A multifunctional metal-organic framework with μ_3-OH⁻ site for gas and vapor

sorption and selective detection of nitrofurantoin

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Content 1: Calculation method

The molecular size of antibiotics was calculated based on the CPK model.[1] The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated using density functional theory (DFT) at the level of B3LYP/6-31G*.[2] To understand better the interaction between the guest molecules and the $Zn_{2.5}$(DDPP)(OH)(H_2O) framework, the Grand Canonical Monte Carlo (GCMC) method was used to simulate the optimal adsorption sites of guest molecules in **1**. The MOF structure was set as rigid with atoms frozen at their crystallographic positions during the GCMC simulations. The Lennard-Jones interactions were calculated with a cut off radius of 12.0 Å. For each state point, GCMC simulation consisted of 2.0×10^7 steps to guarantee equilibration.

References

1. Z. Zhang, Y.-W. Liu, H.-R. Tian, X.-H. Li, S.-M. Liu, Y. Lu, Z.-X. Sun, T. Liu and S.-X. Liu, *Matter*, 2020, 2, 250-260.
2. I. M. Abdellah, T. H. Chowdhury, J.-J. Lee, A. Islam, M. K. Nazeeruddin, M. Grätzel and A. El-Shafei, *Sustainable Energy & Fuels*, 2021, 5, 199-211.

Table S1. Selected bond lengths (Å) and angles (deg) for **1**.

MOF **1**					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn1-O1	2.0545(15)	Zn1-O3¹	2.1306(18)	Zn1-O5	2.1595(19)
Zn1-O6¹	2.0672(18)	Zn1-O9	2.164(2)	Zn1-N1²	2.127(2)
Zn2-O1	1.9818(16)	Zn2-O1³	1.9817(16)	Zn2-O2⁴	2.4212(17)
Zn2-O2¹	2.4212(17)	Zn2-O4¹	2.0040(17)	Zn2-O4⁴	2.0040(17)
Zn3-O1	1.9615(16)	Zn3-O2⁴	1.9893(17)	Zn3-O7	1.9080(18)
Zn3-O8⁵	1.9444(18)				
Angle	(°)	Angle	(°)	Angle	(°)
O1-Zn1-O3¹	87.82(6)	O1-Zn1-O5	91.46(7)	O1-Zn1-O6¹	101.27(7)
O1-Zn1-O9	84.87(7)	O1-Zn1-N1²	168.38(8)	O3¹-Zn1-O5	178.44(7)
O3¹-Zn1-O9	94.22(8)	O5-Zn1-O9	87.09(9)	O6¹-Zn1-O3¹	90.55(7)
O6¹-Zn1-O5	92.07(7)	O6¹-Zn1-O9	84.25(8)	O1³-Zn2-O1	185.07(10)
O1-Zn2-O2⁴	76.62(6)	O1³-Zn2-O2⁴	86.89(6)	O1³-Zn2-O2¹	76.62(6)
O1-Zn2-O2¹	86.89(6)	O1³-Zn2-O4¹	95.17(7)	O1-Zn2-O4¹	98.89(7)
O2¹-Zn2-O2⁴	82.63(8)	O4⁴-Zn2-O2⁴	88.82(7)	O4⁴-Zn2-O2¹	170.51(6)
O4¹-Zn2-O2⁴	170.51(6)	O4¹-Zn2-O2¹	88.82(7)	O4⁴-Zn2-O4¹	99.98(10)
O1-Zn3-O2⁴	88.27(7)	O7-Zn3-O1	113.11(7)	O7-Zn3-O2⁴	117.16(8)
O1-Zn3-O8⁵	116.90(9)	O8⁵-Zn3-O1	110.19(8)	O8⁵-Zn3-O2⁴	107.62(8)
Zn2-O1-Zn1	121.23(8)	Zn3-O1-Zn1	119.53(8)	Zn3-O1-Zn2	103.48(7)
Zn3²-O2-Zn2²	88.62(6)	C1-O2-Zn2²	137.36(16)	C1-O2-Zn3²	129.00(17)

Symmetry codes:1: *1-x, 1/2+y, 1/2-z*; 2: *1/2+x, 1-y, 1/2-z*; 3: *1/2-x, 3/2-y, +z*;4:*-1/2+x,1-y,1/2-z*; 5:*1/2-x,+y,-1/2+z*.

Table S2. Comparison of H_2O vapor adsorption values with some references.

Reported structure	H_2O vapor uptake ($cm^3 g^{-1}$, 298K)	Ref
$Cd_2L_2(TPA)_2] \cdot 12H_2O\}_n$	195	41
$\{[Zn_4L_4(TPA)_4] (DMF) \cdot 16H_2O\}_n$	224	41
$\{[Co_2L_2(TPA)_2] \cdot 12H_2O\}_n$	184	41
$[Cd(bpy)(nbdc)]_n$	163	42
1	281.9	This work

Table S3. Comparison of the Stern-Volmer Constant (Ksv) and DL for antibiotic sensing by different MOFs materials.

Materials	antibiotics	Ksv (M^{-1})	Detection limit	Reference
$\{[Cd_3(TDCPB) 2DMAc] DMAc 4H_2O\}_n$	NFT	1.05×10^5	0.06 mM	45
$\{[Tb(TATMA)(H_2O) 2H_2O\}_n$	NFT	3.35×10^4		46
$[Cd_2Na(L)(BDC)_{2.5}] 9H_2O$	NFT	3.57×10^4	274 ppb	47
$[Cd_2(L)(2,6-NDC)_2] DMF 5H_2O$	NFT	7.19×10^4	131 ppb	47
$[Cd_2(L)(BPDC)_2] DMF 9H_2O$	NFT	6.93×10^4	142 ppb	47
1	NFT	9.60×10^5	0.05 mM	This work
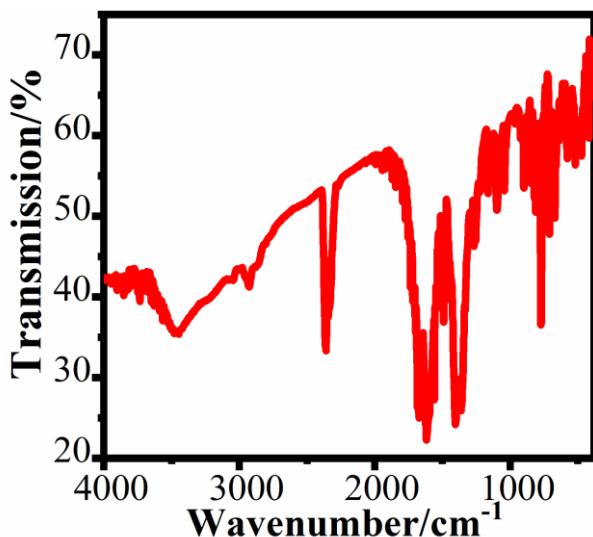
Fig. S1 IR spectrum of **1**.
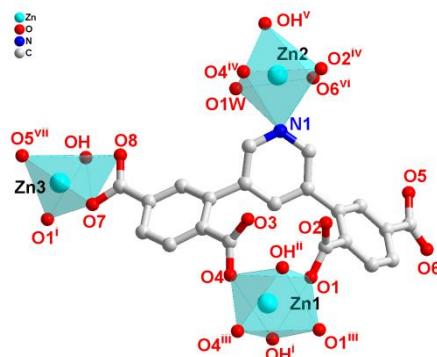
Fig. S2 The Coordination environment of Zn (II) ions. (Symmetry codes: i: 1-x, 1-y, 1-z; ii: -0.5+x, -0.5+y, 1-z; iii: 0.5-x, 0.5-y, z; iv: 1.5-x, 0.5-y, z; v: 2-x, 1-y, 1-z; vi: 0.5+x, 1-y, 0.5-z; vii: 1.5-x, y, 0.5+z. All hydrogen atoms, uncoordinated DMF molecules are omitted for clarity).
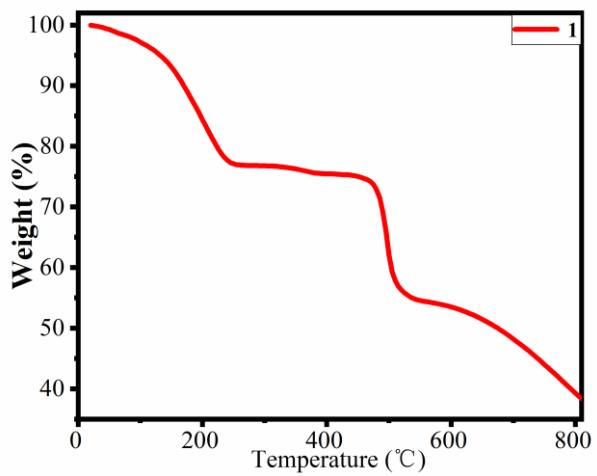
Fig. S3 The TG curve of **1**.
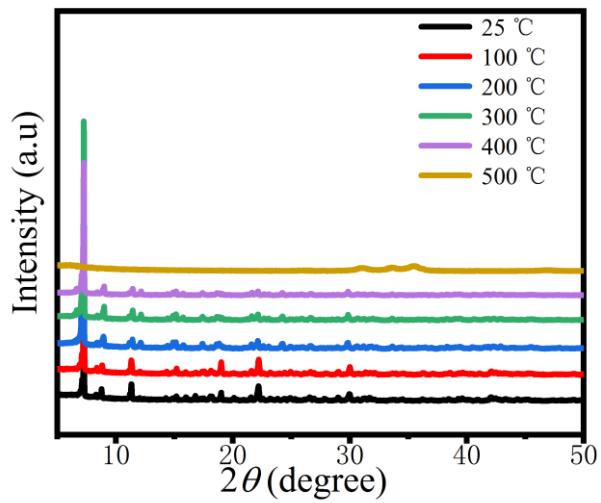
Fig. S4 Variable temperature PXRD patterns of **1**.
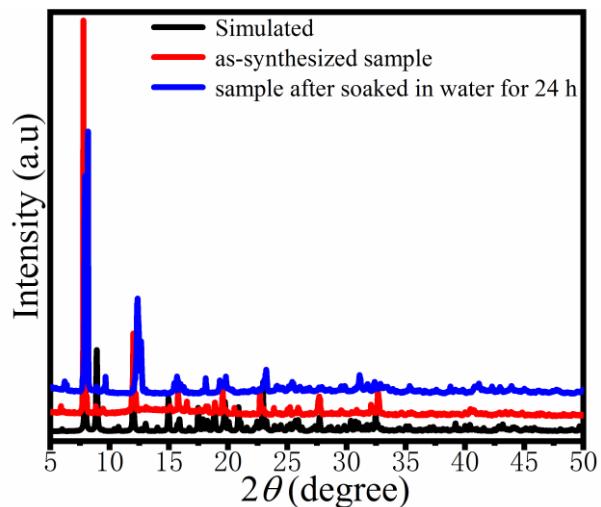

**Fig. S5** PXRD pattern of **1**.
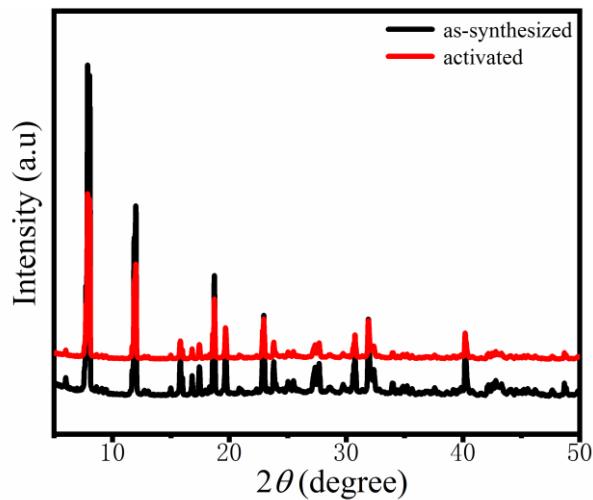
**Fig. S6** PXRD patterns of as-synthesized sample and activated sample.
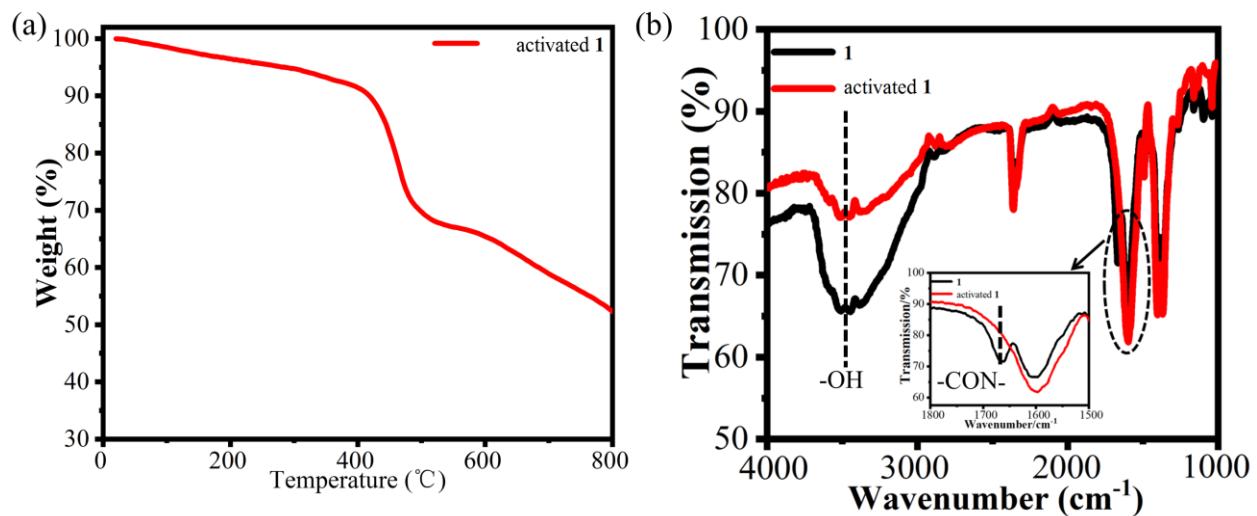
Fig. S7 (a) The TG curve of activated sample. (b) IR spectra of samples before and after being activated.
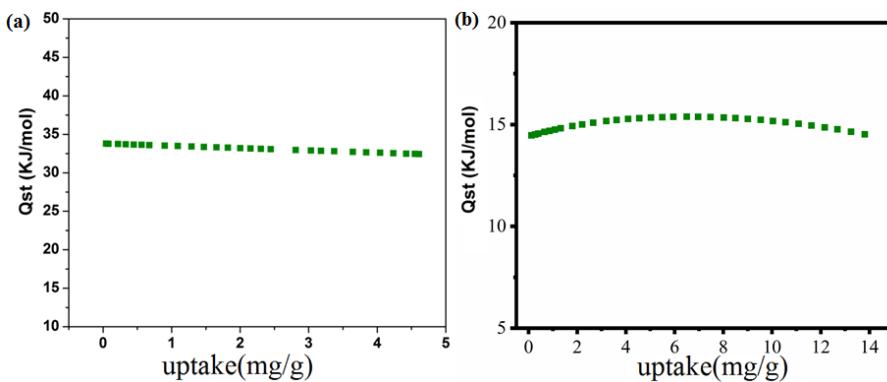

**Fig. S8** Isosteric heat (Q_{st}) of CO_2 (a) and CH_4 (b) adsorption.
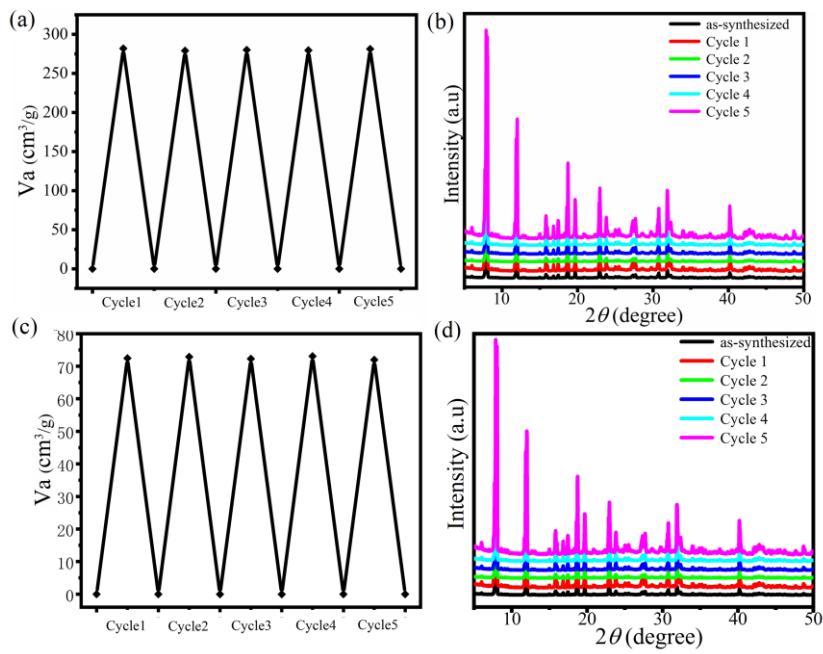
Fig. S9 (a) Water vapor uptake of **1** after five cycle experiments**.** (b) PXRD patterns of **1** after five water vapor cycle experiments. (c) CH$_3$OH vapor uptake of **1** after five cycle experiments**.** (d) PXRD patterns of **1** after five CH$_3$OH vapor cycle experiments.
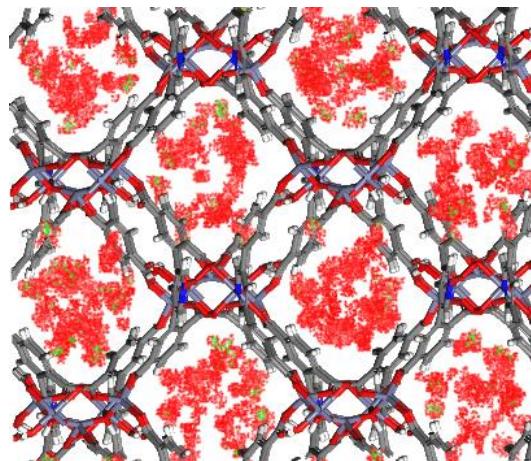

Fig. S10 The Adsorption distribution of water vapor (red points) and CH$_3$OH vapor (green points) in **1** by GCMC calculated at 298 K, 1 bar.
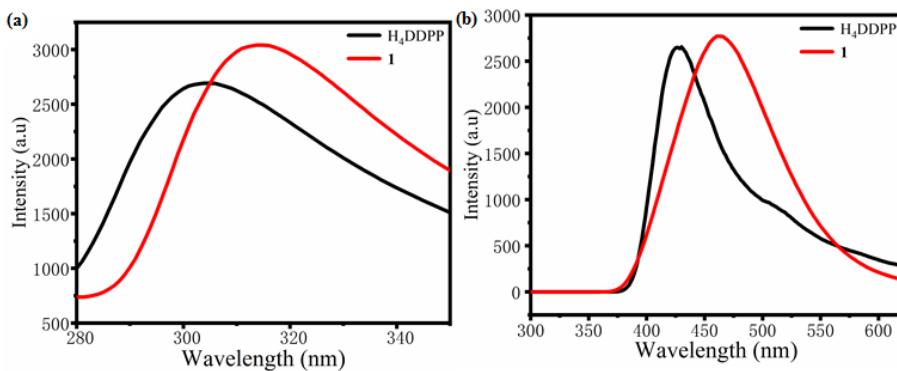

Fig. S11 (a) The excitation spectra of free ligand H$_4$DDPP and **1**. (b) The emission spectra of free ligand H$_4$DDPP and **1**.
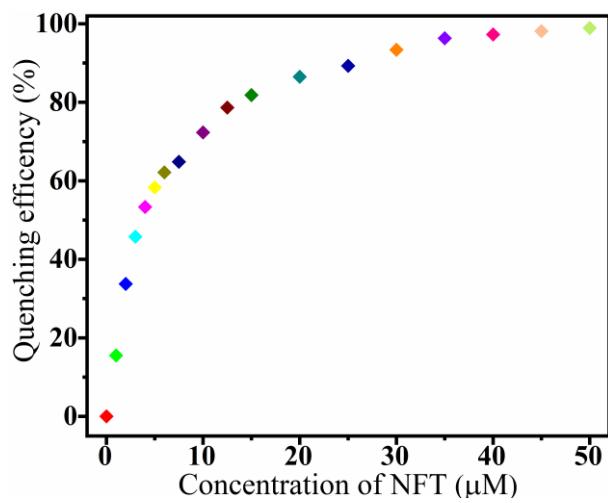
Fig. S12 Quenching rate of NFT for **1**.

$K_{sv}=9.6\times10^5 \text{ M}^{-1}$

$R^2=0.995$
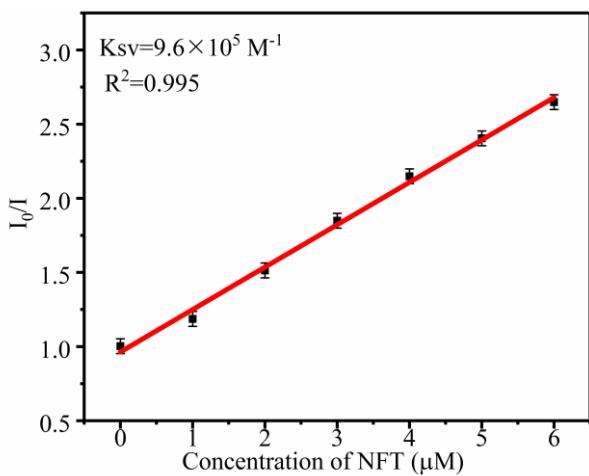
**Fig. S13** Stern–Volmer plot for the fluorescence intensity of **1** upon the addition of NFT in water.
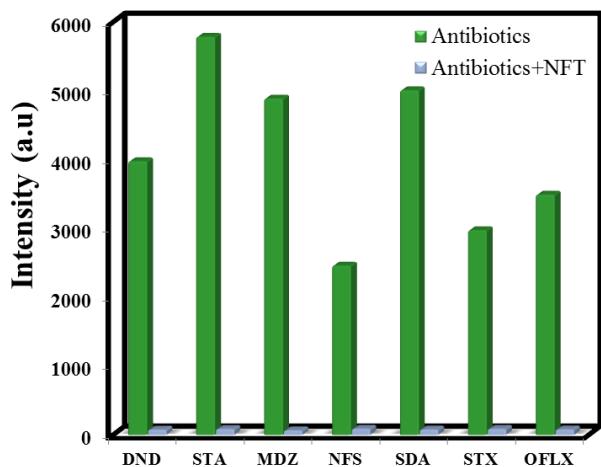
Fig. S14 The competitive quenching experiment of NFT for **1**.
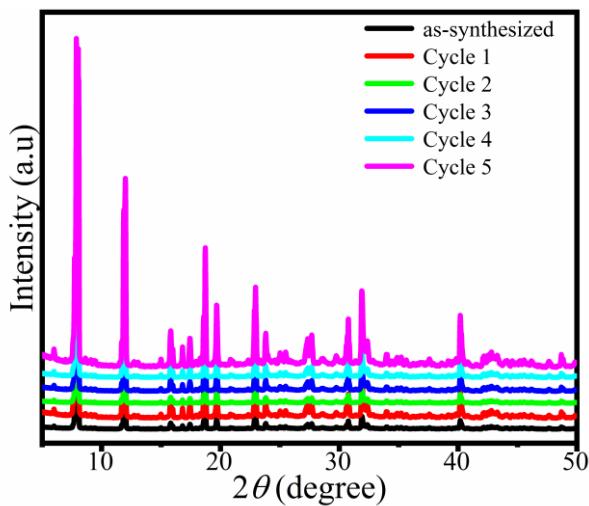
Fig. S15 PXRD patterns of **1** after five runs for NFT.
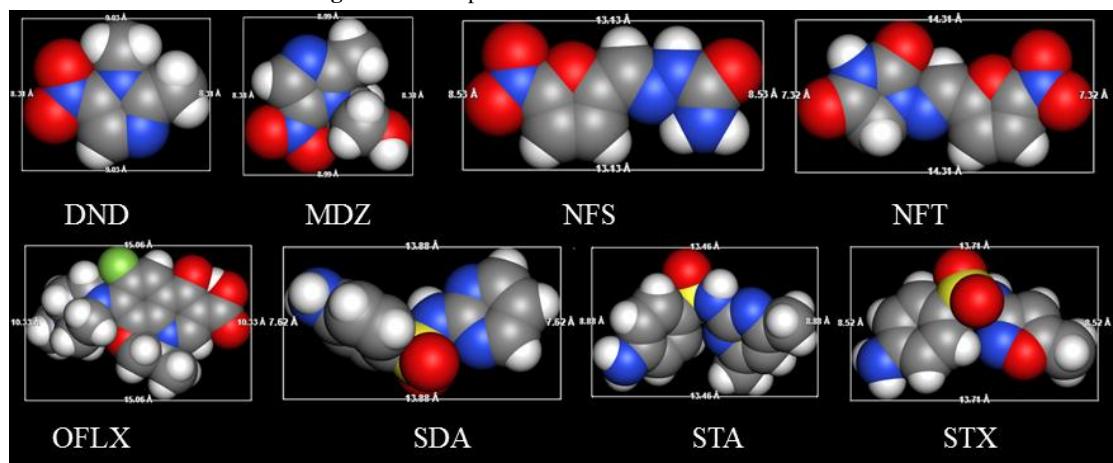
Fig. S16 Molecular Size of Antibiotics.
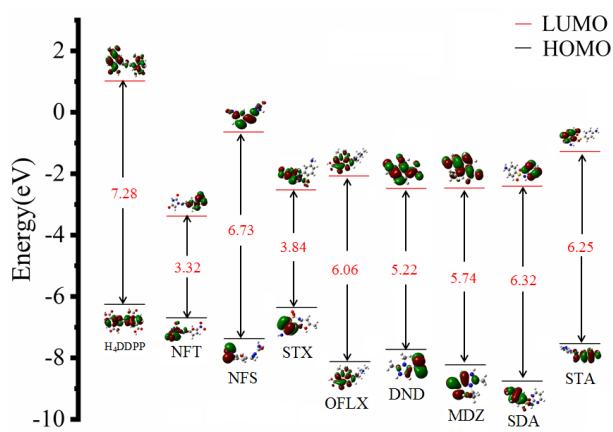
Fig. S17 HOMO and LUMO energies for H$_4$DDPP and antibiotics.