

Supplemental Material

Computational Study of Microhydration in Sulfonated Diels-Alder Poly(Phenylene) Polymers

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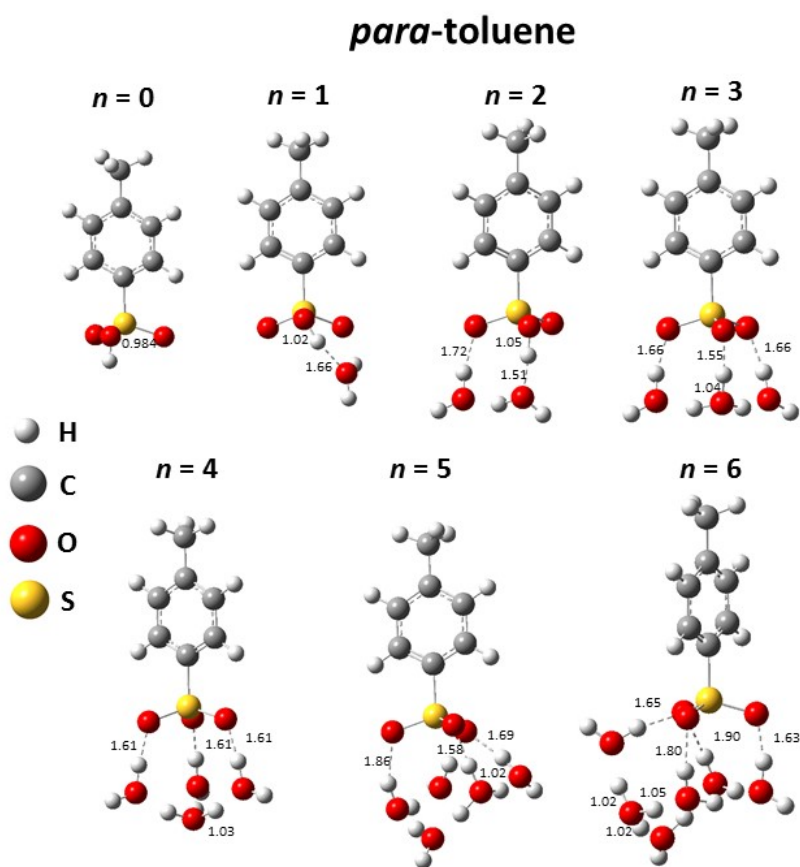


Figure S1. Optimized clusters for the *para*-Tol• n (H₂O) clusters obtained using DFT B3LYP/6-311** methods. Select O-H distances between the sulfonic acid oxygen and the hydrogen bonded water/hydronium protons are shown.

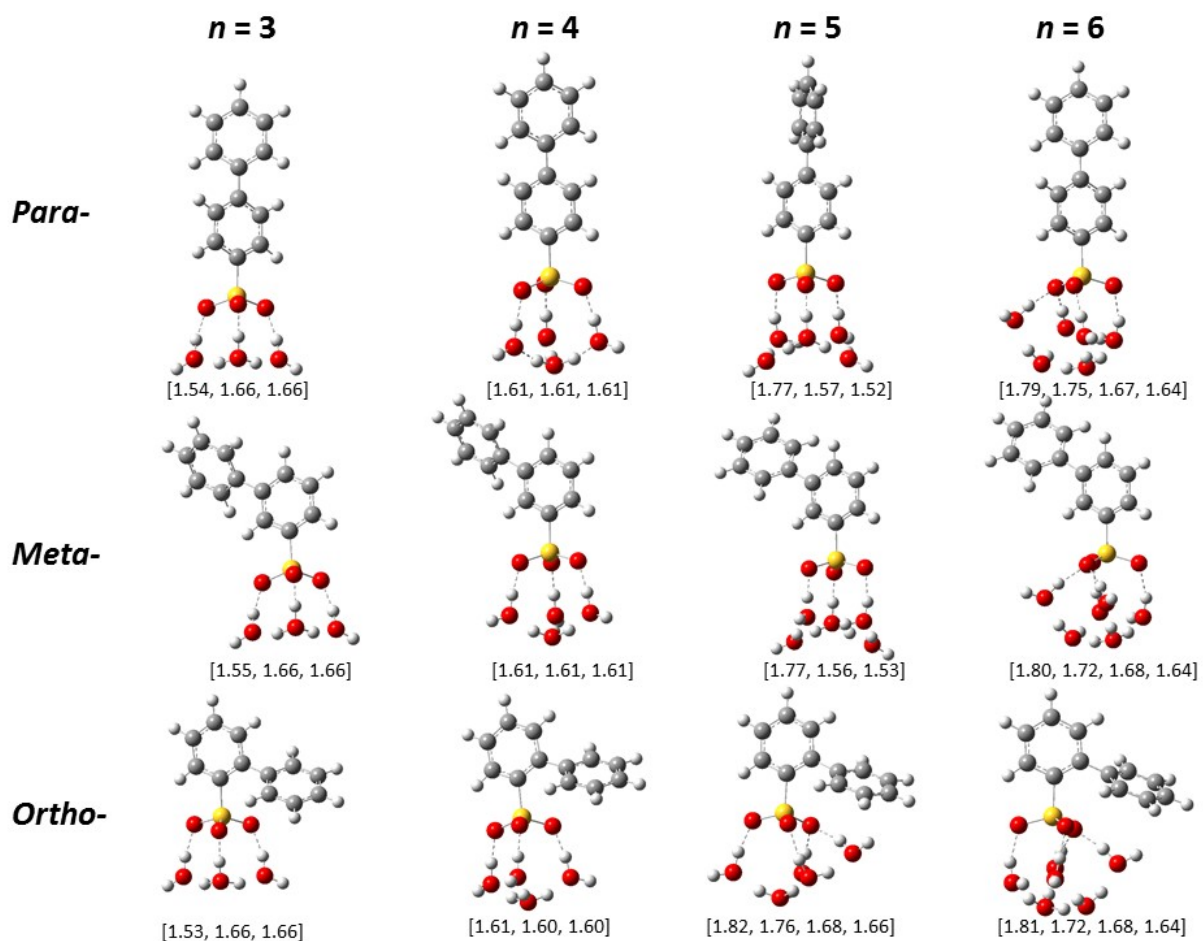


Figure S2. Optimized clusters for the *para*-DIP• n (H₂O), *meta*-DIP• n (H₂O), and *ortho*-DIP• n (H₂O) clusters (for $n = 3, 4, 5$ and 6) obtained using DFT B3LYP/6-311** methods. The $n = 0, 1$ and 2 are not shown, but the structures for those low hydration clusters are nearly identical in the hydrogen bonded network. Select O-H distances between the sulfonic acid oxygen and the hydrogen bonded water/hydronium protons are shown.

Table S1: Micro-hydration Adsorption Energies of Optimized *ortho*-, *meta*-, and *para*-Toluene Sulfonic Acid Clusters.

<i>n</i> H ₂ O	<u><i>p</i>-Tol-SA</u>		<u><i>m</i>-Tol-SA</u>		<u><i>o</i>-Tol-SA</u>	
	ΔE^{Ads} (kcal/mol)	$\Delta E^{Ads} / n$ (kcal/mol)	ΔE^{Ads} (kcal/mol)	$\Delta E^{Ads} / n$ (kcal/mol)	ΔE^{Ads} (kcal/mol)	$\Delta E^{Ads} / n$ (kcal/mol)
1	-16.6	-16.6	-16.7	-16.7	-17.0	-17.0
2	-36.0 (-19.4)	-18.0	-36.0 (-19.3)	-18.0	-36.0 (-19.0)	-18.0
3	-56.0 (-20.0)	-18.7	-56.1 (-20.1)	-18.7	-56.9 (-20.9)	-19.0
4	-77.1 (-21.1)	-19.3	-77.1 (-21.0)	-19.3	-77.8 (-20.9)	-19.5
5	-93.6 (-16.5)	-18.7	-93.7 (16.6)	-18.7	-94.5 (-16.7)	-18.9
6	-112.5 (-18.9)	-18.8	-112.6 (-18.9)	-18.8	113.3 (-18.8)	-18.9

ΔE^{Ads} calculated using Eqn. (1).

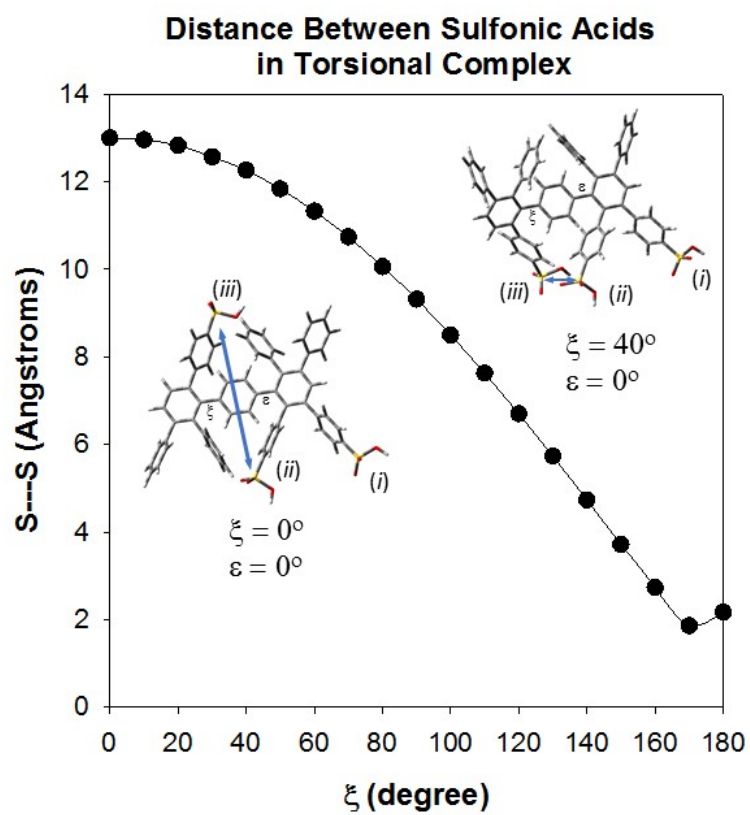


Figure S3: Correlation between the backbone torsional angle ξ (with a fixed $\varepsilon = 0^\circ$) and the S-S distance between the (ii) and (iii) sulfonic acid (“torsional” configuration) in the SDAPP repeat unit.

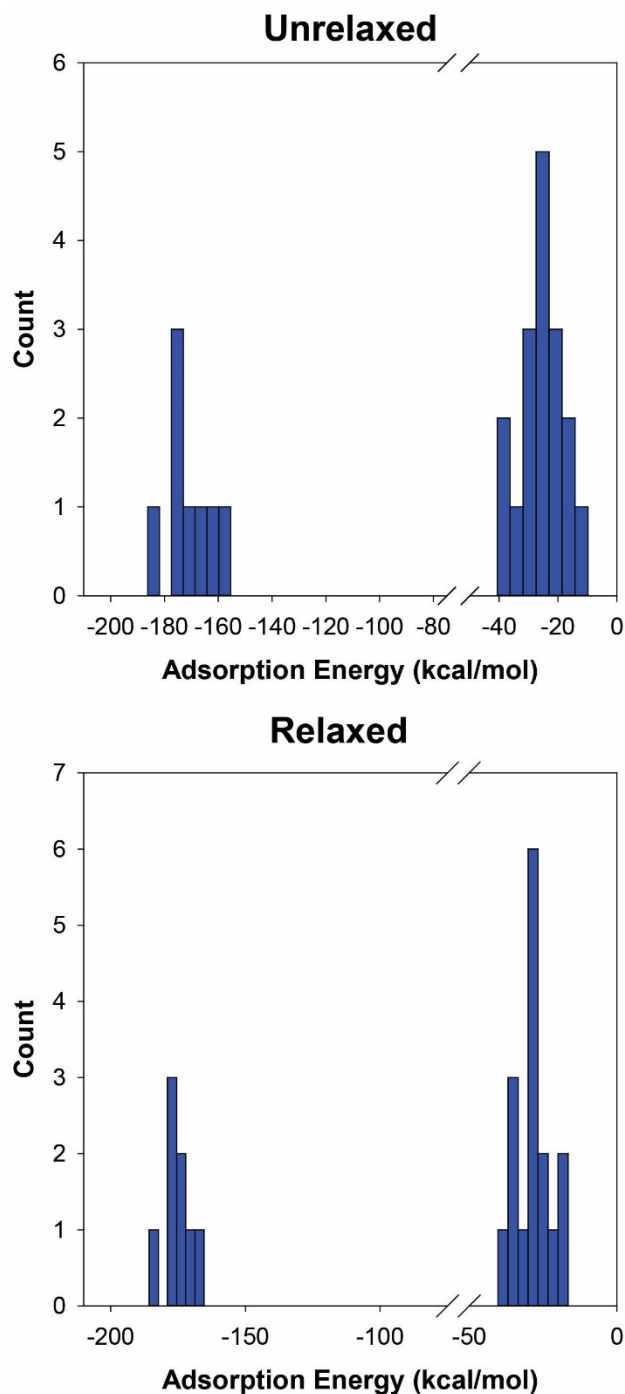


Figure S4: Adsorption energies for the small hydrophilic domain extracted from MD simulations of SDAPP. Unrelaxed structure (as obtained) and re-optimized using HF/6-311**/PM6 ONIOM methods. While there are small changes in the energies, there are no significant changes to the overall distribution and correspondingly the structure of the hydrating water environments. See text for additional discussion.