

## Supplementary Material

### Thermodynamics of $\pi$ - $\pi$ Interactions of Benzene and Phenol in Water

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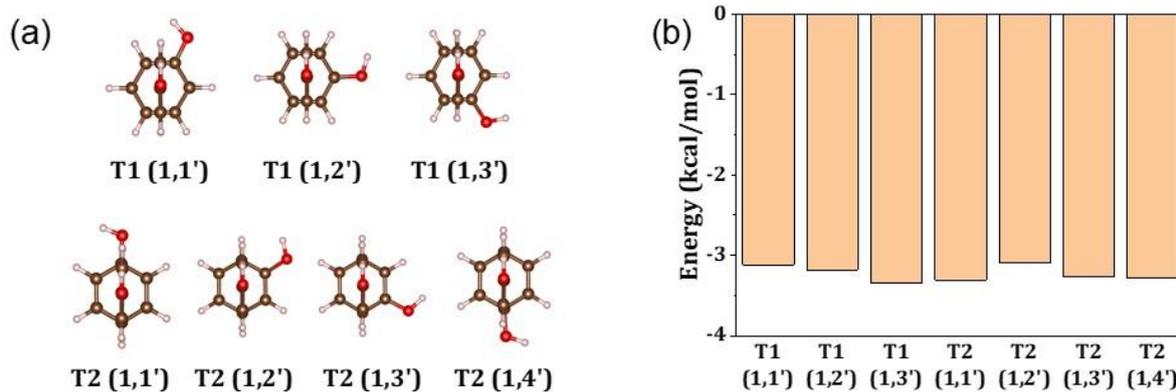
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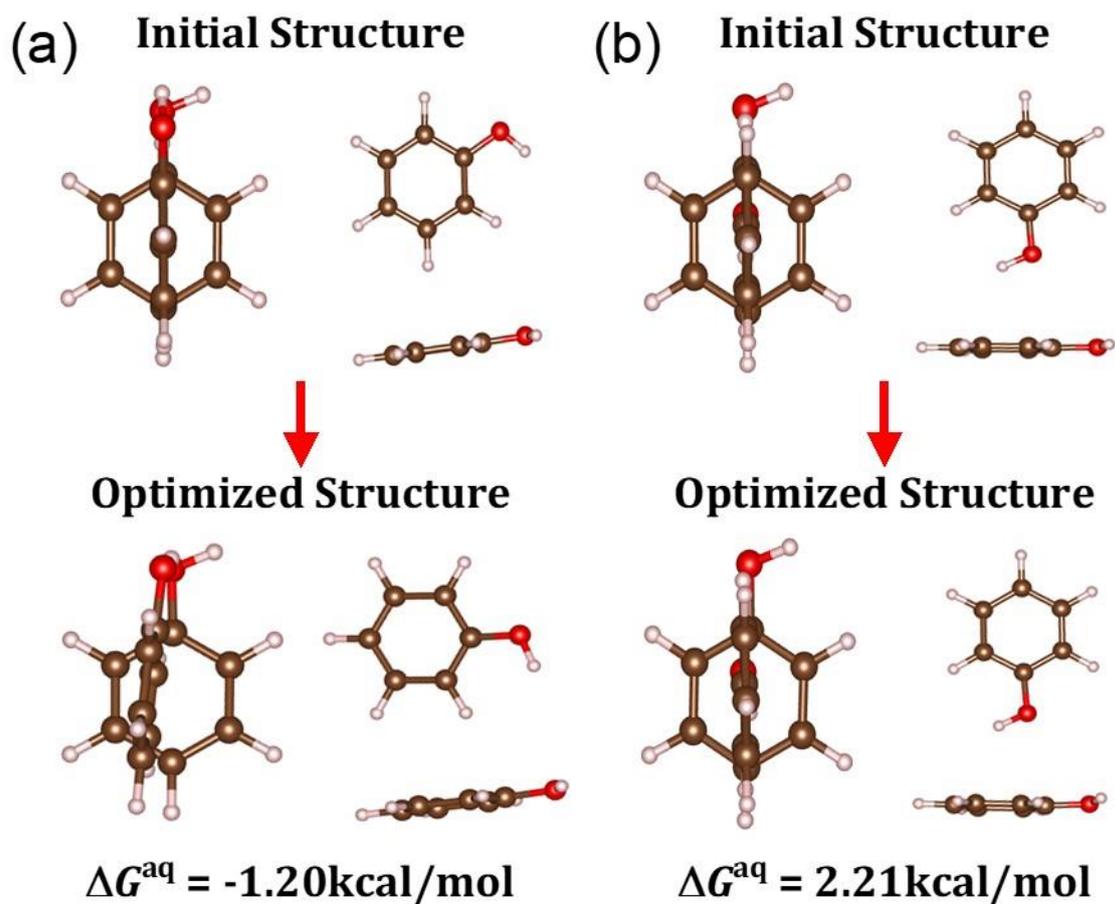
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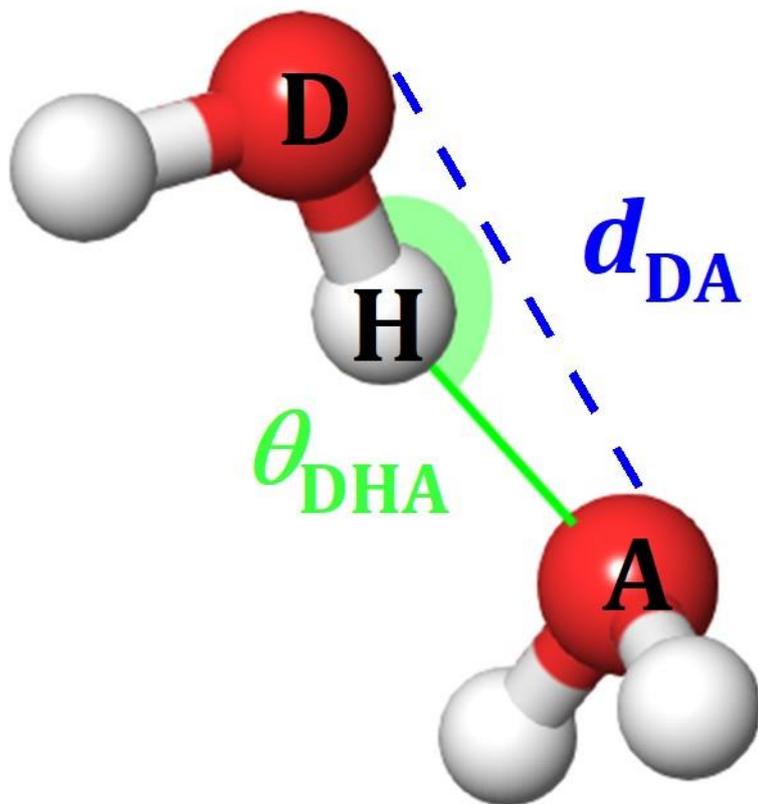
†These authors contributed equally to this work.



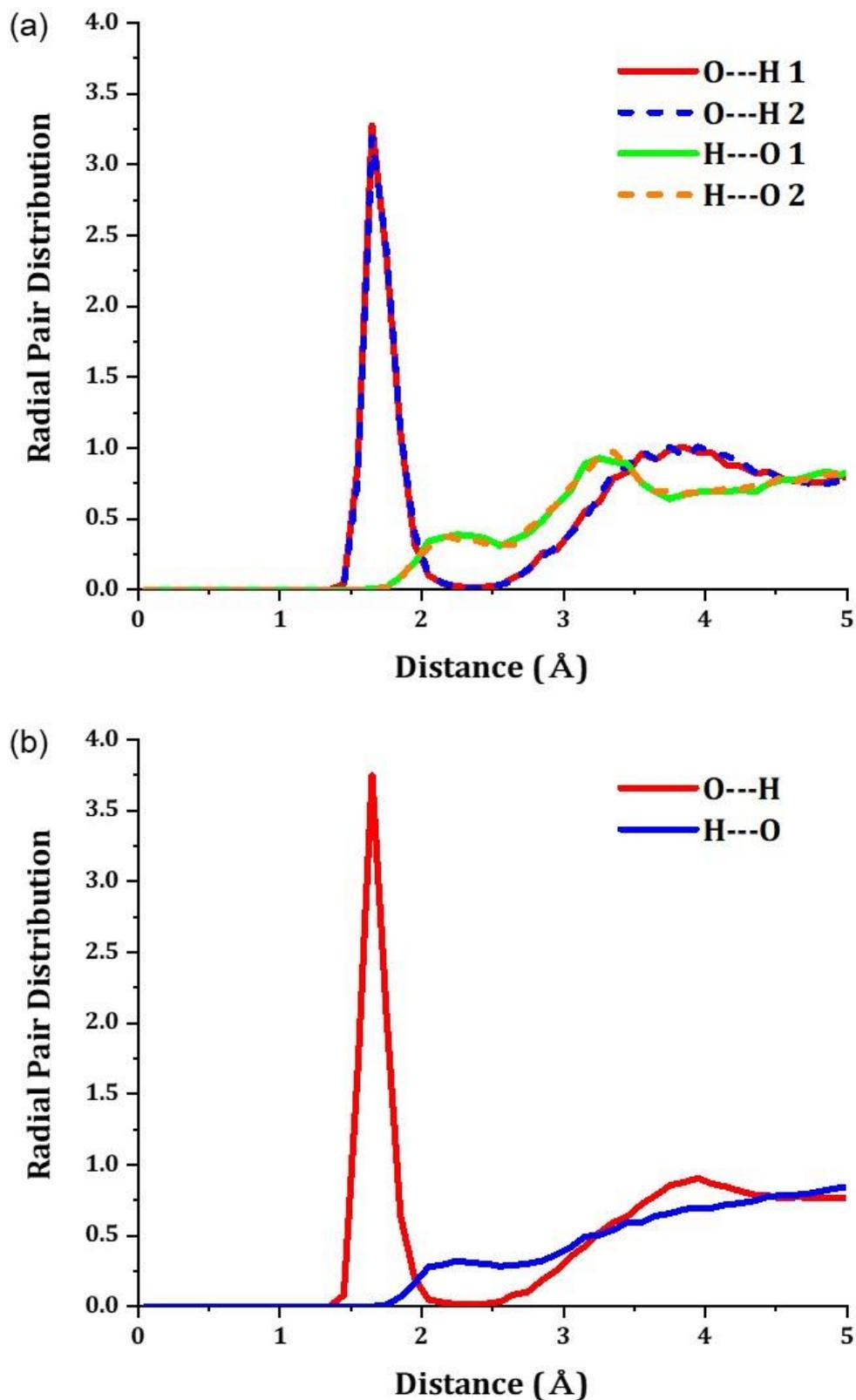
**Figure S1.** (a) Different conformations of phenol dimers with varying the location of OH group in the horizontally laid phenyl ring. The numbers in parenthesis represent the location of hydroxyl groups. (b) Association free energy of phenol dimers calculated in vacuum ( $\Delta G^{\text{vac}}$ ).



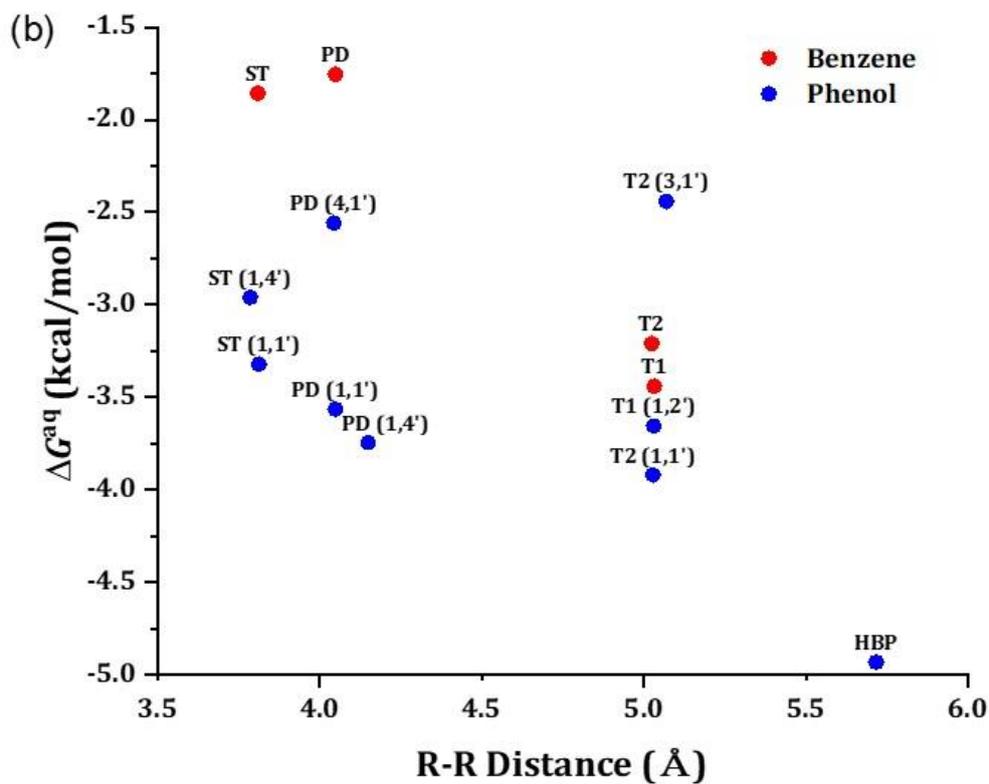
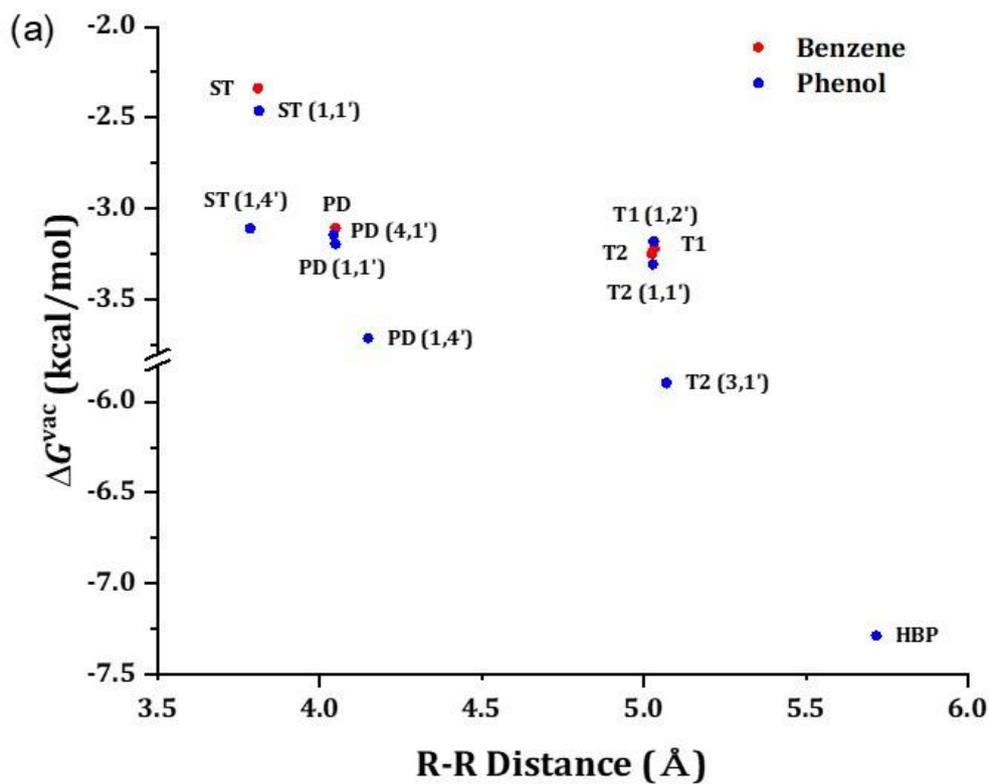
**Figure S2.** Before and after geometry optimizations of (a) T2(2,1') and (b) T2(4,1') conformations in water. T2(2,1') conformation is too unstable to maintain the original conformation, and T2(4,1') shows a positive binding free energy in water, that is  $\Delta G^{\text{aq}} = 2.21$  kcal/mol, disfavoring the dimer association.



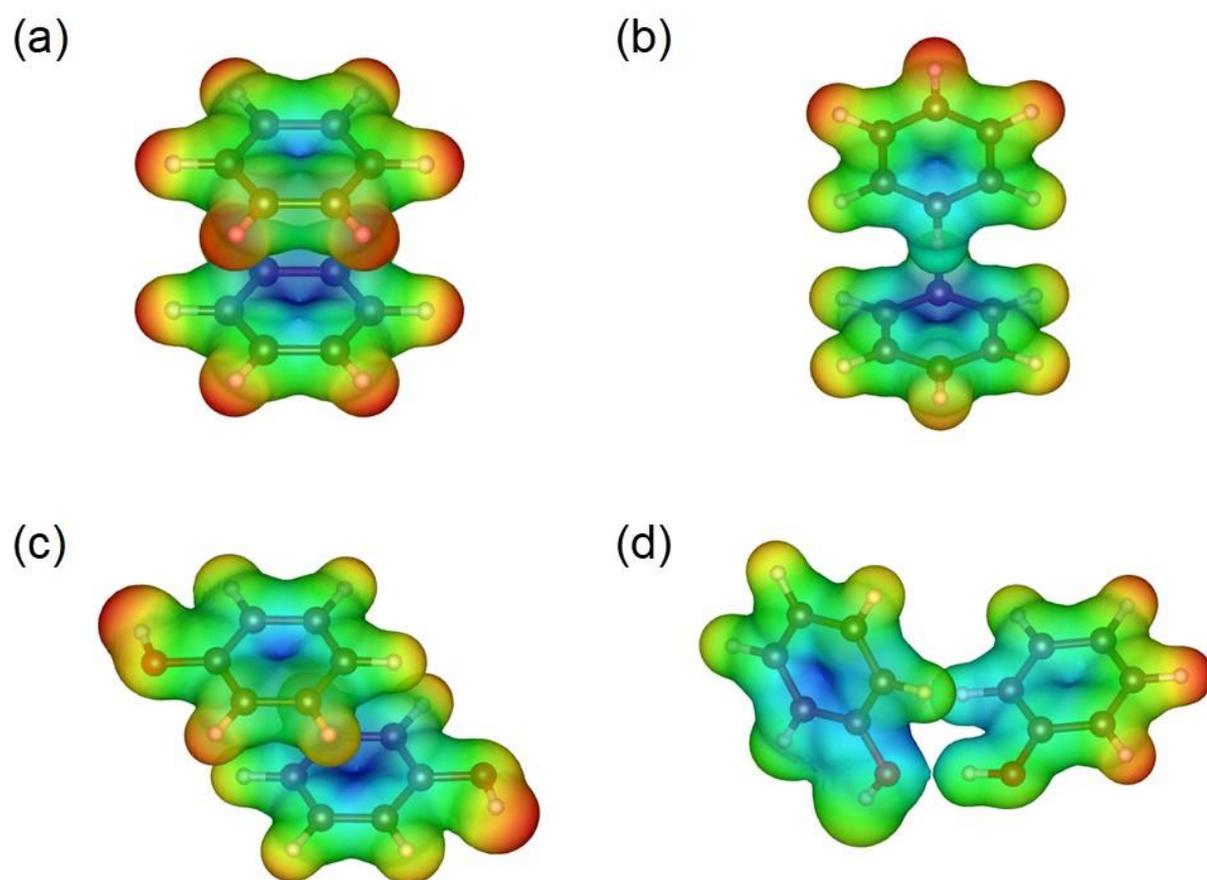
**Figure S3.** The hydrogen bond is defined when the distance between the donor and acceptor oxygen atoms ( $d_{DA}$ ) is shorter than  $3\text{\AA}$  and the angle  $\angle O_A H O_D$  is larger than  $120^\circ$ .



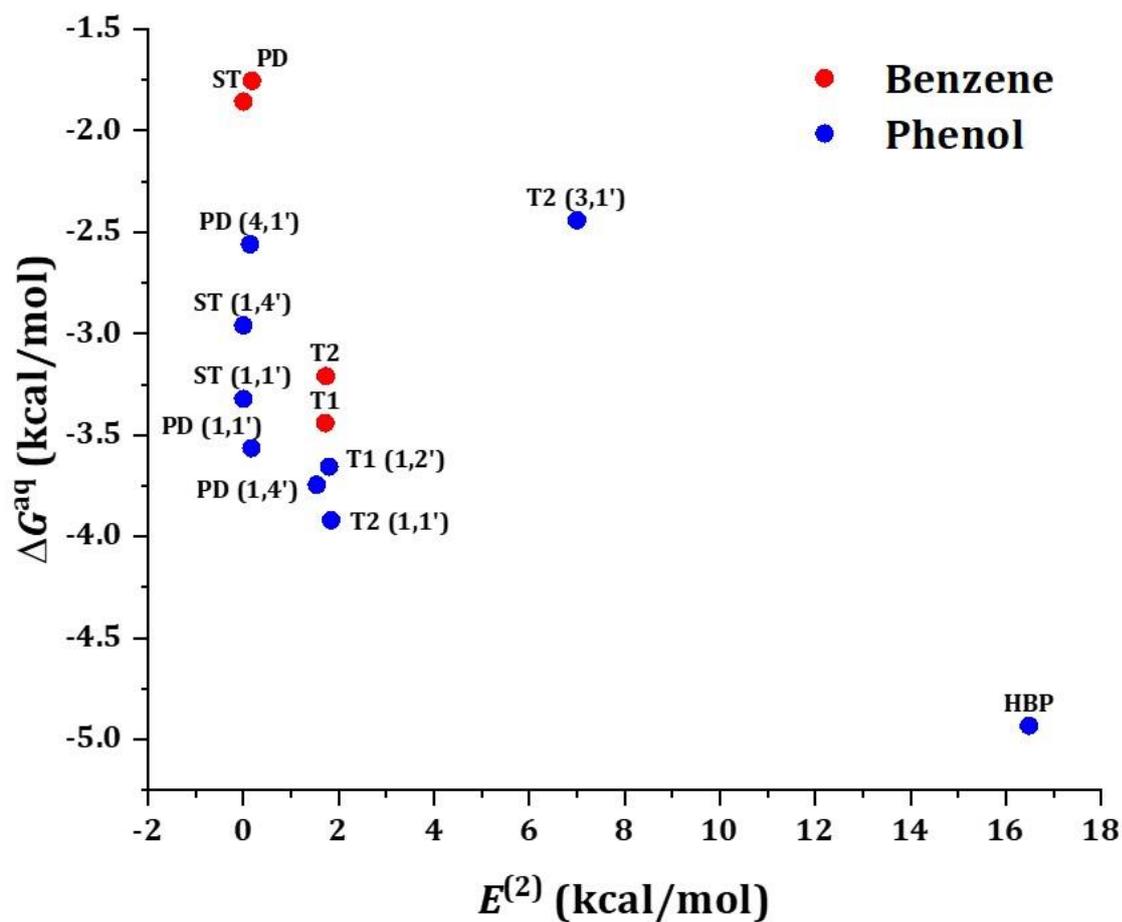
**Figure S4.** Radial pair distributions for (a) PD(4,1') and (b) HBP conformations of phenol dimer; O---H is for the pair of O-atom of the water and H-atom of the hydroxyl group, and H---O is for the pair of H-atom of the water and O-atom of the hydroxyl group.



**Figure S5.** Relationship between ring-to-ring (R-R) distance and association free energies (a) in vacuum ( $\Delta G^{\text{vac}}$ ) and (b) in water ( $\Delta G^{\text{aq}}$ ).



**Figure S6.** Electrostatic potential surfaces of (a) ST, (b) T1 conformations of benzene dimer, and (c) PD(4,1'), (d) HBP conformations of phenol dimer.



**Figure S7.** Relationship between the solute-solute interaction energies ( $E^{(2)}$ ) and association free energies in water ( $\Delta G^{aq}$ ).  $E^{(2)}$  was calculated using the second-order perturbation theory analysis of Fock matrix in natural bond orbital (NBO) basis.