Does the fragments from decomposed ZIF-8 greatly affect some of the intramolecular proton-transfer of Thymine? A quantum chemical study

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Fig. S1 Irreversible change of the pore structure of ZIF-8 caused by water molecules.

Fig. S2 The sketch map of mispairing of GT′.

Fig. S3 The molecular structures of T and T″ investigated.

Fig. S4 The optimized structures of M⁻T-nw-ts in the tautomeric processes.

Fig. S5 The proton-transferred structures of M⁻T′-nw in the tautomeric processes.

Fig. S6 Energy barriers change in the different tautomeric processes including T-nw→T″-nw, MT-nw→MT″-nw and M⁻T-nw→M⁻T″-nw.

Table S1 The Optimized Geometrical Parameters of T and T′ Including the Transition State T-ts

Table S2 NPA Charge Distribution (au) on a Portion of the Critical Atoms in T-nw and MT-nw

Table S3 Relative Energies of Proton-Transferred Complexes based on Initial Structures

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Table S5 Energy Barrier Comparison from B3LYP, CAM-B3LYP and MP2 Methods

Table S6 Energy Barriers of T→T′ Proton-transfer Processes Affected by Hydrated M⁻
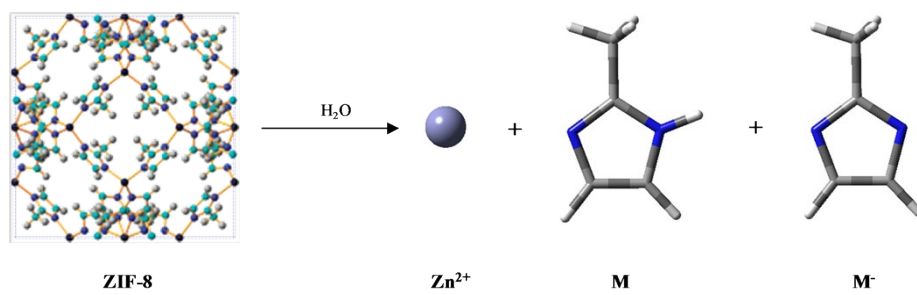
Fig. S1   Irreversible change of the pore structure of ZIF-8 caused by water molecules.
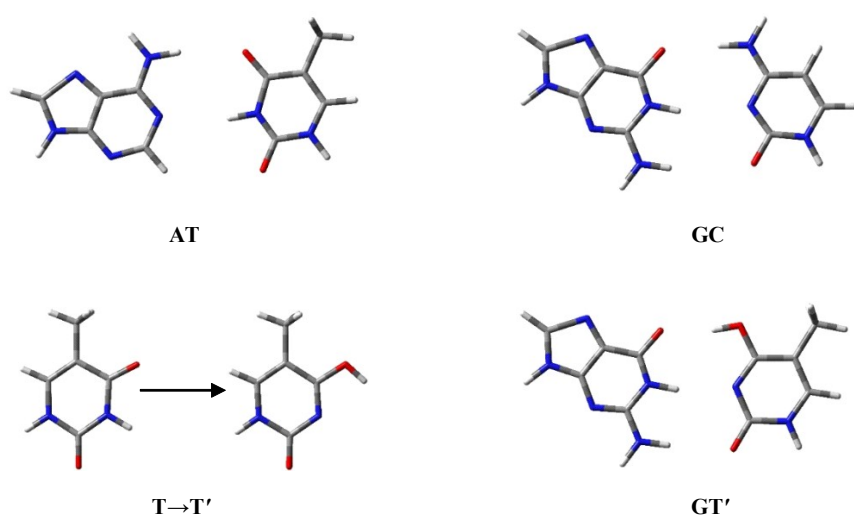
AT

GC

T→T′

GT′

Fig. S2 The sketch map of mispairing of GT′.

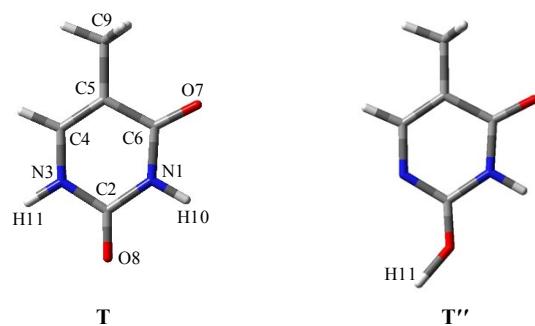**Fig. S3**   The molecular structures of T and T″ investigated. O, C, N atoms are shown in red, gray and blue colors, respectively.

M⁻T-1w-ts

1.462 (1.465)

1.307 (1.352)

M⁻T-2w-ts

1.546 (1.548)

1.411
(1.451)

M⁻T-3w-ts

1.511 (1.512)

1.507
(1.527)

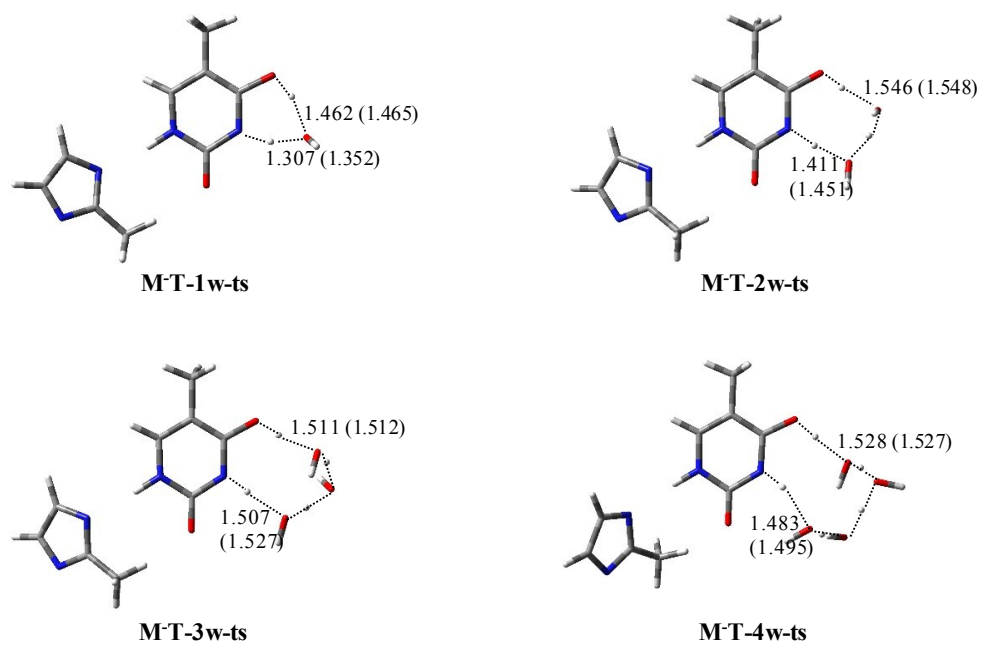**M⁻T-4w-ts**

1.528 (1.527)

1.483
(1.495)

Fig. S4   The optimized structures of M⁻T-nw-ts in the tautomeric processes. The route of proton-transfer are connected by dashed lines. Bond distances in angstrom (Å). Bond distances in parenthesis are obtained from MP2 method.

1.870 (1.930)

1.737
(2.153)

M⁻T′-2w

1.862 (1.937)

1.820 (2.134)

M⁻T′-3w

1.799 (1.812)

1.630
(1.873)

M⁻T′-4w

Fig. S5   The proton-transferred structures of M⁻T′-nw in the tautomeric processes. The route of proton-transfer are connected by dashed lines. Bond distances in angstrom (Å). Bond distances in parenthesis are obtained from MP2 method.
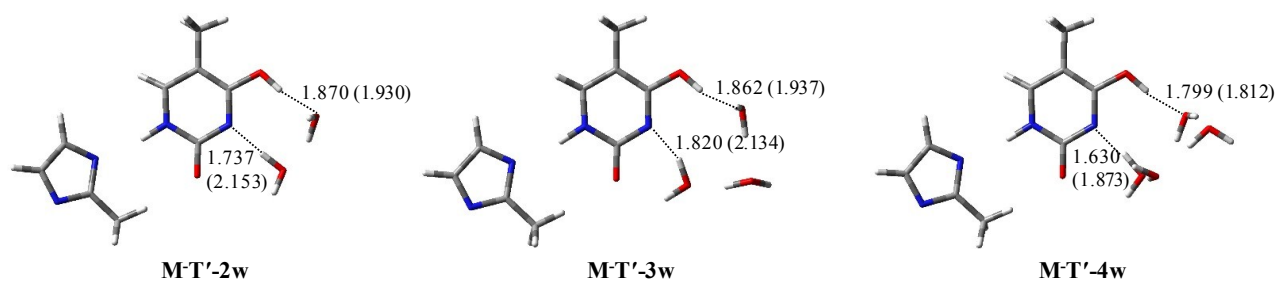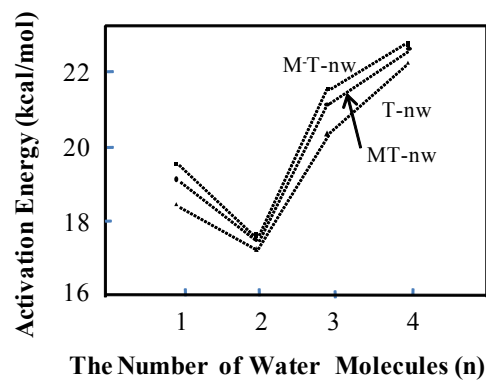
Fig. S6 Energy barriers change in the different tautomeric processes including T-nw→T″-nw, MT-nw→MT″-nw and M⁻T-nw→M⁻T″-nw.

Table S1 The Optimized Geometrical Parameters of T and T′ Including the Transition State T-ts

bond	T	T-ts	T′	Ref. 35	Ref. 36
N1-C2	1.386	1.372	1.379	1.390	1.379
C2-N3	1.388	1.421	1.417	1.391	1.379
N3-C4	1.382	1.367	1.361	1.387	1.375
C4-C5	1.375	1.368	1.366	1.382	1.365
C5-C6	1.468	1.431	1.438	1.470	1.356
C6-N1	1.407	1.350	1.307	1.407	1.379
C6-O7	1.225	1.287	1.348	1.227	1.224
C2-O8	1.221	1.219	1.222	1.220	1.234
C5-C9	1.502	1.503	1.504	1.502	1.502

Bond length in Å.

Table S2   NPA Charge Distribution (au) on a Portion of the Critical Atoms in T-nw and MT-nw (n=0-4)

n	O7	C6	N1	H10	O8	C2	N3	H11
				T-nw / MT-nw [a]				
0	-0.604(-0.619)	0.654(0.652)	-0.671(-0.668)	0.459(0.454)	-0.632(-0.660)	0.808(0.813)	-0.638(-0.647)	0.456(0.477)
1	-0.647(-0.661)	0.663(0.660)	-0.673(-0.669)	0.484(0.479)	-0.626(-0.653)	0.809(0.815)	-0.635(-0.643)	0.456(0.477)
2	-0.669(-0.683)	0.672(0.670)	-0.675(-0.672)	0.486(0.482)	-0.628(-0.654)	0.810(0.815)	-0.634(-0.642)	0.455(0.476)
3	-0.675(-0.686)	0.675(0.671)	-0.674(-0.671)	0.487(0.482)	-0.637(-0.666)	0.811(0.816)	-0.633(-0.640)	0.455(0.476)
4	-0.674(-0.665)	0.676(0.667)	-0.674(-0.675)	0.489(0.475)	-0.646(-0.665)	0.812(0.815)	-0.632(-0.643)	0.456(0.477)

[a] MT-nw data are listed in parenthesis.

Table S3   Relative Energies of Proton-Transferred Complexes based on Initial Structures (0 kcal mol^{-1})

n	T′-nw	MT′-nw	M⁻T′-nw
0	11.0/11.2[a]	12.0	15.1
1	10.5	10.9	12.0
2	8.9	9.2	10.5
3	8.8	9.1	9.6
4	8.4	9.9	10.8

[a] MP2/6-311++G** basis set used in Ref 30. All computed values are zero-point energy corrected.

Table S4 NPA Charge Distribution (au) on the Portion of M⁻T-nw (n=0-4)

n	M⁻	T	w
0	-0.570	-0.430	–
1	-0.510	-0.444	-0.046
2	-0.420	-0.530	-0.050
3	-0.399	-0.540	-0.061
4	-0.415	-0.528	-0.057

Table S5 Energy Barrier Comparison from B3LYP, CAM-B3LYP and MP2 Methods

n	T-nw	MT-nw	M⁻T-nw
1	17.6[a] / 21.3[b] / 16.4[c]	17.7 / 20.3 / 16.5	16.3 / 15.1 / 17.8
2	16.3 / 20.0 / 15.5	16.6 / 21.6 / 15.8	14.4 / 13.4 / 15.1
3	17.8 / 21.6 / 16.3	18.9 / 22.7 / 17.5	15.2 / 14.3 / 16.3
4	20.5 / 24.0 / 18.7	20.8 / 24.3 / 18.3	16.8 / 15.7 / 18.7

[a] obtained by B3LYP. [b] obtained by CAM-B3LYP. [c] obtained by MP2.

Table S6   Energy Barriers of T→T′ Proton-transfer Processes Affected by Hydrated M⁻

Proton-transfer structures	Energy barriers
(monohydrated M⁻)T-1w	16.7
(dihydrated M⁻)T-1w	16.5
(trihydrated M⁻)T-1w	16.4
(monohydrated M⁻)T-2w	15.8
(dihydrated M⁻)T-2w	15.6
(trihydrated M⁻)T-2w	15.5
(monohydrated M⁻)T-3w	17.3
(dihydrated M⁻)T-3w	16.8
(trihydrated M⁻)T-3w	16.6
(monohydrated M⁻)T-4w	20.1
(dihydrated M⁻)T-4w	19.5
(trihydrated M⁻)T-4w	19.3