Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplementary Material

for

Unraveling the Orientation of an Enzyme onto Metal−Organic Framework

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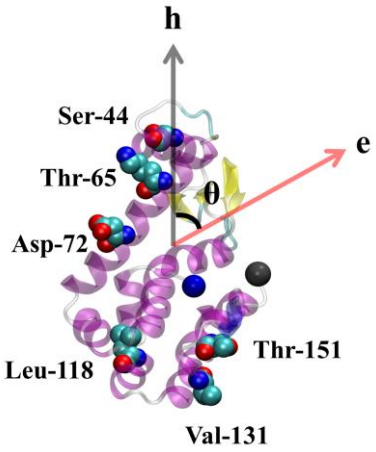

Fig. S1 The crystal structure of T4L, 6 marker sites consistent with the experimental reports are shown in vdW spheres; N-terminal and C-terminal are displayed in blue and black beads, respectively. The grey vector ***h*** and pink vector ***e*** are the unit vectors in the direction of ZIF-8 surface normal and the electrostatic dipole of the T4L

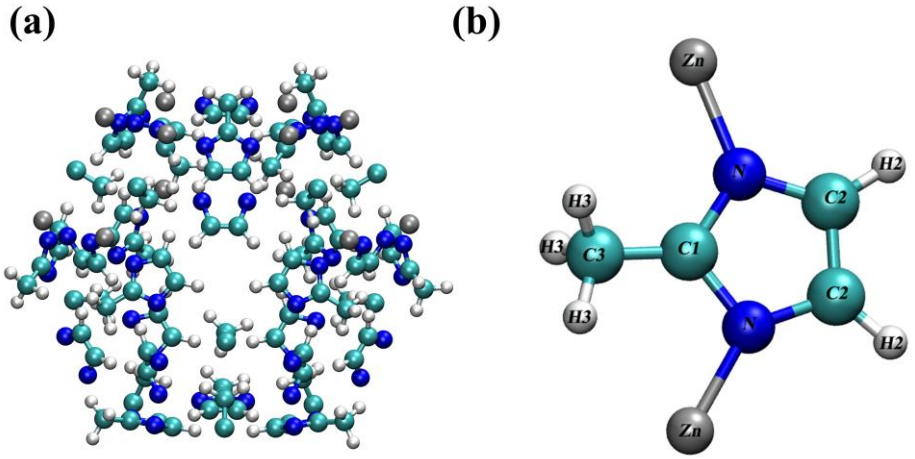

Fig. S2 The unit cell of ZIF-8 (a) and the cluster models for the 2-methylimidazolate (mIm) linker (b)

Table S1. The types and charges of atoms in ZIF-8.

Atom type	Charge	ε(kJ/mol)	σ(nm)
Zn	0.7599	0.196	0.196
N	-0.4312	0.325	0.325
C1	0.4280	0.340	0.340
C2	-0.0571	0.340	0.340
C3	-0.4676	0.340	0.340
H2	0.1083	0.251	0.251
H3	0.1399	0.265	0.265

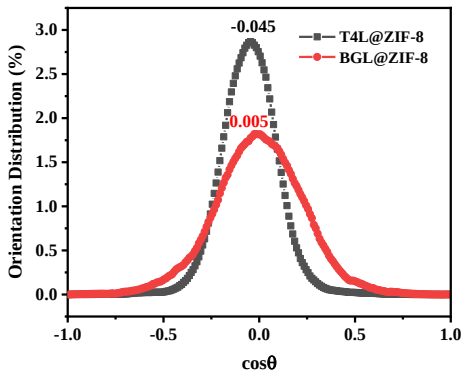

Fig. S3 Adsorption orientation distributions of T4L and BGL on ZIF-8 by MD simulations

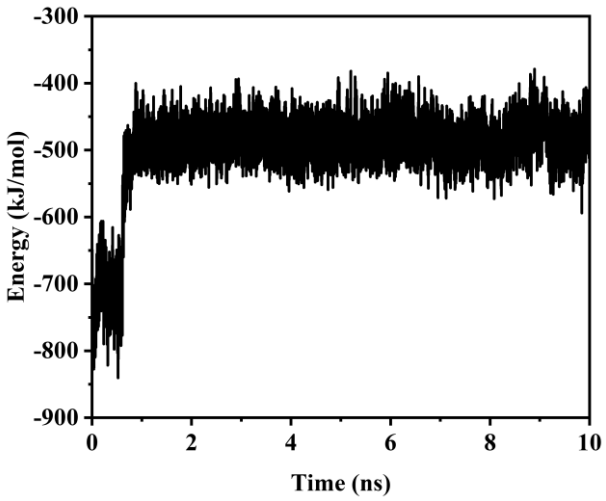

Fig. S4 Interaction energy between BGL and ZIF-8 in a random umbrella window

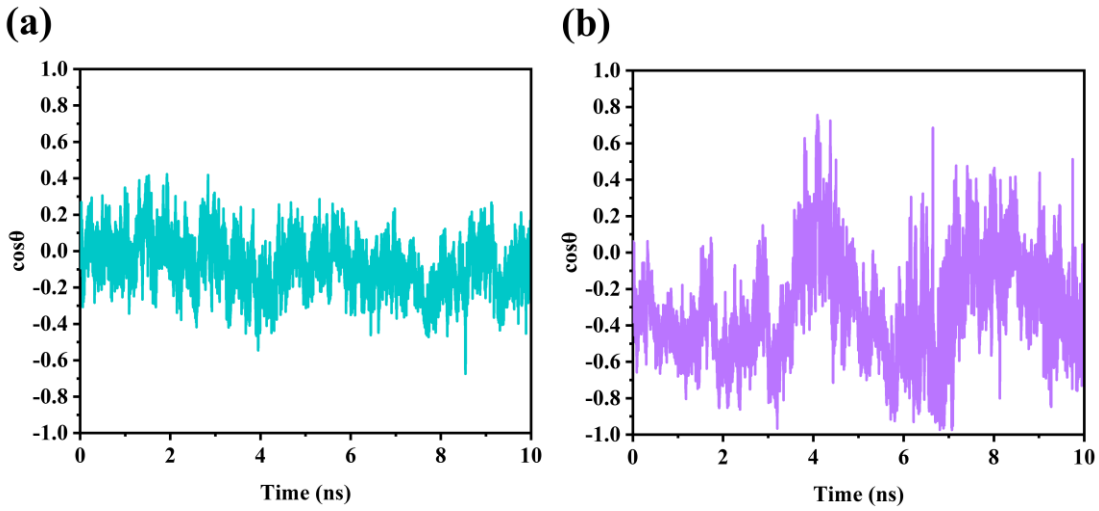

Fig. S5 Time evolutions of cosθ between BGL and ZIF-8 among two representative umbrella windows, the COM distance between BGL and ZIF-8 is about 35 Å (a) and about 70 Å (b)

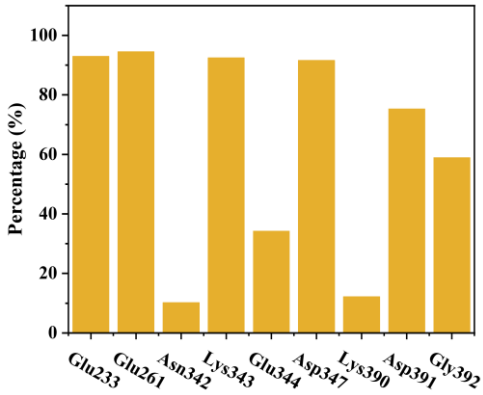

Fig. S6 Proportion of the trajectory each of the key binding residues is in contact with the ZIF-8 surface

Table S2. Adsorption orientations of T4L and BGL obtained by different methods

Proteins / Methods	T4L	BGL
ProtPOS	-0.047	0.199
MD	-0.045	0.005

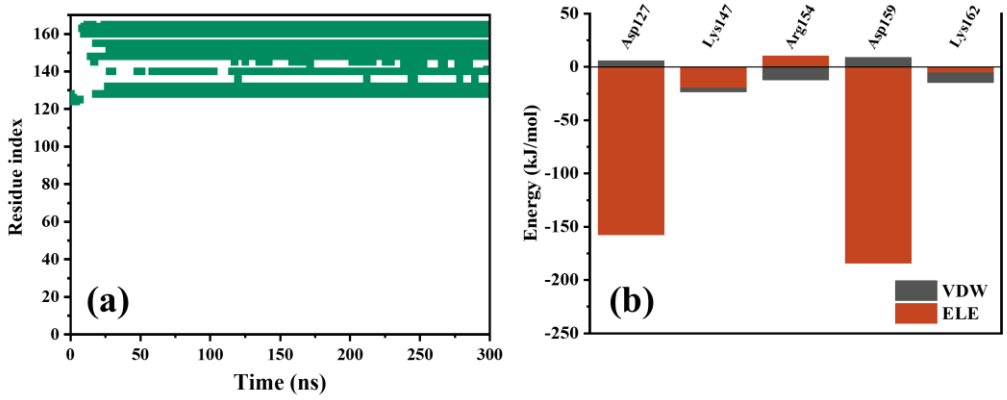

Fig. S7 Residue contact maps of T4L adsorbed on the ZIF-8 surface (a); averaged interaction energy of an individual key residue with the ZIF-8 surface (b)

Residues Asp127, Lys147, Arg154, Asp159 and Lys162 are the key binding sites for T4L on the ZIF-8 surface. After about 30 ns simulation time, they are all stably adsorbed on the ZIF-8 surface. Through negatively charged carboxyl groups, residues Asp127 and Asp159 intact with Zn^{2+} of ZIF-8 (Figure S5a), contribute strong electrostatic energy around -157.35 and -184.26 kJ/mol, respectively; while the positively charged residues Lys147, Arg154 and Lys162 bind with the ZIF-8 surface through relatively weak vdW interactions, with their interaction energies less than −12 kJ/mol. Hence, electrostatic interaction is the dominant driving force for T4L adsorbed on the ZIF-8.

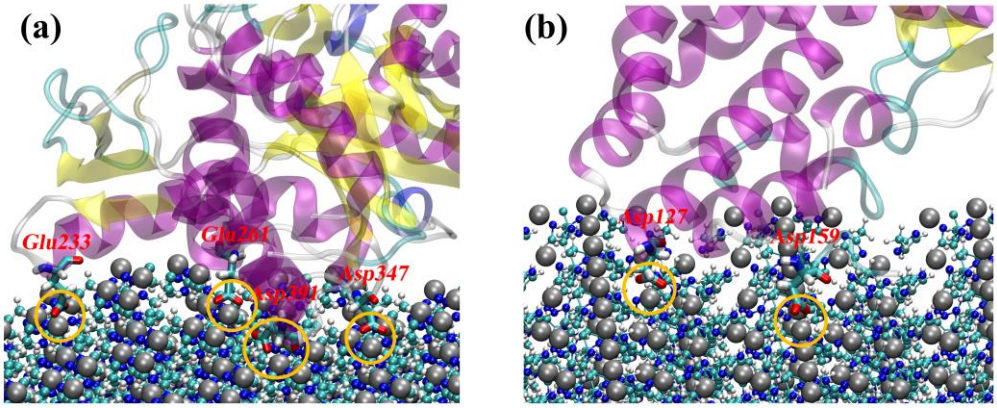

Fig. S8 The binding between deprotonated carboxyl group of acidic amino acids and the Zn^{2+} of ZIF-8, BGL@ZIF-8 system (a) and T4L@ZIF-8 system (b)

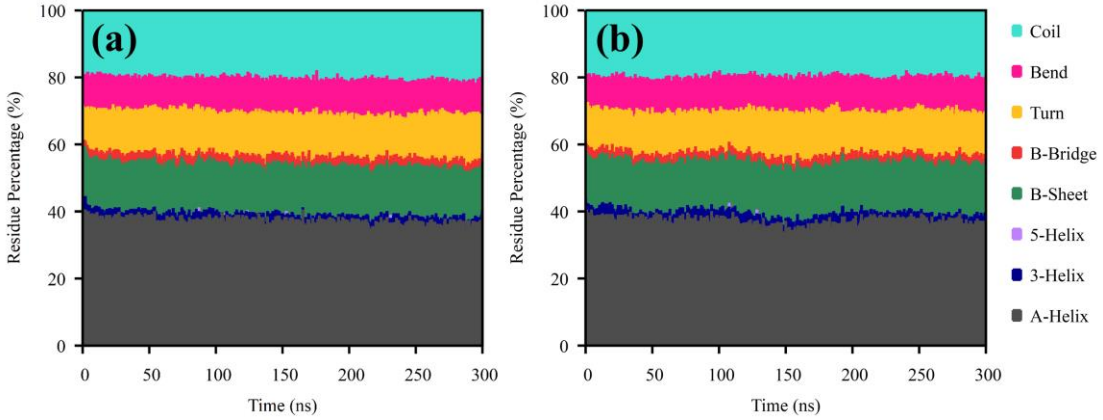

Fig. S9 Average contents of each secondary structure of the BGL for different systems, bulk solution (a) and BGL@ZIF-8 (b)