Supporting Information

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PARAMETERS, PROTOCOLS, AND SIMULATIONS

For the fixed dipole charge scheme, partial charges by geometry were as follows, beginning with the head atom and proceeding around the ring: Triangle, $(-1, 0.5, 0.5)$; Square, $(-1, 0.387, 0.226, 0.387)$; Pentagon, $(-1, 0.353, 0.147, 0.147, 0.353)$; Hexagon, $(-1, 0.378, 0.0, 0.244, 0.0, 0.378)$; Heptagon, $(-1, 0.377, 0.0, 0.123, 0.123, 0.0, 0.377)$; Octagon, $(-1, 0.391, 0.0, 0.0, 0.218, 0.0, 0.0, 0.391)$.

Following are charge distributions for the nitrobenzene and united atom N,N-dimethylaniline analogs, in GROMACS topology file format. Partial charges are in the 7th column.

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Nitrobenzene:
     1         ca      1    TMP     C1      1  -0.08790  12.000000
     2         ca      1    TMP     C2      2  -0.13960  12.000000
     3         ca      1    TMP     C3      3  -0.13960  12.000000
     4         ca      1    TMP     C4      4  -0.06760  12.000000
     5         ca      1    TMP     C5      5  -0.06760  12.000000
     6         ca      1    TMP     C6      6  -0.17620  12.000000
     7         no      1    TMP     N1      7   0.87600  14.000000
     8          o      1    TMP     O1      8  -0.49020  16.000000
     9          o      1    TMP     O2      9  -0.49030  16.000000
    10         ha      1    TMP     H1     10   0.14430   1.000000
    11         ha      1    TMP     H2     11   0.14840   1.000000
    12         ha      1    TMP     H3     12   0.14840   1.000000
    13         ha      1    TMP     H4     13   0.17090   1.000000
    14         ha      1    TMP     H5     14   0.17100   1.000000
Nitrobenzene ``neutral ring'':
     1         ca      1    TMP     C1      1  -0.0  12.000000
     2         ca      1    TMP     C2      2  -0.0  12.000000
     3         ca      1    TMP     C3      3  -0.0  12.000000
     4         ca      1    TMP     C4      4  -0.0  12.000000
     5         ca      1    TMP     C5      5  -0.0  12.000000
     6         ca      1    TMP     C6      6  -0.15520  12.000000
     7         no      1    TMP     N1      7   0.87600  14.000000
     8          o      1    TMP     O1      8  -0.36040  16.000000
     9          o      1    TMP     O2      9  -0.36040  16.000000
    10         ha      1    TMP     H1     10   0.0   1.000000
    11         ha      1    TMP     H2     11   0.0   1.000000
    12         ha      1    TMP     H3     12   0.0   1.000000
    13         ha      1    TMP     H4     13   0.0   1.000000
    14         ha      1    TMP     H5     14   0.0   1.000000
Nitrobenzene ``charged ring'':
     1         ca      1    TMP     C1      1  -0.13725  12.000000
     2         ca      1    TMP     C2      2  -0.13815  12.000000
     3         ca      1    TMP     C3      3  -0.13815  12.000000
     4         ca      1    TMP     C4      4  -0.15150  12.000000
     5         ca      1    TMP     C5      5  -0.15150  12.000000
     6         ca      1    TMP     C6      6  -0.15520  12.000000
     7         no      1    TMP     N1      7   0.87600  14.000000
     8          o      1    TMP     O1      8  -0.36040  16.000000
     9          o      1    TMP     O2      9  -0.36040  16.000000
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    10         ha     1    TMP     H1     10    0.13725   1.000000
    11         ha     1    TMP     H2     11    0.13815   1.000000
    12         ha     1    TMP     H3     12    0.13815   1.000000
    13         ha     1    TMP     H4     13    0.15150   1.000000
    14         ha     1    TMP     H5     14    0.15150   1.000000
UA N,N-dimethylaniline:
     1         ca     1    TMP     C1      1   -0.17060  12.000000
     2         ca     1    TMP     C2      2   -0.09880  12.000000
     3         ca     1    TMP     C3      3   -0.09800  12.000000
     4         ca     1    TMP     C4      4   -0.18170  12.000000
     5         ca     1    TMP     C5      5   -0.18880  12.000000
     6         ca     1    TMP     C6      6    0.15520  12.000000
     7         c3     1    TMP     C7      7    0.29430  12.000000
     8         c3     1    TMP     C8      8    0.29330  12.000000
     9         nh     1    TMP     N1      9   -0.65350  14.000000
    10         ha     1    TMP     H1     10    0.13020   1.000000
    11         ha     1    TMP     H2     11    0.12790   1.000000
    12         ha     1    TMP     H3     12    0.12750   1.000000
    13         ha     1    TMP     H4     13    0.13210   1.000000
    14         ha     1    TMP     H5     14    0.13090   1.000000
UA N,N-dimethylaniline ``neutral ring'':
     1         ca     1    TMP     C1      1   -0.0  12.000000
     2         ca     1    TMP     C2      2   -0.0  12.000000
     3         ca     1    TMP     C3      3   -0.0  12.000000
     4         ca     1    TMP     C4      4   -0.0  12.000000
     5         ca     1    TMP     C5      5   -0.0  12.000000
     6         ca     1    TMP     C6      6    0.15520  12.000000
     7         c3     1    TMP     C7      7    0.24915  12.000000
     8         c3     1    TMP     C8      8    0.24915  12.000000
     9         nh     1    TMP     N1      9   -0.65350  14.000000
    10         ha     1    TMP     H1     10    0.0   1.000000
    11         ha     1    TMP     H2     11    0.0   1.000000
    12         ha     1    TMP     H3     12    0.0   1.000000
    13         ha     1    TMP     H4     13    0.0   1.000000
    14         ha     1    TMP     H5     14    0.0   1.000000
UA N,N-dimethylaniline ``charged ring'':
     1         ca     1    TMP     C1      1   -0.13725  12.000000
     2         ca     1    TMP     C2      2   -0.13815  12.000000
     3         ca     1    TMP     C3      3   -0.13815  12.000000
     4         ca     1    TMP     C4      4   -0.15150  12.000000
     5         ca     1    TMP     C5      5   -0.15150  12.000000
     6         ca     1    TMP     C6      6    0.15520  12.000000
     7         c3     1    TMP     C7      7    0.24915  12.000000
     8         c3     1    TMP     C8      8    0.24915  12.000000
     9         nh     1    TMP     N1      9   -0.65350  14.000000
    10         ha     1    TMP     H1     10    0.13725   1.000000
    11         ha     1    TMP     H2     11    0.13815   1.000000
    12         ha     1    TMP     H3     12    0.13815   1.000000
    13         ha     1    TMP     H4     13    0.15150   1.000000
    14         ha     1    TMP     H5     14    0.15150   1.000000
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In the main text, we also report results for nitrobenzene and N,N-dimethylaniline analogs where the sign of the side group is reversed, but these can trivially be obtained from the above charge distributions by changing the sign of all of the charges on the side group.

Tolerances used for bin occupancy rendering in Figures 2 and 8 are shown in Table I. For Figure 7, tolerances were 0.25

Geometry	Case	O Tolerance	H Tolerance
Hexagon	Negative	0.25	0.25
	Positive	0.5	0.6
Linear	(1)(2)	0.4	0.4
	(1)(3)	0.4	0.4
	(1)(4)	0.4	0.4
	(2)(1)	0.25	0.25
	(3)(1)	0.25	0.25
	(4)(1)	0.25	0.25

TABLE I: **Tolerance settings for bin occupancy rendering.** Shown are the tolerances used for rendering the solvent oxygen and hydrogen occupancy regions around the specified solutes. The O and H tolerances are the fractional cutoff for including a particular bin in the displayed atomic occupancy; i.e. the fractional population (as a function of the most populated bin) is calculated for each bin, and only those with a population greater than the tolerance value are included in the displayed occupancy. The case nomenclature for the linear geometry is: First number - position of the negative charge. Second number - position of the positive charge.

(light), 0.5 (medium), and 0.75 (dark).

RESULTS

Raw Data

Table III shows computed hydration free energies and hydration free energy asymmetries for the various linear geometries examined here and plotted in the main text. Table II shows computed hydration free energies for all of the bracelet cases discussed in the main text, as well as some additional bracelet cases where Lennard-Jones (LJ) radii were uniformly increased by a constant scaling factor. When radii were increased, trends stayed roughly the same, but overall hydration free energies (and hydration free energy asymmetries) were smaller in magnitude.

Additional Data for Rods

Table IV shows the enthalpy of hydration for various linear rods. Combined with Table III, this shows that the hydration free energy asymmetries are largely enthalpically driven, except for the last two cases in Table IV, where the asymmetry is nearly zero but the ΔH_{solv} values are different, indicating that entropy and enthalpy nearly compensate.

Additional Figures

Figure 1 shows hydration free energies and asymmetry free energies for the various charge distributions, as in the main text, but with additional Lennard-Jones radii that are scaled up from the original values.

In the main text, we examined hydration free energies and asymmetries only for bracelets where the largest partial charge was ± 1, and the other charges compensated to make the solute net neutral. However, we found that asymmetries are present for *any* smaller magnitude head charge as well. We took all of the hexagon partial charge distributions, and scaled the charges back linearly by some constant prefactor. We then computed the free energy of increasing the partial charges (which here is equivalent to evaluating the change in hydration free energies on increasing the partial charges), and found that this free energy exhibits the same asymmetries. Shown in Figure 2 are these free energy changes. For example, the first point, at a scale factor of 0.1, shows the free energy ($\Delta\Delta G_{elec}$) of increasing the partial charges from net neutral to +/-0.1 on the head atom, and -/+0.1/5 on the other atoms. The sum of these $\Delta\Delta G_{elec}$ values up to a particular partial charge scale factor gives the electrostatic component of the hydration free energy for that charge distribution.

Figure 3 shows cylindrical radial distribution functions (within 5Å of the rod) and water dipole orientations around several different rods. It is interesting to note (as in Figure 7 of the main text) that there is usually a bridging structure between the positively and negatively charged beads, as shown by the connected regions of oriented dipoles in the dipole plots. It is also interesting to note that the charges lead to significant local water density fluctuations around the rod.

Geometry	Radius scalefactor	P-bracelet	N-bracelet
TIP4P-EW water, distributed charge scheme			
triangle	1.0	-18.35±0.07	-29.47±0.14
square	1.0	-17.35±0.06	-30.15±0.13
pentagon	1.0	-17.99±0.06	-33.88±0.10
heptagon	1.0	-20.14±0.07	-40.75±0.11
octagon	1.0	-21.92±0.07	-44.02±0.11
TIP5P-E water, distributed charge scheme			
triangle	1.0	-13.65±0.04	-15.53±0.04
square	1.0	-14.14±0.04	-16.53±0.04
pentagon	1.0	-15.61±0.03	-18.59±0.04
heptagon	1.0	-19.64±0.04	-23.61±0.04
octagon	1.0	-21.46±0.04	-25.93±0.05
TIP3P water, distributed charge scheme			
triangle	1.0	-13.91±0.02	-19.15±0.03
square	1.0	-13.71±0.04	-20.37±0.04
pentagon	1.0	-14.83±0.03	-22.97±0.04
heptagon	1.0	-17.89±0.04	-28.80±0.04
octagon	1.0	-19.28±0.04	-31.55±0.04
triangle	2.0	0.52±0.03	0.31±0.03
square	2.0	-2.62±0.03	-2.90±0.03
pentagon	2.0	-5.60±0.04	-6.01±0.04
heptagon	2.0	-11.97±0.04	-12.62±0.04
octagon	2.0	-13.86±0.04	-14.65±0.04
TIP3P water, fixed dipole charge scheme			
triangle	1.0	-14.13±0.03	-19.14±0.03
square	1.0	-11.31±0.03	-18.20±0.04
pentagon	1.0	-9.91±0.03	-17.57±0.04
heptagon	1.0	-7.39±0.03	-15.48±0.04
octagon	1.0	-6.19±0.02	-13.94±0.04
triangle	1.5	-3.16±0.02	-4.01±0.02
square	1.5	-3.57±0.02	-4.84±0.02
pentagon	1.5	-4.15±0.03	-5.50±0.03
heptagon	1.5	-4.76±0.03	-6.13±0.03
octagon	1.5	-4.63±0.03	-5.82±0.03
triangle	2.0	0.51±0.03	0.35±0.03
square	2.0	-2.07±0.03	-2.37±0.03
pentagon	2.0	-4.33±0.04	-4.62±0.04
heptagon	2.0	-9.06±0.04	-9.37±0.04
octagon	2.0	-10.07±0.04	-10.32±0.04
TIP3P water, opposing charge scheme			
triangle	1.0	-14.03±0.02	-19.28±0.03
square	1.0	-8.19±0.03	-14.35±0.04
pentagon	1.0	-35.36±0.05	-42.00±0.05
heptagon	1.0	-53.07±0.06	-59.10±0.07
octagon	1.0	-45.76±0.06	-56.76±0.06
triangle	1.5	-3.13±0.02	-4.02±0.02
square	1.5	-2.02±0.02	-3.08±0.02
pentagon	1.5	-14.91±0.04	-16.34±0.04
heptagon	1.5	-25.66±0.04	-27.15±0.04
octagon	1.5	-23.28±0.04	-26.63±0.04
triangle	2.0	0.50±0.03	0.35±0.03
square	2.0	-1.19±0.03	-1.44±0.03
pentagon	2.0	-10.05±0.04	-10.42±0.04
heptagon	2.0	-20.69±0.04	-21.11±0.04
octagon	2.0	-20.81±0.04	-21.98±0.04

TABLE II: **Hydration free energies for different bracelets.** Shown are all computed hydration free energies for bracelets of different geometries, for both P- and N-bracelets. The radius scalefactor column denotes the scaling factor applied to Lennard-Jones radii for the calculation. A value of 1.0 corresponds to the original LJ radii as in the main text; values of 1.5 and 2.0 used LJ radii scaled up by those factors.

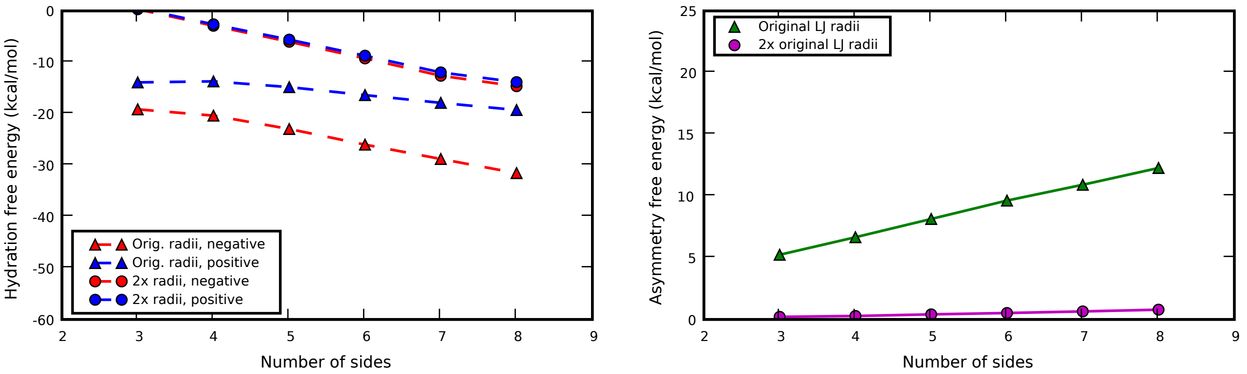
Configuration	ΔG_{solv} (kcal/mol)
5 atom chains	
(-)(+)( )( )( )	-21.33±0.04
(+)(-)( )( )( )	-18.01±0.04
Asymmetry	3.32±0.04
(-)( )(+)( )( )	-61.73±0.08
(+)( )(-)( )( )	-59.07±0.07
Asymmetry	2.66±0.11
(-)( )( )(+)( )	-90.81±0.12
(+)( )( )(-)( )	-87.29±0.12
Asymmetry	3.52±0.18
( )(-)(+)( )( )	-14.43±0.04
( )(+)(-)( )( )	-14.64±0.04
Asymmetry	-0.21±0.04
6 atom chains	
(-)(+)( )( )( )( )	-21.24±0.04
(+)(-)( )( )( )( )	-17.79±0.04
Asymmetry	3.44±0.05
(-)( )(+)( )( )( )	-61.46±0.08
(+)( )(-)( )( )( )	-58.75±0.08
Asymmetry	2.71±0.11
(-)( )( )(+)( )( )	-90.58±0.12
(+)( )( )(-)( )( )	-87.13±0.12
Asmmetry	3.45±0.17
(-)( )( )( )(+)( )	-108.35±0.15
(+)( )( )( )(-)( )	-105±0.14
Asymmetry	3.35±0.21

TABLE III: **Hydration free energies for different rods.** Shown are computed hydration free energies (in TIP3P water) for different linear geometries, grouped in charge-image pairs. Following each pair is shown the asymmetry for that particular geometry. The geometries are denoted by parentheses filled with a space for every neutral atom, and with a plus or minus for every charged atom. Five-atom and six-atom chains are shown.

Configuration	ΔH_{solv} (kcal/mol)
(-)(+)( )( )( )	-30.4±0.3
(+)(-)( )( )( )	-24.6±0.3
(-)( )(+)( )( )	-76.2±0.3
(+)( )(-)( )( )	-71.2±0.3
(-)( )( )(+)( )	-108.0±0.3
(+)( )( )(-)( )	-101.4±0.3
( )(-)(+)( )( )	-21.8 ±0.3
( )(+)(-)( )( )	-24.5 ±0.3

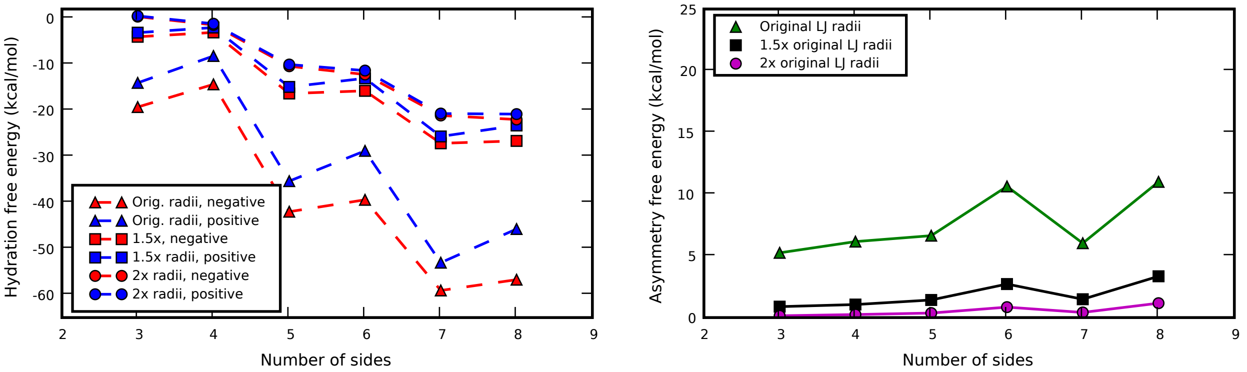
TABLE IV: ΔH_{solv} **for different rods.** Shown are computed enthalpies of hydration (in TIP3P water) for different linear geometries, grouped in charge-image pairs. The geometries are denoted by parentheses filled with a space for every neutral atom, and with a plus or minus for every charged atom.

In the main text, we decomposed the hydration free energy of several solutes into entropic and enthalpic components. To do so, we needed to converge the calculation of the average enthalpy of hydration. Doing this required long simulations. In Figure 4 we show a sample convergence plot for the mean ΔH of hydration over the course of our simulations. The value at each point was obtained by taking the average enthalpy (up to that time point) for the fully interacting system, and subtracting the same quantity for the system where the solute does not interact with the solvent. Uncertainties were obtained as the standard error in the mean, where the effective number of samples is computed considering the statistical inefficiency as obtained from autocorrelation analysis.



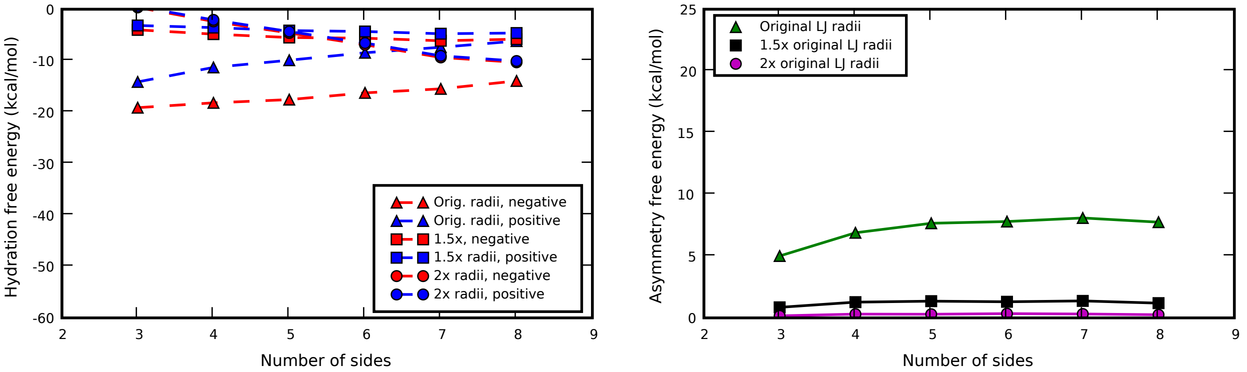
(a)Hydration free energies, distributed case

(b)Asymmetry free energies, distributed case



(c)Hydration free energies, opposing case

(d)Asymmetry free energies, opposing case



(e)Hydration free energies, fixed dipole case

(f)Asymmetry free energies, fixed dipole case

FIG. 1: **Asymmetries for the opposing and fixed dipole bracelets, as a function of size.** Shown, as a function of bracelet size, are asymmetries in TIP3P water for (a) the opposing case, where the neutralizing charges are of magnitude 0.5 and as far from the large large as possible, and (b) for the case where the neutralizing charges are distributed to keep the dipole moment of the solute fixed to the value for the triangle case. Original Lennard-Jones radii are shown, as well as with Lennard-Jones radii scaled by 1.5x (in some cases) and 2.0x. In the legend, positive and negative denote the sign of the largest charge. Lines are a guide for the eye.

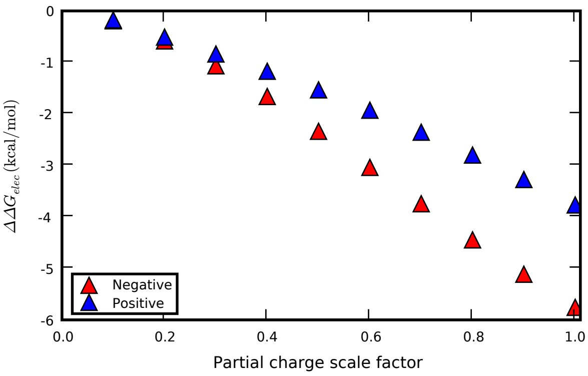
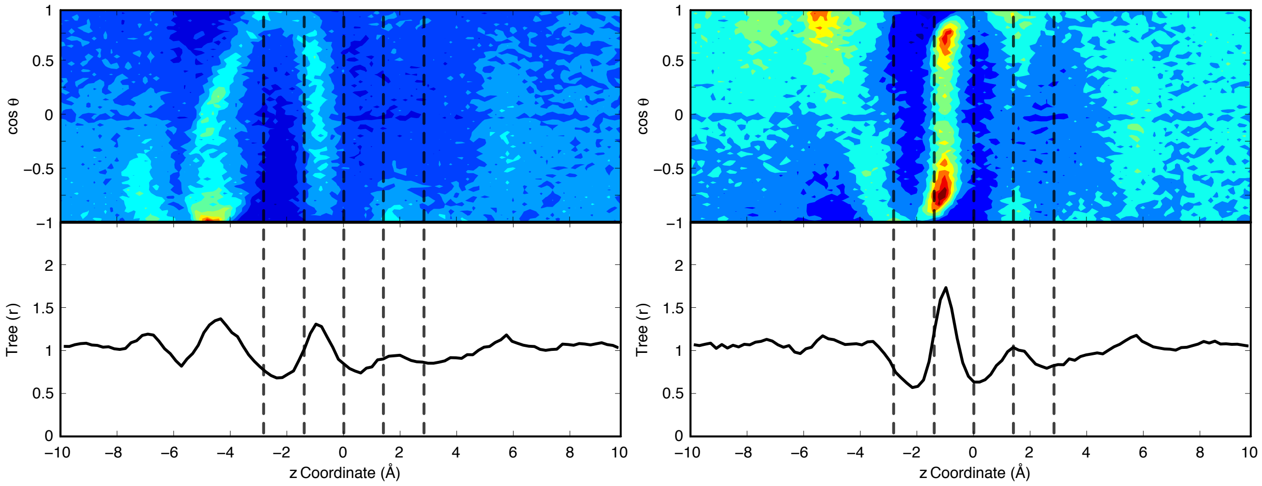
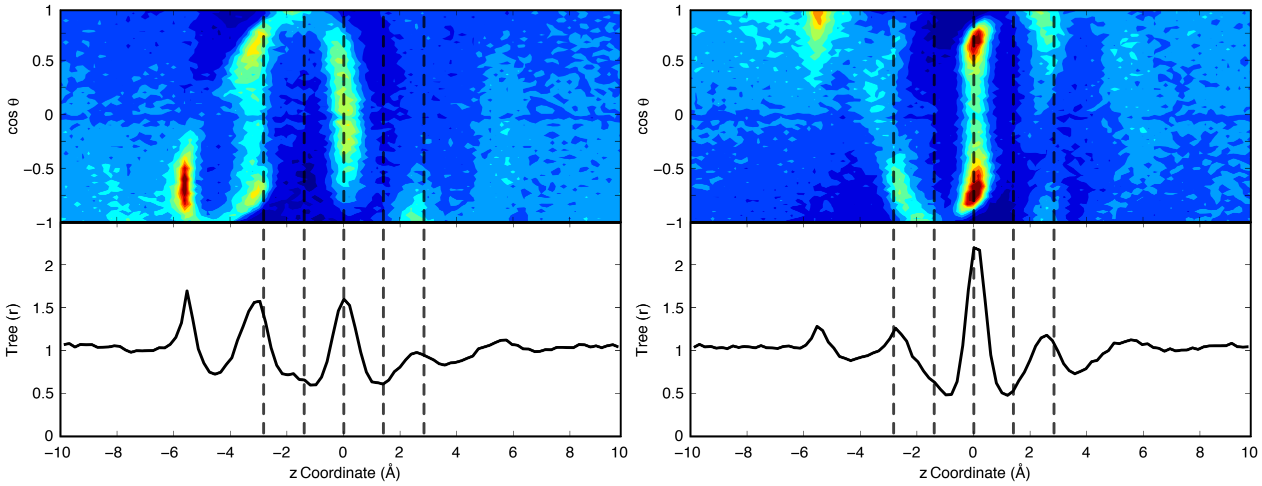


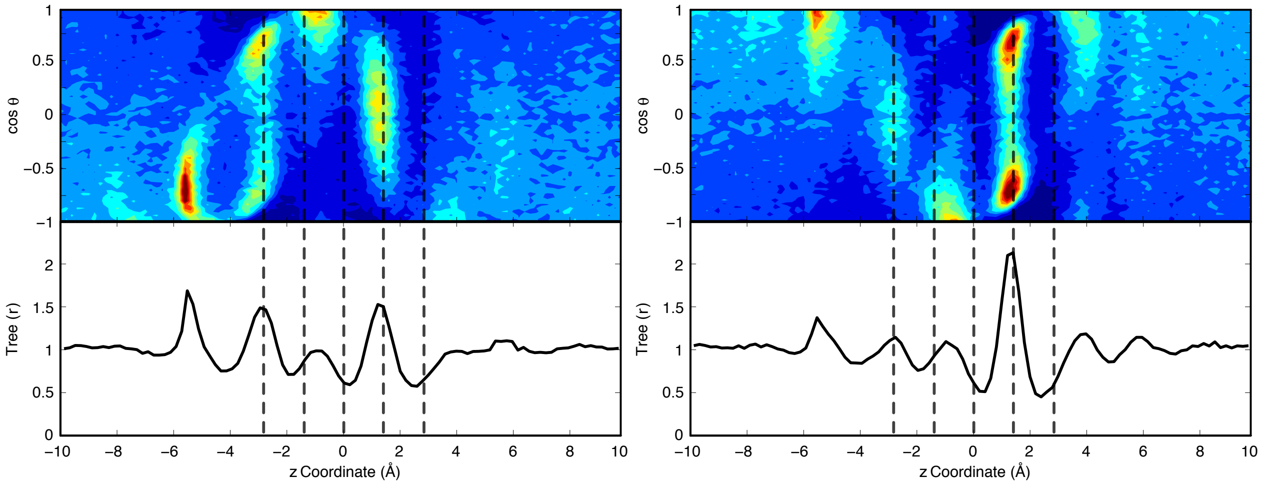
FIG. 2: **Free energy of increasing the magnitude of the partial charges** Shown are $\Delta\Delta G_{elec}$ values for various different scaled charge distributions, for the hexagonal bracelet with the distributed charge scheme. In these charge distributions, the scale factor is a constant prefactor which multiplies all of the partial charges, so a value of 1.0 gives the full charge distribution as in the main text. $\Delta\Delta G_{elec}$ is the difference in hydration free energies on increasing the partial charges.



(a)(-)(+)( )( )( ) (left) and (+)(-)( )( )( )



(b)(-)( )(+)( )( ) (left) and (+)( )(-)( )( )



(c)(-)( )( )(+)( ) (left) and (+)( )( )(-)( )

FIG. 3: **Dipole orientations and radial distribution functions for some rods.** Shown are (top) average water dipole orientations and occupancies and water radial distribution functions in cylindrical coordinates (bottom, “Tree(r)”, showing occupancy within 5Å around the rod) around several different rods. The Z-coordinate lies along the center of the rod, and the dashed lines denote the bead positions. Water dipole orientations are shown by the value of $cos\theta$, where a value of -1 has the dipole pointing to the right along the rod; 0 is perpendicular to the axis of the rod, and +1 is left along the rod.

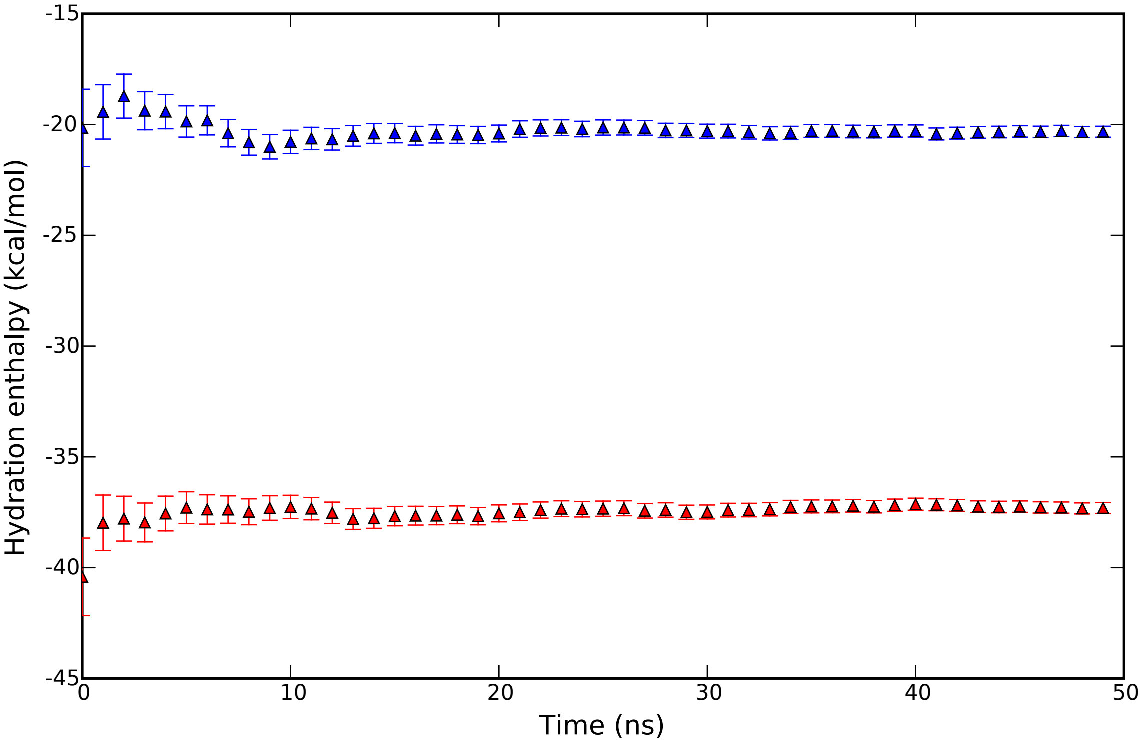


FIG. 4: ΔH **of solvation for the hexagonal N- and P-bracelets**. Shown are the average enthalpies of solvation for the hexagonal N- and P-bracelets as a function of simulation time, to demonstrate convergence. Also shown are error bars representing the uncertainty in the mean, based on autocorrelation analysis. Red symbols denote the N-bracelet and blue symbols the P-bracelet.