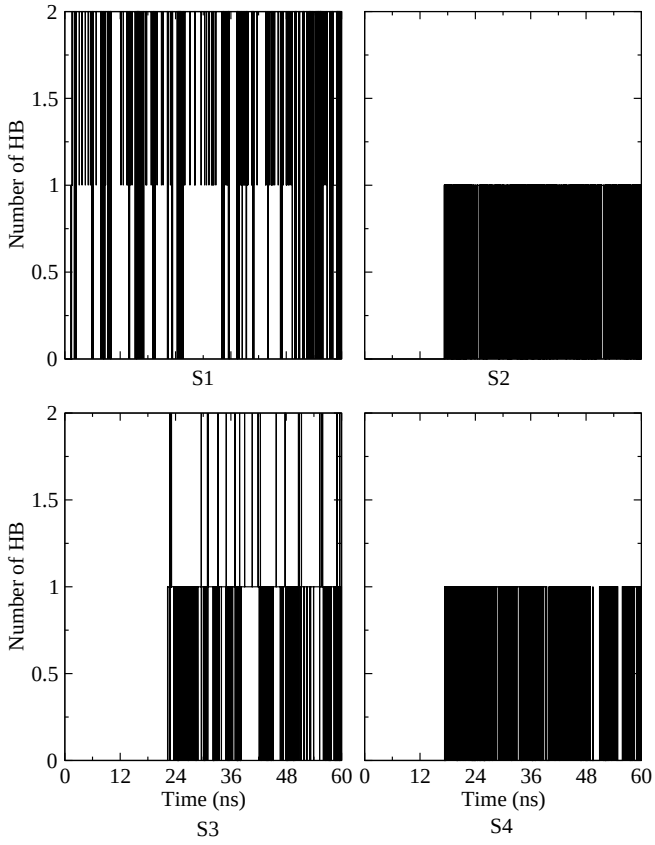

FIG. S2: Host-inserted guest intermolecular hydrogen bonds (HB) value vs. simulation time for different systems.

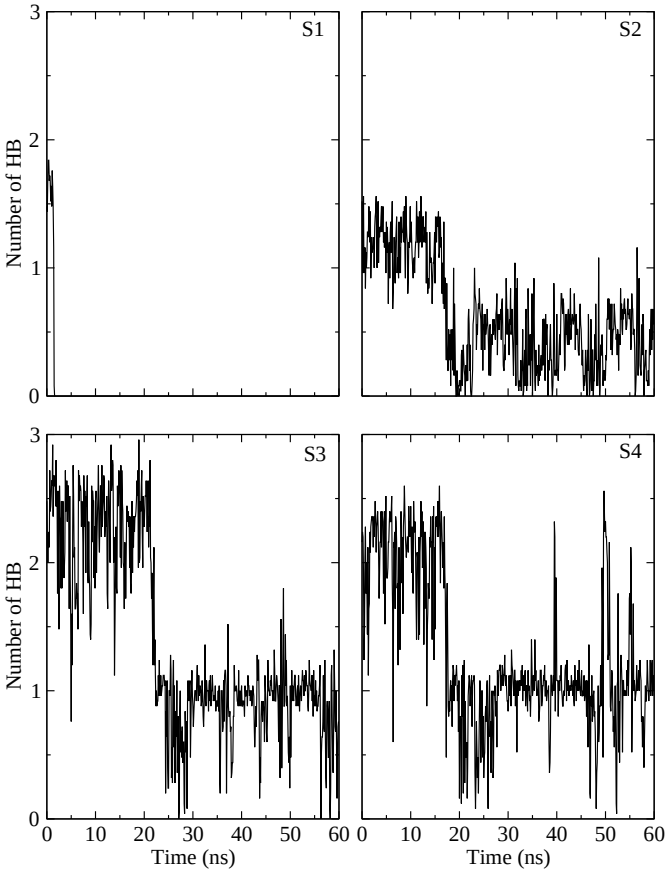

FIG. S3: Water-inserted guest intermolecular hydrogen bonds (HB) as a function of simulation time for different systems.

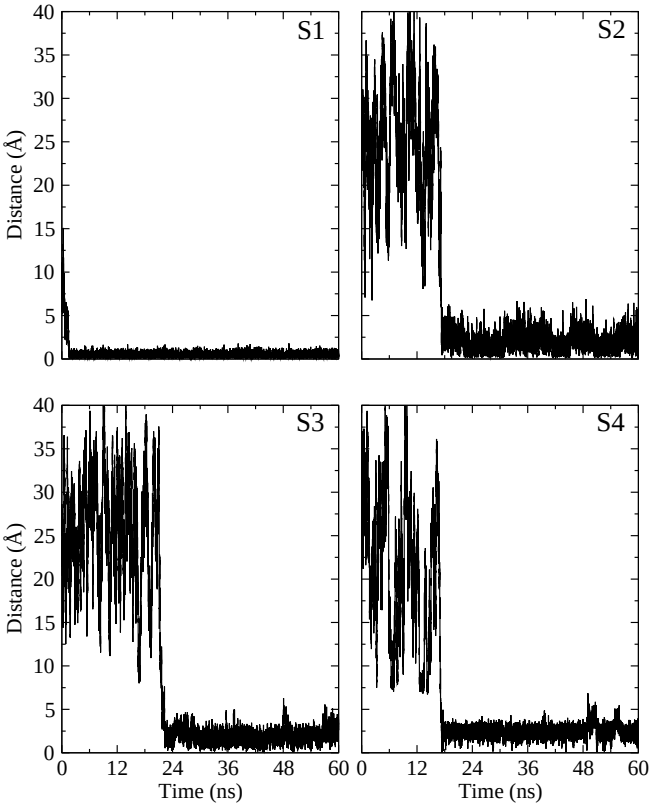

FIG. S4: Host-inserted guest center of mass to center of mass (COM-COM) distance as a function of simulation time for different systems.

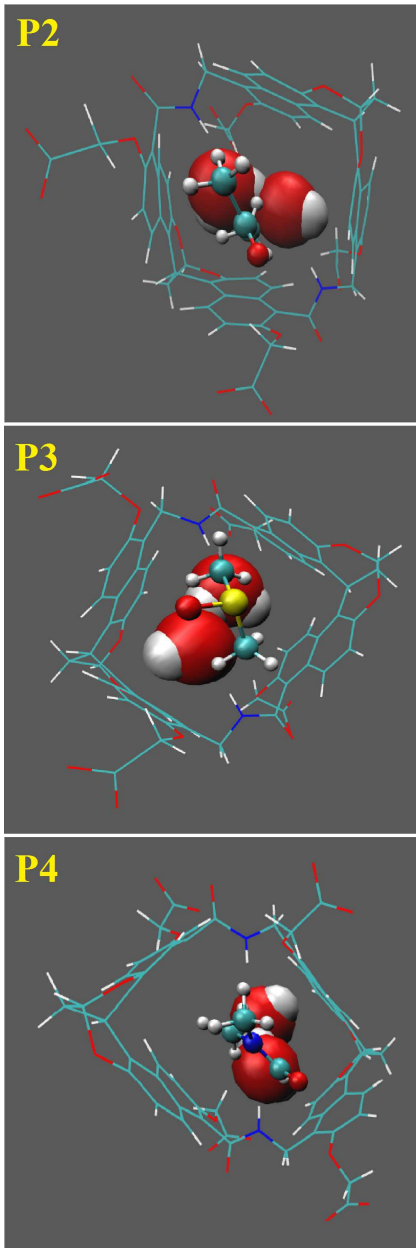

FIG. S5: The visualization of solvent-separated-minimum (SSM) structures for P2, P3 and P4 systems. These snapshots are prepared when the distance between the center-of-mass of host and the center-of-mass of guest is 5Å . Only the water molecules (represented as VDW) present between the host-1b (represented as lines) and the guest molecules (represented as CPK) are considered. Other water molecules are left-off to enhance the visual clarity.

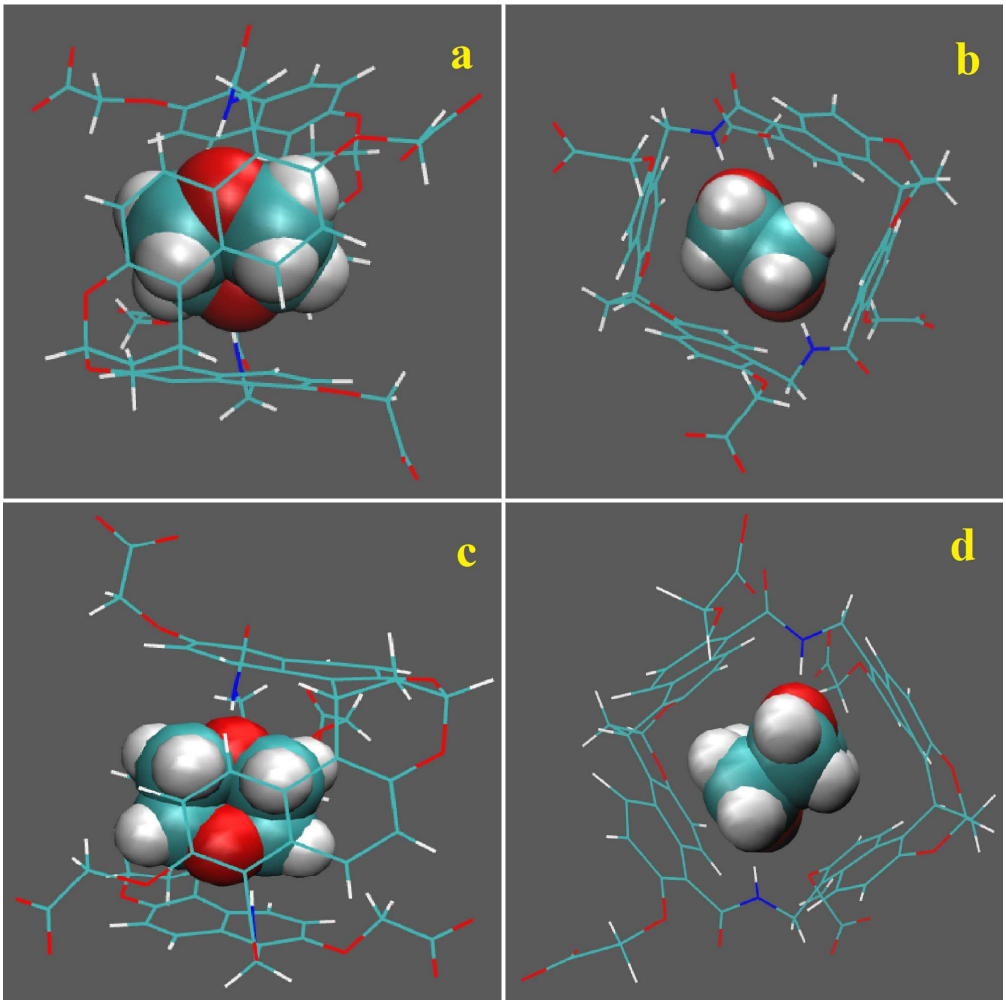

FIG. S6: (a) and (b) are the snapshots for system S1 and (c) and (d) are the snapshots for system S1-test. Left and right panels represent side and top view, respectively.

TABLE S1: Partial charges of different atomic sites of host-1b and ammonium ion. e is the elementary charge.

Host-1b							
Atom	Charge (e)	Atom	Charge (e)	Atom	Charge (e)	Atom	Charge (e)
O5, O6	-0.6651	C85	-0.6899	C68	0.5877	H97, H98	0.0123
C20	0.5716	C84	0.5877	C66	-0.6117	H81	0.1708
C13	1.0925	C82	-0.6117	C65	-0.2608	O101, O102	-0.5940
C99, C100	-0.6651	C80	-0.2608	H103	0.1708	H14	-0.0695
C36	0.5716	C79	0.4658	H67	0.3942	C15	-1.0468
C37	-0.3272	O9, O10	-0.5802	H59	0.1657	H16, H17	0.1888
H38	0.1814	C72	0.8542	H61, H90	0.1740	H54, H55	0.0123
C39	-0.2464	C29	-0.2464	C77	0.9714	C18	1.0382
H40	0.1632	C64	0.4658	C74	-0.7070	H19	-0.1261
C41	0.2421	C63	-0.4062	H75, H76	0.0996	C21, C49	-0.5908
C42	-0.6232	C62	-0.0491	H32	0.1814	C22	0.1891
C43	0.4809	C60	-0.2565	H78	-0.1762	C23	-0.2887
O7, O8	-0.1990	C58	-0.2864	C92	-0.4062	H24	0.1635
C50	-0.2490	C57	0.5118	C91	-0.0491	C25	-0.2642
H51, H52	0.0636	O11, O12	-0.3156	C89	-0.2565	H104	0.1653
C96	0.5277	C69	0.0133	C87	-0.2864	C26	0.4809
C111	1.1483	H70, H71	-0.0031	C86	0.5118	H2	0.5133
O114, O116	-0.9397	H83	0.3942	H88	0.1657	C33	-0.2490
N1, N3	-1.1261	C112	1.0887	C93	0.0133	H34, H35	0.0636
C44	-0.2642	O113, O115	-0.9441	H94, H95	-0.0031	H4	0.5133
H45	0.1653	H73	-0.0469	C31	-0.3272	C105	1.1483
C46	-0.2887	C56	-0.6899	C106	1.0887	O107	-0.9397
H47	0.1635	C53	0.5277	O108, O110	-0.9441	O109	-0.9397
C48	0.1891	H30	0.1632	C28	0.2421	C27	-0.6232
Ammonium ion							
N1	-0.8762	H2, H3, H4, H5	0.4691				

TABLE S2: Average number of host-water hydrogen bonds for different systems. For calculating host-water hydrogen bonds the N1 and N3 atomic sites (as well as hydrogen atoms attached to them) of host-1b are considered.

	Average value of hydrogen bonds	
System	N1 atom	N3 atom
S0	0.85	0.67
S1	0.02	0.01
S2	0.42	0.31
S3	0.71	0.51
S4	0.32	0.23

TABLE S3: Average number of host-inserted guest hydrogen bonds for different systems.

System	Average value of hydrogen bonds
S1	1.91
S2	0.57
S3	0.57
S4	0.58

TABLE S4: Average internal diameter-1 and internal diameter-2 of host-1b for S1 and S1-test system.

System	Average value of diameter-1 (Å)	Average value of diameter-2 (Å)
S1	13.04	9.80
S1-test	13.07	9.79

TABLE S5: The binding free energy values of S1 and S1-test system. All energy values are expressed in kcal/mol unit.

System	ΔE_{vdw}	ΔE_{ele}	ΔG_{PB}	ΔG_{NP}	ΔG^{0}_{bind}
S1	-27.98	-10.17	12.43	-19.15	-44.87
S1-test	-27.99	-10.12	12.46	-19.10	-44.75

* Electronic address: sandipp@iitg.ernet.in

References:

[1] J. Timko, D. Bucher, S. Kuyucak, *J. Chem. Phy.*, 2010, **132**, 114510-1-8.

[2] J. S. Patel, F. M. Ytreberg, *J. Chem. Theory Comput.*, 2018, **14**, 991-997.