Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information for

Molecular Dynamic Simulation of a DOPA/ST Monolayer on Au (111) Surface

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Single molecule simulation method:

An NVT simulation run of a single molecule on a gold surface (57.68 Å×49.95 Å) at 300 K of 100 ps has been performed. After that, the gold-molecule interaction energy has been calculated following the procedure described in a previous study[1]. The geometry and adsorption sites are supported by previous research[2,]

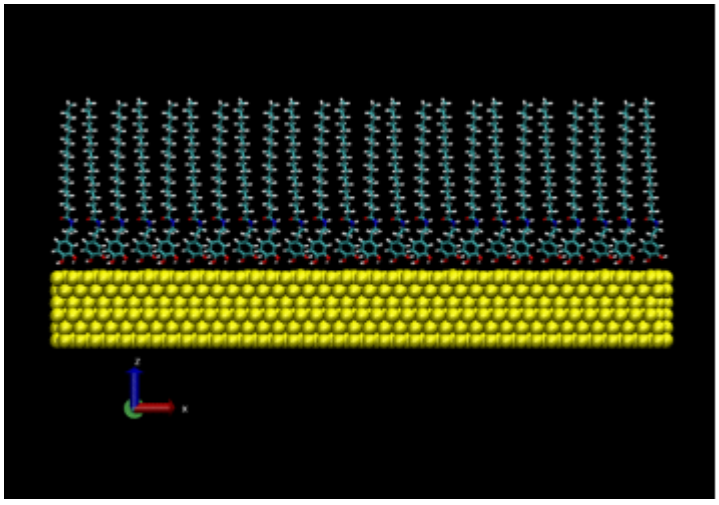


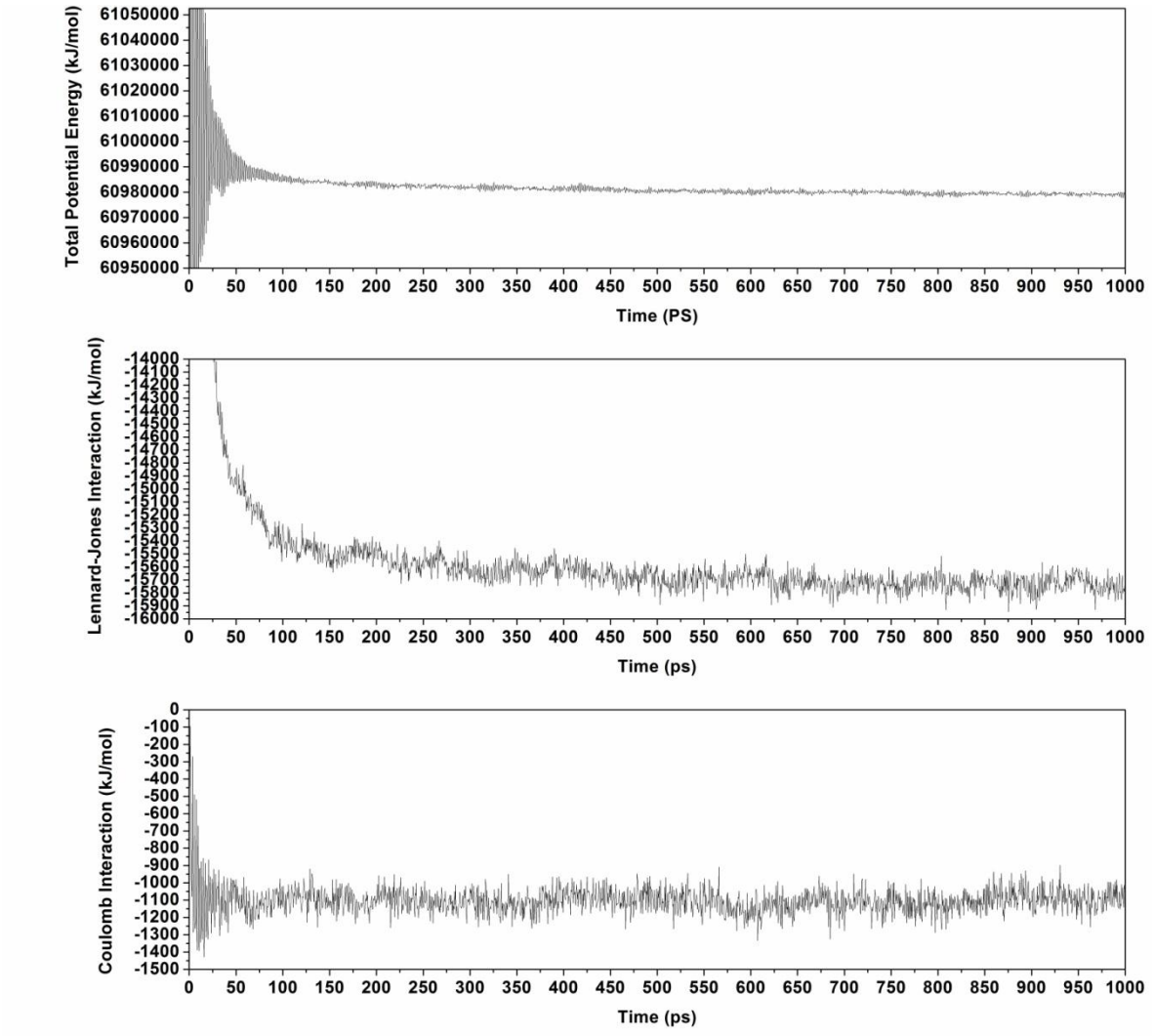
Figure S1 Example of the initial structure employed in the NVT simulations. The molecules are oriented perpendicular to the surface in order to reflect the situation for Langmuir–Blodgett transfer.

Verify the reliability of the simulation time

The equilibration time for the system is 1 ns. To test the equilibration, we have employed the distances of catechol groups to gold surface in DOPA30 (Total number of DOPA is 391. Also See Table 2). Two time periods have been chosen. One is the last 100ps of equilibrium run (A). The other is the NVT production run of 100 ps (B). The results are listed as follows. All the statistic results are average by the simulation time of 100 ps.

	# of Catechols in >10 Å	# of Catechols in >10 Å	# of Catechols in >10 Å
A	93.7 (24.0%)	165.2 (42.3%)	132.1 (33.8%)
B	89.1 (22.8%)	171.6 (43.9%)	130.2 (33.3%)

The result shows that the statistics of catechol groups in the two time periods are similar. The change of the total potential energy, the L-J interaction, and the Coulomb interaction with the time evolution are also listed to verify the method:



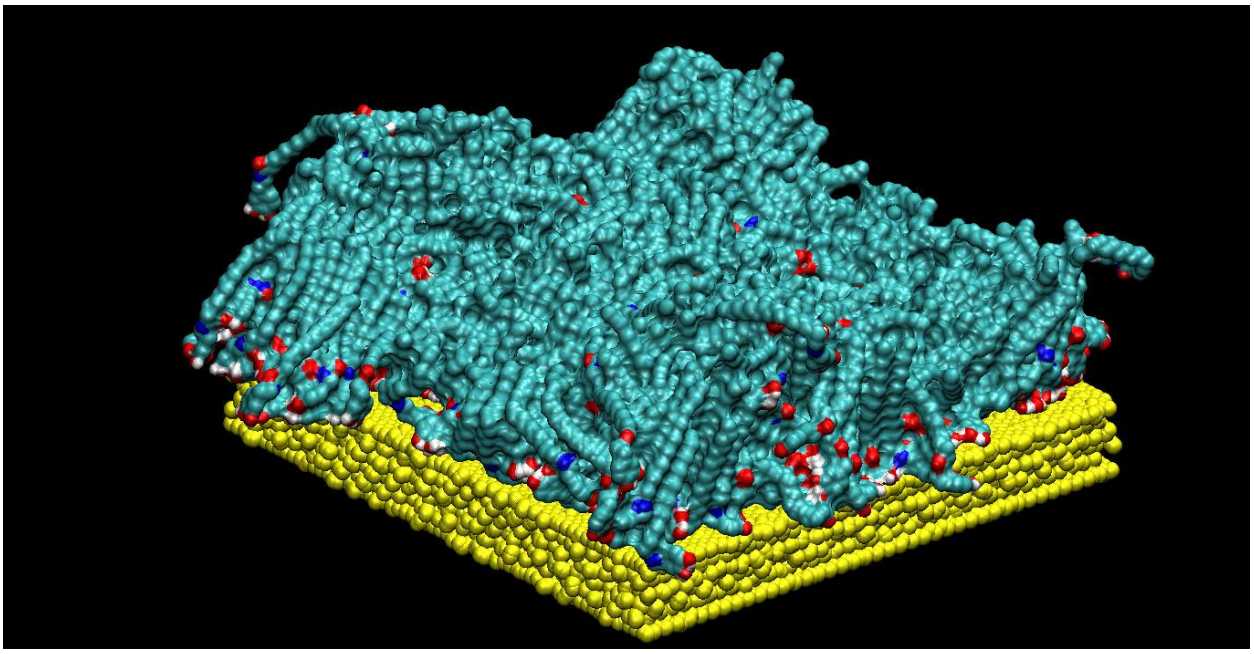


Figure S2. An example of simulated surface (DOPA molecules with a surface area of 30 $Å^2$ per molecule). In this graph, C is represented in green. N is represented in blue. O is represented in red.

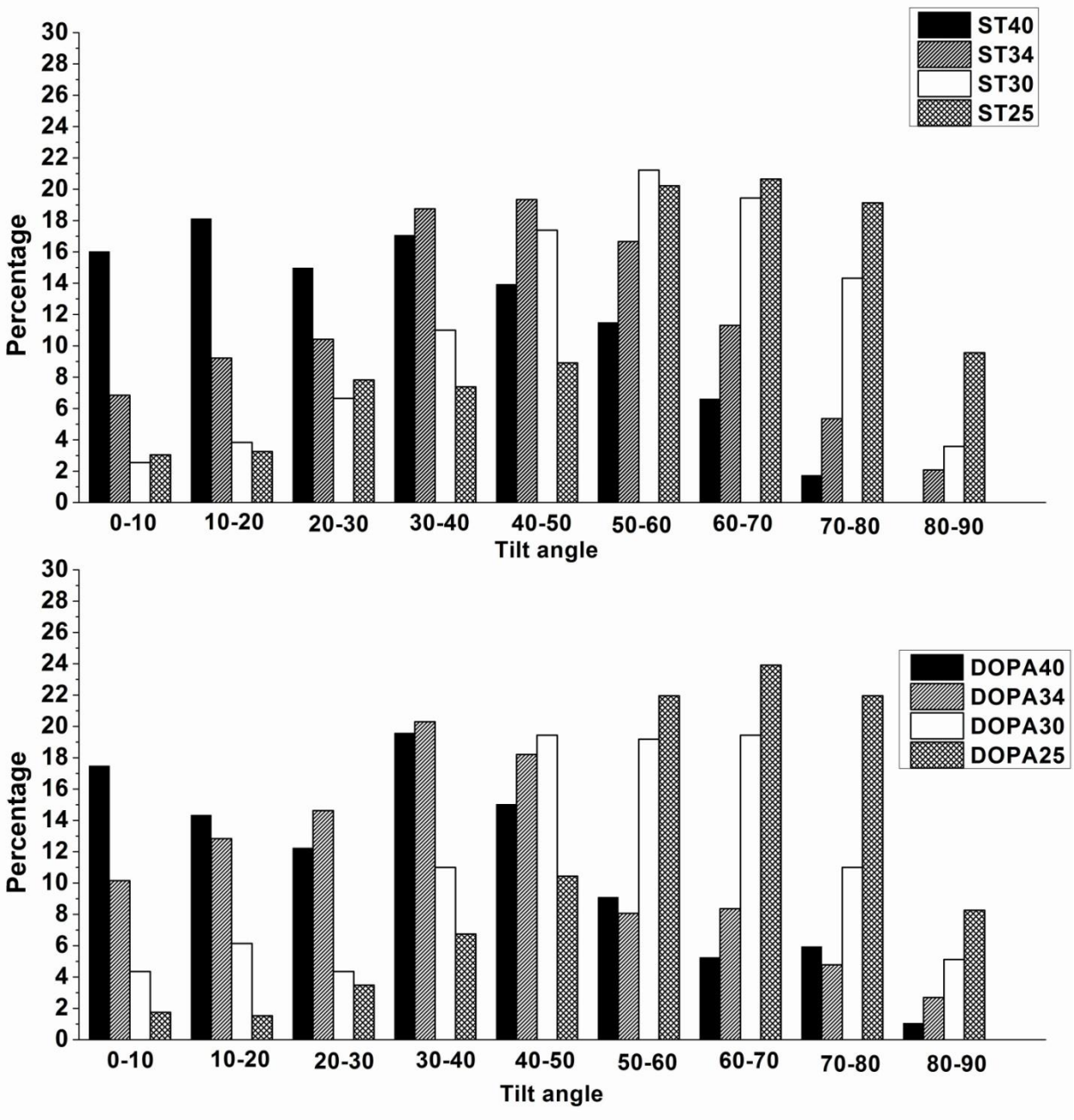


Figure S3 Distributions of tilt angle (α_t) of alkyl tails.

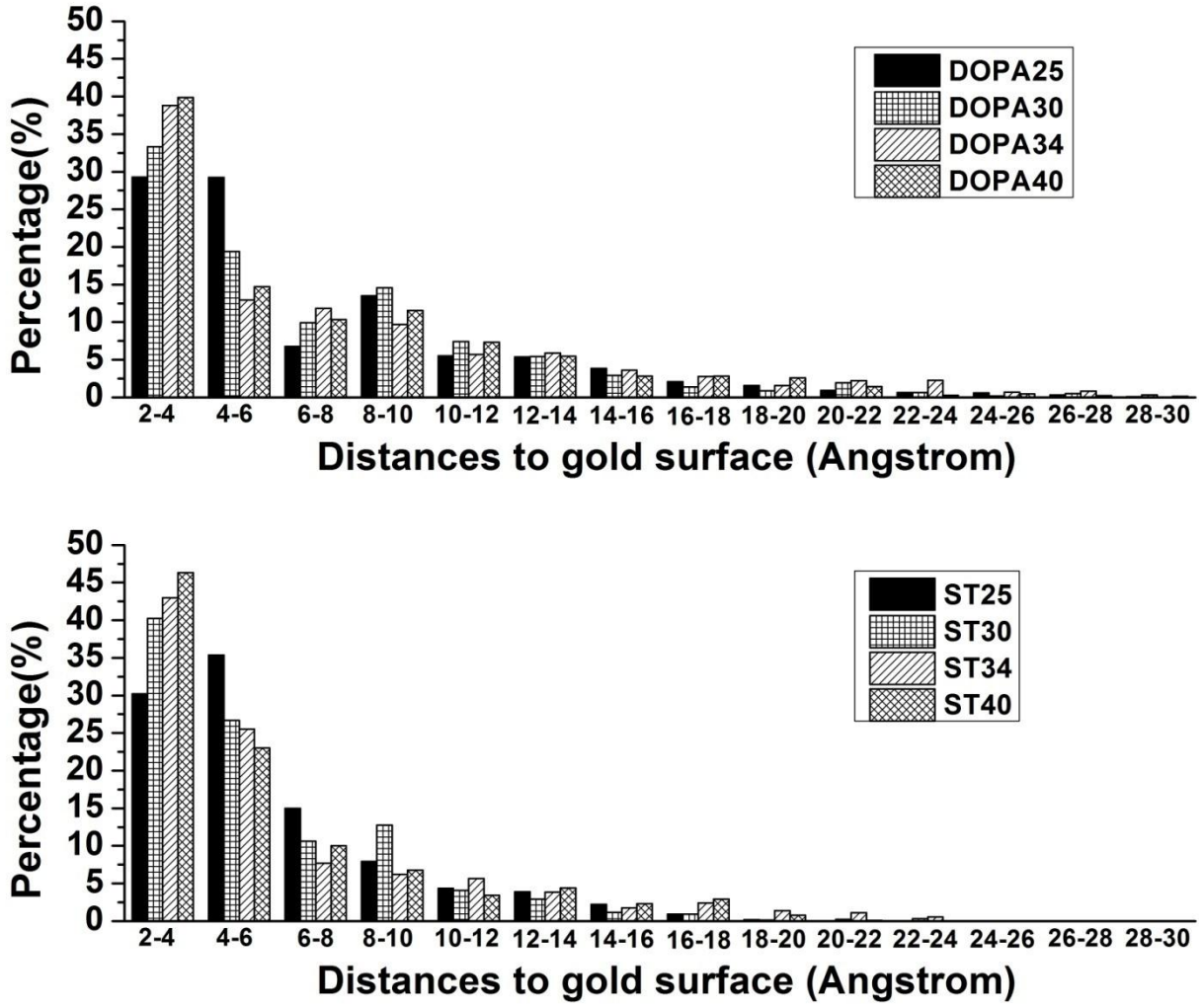


Figure S4 Statistics of distances from the geometric center of aromatic rings to gold surface.

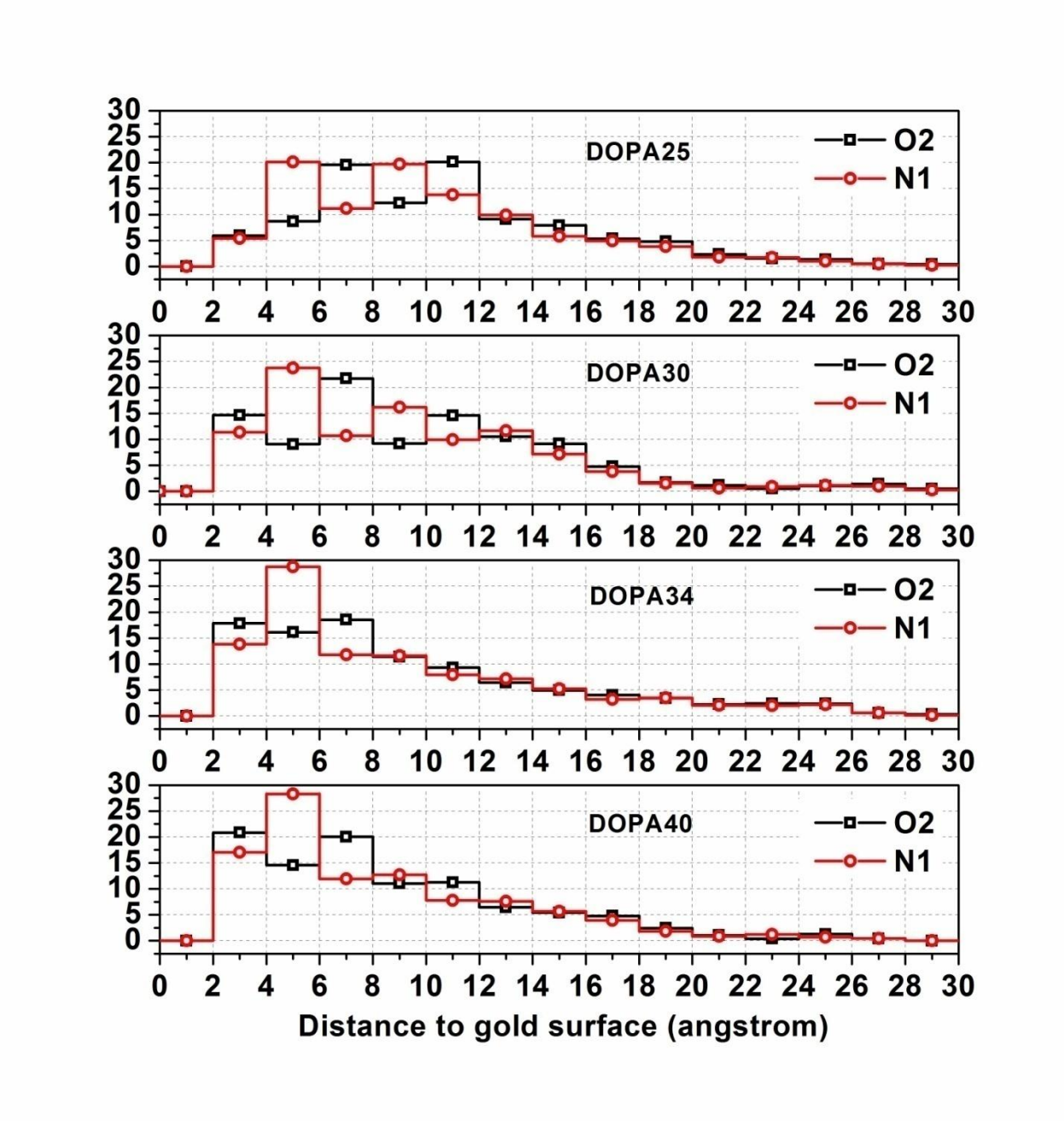


Figure S5 Statistics of distance distribution: O2 and N from the amide groups in DOPA to the gold surface.

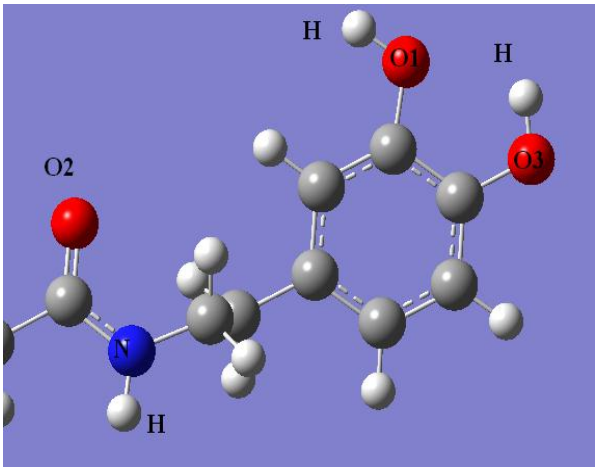


Figure S6 Illustration of hydrogen bonds in DOPA and ST. Type1 is hydrogen bonds between two amide groups, including N-H···O2 and N-H···N; Type 2 is hydrogen bonds between an amide group and a hydroxyl, including O1/O3-H···O2, N-H···O1/O3, and O1/O3-H···N; Type 3 is hydrogen bonds between two hydroxyls, including O1/O3-H···O1/O3; For ST only the type 3 exists.

References:

[1] Iori, F.; Di Felice, R.; Molinari, E.; Corni, S. *Journal of Computational Chemistry* **2009**, *30*, 1465-1476.

[2] Weinhold, M.; Soubatch, S.; Temirov, R.; Rohlfing, M.; Jastorff, B.; Tautz, F. S.; Doose, C. *The Journal of Physical Chemistry B* **2006**, *110*, 23756-23769.