Supporting Information

From CAT-like to POD-like Enzymatic Activity of Cu-BHT Tuning by Substrate Engineering

Ting Wang[1,2], Liyuan Wang[1], Hongsheng Liu*[1], Zhongran Wei*[2], Vitaly Ksenevich[3], Juan Hou[2], Junfeng Gao[1]*.

1. Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, School of Physics, Dalian 116024, China

2. College of Sciences/State Key Laboratory of Advanced Energy Storage Materials and Technology, Shihezi University, Xinjiang, Shihezi, 832003, China.

3. Faculty of Physics, Belarusian State University, Nezalezhnastsi av.4, Minsk 220030, Belarus

liuhongsheng@dlut.edu.cn

S1 AIMD energy evolution for Cu-BHT.

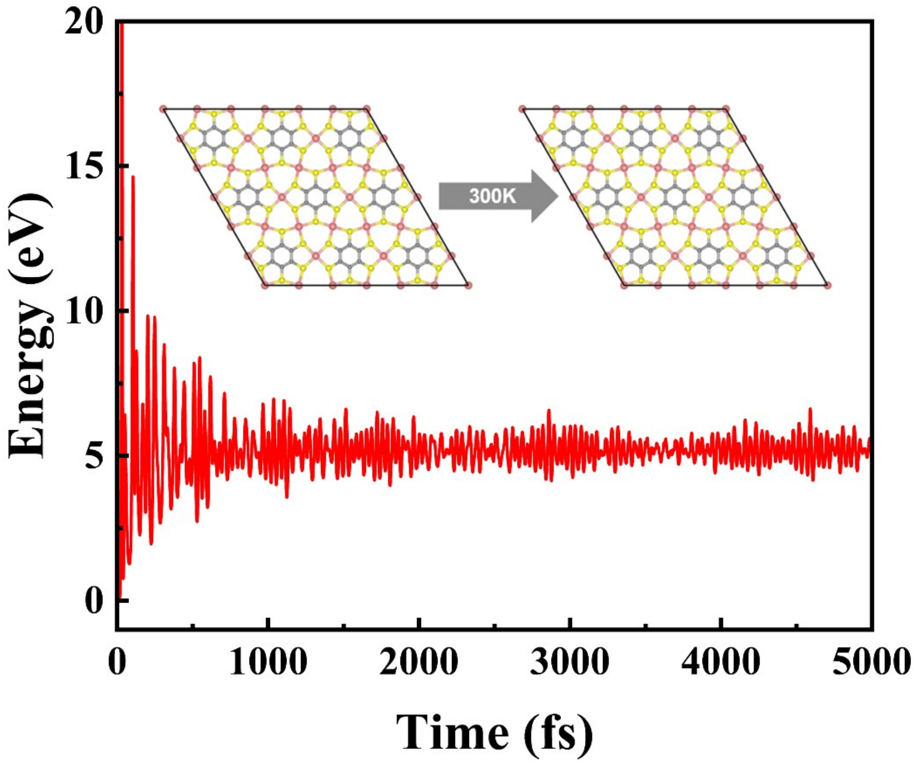

Figure S1. AIMD results for Cu-BHT in the NVT ensemble at 300 K, demonstrating stable energy/structure evolution.

S2 Top view of the optimized geometries of the H atoms adsorbed on the surface of Cu-BHT.

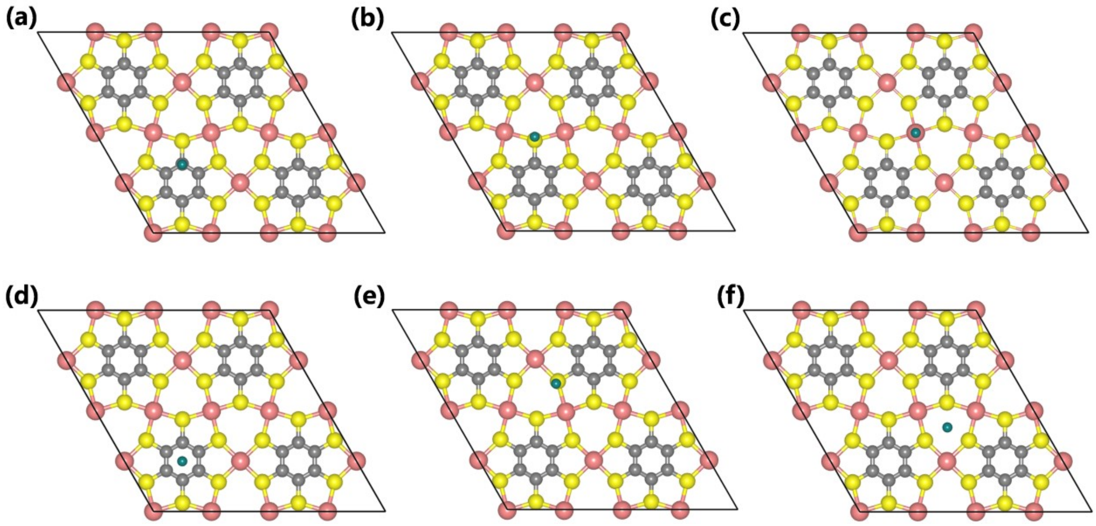

Figure S2. Top view of the optimized geometries of the H atoms adsorbed on the surface of Cu-BHT. The H atom adsorbed in the ‘C top’ (a), ‘S top’ (b), ‘Cu top’ (c), ‘top of the center of the benzene ring’ (d), “top of the ‘CuC2S2 ring’” (e) and “top of the center of ‘S3Cu3 ring’” (f).

S3 Top view of the optimized geometries of the OH atoms adsorbed on the surface of Cu-BHT.

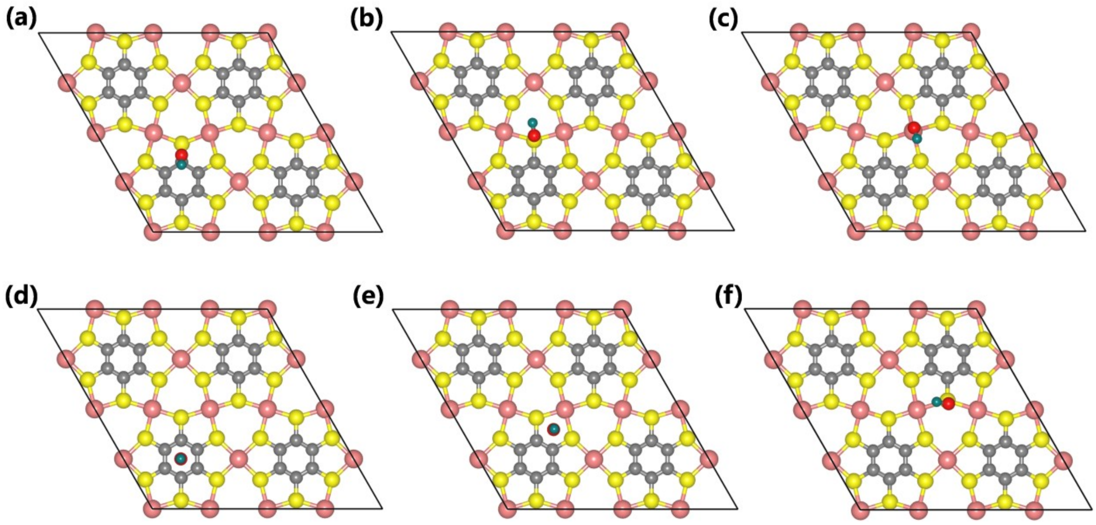

Figure S3. Top view of the optimized geometries of the OH atoms adsorbed on the surface of Cu-BHT. The OH atom adsorbed in the ‘C top’ (a), ‘S top’ (b), ‘Cu top’ (c), ‘top of the center of the benzene ring’ (d), “top of the ‘CuC2S2 ring’” (e) and “top of the center of ‘S3Cu3 ring’” (f).

S4 Top view of the optimized geometries of the H_2O_2 atoms adsorbed on the surface of Cu-BHT.

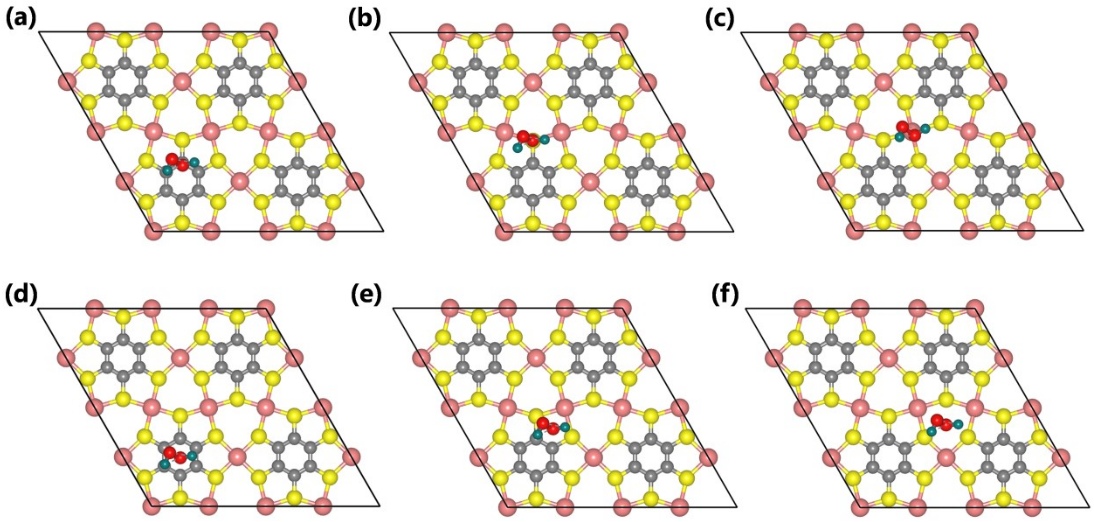

Figure S4. Top view of the optimized geometries of the H_2O_2 atoms adsorbed on the surface of Cu-BHT. The H_2O_2 atom adsorbed in the 'C top' (a), 'S top' (b), 'Cu top' (c), 'top of the center of the benzene ring' (d), "top of the 'CuC2S2 ring'" (e) and "top of the center of 'S3Cu3 ring'" (f).

Table S1 Adsorption energies ΔE (eV) of different adsorbates O, OH, and H_2O_2 on Cu-BHT. Red values indicate the most stable adsorption sites.

Adsorbed Sites	**H (eV)**	**OH (eV)**	**H_2O_2 (eV)**
C top	-0.334	-1.566	-0.508
S top	-2.536	-1.529	-0.499
Cu top	-1.307	-0.903	-0.638
top of the center of the benzene ring	-0.336	0.143	-0.506
top of the 'CuC2S2 ring'	-2.561	-0.965	-0.516
top of the center of 'S3Cu3 ring'	-0.336	-1.559	-0.521

Table S2 Adsorption energies ΔE (eV) of different adsorbates O, OH, and H_2O_2 on Cu-BHT/SiO_2. Red values indicate the most stable adsorption sites.

Adsorbed Sites	**H (eV)**	**OH (eV)**	**H_2O_2 (eV)**
C top	0.048	-0.828	-0.147
S top	-2.178	-1.186	-0.169
Cu top	-2.203	-1.186	-0.418
top of the center of the benzene ring	0.047	-1.126	-0.128
top of the 'CuC2S2 ring'	-2.188	-2.312	-0.192
top of the center of 'S3Cu3 ring'	-2.105	-1.376	-0.320

S5 Top view of the optimized geometries of the H atoms adsorbed on the surface of SiO_2/Cu-BHT.

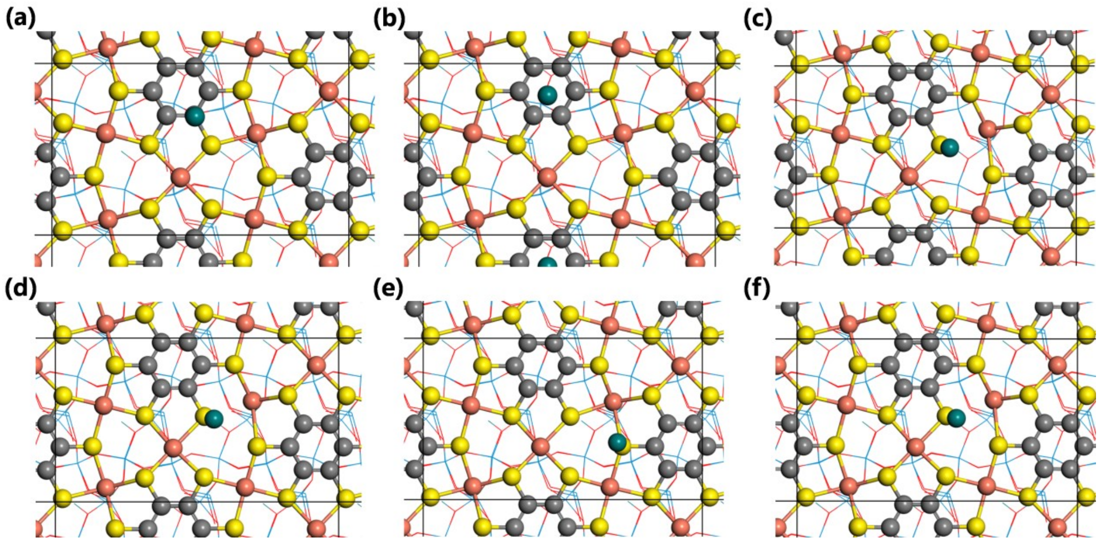

Figure S5. Top view of the optimized geometries of the H atoms adsorbed on the surface of SiO_2/Cu-BHT. The H atom adsorbed in the 'C top' (a), 'top of the center of the benzene ring' (b), 'Cu top' (c), "top of the 'CuC2S2 ring'" (d), "top of the center of 'S3Cu3 ring'" (e) and 'S top'(f).

S6 Top view of the optimized geometries of the OH atoms adsorbed on the surface of SiO_2/Cu-BHT.

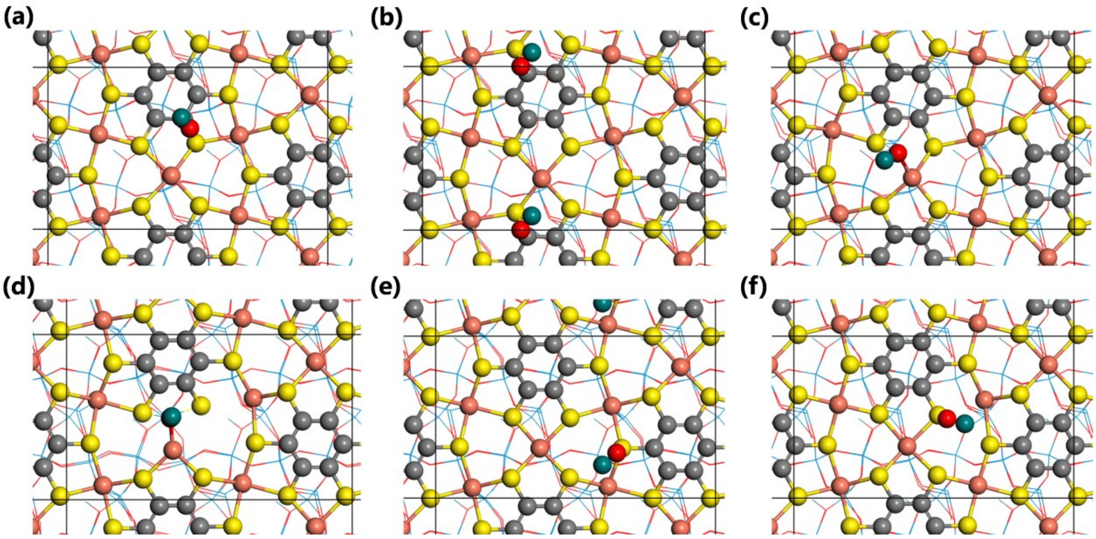

Figure S6. Top view of the optimized geometries of the OH atoms adsorbed on the surface of SiO_2/Cu-BHT. The OH atom adsorbed in the 'C top' (a), 'top of the center of the benzene ring' (b), 'Cu top' (c), "top of the 'CuC2S2 ring'" (d), "top of the center of 'S3Cu3 ring'" (e) and 'S top'(f).

S7 Top view of the optimized geometries of the H_2O_2 atoms adsorbed on the surface of SiO_2/Cu-BHT.

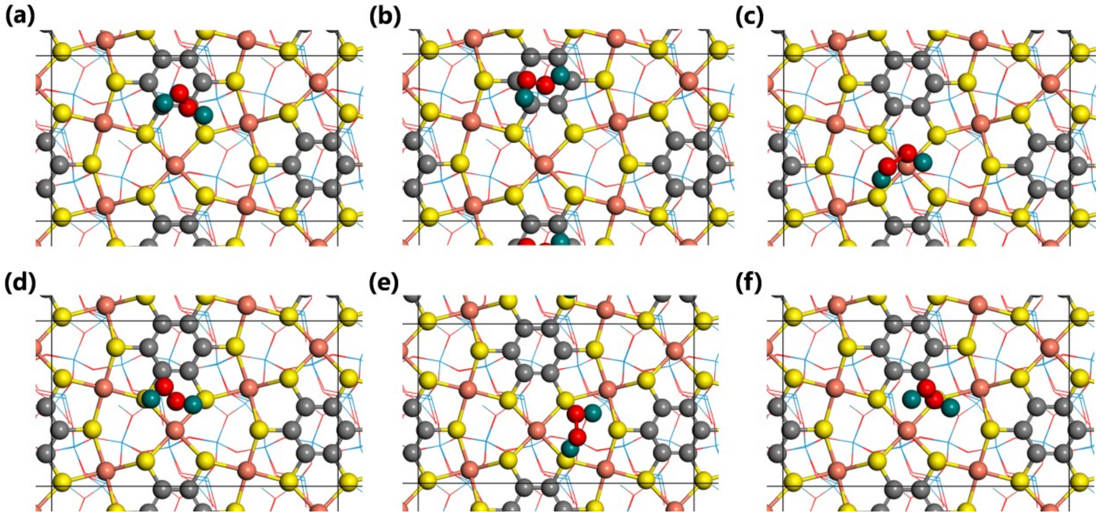

Figure S7. Top view of the optimized geometries of the H_2O_2 atoms adsorbed on the surface of SiO_2/Cu-BHT. The H_2O_2 atom adsorbed in the 'C top' (a), 'top of the center of the benzene ring' (b), 'Cu top' (c), "top of the 'CuC2S2 ring'" (d), "top of the center of 'S3Cu3 ring'" (e) and 'S top'(f).

Table S3 Bader charge variation and electron transfer direction.

System	Site	$\Delta Q\ (e^-)$	Electron transfer direction
SiO_2/Cu-BHT	Cu	+0.058	$SiO_2 \rightarrow$ Cu-BHT
SiO_2/Cu-BHT	Interfacial Cu	+0.174	$SiO_2 \rightarrow$ interfacial Cu
SiO_2/Cu-BHT + H_2O_2	O atoms in adsorbed H_2O_2	+0.037	SiO_2/Cu-BHT $\rightarrow H_2O_2$

S8 Projected density of states (PDOS) of Cu_3d orbitals in Cu-BHT and SiO_2/Cu-BHT.

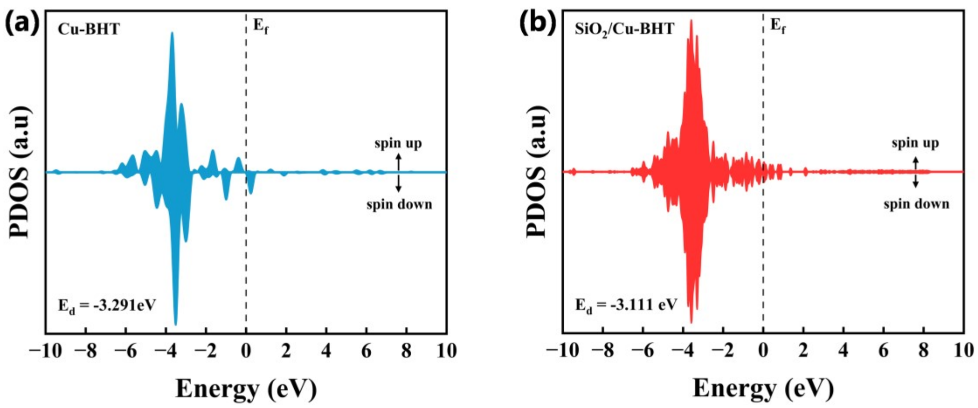

Figure S8. (a) PDOS of Cu_3d orbitals in pristine Cu-BHT and (b) in the SiO_2/Cu-BHT. The vertical dashed line at 0 eV marks the Fermi level. The d-band center values are given in the lower-left corner of each panel, which shift from -3.29 eV in (a) to -3.11 eV in (b). The upward shift of the d-band center upon SiO_2 integration indicates enhanced electron-donating ability of the Cu centers.