

Supporting Information

Growth of Two-Dimensional Covalent Organic Frameworks on Substrates: Insight from Microsecond Atomistic Simulations

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The angular distribution of CHP with respect to the metal substrate is calculated as follows:

i. We first calculate the vector pointing to the (1, 0, -1) direction of the metal (red arrow in **Figure S1**).

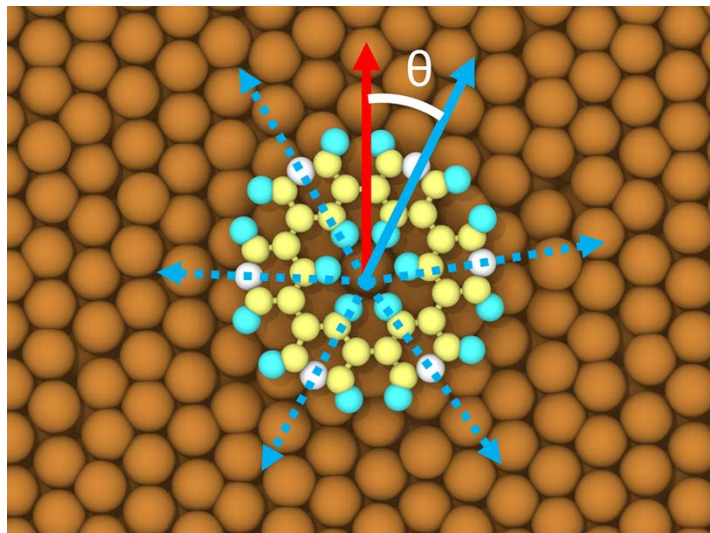


Figure S1. Schematic diagram of the calculation of the angle of CHP on the metal surface. Red arrow represents the (1,0, -1) direction on the metal. Blue arrows represent vectors from the center of CHP to each carbon radical. The blue solid arrow is the one used to represent the angle of CHP with respect to the metal surface.

ii. We determine six vectors for one CHP, each pointing from its molecular center to one of its carbon radicals (blue arrows in **Figure S1**).

iii. The angles (θ) between the red arrows and each of the blue arrows are calculated. The value falling within the range of [0-60] degrees is recorded as the angle of CHP with respect to the substrate, as indicated by the blue solid arrow in **Figure S1**.

iv. Steps ii and iii were performed for each CHP, leading to a collection of degrees $\{\theta\}$ of size N .

v. We then divide the [0-60] degree value range into 120 windows, and the percentage of θ in each window is calculated as:

$$P_0 = \frac{N_i}{N} \times 100\% \quad (\text{S1})$$

where N_i is the number of θ that falls within the i^{th} interval.

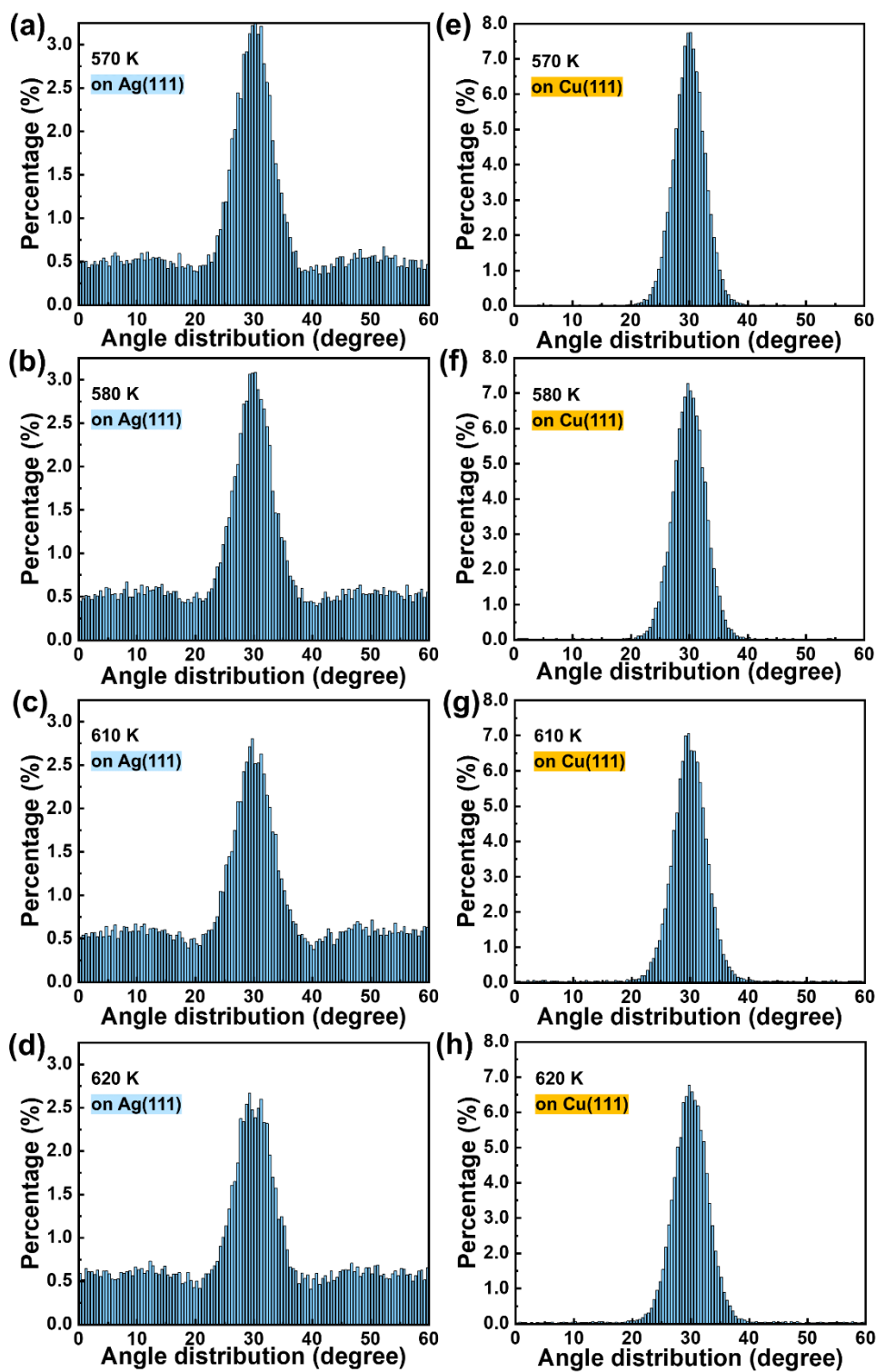


Figure S2. (a-h) Angular distribution of CHP on metal substrates at different temperatures.

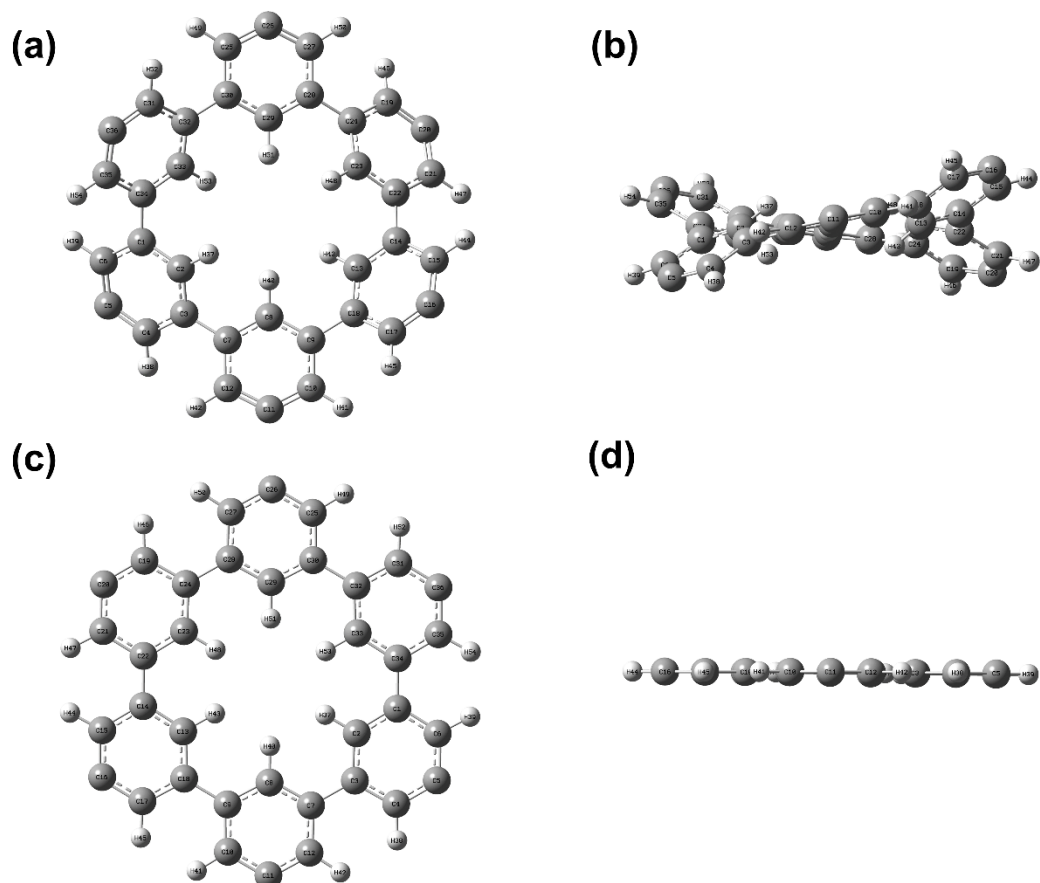


Figure S3. (a) Top and (b) side views of the CHP radical. (c) Top and (d) side views of the CHP radical on a metal substrate.

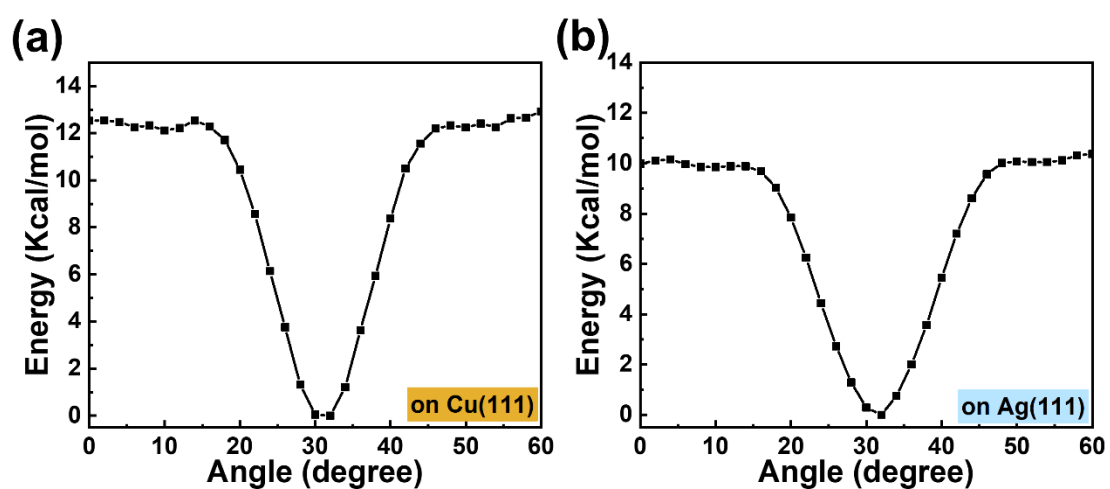


Figure S4. Potential energies of a CHP radical rotating around its center on (a) Cu (111) and (b) Ag (111) surfaces, as calculated based on the force field.

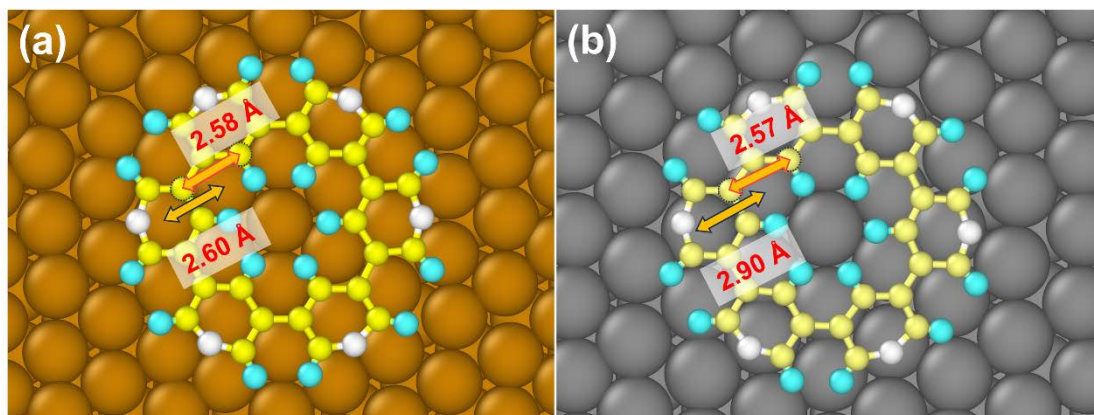


Figure S5. Illustrations of the geometrical structure of CHP radicals on (a) Cu (111) and (b) Ag (111) surfaces. Arrows with red outlines give the distance between carbon atoms within the CHP radical. Arrows with black outlines show the distance between metal atoms.

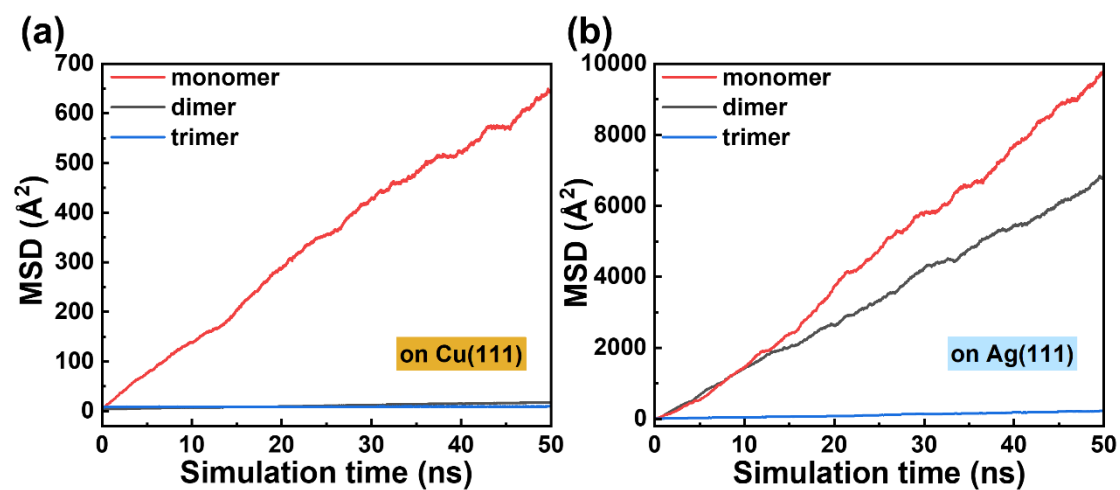


Figure S6. Evolutions of the mean square displacements (MSDs) as a function of time for monomers, dimers, and trimers on (a) Cu (111) and (b) Ag (111) surfaces at 600 K.

Table S1. Diffusion coefficients for monomers, dimers, and trimers on metal surfaces. All units are in 10^{-6} cm²/s, as calculated based on the force field.

Structure	on Ag (111) surface	on Cu (111) surface
Monomer	4.734	0.335
Dimer	3.389	0.010
Trimer	0.111	0.007

Table S2. Calculated binding energies of the monomer on the substrate based on the force field. All units in kcal/mol.

Energy	Cu (111)	Ag (111)
total	-9821.8602	322993.71
slab	-9827.3824	322852.58
monomer	41.146801	173.59799
binding energy	-35.624601	-32.46799

The binding energy E_b between the monomer and the substrate is calculated by the following equation:

$$E_b = E_{total} - (E_{monomer} + E_{slab}) \quad (S2)$$

Here, E_{slab} and E_{total} are the total energies of the metal substrate and that with monomer adsorbed on it, respectively, and $E_{monomer}$ is the energy of standalone monomer. Therefore, in our convention, a negative binding energy corresponds to an attractive interaction. The calculated binding energies based on the force field for the CHP radical are -35.62 and -32.47 kcal/mol on Cu (111) and Ag (111) surfaces, respectively.

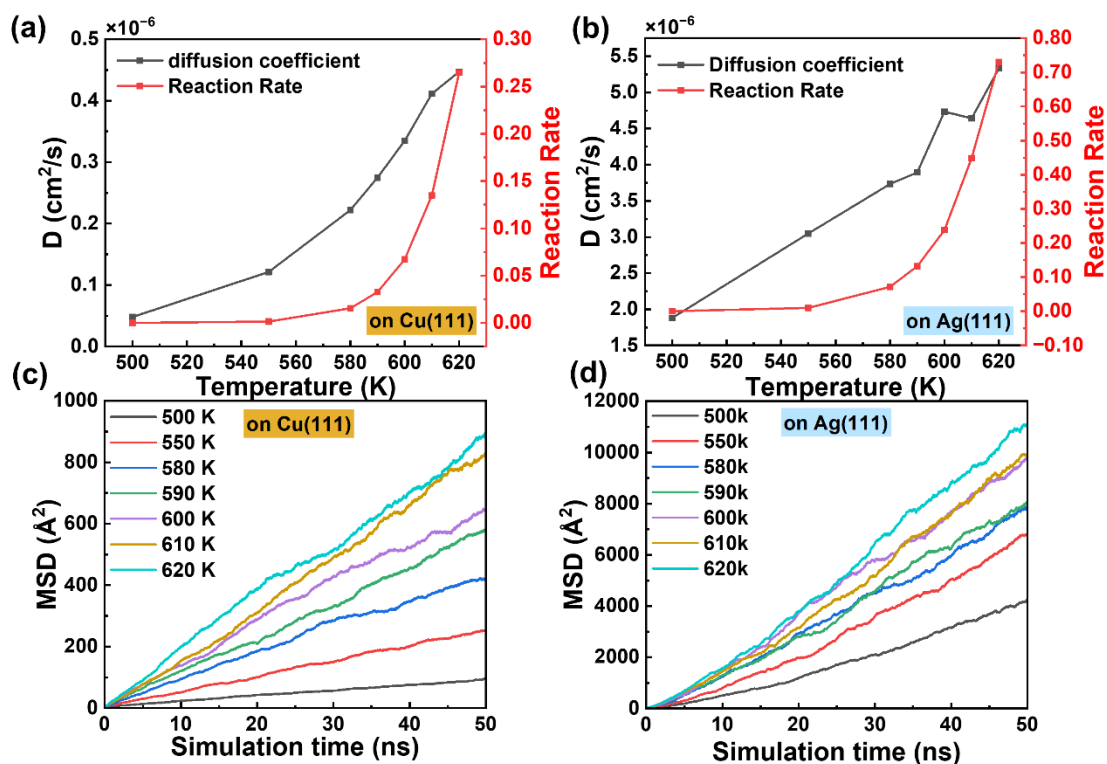


Figure S7. Evolution of the diffusion coefficients and bond formation rates at different temperatures on (a) Cu (111) and (b) Ag (111) surfaces. MSDs of CHP radicals on (c) Cu (111) and (d) Ag (111) surfaces at different temperatures (note the large difference in y-axis range between the two panels).

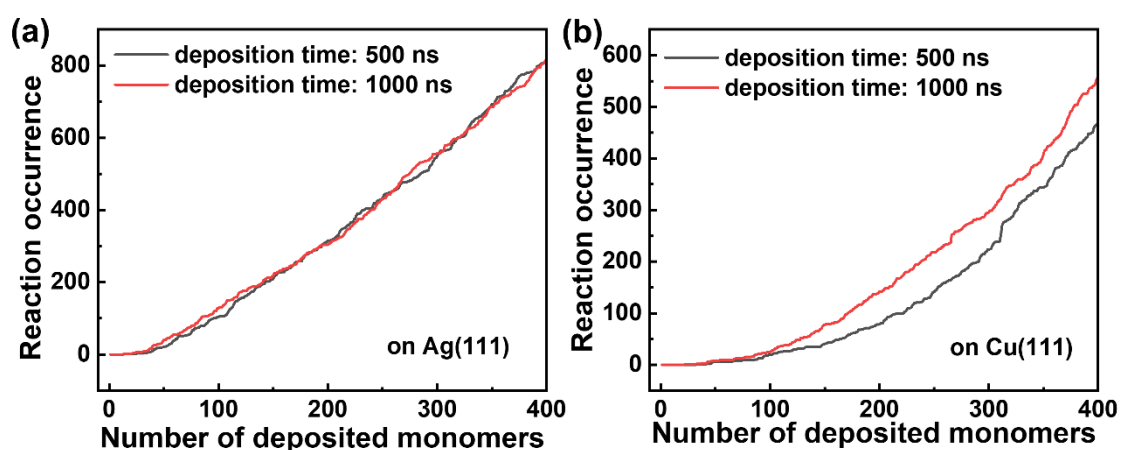


Figure S8. Number of reactions with respect to the number of deposited monomers at different deposition rates on (a) Ag (111) and (b) Cu (111) surfaces.

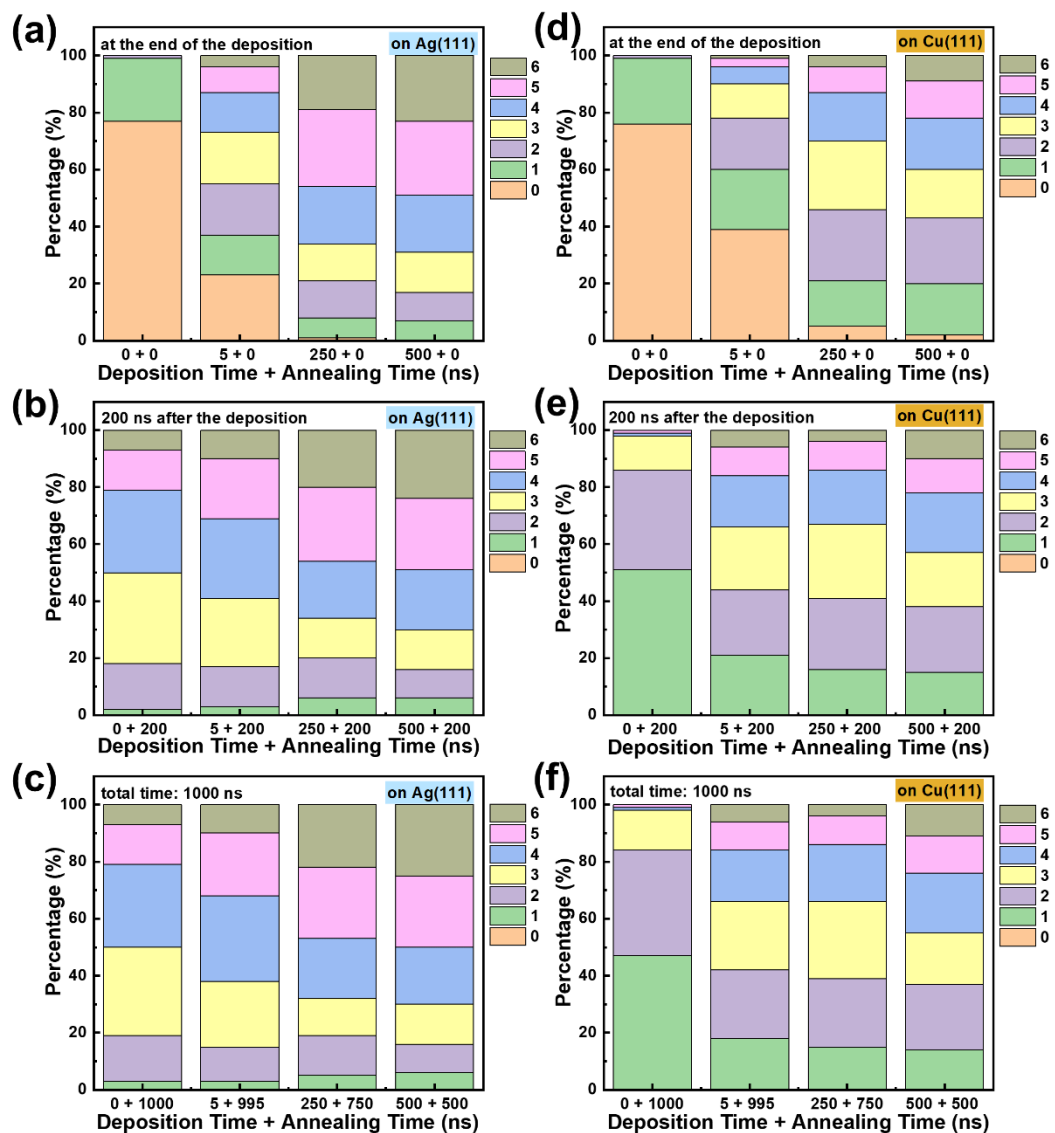


Figure S9. Ratios of monomers with different numbers of connections at different stages on the Ag (111) substrate: (a) at the end of the deposition stage, (b) at 200 ns after the deposition stage, and (c) at a total time of 1000 ns. Ratios of monomers with different number of connections at different stages on the Cu (111) substrate: (d) at the end of the deposition stage, (e) at 200 ns after the deposition stage, and (f) at a total time of 1000 ns.

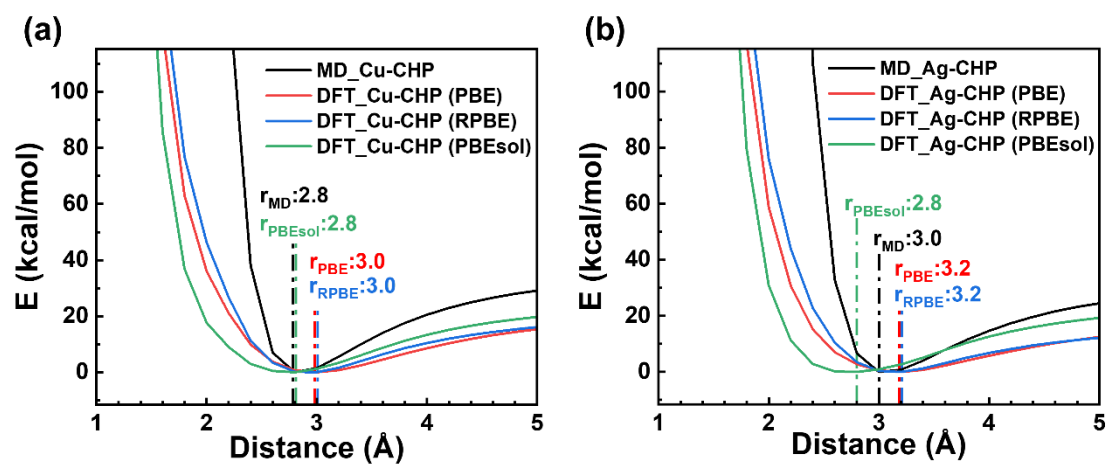


Figure S10. Evolution of the energy of the CHP at different distances from (a) Cu (111) and (b) Ag (111) surfaces, as calculated with the GAFF/EAM force field and at the DFT level with the PBE, RPBE, and PBEsol functionals.

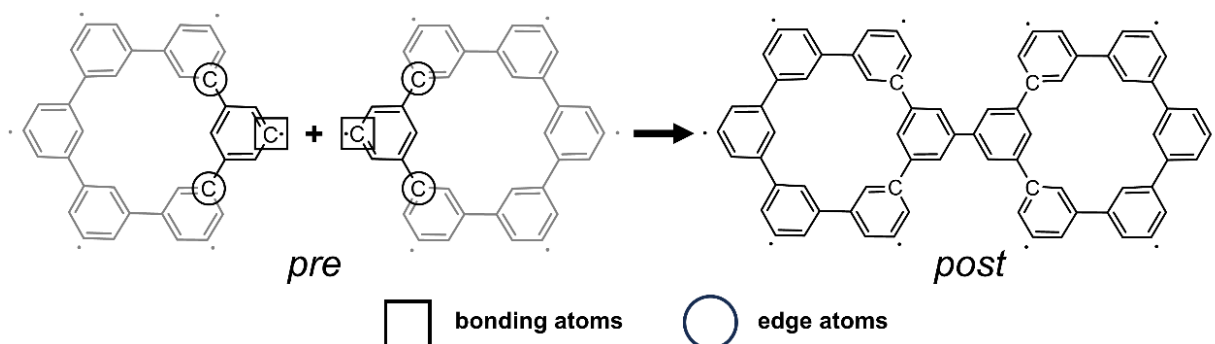


Figure S11. Illustration of the molecular reactions between CHP radicals in the REACTER algorithm.

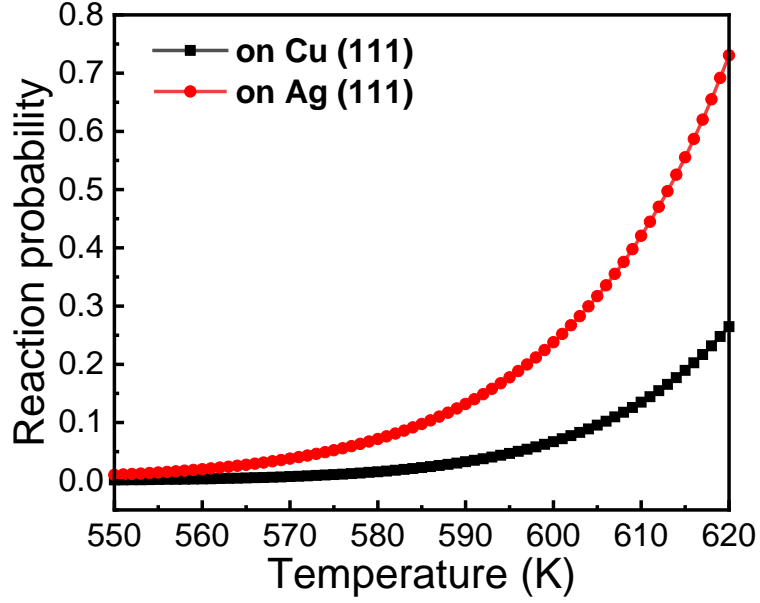


Figure S12. Reaction probabilities (checked every 100 fs) at the different temperatures used in the simulations.

We calculate the bonding probability between CHP reaction sites based on the Arrhenius relationship:

$$k = AT^n e^{-E_a/k_B T} \quad (1)$$

where E_a is the activation energy. According to the work by Bieri et al.,¹ the energy barriers for bonding between monomers on Cu (111) and Ag (111) surfaces are 2.2 eV and 1.8 eV, respectively. We adjust the value of A so that reaction probability falls within the range of (0,1) in the temperature range considered. Specifically, the prefactor is set to 1.954×10^{17} and n is 0 for bonding between monomers on Cu (111); this results in a reaction probability of 0.067 at 600 K. On Ag (111), we set A to 3.042×10^{14} and n to 0; this results in a reaction probability of 0.238 at 600 K.

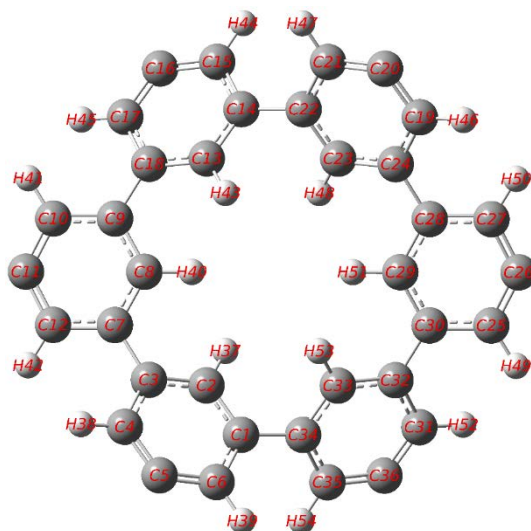


Figure S13. Atomic labels of CHP.

The RESP charge was calculated at the M062X/6-311+G(d, p)⁸ level and shown in **Table S3**.

Table S3. RESP charge of CHP.

Atom	Charge	Atom	Charge	Atom	Charge
C1	0.058459455	C19	-0.15721	H37	0.131122
C2	-0.188038829	C20	-0.03882	H38	0.146618
C3	0.058459455	C21	-0.15721	H39	0.146618
C4	-0.15721002	C22	0.058459	H40	0.131122
C5	-0.038818499	C23	-0.18804	H41	0.146618
C6	-0.15721002	C24	0.058459	H42	0.146618
C7	0.058459455	C25	-0.15721	H43	0.131122
C8	-0.188038829	C26	-0.03882	H44	0.146618
C9	0.058459455	C27	-0.15721	H45	0.146618
C10	-0.15721002	C28	0.058459	H46	0.146618
C11	-0.038818499	C29	-0.18804	H47	0.146618
C12	-0.15721002	C30	0.058459	H48	0.131122
C13	-0.188038829	C31	-0.15721	H49	0.146618
C14	0.058459455	C32	0.058459	H50	0.146618
C15	-0.15721002	C33	-0.18804	H51	0.131122
C16	-0.038818499	C34	0.058459	H52	0.146618
C17	-0.15721002	C35	-0.15721	H53	0.131122
C18	0.058459455	C36	-0.03882	H54	0.146618

Reference

- (1) Bieri, M.; Nguyen, M.-T.; Gröning, O.; Cai, J.; Treier, M.; Ait-Mansour, K.; Ruffieux, P.; Pignedoli, C. A.; Passerone, D.; Kastler, M.; Müllen, K.; Fasel, R. Two-Dimensional Polymer Formation on Surfaces: Insight into the Roles of Precursor Mobility and Reactivity. *J. Am. Chem. Soc.* **2010**, *132* (46), 16669–16676.