Available online at website: https://journal.bcrec.id/index.php/bcrec

Bulletin of Chemical Reaction Engineering & Catalysis, 19 (2) 2024, 190-214

Research Article

Investigating the Structure of Defects in Heterometallic Zeolitic Imidazolate Frameworks ZIF-8(Zn/Cd) and Its Interaction with CO_2 Using First-Principle Calculations

Fajar Inggit Pambudi*, S. Sutarno, Adhi Dwi Hatmanto, Mita Patmawati, Tika Dwi Utari

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara Bulaksumur Yogyakarta 55281, Indonesia.

Received: 2nd March 2024; Revised: 28th March 2024; Accepted: 28th March 2024
Available online: 9th April 2024; Published regularly: August 2024

SUPPORTING INFORMATION

Table S1. The electronic and bandgap energy of selected structures with and without considering spin effect.

MOFs type	Energy (E)				Band gap energy	
	Without spin (a.u.)	With spin (a.u.)	Delta E (a.u.)	Delta E (eV)	Without spin	With spin
Non-defective ZIF-8(Cd/Zn)-Trimer (T)	-867.769394	-867.769396	1.247×10^{-06}	0.000034	4.51	4.51
Defect due to missing Cd (1DM)	-822.872476	-822.872478	1.597×10^{-06}	0.000043	4.23	4.23
Defect due to missing imidazolate (1TL)	-855.984527	-855.984529	2.660×10^{-06}	0.000072	3.96	3.96

Table S2. Calculated unit cell dimensions of non-defective and defective structures

MOFs	a(Å)	b(Å)	c(Å)	Average Lattice length (Å)	Volume(Å^3)
ZIF-8(Zn)	14.840	14.842	14.844	14.842	2516.854
ZIF-8(Cd)	15.834	15.834	15.843	15.837	3057.832
D	15.322	15.335	15.318	15.325	2770.710
T	15.385	15.155	15.387	15.309	2761.790
1DL	14.906	15.215	15.310	15.144	2672.943
2DL	15.633	14.567	15.172	15.124	2659.792
1TL	15.141	14.607	15.532	15.093	2644.418

2TL	15.275	14.754	15.361	15.130	2665.134
3TL	15.246	15.175	15.221	15.214	2710.809
4TL	14.832	14.975	15.513	15.107	2652.549
5TL	15.455	15.213	14.851	15.173	2687.930
6TL	14.477	15.557	15.338	15.124	2659.285
1DM	15.247	15.336	14.997	15.193	2699.564
2DM	15.410	15.384	15.353	15.383	2801.979
1TM	15.128	15.190	15.263	15.193	2699.767
2TM	15.303	14.921	15.314	15.179	2691.740
3TM	15.275	15.255	15.548	15.359	2789.072
4TM	15.561	15.191	15.334	15.362	2790.254

Table S3. Comparison between calculated and experimental reported unit cell for ZIF-8(Zn), ZIF-8(Cd) and ZIF-8(Zn/Cd).

MOFs	Calculated unit cell (Å) (simplified structure)	[c] %Δ1	Experimental unit cell (Å) (Cubic structure)	[c] %Δ2	%Δ1 -%Δ2
ZIF-8(Zn)	14.842	6.3	17.0400	5.4	0.9%
[a]ZIF-8(Zn/Cd)-D	15.325	3.2	[b]17.4954	2.9	0.3% - 0.4%
[a]ZIF-8(Zn/Cd)-T	15.309	3.3			
ZIF-8(Cd)	15.837	-	18.0173	-	

Note:
a = Structure D and T have the same number of Zn and Cd in a unit cell
b = Experimental unit cell where the ratio of Zn and Cd is the same which is close to our D and T structure
c = %Δ is calculated based on the following equation $\%\Delta = \frac{(ZIF8Cd - ZIF8Zn)}{ZIF8Cd} * 100\%$

Table S4. The electronic energy difference between D and T structures

MOFs type	Energy (a.u.)	ΔE (a.u.)	ΔE (eV)
ZIF-8(Cd/Zn)-D	-867.76899537	0.00039898	0.01086
ZIF-8(Cd/Zn)-T	-867.76939435	0.00000000	0.00000

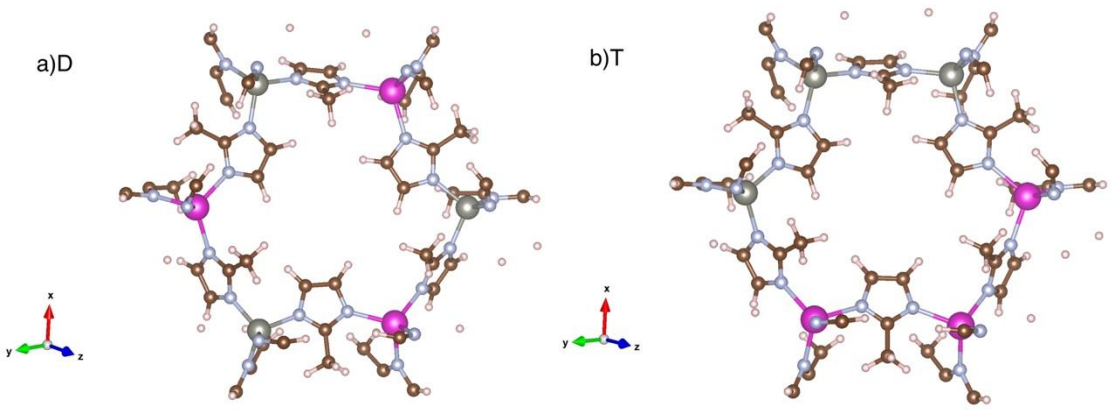

Figure S1. The structure of Zn3Cd3-ZIF-8 with D (a) and T (b) configurations. D and T are disperse and trimer structure, respectively. Zn, Cd, N, C and H are grey, magenta, cyan, brown and pink, respectively.

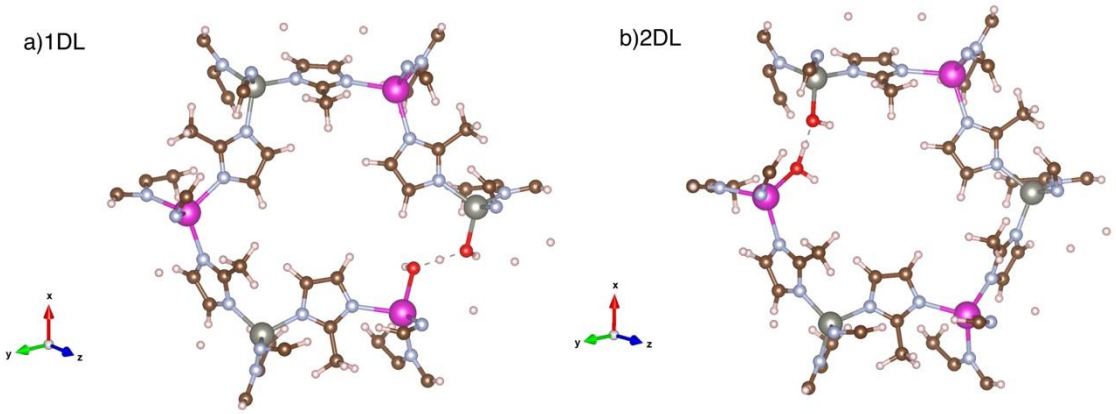

Figure S2. The structure of Zn3Cd3-ZIF-8 with missing linkers annotated as 1DL (a) and 2DL (b). DL is a disperse configuration with missing linker. The missing imidazolate (Im) is from the same Cd-Im-Zn but Im has different orientations. Zn, Cd, O, N, C and H are grey, magenta, red, cyan, brown and pink, respectively.

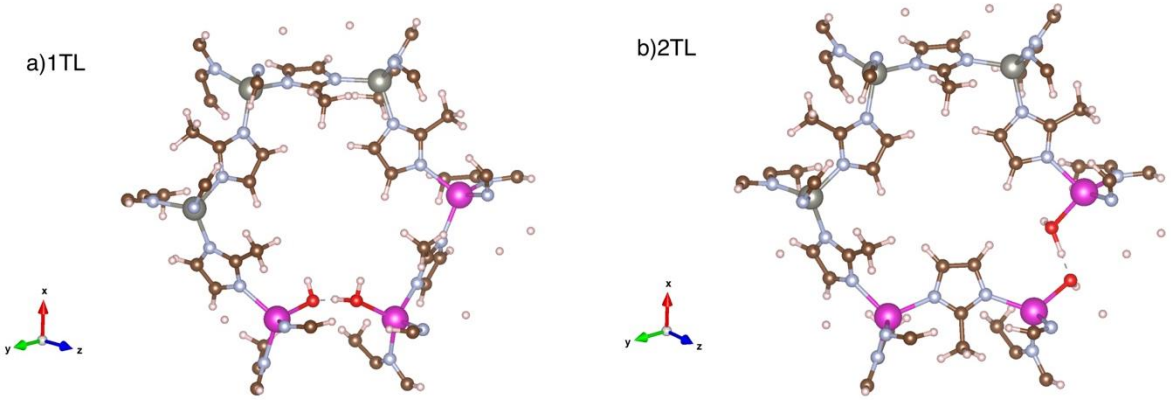

Figure S3. The structure of Zn3Cd3-ZIF-8 with missing linkers annotated as 1TL (a) and 2TL (b). TL is a trimer configuration with missing linker. The missing imidazolate (Im) is from the same Cd-Im-Cd but Im has different orientations. Zn, Cd, O, N, C and H are grey, magenta, red, cyan, brown and pink, respectively.

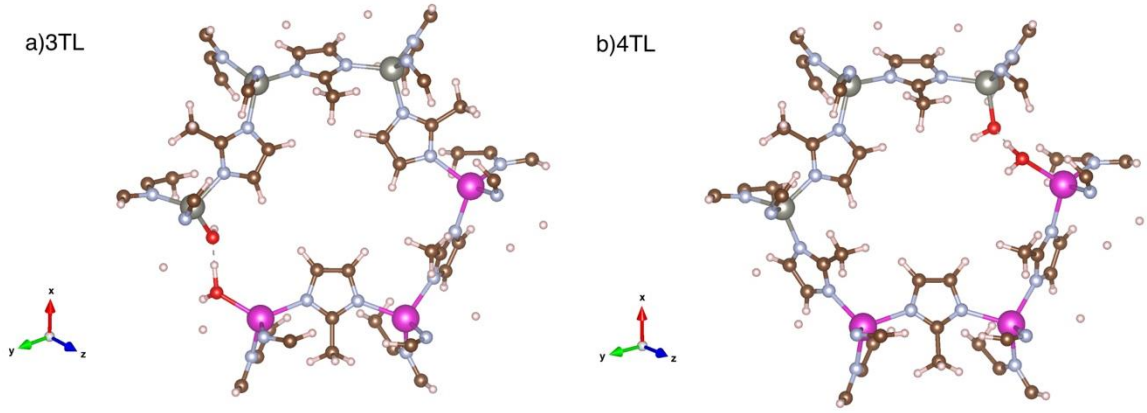

Figure S4. The structure of Zn3Cd3-ZIF-8 with missing linkers annotated as 3TL (a) and 4TL (b). TL is a trimer configuration with missing linker. The missing imidazolate (Im) is from the same Cd-Im-Zn but Im has different orientations. Zn, Cd, O, N, C and H are grey, magenta, red, cyan, brown and pink, respectively.

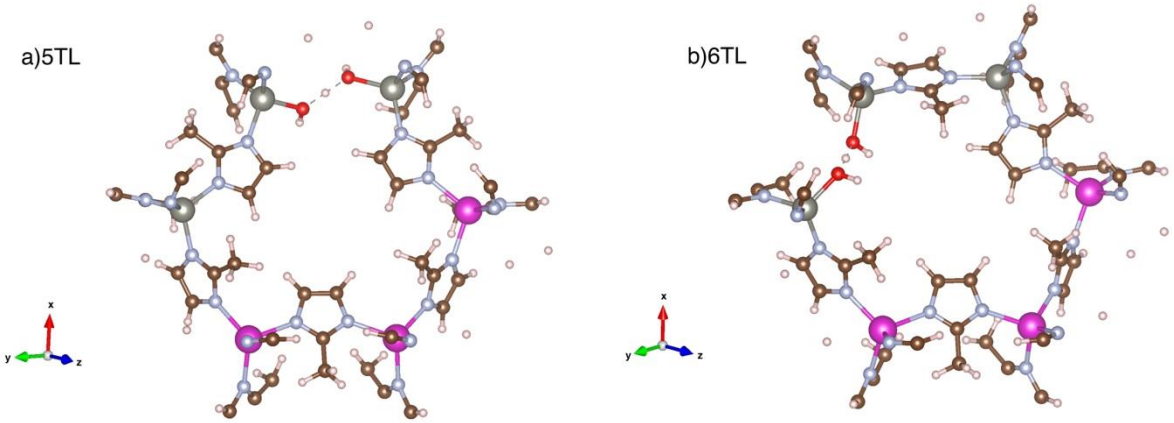

Figure S5. The structure of Zn3Cd3-ZIF-8 with missing linkers annotated as 5TL (a) and 6TL (b). TL is a trimer configuration with missing linker. The missing imidazolate (Im) is from the same Zn-Im-Zn but Im has different orientations. Zn, Cd, O, N, C and H are grey, magenta, red, cyan, brown and pink, respectively.

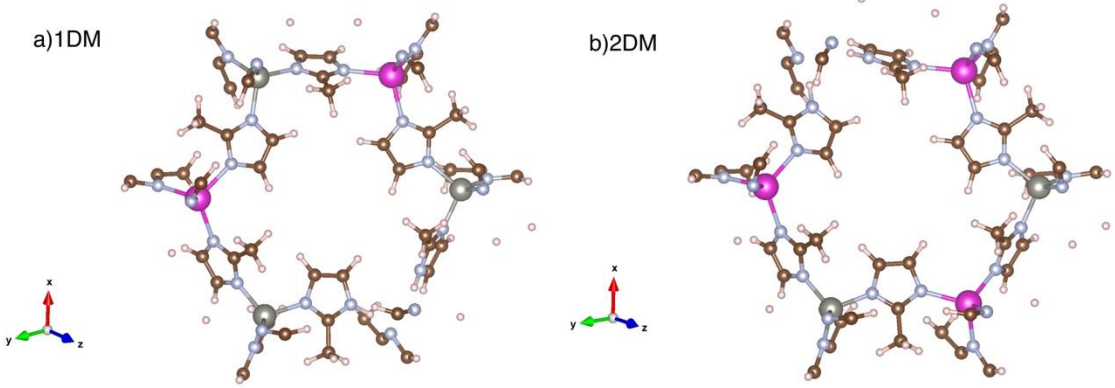

Figure S6. The structure of Zn3Cd3-ZIF-8 with missing metals annotated as 1DM (a) and 2DM (b). DM is a disperse configuration with missing metal. The missing metal centre is Cd^{2+} for 1DM and Zn^{2+} for 2DM. Zn, Cd, N, C and H are grey, magenta, cyan, brown and pink, respectively.

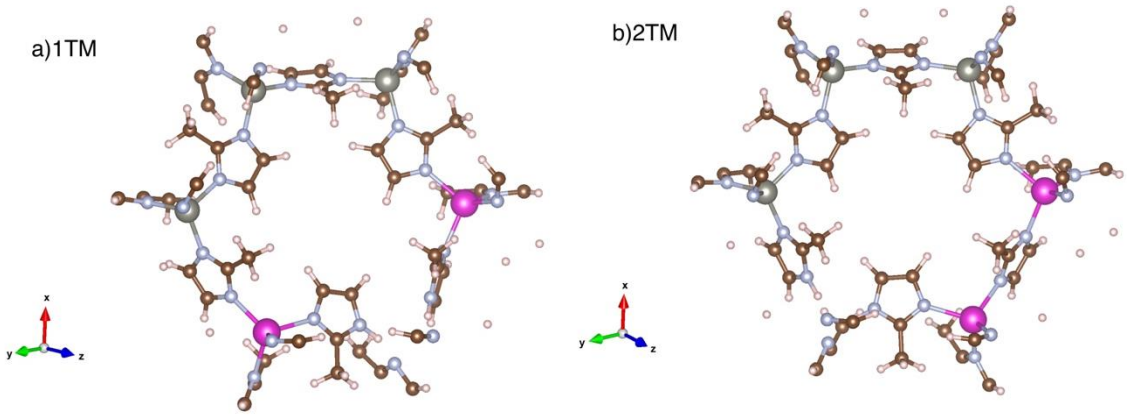

Figure S7. The structure of Zn3Cd3-ZIF-8 with missing metals annotated as 1TM (a) and 2TM (b). TM is a trimer configuration with missing metal. The missing metal centre is Cd^{2+} for both 1TM and 2TM, but the location of each Cd^{2+} is different. Zn, Cd, N, C and H are grey, magenta, cyan, brown and pink, respectively.

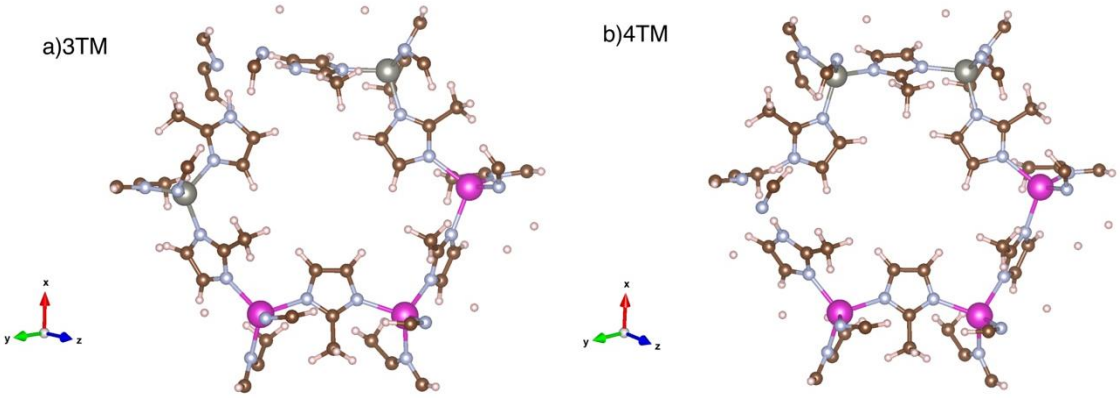

Figure S8. The structure of Zn3Cd3-ZIF-8 with missing metals annotated as 3TM (a) and 4TM (b). TM is a trimer configuration with missing metal. The missing metal centre is Zn^{2+} for both 3TM and 4TM, but the location of each Zn^{2+} is different. Zn, Cd, N, C and H are grey, magenta, cyan, brown and pink, respectively.

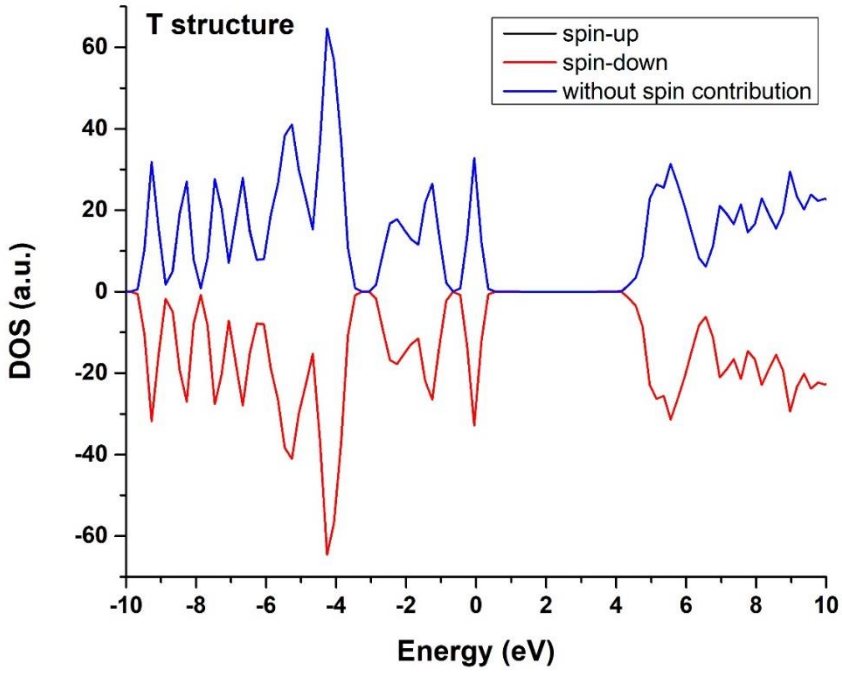

Figure S9. The total DOS of the T configuration. The total DOS for calculation without spin contribution is overlap with the total DOS of spin up.

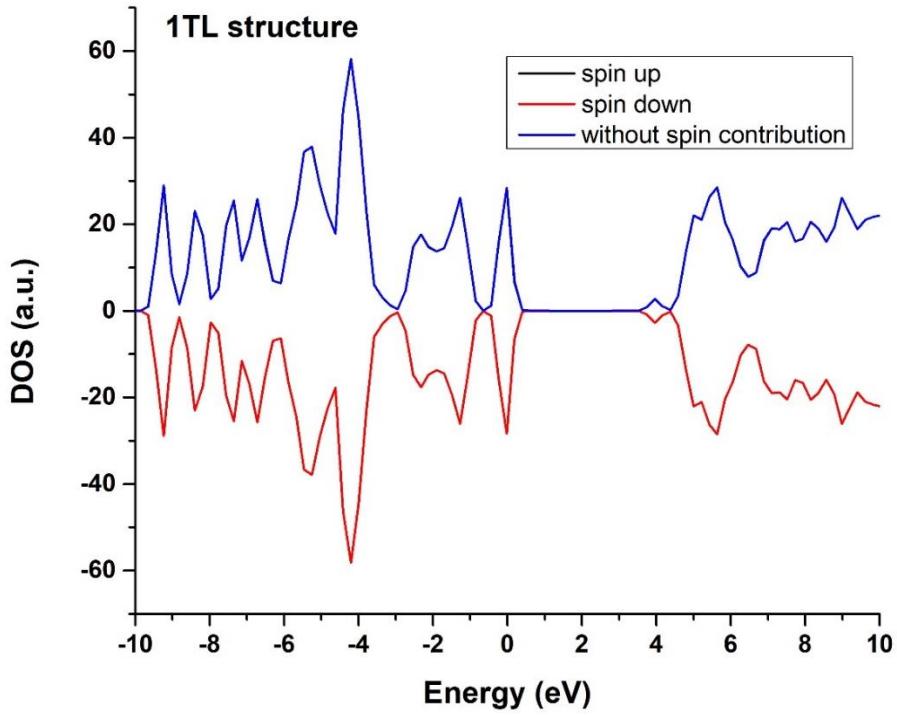

Figure S10. The total DOS of the defective 1TL configuration due to missing imidazolate linker. The total DOS for calculation without spin contribution is overlap with the total DOS of spin up.

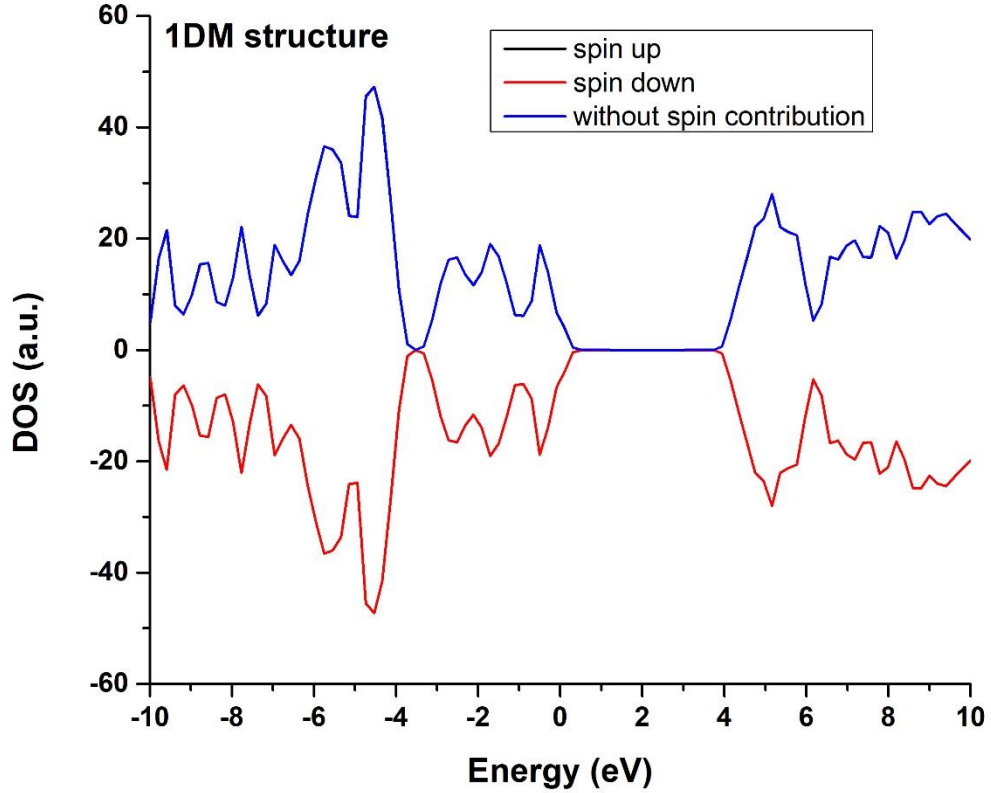

Figure S11. The total DOS of the defective 1DM configuration due to missing metal ion. The total DOS for calculation without spin contribution is overlap with the total DOS of spin up.

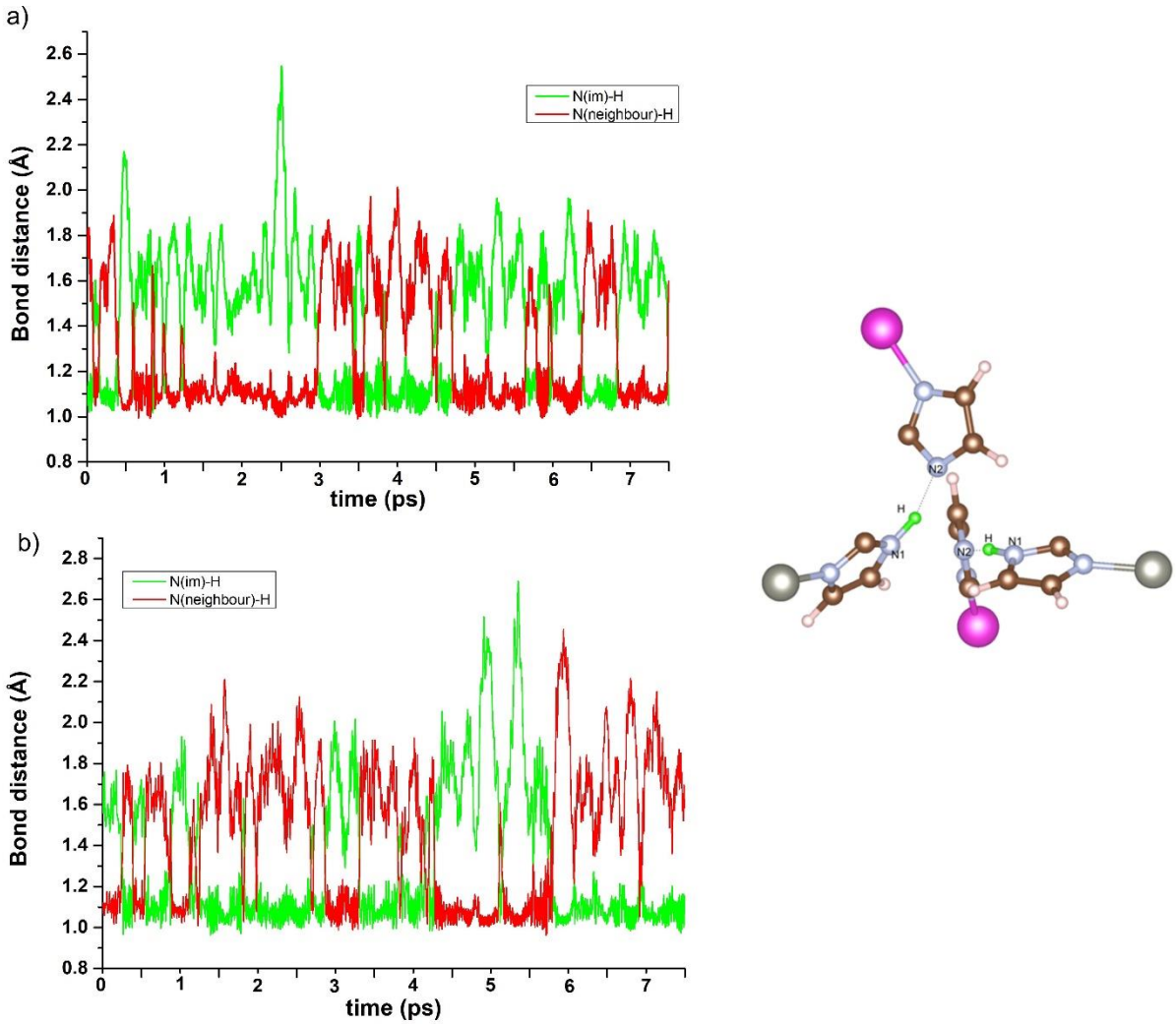

Figure S12. The AIMD trajectory showing the distance between N of MeIm ligand to H atom at the defect sites of missing metal ion at 298K (a) and 500K (b). A cluster of missing Cd^{2+} ion is shown in (f) indicating the hydrogen bond between H and N (N1 and N2). The structure in figure (f) is simplified to show the defect site.

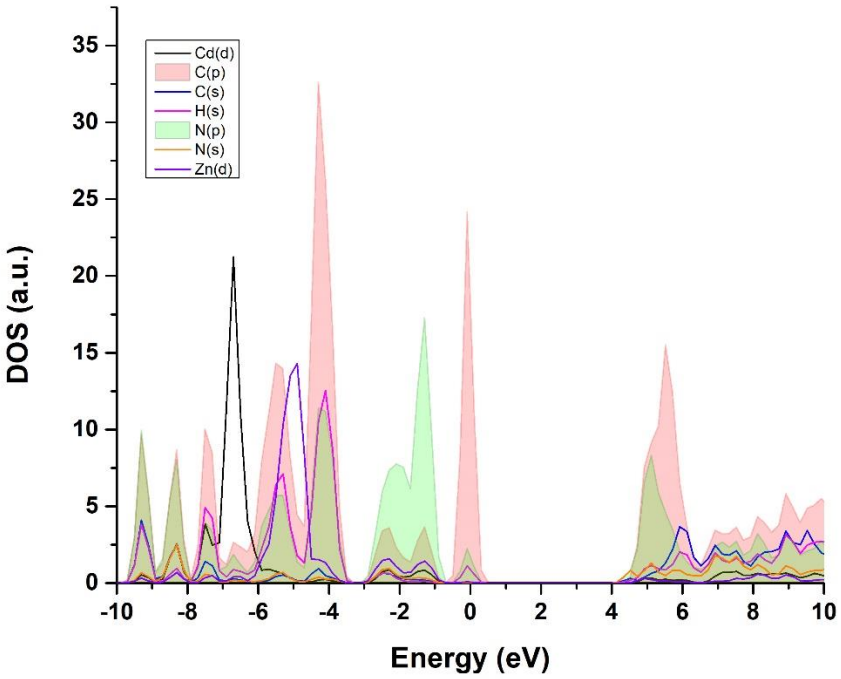

Figure S13. Projected DOS of the D structure.

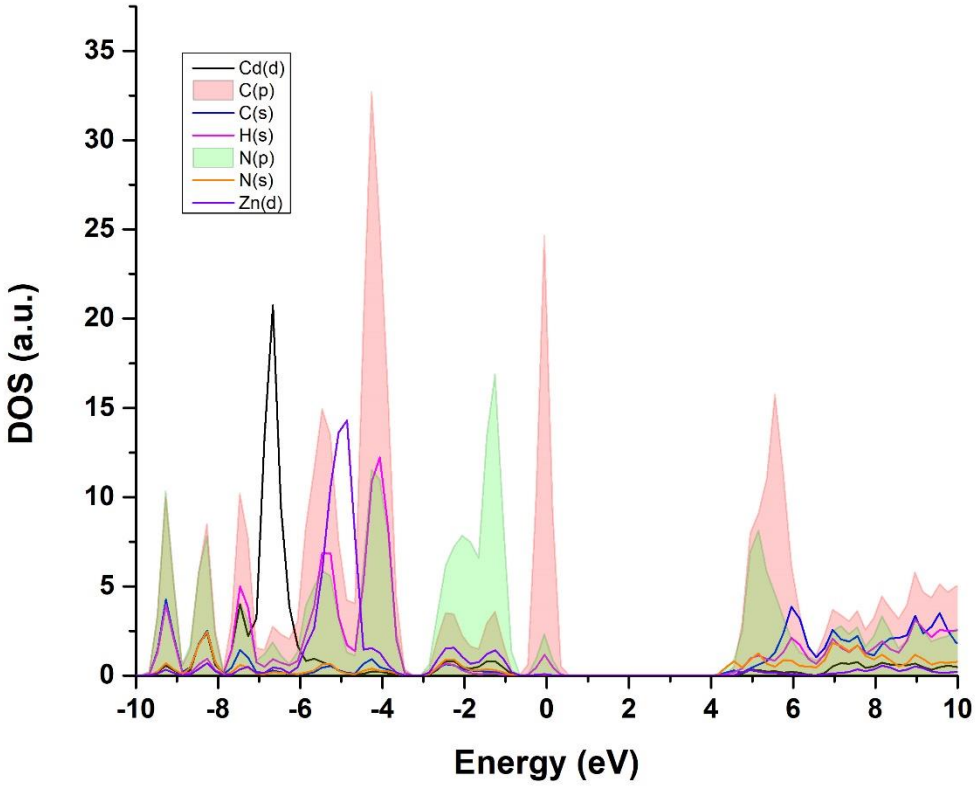

Figure S14. Projected DOS of the T structure.

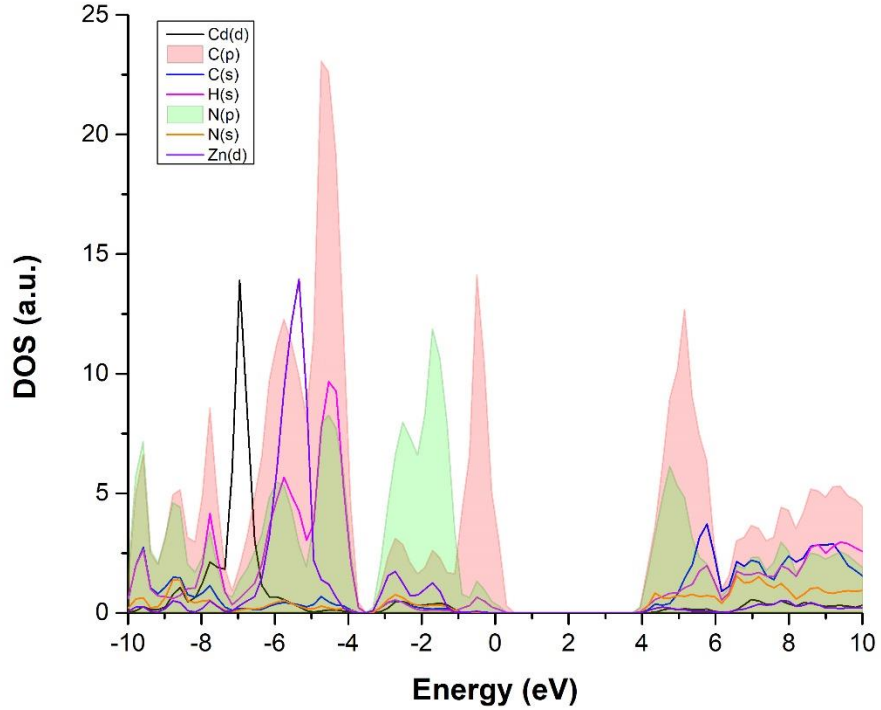

Figure S15. Projected DOS of the 1DM structure.

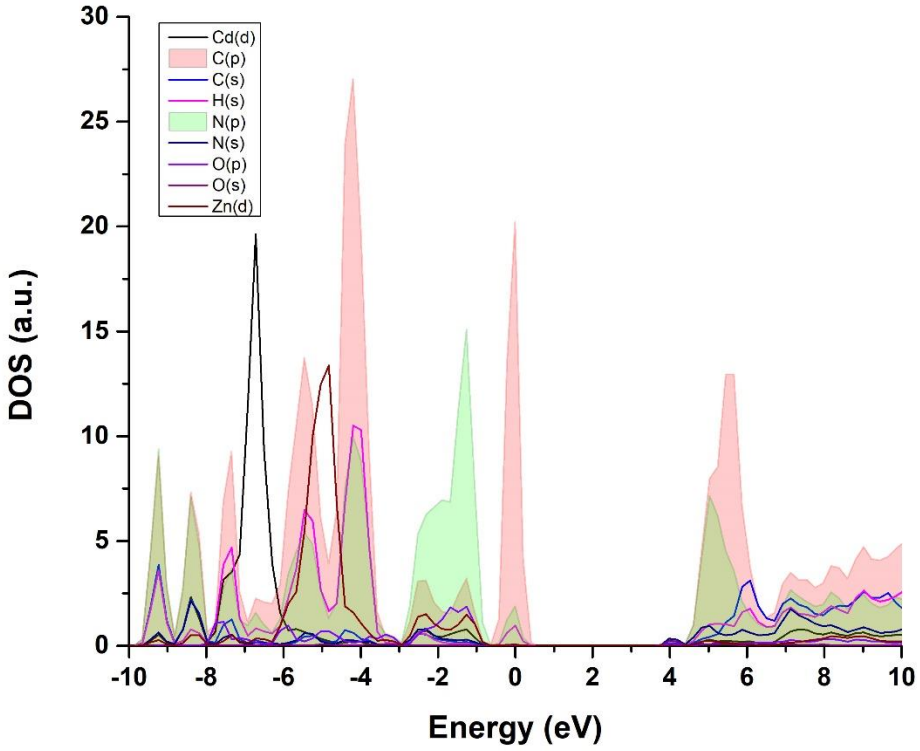

Figure S16. Projected DOS of the 1DL structure.

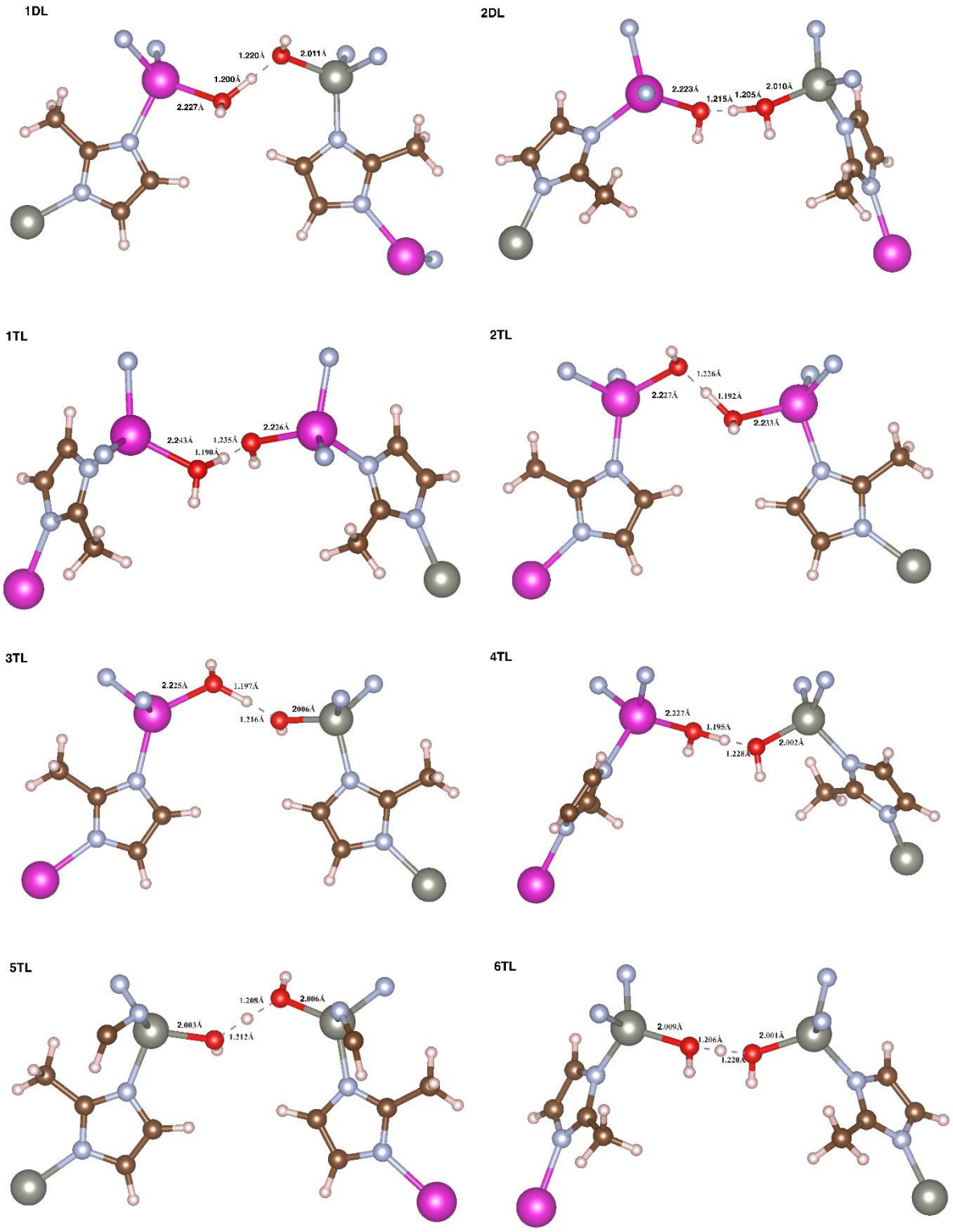

Figure S17. The structure of defective site of ZIF-8(Zn/Cd) due to missing linker. The structure is simplified to highlight the defect site. Cd, Zn, C, N, H are coloured pink, grey, brown, light blue, and pink, respectively.