Supporting Information

Xe Affinities of Water-Soluble Cryptophanes and the Role of Confined Water

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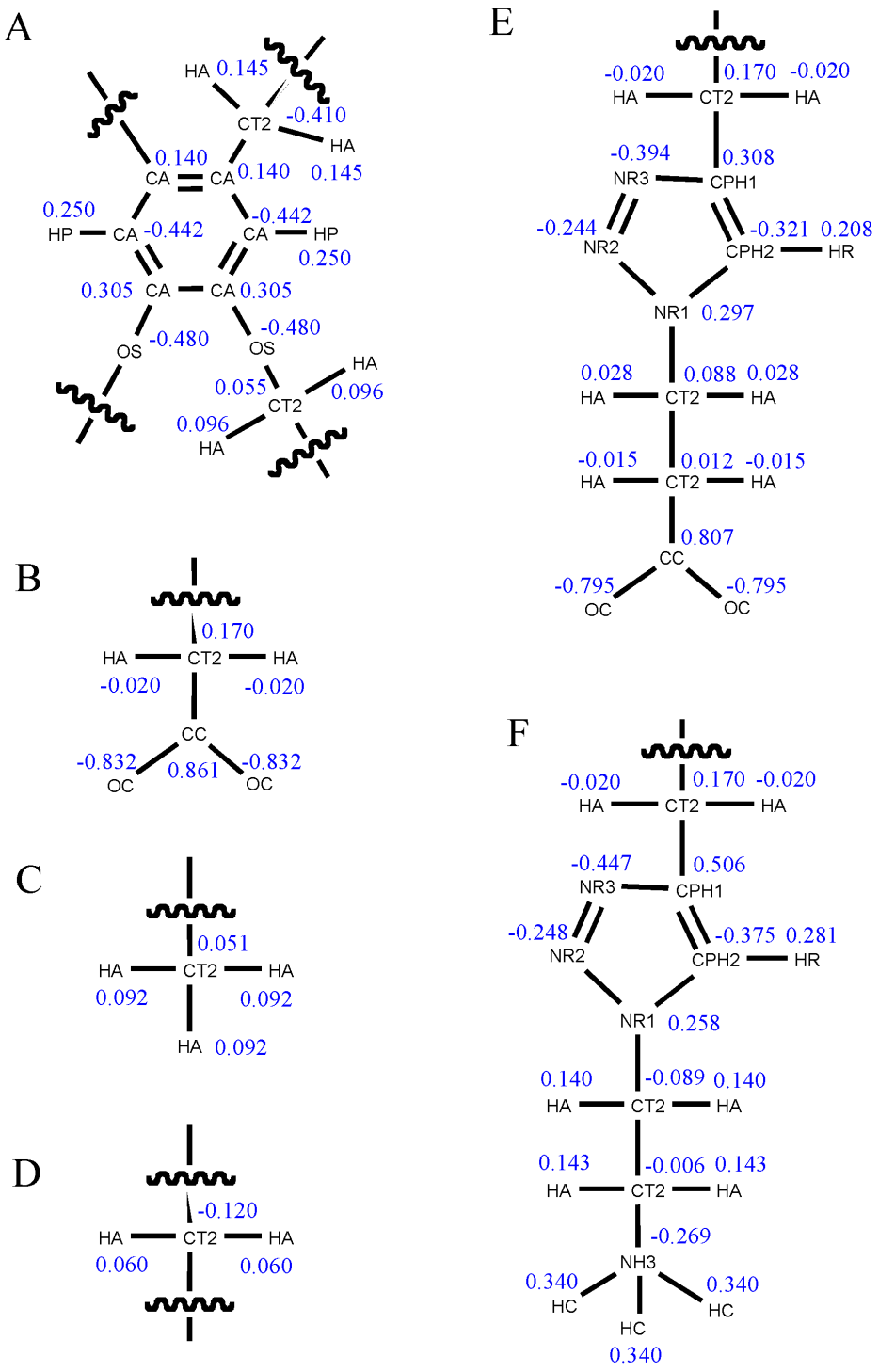

Figure S1. Molecular segments labeled by atom types and electrostatic charges. Segment **(A)** is the cryptophane backbone and is thus included in all cryptophane molecules. Segment **(B)** is the carboxyl side chain in TAAC, *m2n2*, *m2n3* and *m3n3*. Segment **(C)** is the methyl side chain in TAAC and TTPC. Segment **(D)** is the additional methylene group in the middle of the propyl linkers of *m2n3* and *m3n3*. Segment **(E)** is the long side chain in TTPC. Segment **(F)** is the long side chain in TTEC.

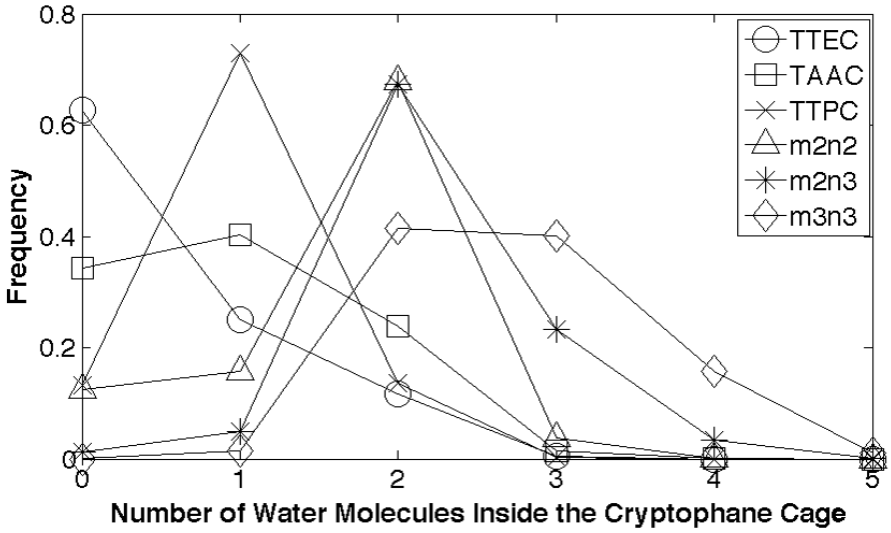

Figure S2. The histograms of number of water molecules inside the cryptophane molecules. The radius cutoff is set at 4 Å relative to the center of mass of the carbons in the six aromatic rings of each cryptophane molecule. The average numbers of interior water molecules are 0.50 for TTEC, 0.92 for TAAC, 1.01 for TTPC, 1.63 for *m2n2*, 2.23 for *m2n3*, and 2.73 for *m3n3*, respectively.

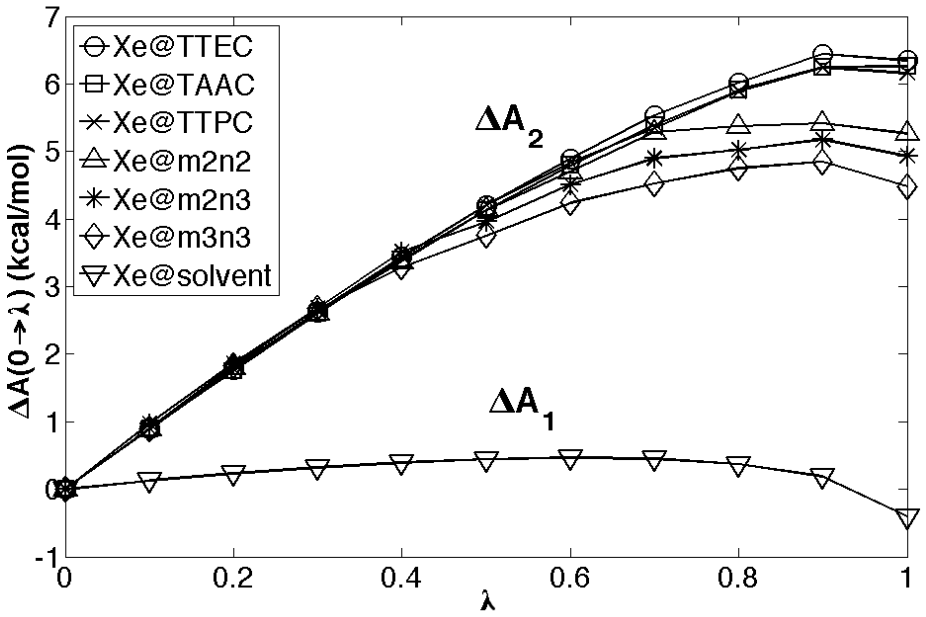

Figure 3. Helmholtz free energy changes ΔA_1 and ΔA_2 as functions of the decoupling parameter λ.

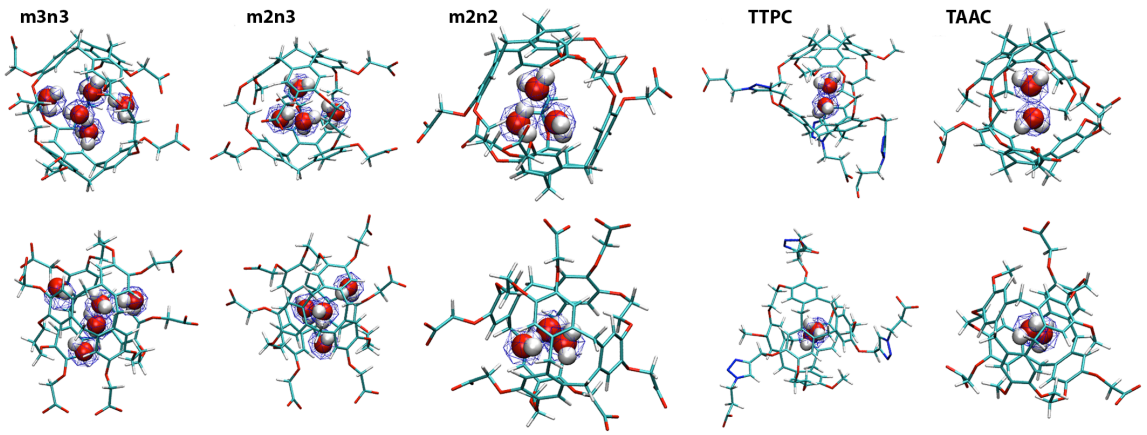

Figure 4. Water maps for water molecules inside *m3n3*, *m2n3*, *m2n2*, TTPC and TAAC. Side view (**top**) and top view (**bottom**). For each position cluster marked by a blue wireframe sphere with radius of 1 Å, 1 water molecule representing the highest orientation cluster is shown.

Table 1. Potential energy (force field) parameters[b]

bond	b_0 (Å)	k_b (kcal/mol/ Å^2)
CA—OS [a]	1.364	450
CT2—CPH1	1.480	324
CPH1—CPH2	1.388	366
CPH1—NR3	1.364	325
CPH2—NR1	1.356	379
CPH2—HR	1.086	332
NR1—NR2	1.356	280
NR1—CT2	1.472	286
NR2—NR3	1.338	306
angle	θ_0 (deg)	k_θ (kcal/mol/ rad^2)
CA—OS—CT2 [a]	113	35
CA—CT2—CA [a]	114	80
CA—CA—OS [a]	120	70
OS—CT2—CC [a]	110	80
OS—CT2—CPH1	110	50
HA—CT2—CPH1	109	29
CT2—CPH1—CPH2	129	26
CT2—CPH1—NR3	121	29
CPH2—CPH1—NR3	110	30
CPH1—CPH2—NR1	104	25
CPH1—CPH2—HR	134	18
NR1—CPH2—HR	122	20
CPH2—NR1—NR2	112	33
CPH2—NR1—CT2	129	27
NR2—NR1—CT2	119	30
NR1—NR2—NR3	107	46
CPH1—NR3—NR2	108	44
NR1—CT2—HA	108	34
NR1—CT2—CT2	110	50

dihedral angle	δ (deg)	k_δ (kcal/mol)	n
CT2—OS—CA—CA [a]	180	0.90	2
NR1—NR2—NR3—CPH1	180	3.82	1
X—CT2—CPH1—X	0	0	2
X—CT2—NR1—X	0	0	2
X—CPH1—CPH2—X	180	5.38	2
X—CPH1—NR3—X	180	2.40	2
X—CPH2—NR1—X	180	0.62	2
X—NR1—NR2—X	180	0.77	2
improper	ω_0 (deg)	k_ω (kcal/mol/ rad^2)	
CA OS CA CA	0	10	

[a] Previous calculated results[1]

[b] The results are then formatted into CHARMM type as

$$U_{bonded} = \sum_{bonds} k_b(b-b_0)^2 + \sum_{angles} k_\theta(\theta-\theta_0)^2 + \sum_{dihedrals} k_\phi[1+\cos(n\phi-\delta)] + \sum_{impropers} k_\omega(\omega-\omega_0)^2$$

(1) Kirchhoff, P.; Bass, M.; Hanks, B.; Briggs, J.; Collet, A.; McCammon, J. *J. Am. Chem. Soc.* **1996**, *118*, 3237.

Table 2. Residence Time of Water Molecules Inside the Cryptophane Molecules[a]

	Residence Time (ps)	
	Average Value	Maximum Value
TTEC	36.04	2014.8
TAAC	35.41	1011.4
TTPC	84.69	2338.4
m2n2	33.11	2507.6
m2n3	19.90	1862.4
m3n3	17.50	2012.6

[a] The radius cutoff is set at 4 Å relative to the mass weighted center of cryptophane molecules.