

Supplementary Information

**A new insight into π - π stacking involving remarkable
orbital interactions**

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Energy decompositions for benzene-phenol and benzene-benzonitrile dimers

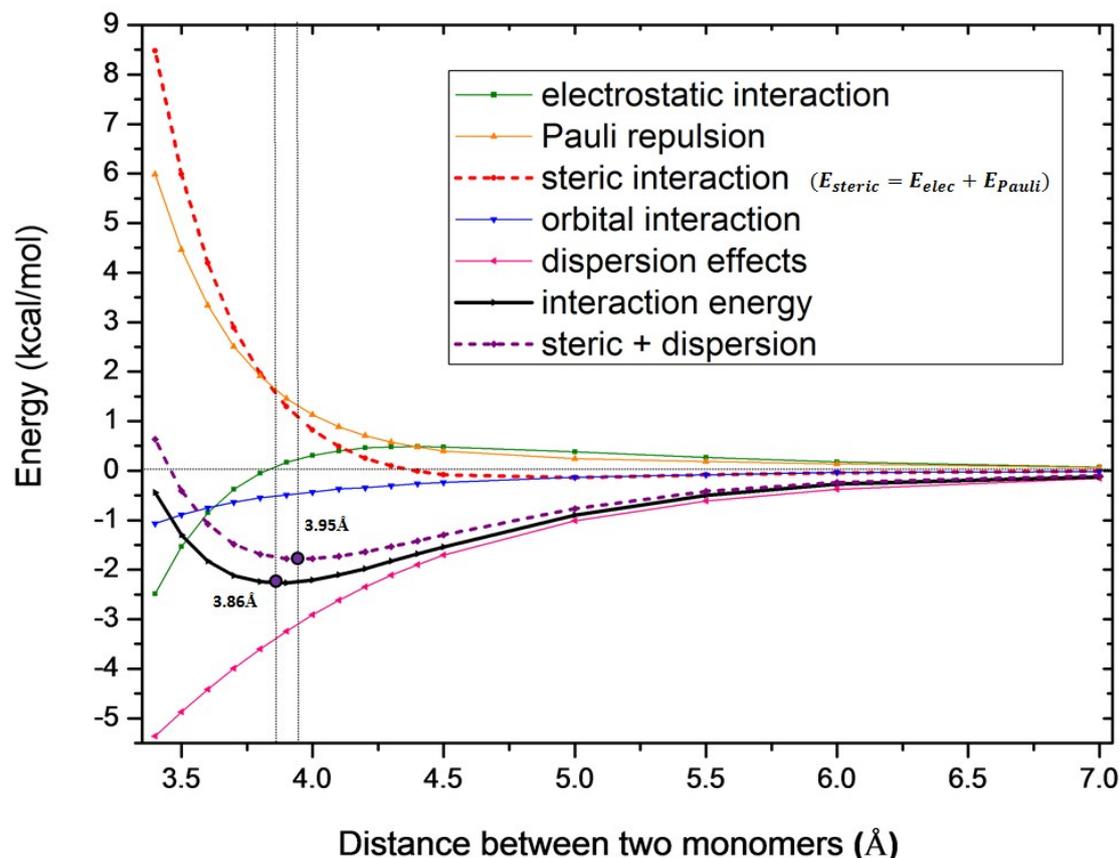


Fig. S1. Decomposition of the interaction energy for the benzene-phenol dimer at different interaction distances. The single-point calculations are done using the “PBE/ET-pVQZ + dispersion correction” recipe and the basis set superposition error (BSSE) has been taken into account. The black line indicates 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.

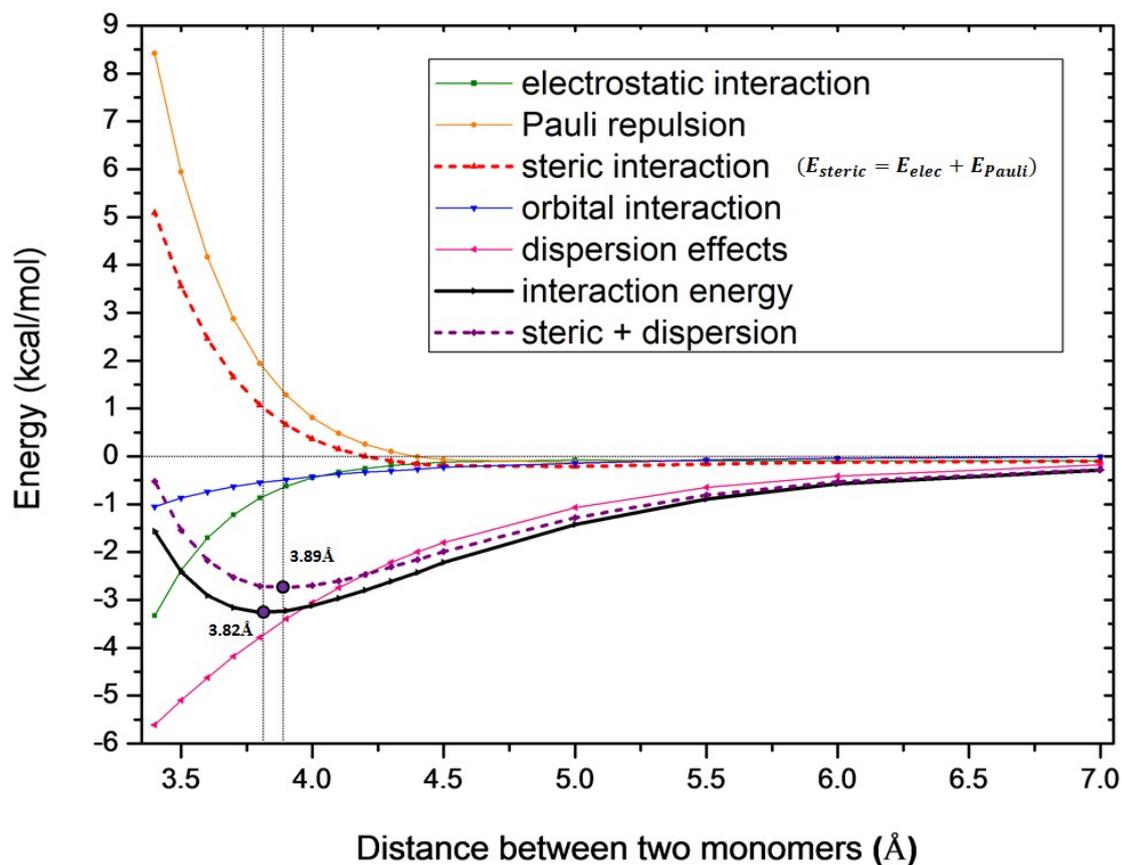


Fig. S2. Decomposition of the interaction energy for the benzene-benzonitrile dimer at different interaction distances. The single-point calculations are done using the “PBE/ET-pVQZ + dispersion correction” recipe and the basis set superposition error (BSSE) has been taken into account. The black line 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.

The energy decomposition scheme adopted here obeys the following equations:

$$E_{int} = E_{orb} + E_{steric} + E_{disp}$$

$$E_{steric} = E_{elec} + E_{Pauli}$$

It is shown that the dispersion effect make the largest contribution to the intermolecular interaction energy but are largely canceled by the Pauli repulsion at the equilibrium distance.

Interaction energies at the equilibrium distances

	$R(\text{\AA})$	E_{elec}	E_{Pauli}	E_{steric}	E_{orb}	$E_{int}(kcal/mol)$
<i>Benzene-benzene</i>	3.76	(0.13	-0.34)	-0.21	-0.36	-0.57
<i>Benzene-phenol</i>	3.73	(-0.07	-0.49)	-0.56	-0.43	-0.99
<i>Benzene-toluene</i>	3.74	(0.02	-0.49)	-0.47	-0.37	-0.84
<i>Benzene-fluorobenzene</i>	3.73	(-0.40	-0.41)	-0.81	-0.47	-1.28
<i>Benzene-benzonitrile</i>	3.72	(-1.06	-0.40)	-1.46	-0.45	-1.91

Table S1. Decompositions of the interaction energies at the equilibrium distances using the hybrid functional M06-2X. Single-point calculations are done using the “M06-2X/ET-pVQZ” recipe, with the BSSE correction incorporated.

Frontier molecular orbitals

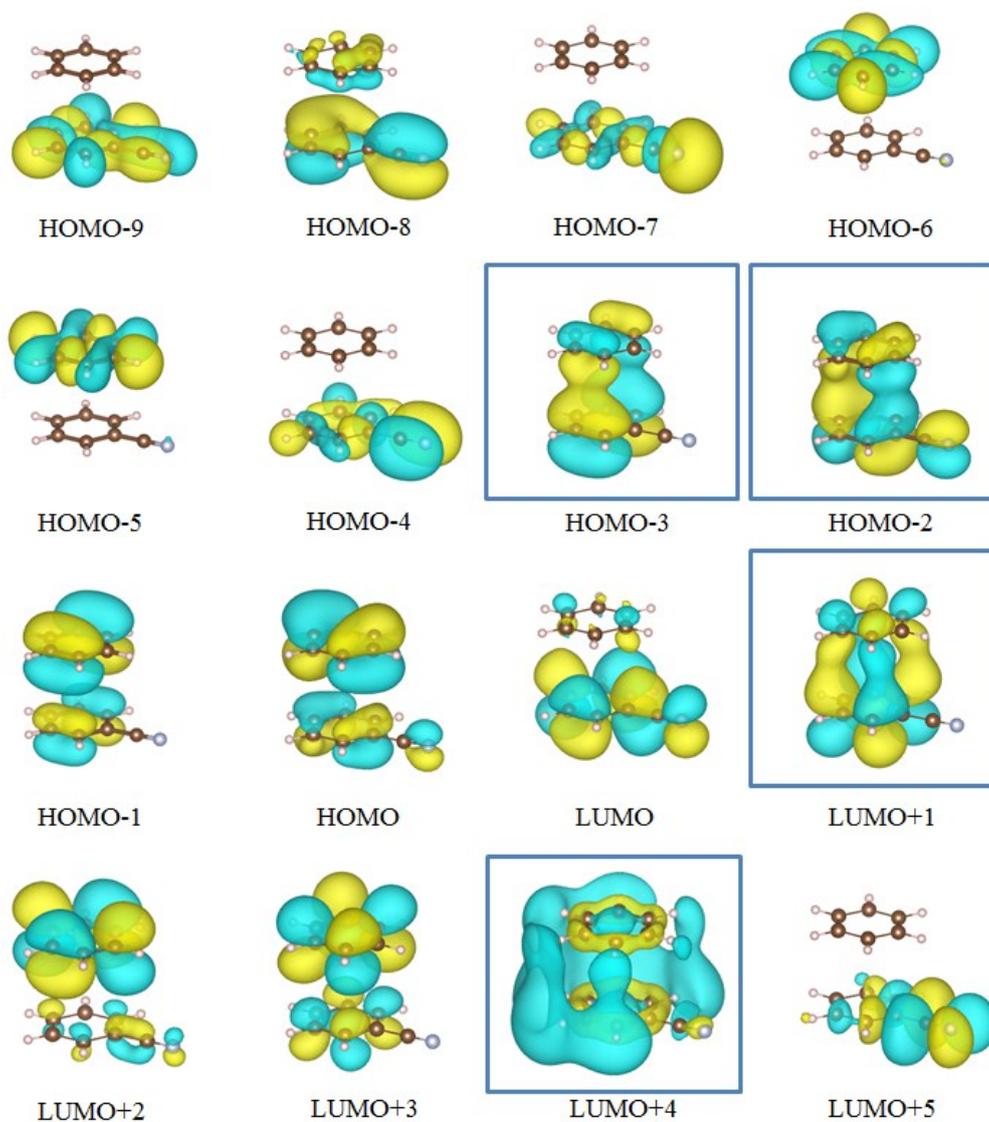


Fig. S3. The frontier molecular orbitals of the benzene-benzonitrile dimer (Isovalue=0.02 au) using the “PBE/ET-pVQZ + dispersion correction” method. Relatively strong orbital interactions can be found on HOMO-3, HOMO-2, LUMO+1, and LUMO+4, which are highlighted with frames.

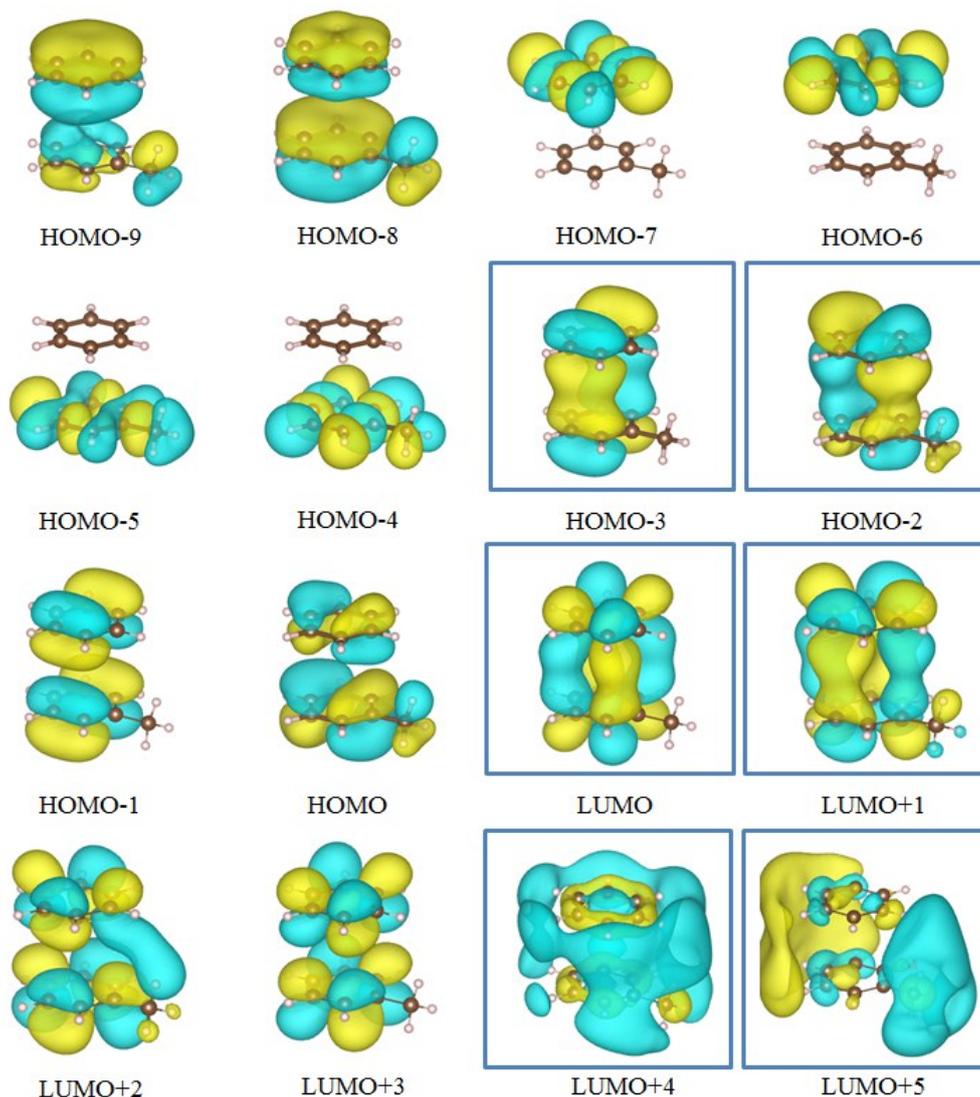


Fig. S4. The frontier molecular orbitals of the benzene-toluene dimer (Isovalue=0.02 au) using the “PBE/ET-pVQZ + dispersion correction” method. Relatively strong orbital interactions can be found on HOMO-3, HOMO-2, LUMO, LUMO+1, LUMO+4, and LUMO+5, which are highlighted with frames.

Note that the orbital interaction features showing here depend on the value of isosurface we choose, which is tunable. Usually we choose an appropriate value that may offer the relatively best illustration, but this is not the only choice. For instance, the LUMO plotted in Fig. S1 and the HOMO-9 plotted in Fig. S2 would also show orbital overlap if we chose a smaller isosurface such as 0.01au. But for HOMO-1 and HOMO in both the two figures, any value of isosurface will not lead to orbital overlap.

Orbital analysis for benzene-phenol dimer

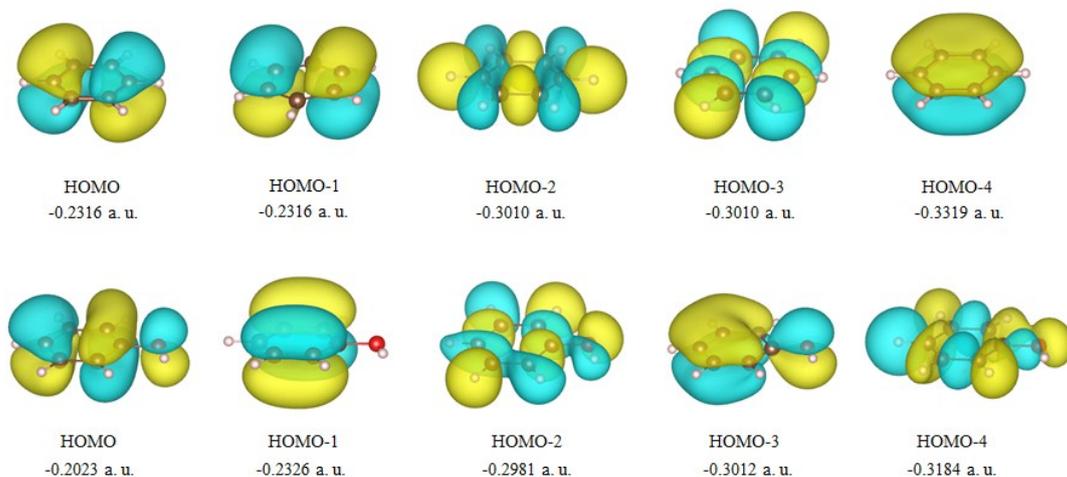


Fig. S5. The occupied orbitals (with the corresponding energy levels) of the benzene and phenol monomers. The optimizations and single-point calculations are done using the “PBE/ET-pVQZ + dispersion correction” recipe. The highest occupied molecular orbital (HOMO) of the benzene monomer is two-fold degenerate. On the other hand, the HOMO of the phenol monomer consists of electrons on both the ring and hydroxyl, while the HOMO-1 is only contributed by the electrons on the ring. Comparing Fig. 2 with Fig. S3, we easily find that the HOMO and HOMO-2 of the dimer must contain the ingredient of the HOMO of the phenol.