

## Supplementary Information

### Beyond the electrostatic model: the significant roles of orbital interaction and the dispersion effect in aqueous- $\pi$ systems

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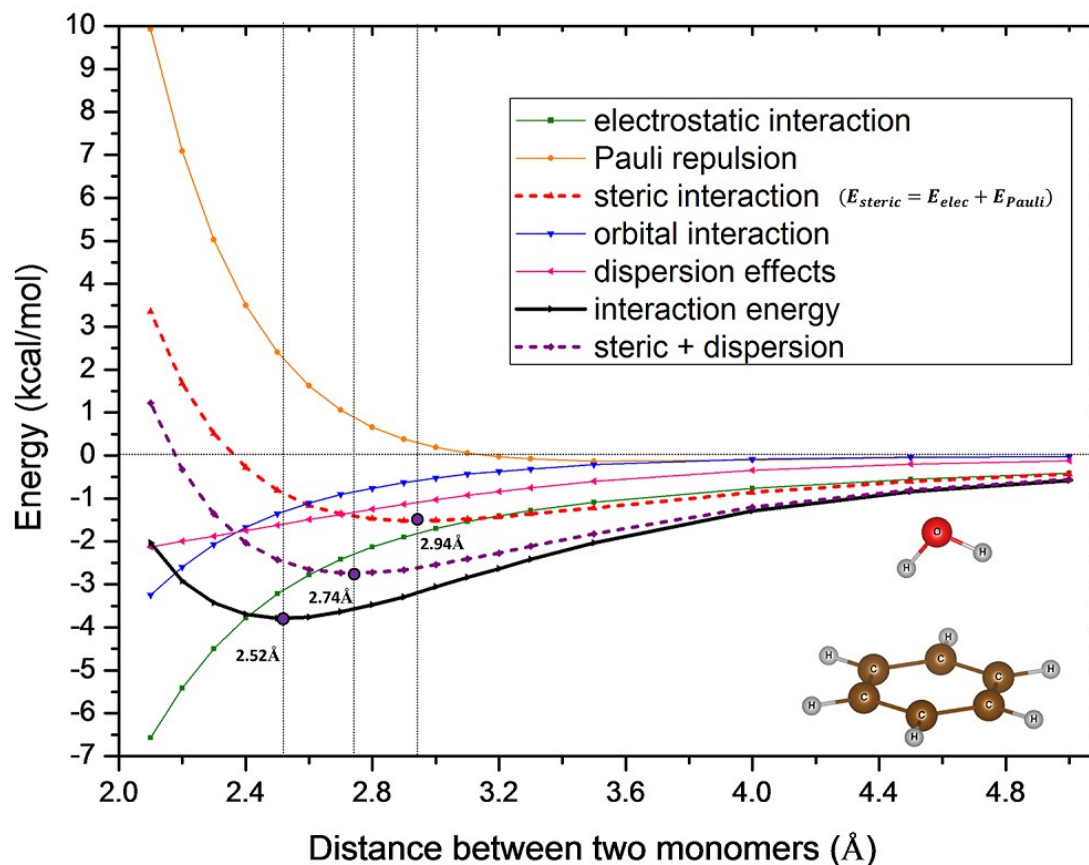
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### Supplementary materials 1: counter-examples calculated by other theoretical methods

	$E_{int}(kcal/mol)$
benzene • H <sub>2</sub> O	-3.67
a1 • H <sub>2</sub> O	-3.95
a2 • H <sub>2</sub> O	-3.76
a3 • H <sub>2</sub> O	-3.44
b1 • H <sub>2</sub> O	-3.29
b2 • H <sub>2</sub> O	-2.15
c1 • H <sub>2</sub> O	-4.19
c2 • H <sub>2</sub> O	-4.51
c3 • H <sub>2</sub> O	-5.04
d1 • H <sub>2</sub> O	-3.17
d2 • H <sub>2</sub> O	-1.80
d3 • H <sub>2</sub> O	-2.99
e1 • H <sub>2</sub> O	-2.51
e2 • H <sub>2</sub> O	-3.64
e3 • H <sub>2</sub> O	-7.15

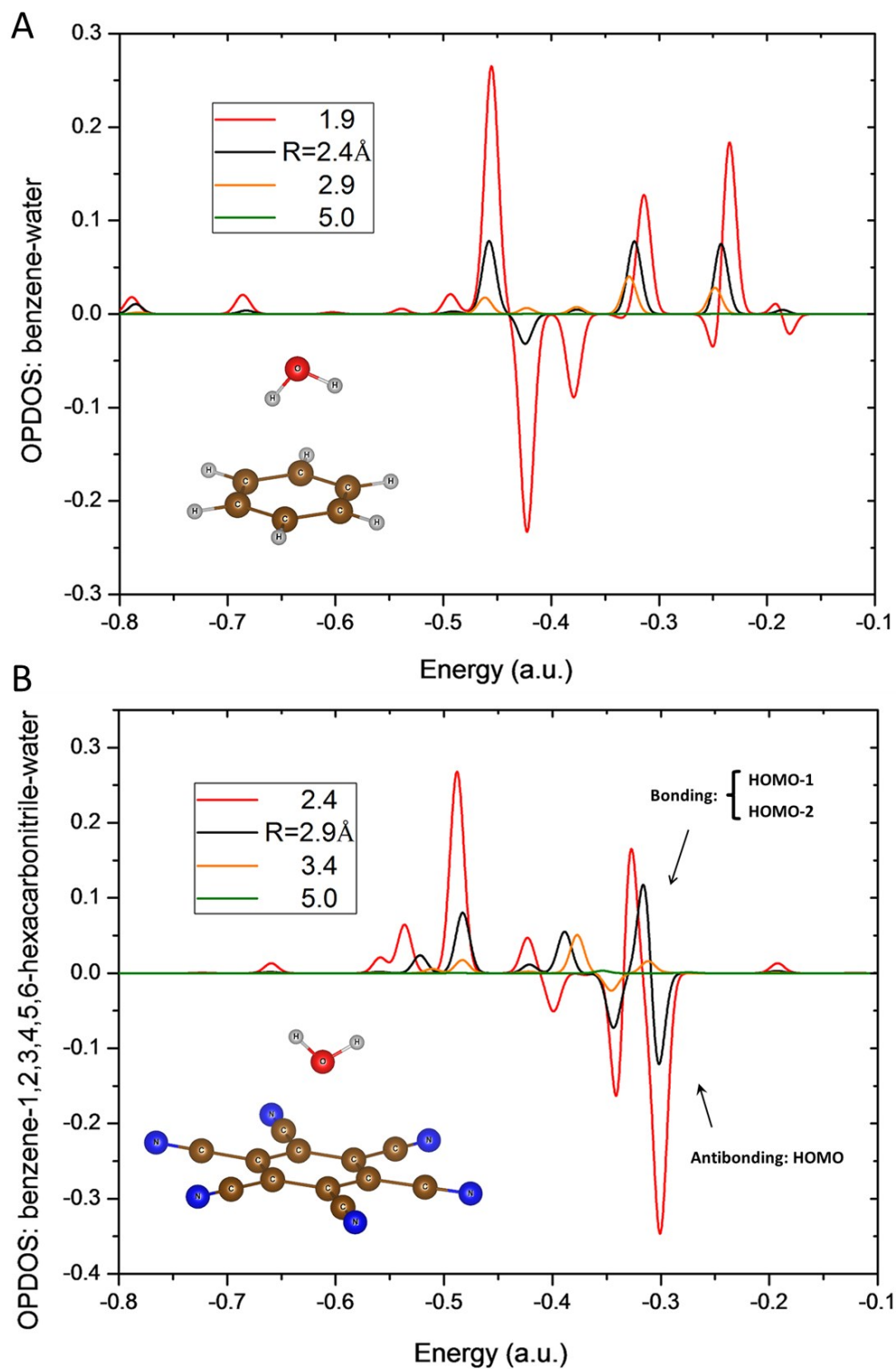
**Table S1.** Interaction energies between water molecule and different substituted aromatic rings calculated with the M06-2X/cc-pVQZ recipe. The groups of a, b, c, d, e are all plotted in Figure 1 in the main text.

## Supplementary materials 2: energy decompositions for benzene-water dimer



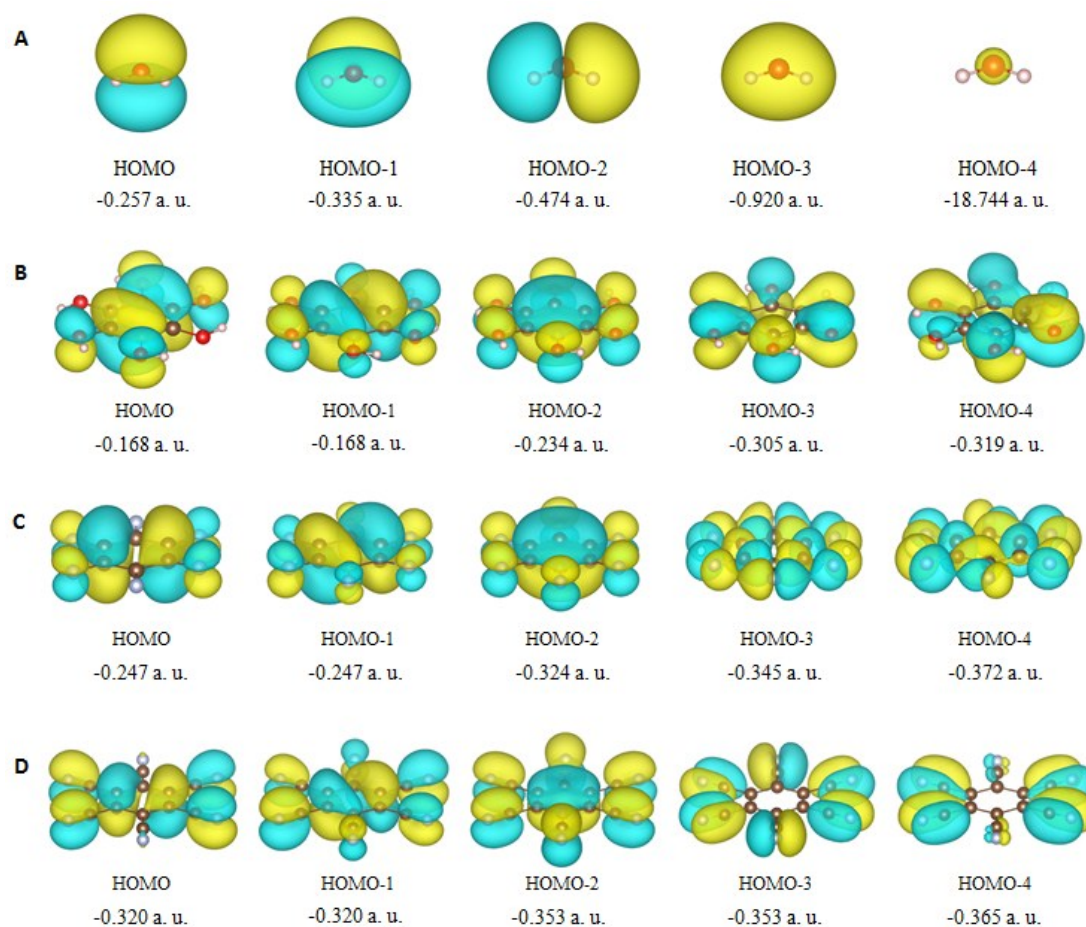
**Fig. S1 Decomposition of the interaction energy for the benzene-water dimer at different interaction distances.** The single-point calculation is conducted using the “PBE/ET-pVQZ + dispersion correction” recipe and the basis set superposition error (BSSE) has been taken into account. The black line indicates interaction energy, which is the sum of the electrostatic interaction (green line), Pauli repulsion (orange line), orbital interaction  $E_{orb}$  (blue line), and dispersion (pink line) energies. The steric interaction (the red dashed line) consists of the electrostatic interaction and Pauli repulsion energies. The sum (purple dashed line) of the steric interaction and dispersion energies are also plotted. Equilibrium distance is labeled by the purple circle.

### Supplementary materials 3: orbital analysis



**Fig. S2** The OPDOS between water monomer and the two aromatic monomers (benzene and benzene-1,2,3,4,5,6-hexacarbonitrile), at different interaction distances  $R$ . The black lines (corresponding to  $R=2.4 \text{ \AA}$  and  $R=2.9 \text{ \AA}$ ) show the bonding near the equilibrium distance; the

green lines show that the intermolecular bonding nature gradually disappears as the distance increases. **A.** The benzene-water dimer does not show obvious intermolecular interaction. **B.** For the benzene-1,2,3,4,5,6-hexacarbonitrile-water dimer, the HOMO (about -0.303 a.u.) can be taken as the antibonding orbital while the HOMO-1 (about -0.311 au) and HOMO-2 (about -0.314 a.u.) can be taken as the bonding orbital. This is because the orbital energy of the HOMO (about -0.335 a.u.) in the water monomer is close to that of the HOMO and HOMO-1 (these two orbitals are degenerate, each with an orbital energy of around -0.320 a.u.) in benzene-1,2,3,4,5,6-hexacarbonitrile.



**Fig. S3 The occupied orbitals (with the corresponding energy levels) of the water, hexahydroxybenzene, hexafluorobenzene and benzene-1,2,3,4,5,6-hexacarbonitrile monomers.** All the optimizations and single-point calculations are conducted using the “PBE/cc-pVQZ + dispersion correction” recipe.