Computational exploration of the newly synthesized zirconium metal organic frameworks UiO-66 to -68 and its analogues

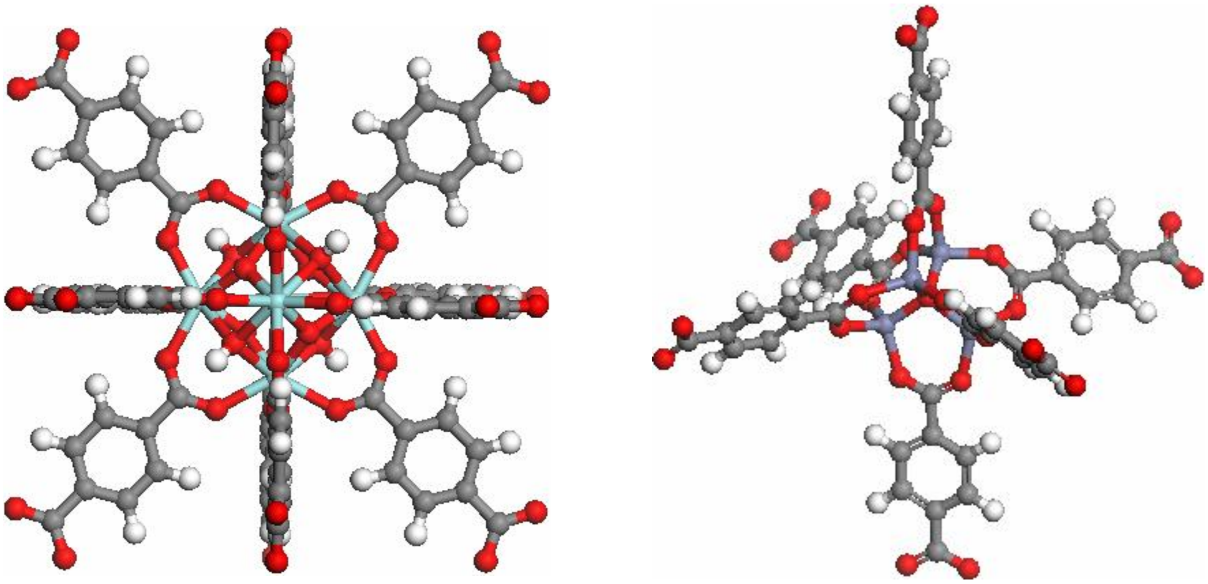
Li-Ming Yang*[†], Eric Ganz,[§] Stian Svelle[||], and Mats Tilset*[†]

Supporting Information

[†] *Center of Theoretical and Computational Chemistry, Department of Chemistry, University of Oslo, P.O.Box 1033 Blindern, N-0315 Oslo, Norway,* [§] *Department of physics, University of Minnesota, Minneapolis, Minnesota, USA,* [||] *inGap Center of Research Based Innovation, Department of Chemistry, University of Oslo, P.O.Box 1033 Blindern, N-0315, Oslo, Norway.*

(E-mail of corresponding authors: *lmyang.uio@gmail.com* and *mats.tilset@kjemi.uio.no*; Fax: +47 22855441)

Page 2, **Fig. S1**. The comparison of the topology (connection relationship) between nodes and linkers in UiO-66 and prototypical MOF-5.
Page 3, **Table S1.** The VASP optimized structural parameters as well as the experimental data for Zr-UiO-66.
Page 5, **Scheme S1**. The atomic labels of *M*-UiO-66 (a), -67 (b), and -68 (c) (*M* = Ti, Zr, and Hf) for the description of key geometry parameters, i.e., bond length (Å) and bond angles (°).
Page 6, **Table S2**. Some optimized geometry parameters, i.e., bond length (Å) and bond angles (°) for *M*-UiO-66 to -68 (*M* = Ti, Zr, and Hf) at their equilibrium volumes.
Page 10, **Fig. S2.** The simulated PXRD pattern for Ti-UiO-66, 67, 68, Zr-UiO-68, Hf-UiO-67, 68.
Page 11, **Fig. S3.** The calculated TDOS and PDOS for Zr-UiO-67.
Page 12, **Fig. S4.** The calculated TDOS and PDOS for Zr-UiO-68.
Page 13, **Fig. S5.** The calculated TDOS and PDOS for Ti-UiO-66
Page 14, **Fig. S6.** The calculated TDOS and PDOS for Ti-UiO-67
Page 15, **Fig. S7.** The calculated TDOS and PDOS for Ti-UiO-68
Page 16, **Fig. S8.** The calculated TDOS and PDOS for Hf-UiO-66
Page 17, **Fig. S9.** The calculated TDOS and PDOS for Hf-UiO-67
Page 18, **Fig. S10.** The calculated TDOS and PDOS for Hf-UiO-68
Page 19, **Scheme S1**. The comparison of the positions of O atoms with and without protons
Page 20, **Scheme S3.** Perspective plots of side, tilted side, and top views of UiO-66 framework
Page 21, **Fig. S11.** Calculated charge density, charge transfer, and ELF plots for Zr-UiO-67
Page 22, **Fig. S12.** Calculated charge density, charge transfer, and ELF plots for Zr-UiO-68
Page 23, **Fig. S13.** Calculated charge density, charge transfer, and ELF plots for Ti-UiO-66
Page 24, **Fig. S14.** Calculated charge density, charge transfer, and ELF plots for Ti-UiO-67
Page 25, **Fig. S15.** Calculated charge density, charge transfer, and ELF plots for Ti-UiO-68
Page 26, **Fig. S16.** Calculated charge density, charge transfer, and ELF plots for Hf-UiO-66
Page 27, **Fig. S17.** Calculated charge density, charge transfer, and ELF plots for Hf-UiO-67
Page 28, **Fig. S18.** Calculated charge density, charge transfer, and ELF plots for Hf-UiO-68
Page 29, **Table S3.** The calculated Hirshfeld charge (HC), Mulliken effective charge (MEC), bond overlap populations (BOP) for M-UiO-66 and -68 (M = Ti, Zr, and Hf).
Page 33, **Fig. S19.** Calculated optical properties for Zr-UiO-68
Page 34, **Fig. S20.** Calculated optical properties for Ti-UiO-66
Page 35, **Fig. S21.** Calculated optical properties for Ti-UiO-68
Page 36, **Fig. S22.** Calculated optical properties for Hf-UiO-66
Page 37, **Fig. S23.** Calculated optical properties for Hf-UiO-68
Page 38, **Fig. S24.** The electronic band structure of Zr-UiO-66
Page 39, **Fig. S25.** The electronic band structure of Zr-UiO-68
Page 40, **Fig. S26.** The electronic band structure of Ti-UiO-66
Page 41, **Fig. S27.** The electronic band structure of Ti-UiO-68
Page 42, **Fig. S28.** The electronic band structure of Hf-UiO-66
Page 43, **Fig. S29.** The electronic band structure of Hf-UiO-68



(a) $Zr_6O_4(OH)_4(BDC)_{12}$

(b) $Zn_4O(BDC)_6$

Figure S1. Comparison of the topology between nodes and linkers in UiO-66 and prototypical MOF-5 is illustrated in (a) and (b). (a) The $Zr_6O_4(OH)_4$ node is connected to twelve BDC linkers; (b) The Zn_4O node is connected to six BDC linkers. O is red , C is gray, H is white, Zr is light blue, Zn is dark blue.

Table S1. The VASP optimized structural parameters as well as the experimental data for Zr-UiO-66

Property	PBE-GGA (VASP code)[a]	B3LYP (CRYSTAL code)[b]	Expt. (PXRD)[c]
Materials	UiO-66	UiO-66	UiO-66
Crystal system	*Face-Centered Cubic (FCC)*	*Face-Centered Cubic (FCC)*	*Face-Centered Cubic (FCC)*
Space group	*F-43m* (*216*)	*F-43m* (*216*)	*Fm-3m* (*225*)
Atoms/cell	114	114	110
a (Å)	20.9616	21.0171	20.7551,[d] 20.7004[e]
Atom type	Atomic positions (x, y, z)		
Zr1 (24*f*)	0.12003, -1/2, 1/2	0.12035, 0.00000, 0.00000	0.11989, 0., 0.
O1 (96*i*)	0.17094, -0.59417, 0.50275	0.17072, 0.00262, 0.09458	0.17047, 0., 0.0953
O2 (16*e*)	0.04993, -0.04993, 0.04993	0.04941, -0.04941, -0.04941	0.0561, -0.0561, -0.0561
O3 (16*e*)	0.93293, -0.56707, 0.56707	0.06727, -0.06727, 0.06727	
C1 (96*i*)	0.26748, -0.68559, 0.50682	0.15234, -0.00410, -0.15234	0.1536, 0., -0.1536
C2 (48*h*)	0.20276, -0.20276, 0.00636	0.20286, 0.00623, 0.20286	0.2050, 0., 0.2050
C3 (48*h*)	0.00417, -0.15225, 0.15225	0.26743, 0.00659, 0.18567	0.2675, 0., 0.1844
H1 (16*e*)	0.59381, -0.90619, 0.59381	0.09377, -0.09377, 0.09377	
H2 (96*i*)	0.63515, -0.28006, 0.50682	0.13555, -0.28000, -0.00649	

[a] The data from present work.

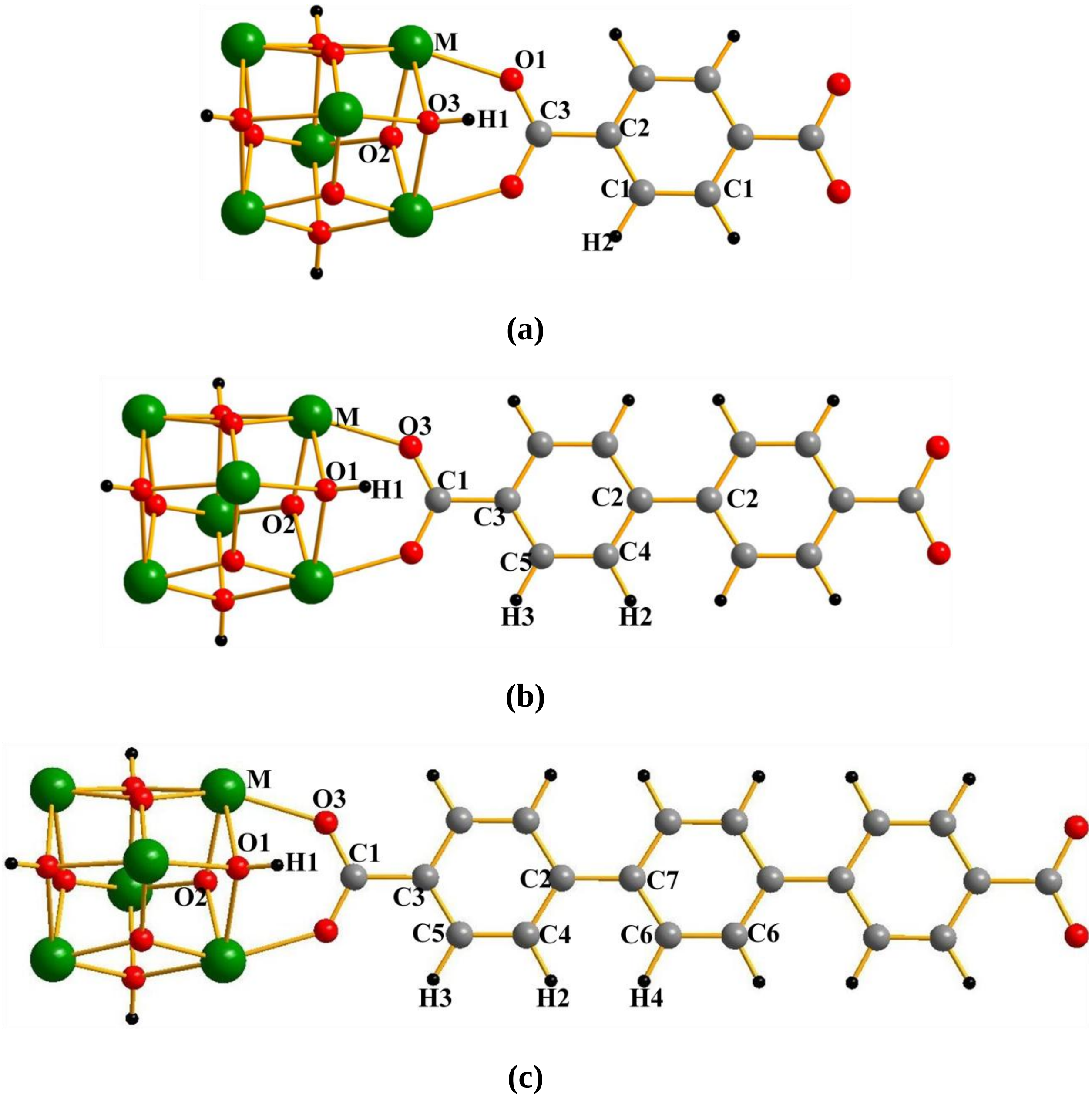
[b] Theoretical results from Ref: Valenzano, L.; Civalleri, B.; Chavan, S.; Bordiga, S.; Nilsen, M. H.; Jakobsen, S.; Lillerud, K. P.; Lamberti, C. *Chem. Mater*. **2011**, *23*, 1700.

[c] Experimental data (non-hydrogen, only heavy atoms could be seen clearly in PXRD) from Ref: Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. *J. Am. Chem. Soc*. **2008**, *130*, 13850.

[d] The experimental lattice parameter for the as-synthesized material.

[e] The experimental lattice parameter for the calcined material.

Note that XRD cannot determine accurately H-atom positions.



Scheme S1. We schematically list the atomic labels of *M*-UiO-66 (a), -67 (b), and -68 (c) (*M* = Ti, Zr, and Hf) for the description of key geometry parameters, i.e., bond length (Å) and bond angles (°). Note that the atomic labels for UiO-66, -67, and -68 are *different*. Within the same subseries (e.g., in *M*-UiO-66), the atomic labels are the same for different metals (e.g., *M* = Ti, Zr, and Hf). For UiO-66 and -68, the atomic labels are followed as that in **Fig. 1**. Whereas, for UiO-67, we did not distinguish atomic labels in **Fig. 1** due to the huge number of atoms in the unit cell. For the convenience of our discussion for the key geometry parameters, here, we just label the atoms of UiO-67. Note that we did not display all twelve -CO_2 around the metal cluster, alternatively we selectively keep several -CO_2 around the metal cluster for the convenience of description of bond angles (°), which will be listed in **Table S2**. O is red, C is gray, H is black, M is green.

Table S2. Some optimized geometry parameters, i.e., bond length (Å) and bond angles (°) for *M*-UiO-66 to -68 (*M* = Ti, Zr, and Hf) at their equilibrium volumes. Note that the atomic labels for UiO-66, -67, and -68 are *different*. Within the same subseries (e.g., in *M*-UiO-66), the atomic labels are the same for different metals (e.g., *M* = Ti, Zr, and Hf). For UiO-66 and -68, the atomic labels are followed as that in **Fig. 1**. Whereas, for UiO-67, we did not distinguish atomic labels in **Fig. 1** due to the huge number of atoms in the unit cell. For the convenience of our discussion for the key geometry parameters, we just label the atoms of UiO-67 as in **Scheme S1**. It should be pointed out that the experimental PXRD crystal structures are highly symmetric *Fm-3m* (no. 225) for Zr-UiO-66, -67, and -68. However, the crystal structures are lower symmetry, i.e., *F-43m* (no. 216) for *M*-UiO-66 and -68, as well as *P-43m* (no. 215) for *M*-UiO-67, respectively. Thus, the number of atomic types are different.

M-UiO-66	**M-O1**	**M-O2**	**M-O3**	**O3-H1**	**C3-O1**	**C1-H2**	**C1-C2**	**C2-C3**	**C1-C1**	**H1-O3-M**	**H2-C1-C2**	**M-O1-C3**
Ti	2.127	1.966	2.142	0.972	1.279	1.090	1.403	1.499	1.391	115.610	118.876	131.333
Zr	2.245	2.086	2.277	0.971	1.280	1.089	1.404	1.498	1.391	115.559	118.861	133.780
	(2.137)[a]	(2.083)[b]	(2.083)[b]	*[c]	(1.305)	*	(1.408)	(1.515)	(1.415)	*	*	(132.325)
Hf	2.217	2.056	2.250	0.970	1.280	1.090	1.404	1.497	1.391	115.954	118.868	133.330

M-UiO-66	**M-O2-M**	**M-O3-M**	**O1-M-O2**	**O1-M-O3**	**O2-M-O3**	**O1-C3-O1**	**O1-C3-C2**	**C1-C2-C3**	**C2-C1-C1**
Ti	116.576	102.695	84.393	74.277	70.260	126.265	116.859	120.106	120.109
Zr	117.082	102.755	83.152	72.824	69.912	125.616	117.186	120.139	120.141
	(107.942)[b]	(107.942)[b]	(77.113)[b]	(77.113)[b]	(71.997)	(124.165)	(117.917)	(121.557)	(121.557)
Hf	116.964	102.280	83.445	72.886	70.246	125.502	117.242	120.156	120.159

M-UiO-67	**M-O1**	**M-O2**	**M-O3**	**O1-H1**	**C1-O3**	**C4-H2**	**C5-H3**	**C1-C3**	**C3-C5**	**C5-C4**	**C4-C2**	**C2-C2**
Ti	2.144	1.963	2.127	0.971	1.279	1.089	1.090	1.496	1.403	1.390	1.410	1.486
Zr	2.277	2.087	2.249	0.971	1.282	1.089	1.090	1.493	1.401	1.389	1.411	1.486
	(2.036)[b]	(2.036)[b]	(2.110)	*	(1.416)	*	*	(1.530)	(1.508)	(1.359)	(1.397)	(1.567)
Hf	2.248	2.054	2.213	0.970	1.280	1.089	1.090	1.496	1.402	1.390	1.410	1.488

M-UiO-67	**H1-O1-M**	**M-O3-C1**	**M-O1-M**	**M-O2-M**	**O1-M-O2**	**O1-M-O3**	**O2-M-O3**	**O3-C1-O3**	**O3-C1-C3**
Ti	115.846	131.558	102.445	116.646	70.257	74.305	84.410	125.960	116.966
Zr	115.357	133.552	103.163	117.127	69.686	73.031	83.363	125.844	117.070
	*	(124.253)	(105.718)[b]	(105.718)[b]	(73.943)	(79.575)[b]	(79.575)[b]	(130.013)	(114.994)
Hf	115.864	133.473	102.403	117.102	70.115	73.007	83.563	125.297	117.337

M-UiO-67	**C1-C3-C5**	**C3-C5-C4**	**C5-C4-C2**	**C4-C2-C2**	**C2-C4-H2**	**C3-C5-H3**
Ti	120.585	120.678	121.586	121.555	120.438	118.790
Zr	120.683	120.569	121.678	121.561	120.285	118.854
	(122.521)	(119.549)	(123.663)	(120.691)	*	*
Hf	120.795	120.659	121.792	121.649	120.260	118.856

M-UiO-68	**M-O1**	**M-O2**	**M-O3**	**O1-H1**	**C1-O3**	**C4-H2**	**C5-H3**	**C6-H4**	**C1-C3**	**C3-C5**	**C5-C4**	**C4-C2**	**C2-C7**
Ti	2.142	1.966	2.127	0.972	1.280	1.089	1.090	1.089	1.494	1.402	1.390	1.411	1.483
Zr	2.277	2.085	2.244	0.970	1.281	1.089	1.090	1.089	1.493	1.402	1.390	1.411	1.482
	(2.054)[b]	(2.054)[b]	(2.105)	*	(1.296)	*	*	*	(1.484)	(1.401)	(1.397)	(1.417)	(1.519)
Hf	2.251	2.055	2.217	0.969	1.280	1.089	1.090	1.089	1.493	1.402	1.390	1.411	1.482

M-UiO-68	**C7-C6**	**C6-C6**	**H1-O1-M**	**M-O3-C1**	**M-O1-M**	**M-O2-M**	**O1-M-O2**	**O1-M-O3**	**O2-M-O3**	**O3-C1-O3**
Ti	1.409	1.389	115.616	131.315	102.687	116.616	70.240	74.244	84.494	126.293
Zr	1.409	1.390	115.559	133.798	102.756	117.130	69.882	72.757	83.301	125.555
	(1.412)	(1.397)	*	(131.259)	(107.002)[b]	(107.002)[b]	(72.844)	(76.937)[b]	(76.937)[b]	(125.009)
Hf	1.409	1.389	115.966	133.335	102.266	117.002	70.229	72.804	83.565	125.502

M-UiO-68	**O3-C1-C3**	**C1-C3-C5**	**C3-C5-C4**	**C5-C4-C2**	**C4-C2-C7**	**C2-C7-C6**	**C7-C6-C6**	**C2-C4-H2**	**C3-C5-H3**
Ti	116.845	120.629	120.490	121.696	121.553	122.009	122.009	120.212	118.886
Zr	117.217	120.698	120.584	121.663	121.546	121.995	121.995	120.227	118.809
	(117.495)	(120.762)	(120.857)	(121.522)	(121.617)	(121.745)	(121.745)	*	*
Hf	117.243	120.685	120.581	121.641	121.535	121.994	121.994	120.246	118.812

M-UiO-68	**C7-C6-H4**
Ti	120.293
Zr	120.315 *
Hf	120.276

[a] The experimental data in (braces) are from ref[2]. It should be pointed out that the experimental PXRD is highly symmetric *Fm-3m* (no. 225), so the number of the type of atoms are different from the computational results, e.g., only two types of O atoms (i.e., O1 and O2) in the *Fm-3m* symmetry, whereas three types of O atoms (i.e., O1, O2, and O3) in the *F-43m* (no. 216) symmetry.

[b] Note that O2 and O3 are equivalent in the experimental PXRD structure (*Fm-3m*, 225) of Zr-UiO-66 since no hydrogen atoms connected to O3, whereas O2 and O3 are different due to the proton on O3 in the computational crystal structure (*F-43m*, 216). This is also the case for Zr-UiO-67, and -68. O1 and O2 are equivalent in the experimental PXRD structures of Zr-UiO-67 and -68, however, they are different in the calculated crystal structures due to the proton on O1 in Zr-UiO-67 and -68.

[c] Note that the experimental PXRD data cannot determine the hydrogen position, so, we show * in the positions of geometry parameters relevant to hydrogen atoms.

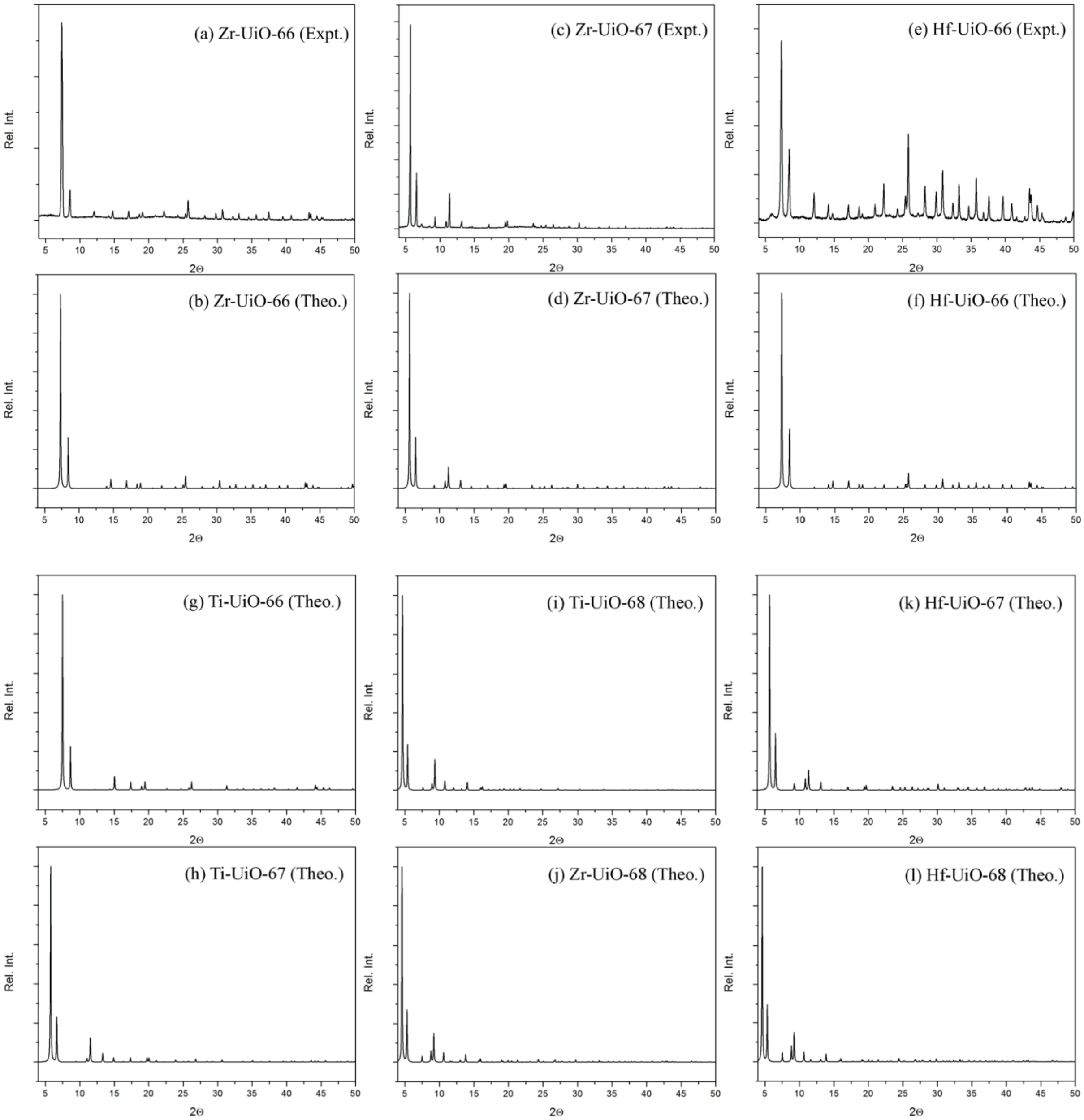


Figure S2. The comparison between experimental and simulated powder X-ray diffraction pattern (PXRD) for Zr-UiO-66 (a and b), Zr-UiO-67 (c and d), and Hf-UiO-66 (e and f), respectively. The calculated PXRD plots for (g) Ti-UiO-66, (h) -67, (i) -68, (j) Zr-UiO-68, (k) Hf-UiO-67, and (l) -68.

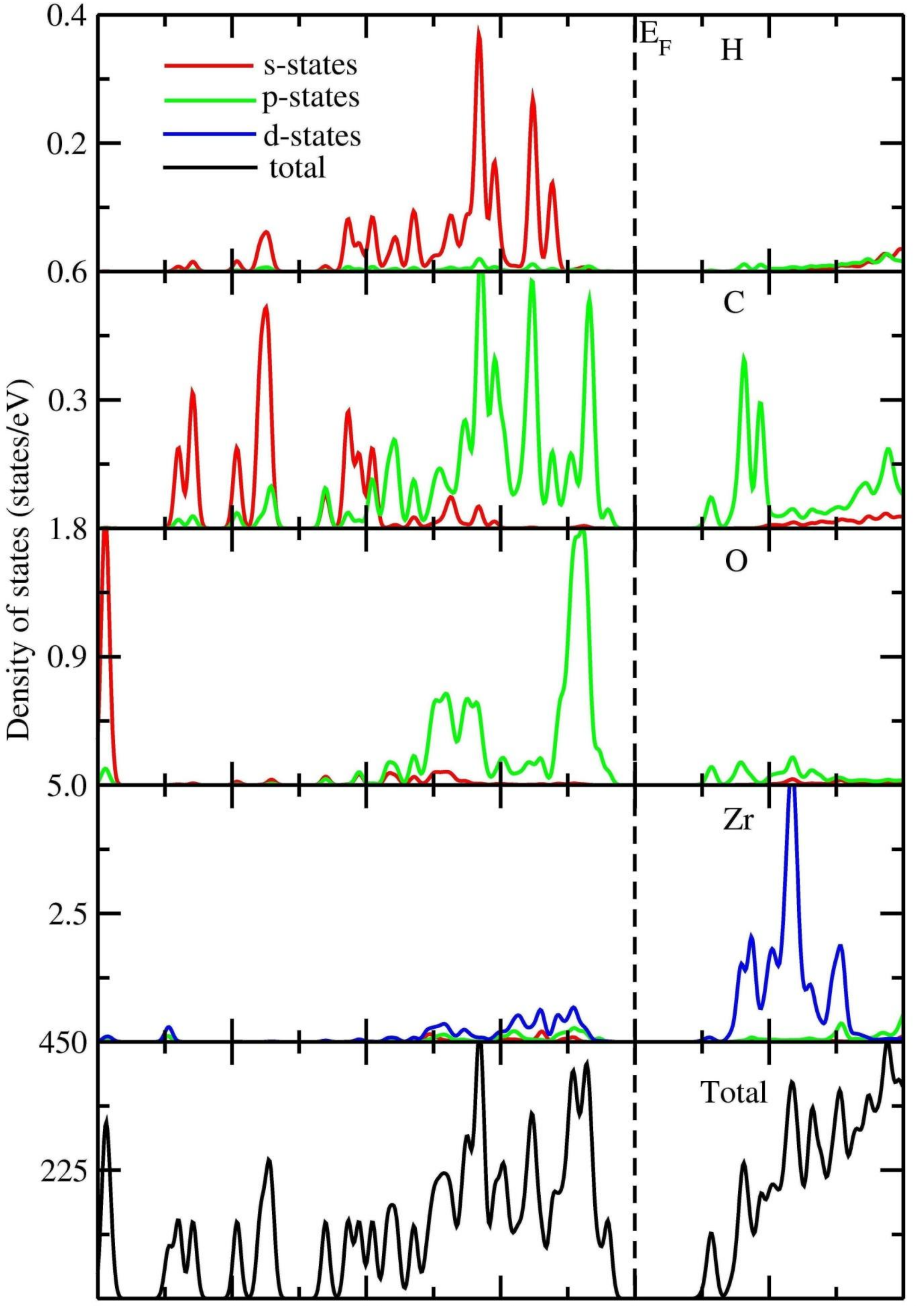


Figure S3. The calculated total density of states (TDOS) and partial density of states (PDOS) for Zr-UiO-67 in the Simple Cubic *P-43m* (no. 215) symmetry. Note that, for the UiO-67, we did not distinguish different crystallographic sites, we just distinguish each element, and sum the result.

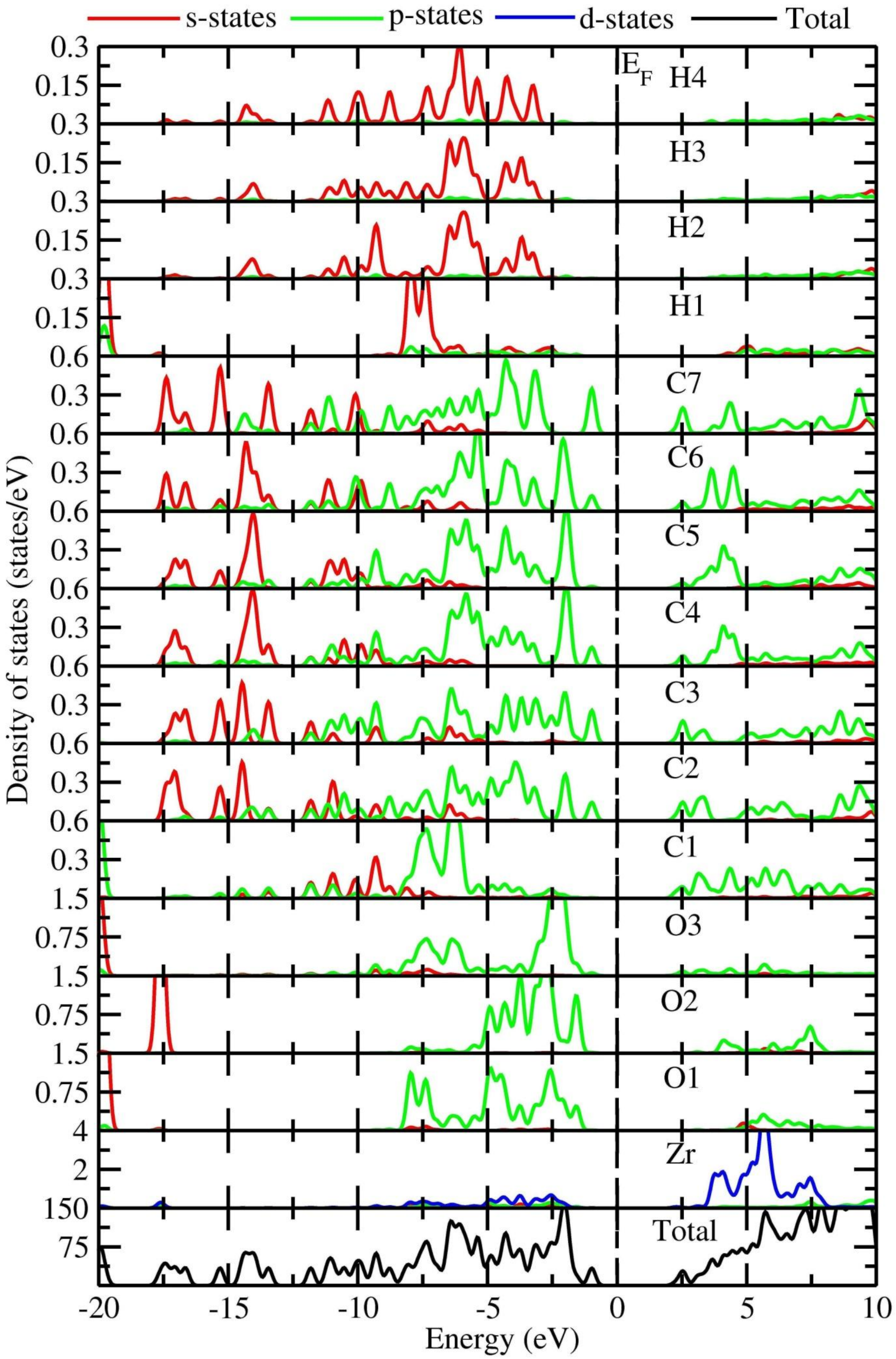


Figure S4. The calculated total density of states (TDOS) and partial density of states (PDOS) for Zr-UiO-68 in the Face-Centered Cubic (FCC) *F-43m* (no. 216) symmetry.

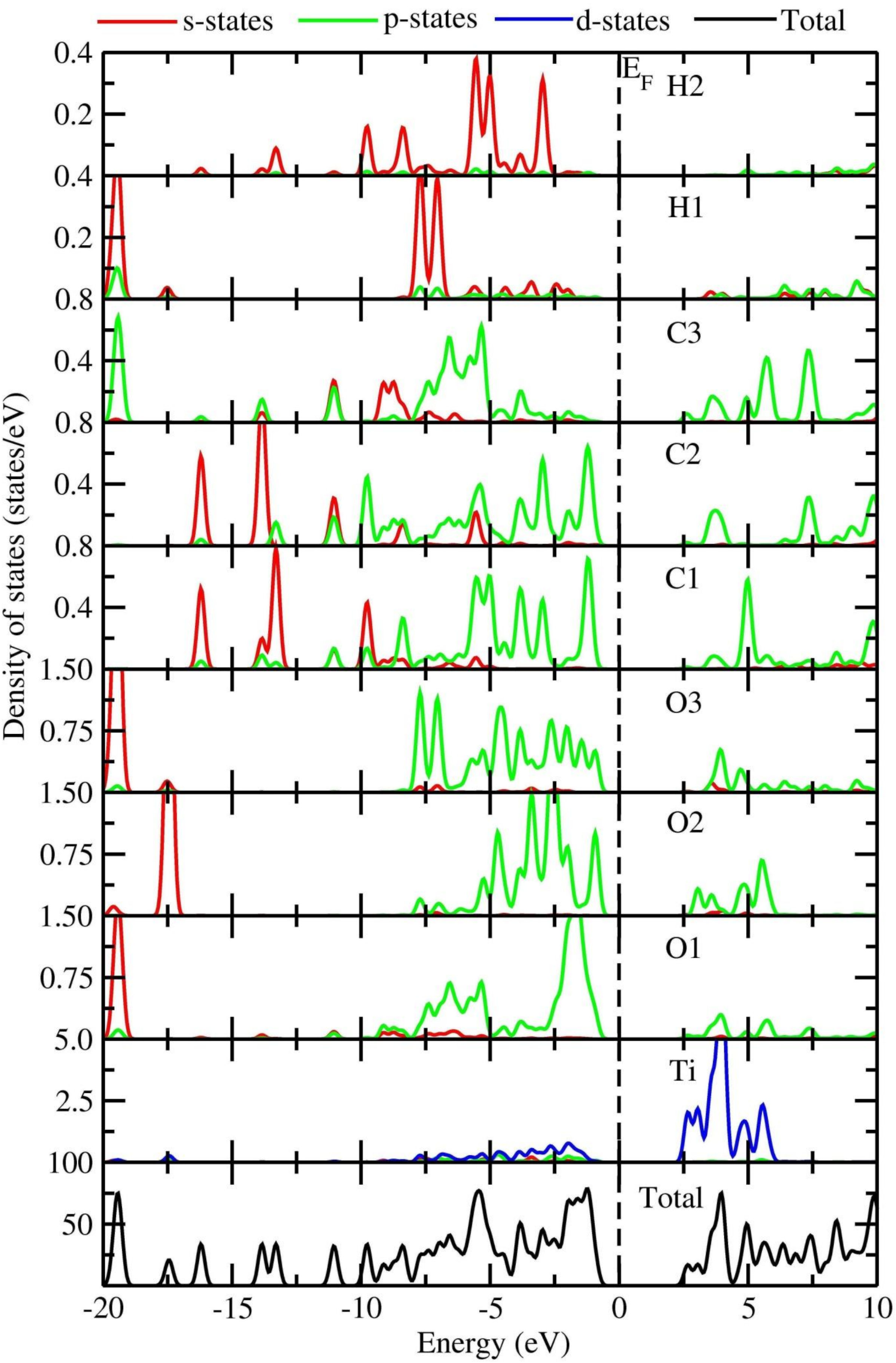


Figure S5. The calculated total density of states (TDOS) and partial density of states (PDOS) for Ti-UiO-66 in the face-centered cubic *F-43m* (no. 216) symmetry.

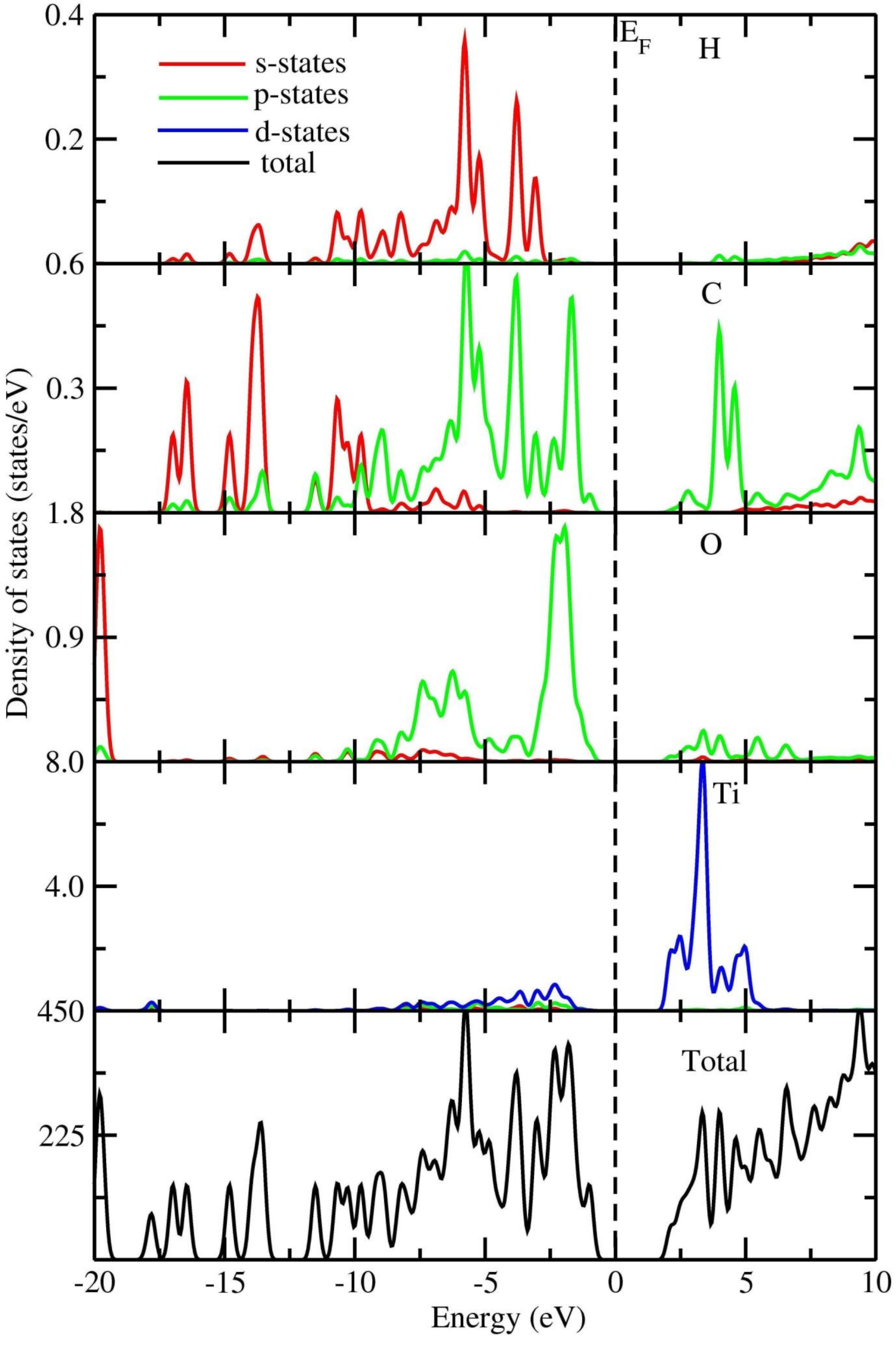


Figure S6. The calculated total density of states (TDOS) and partial density of states (PDOS) for Ti-UiO-67 in the simple cubic *P-43m* (no. 215) symmetry.

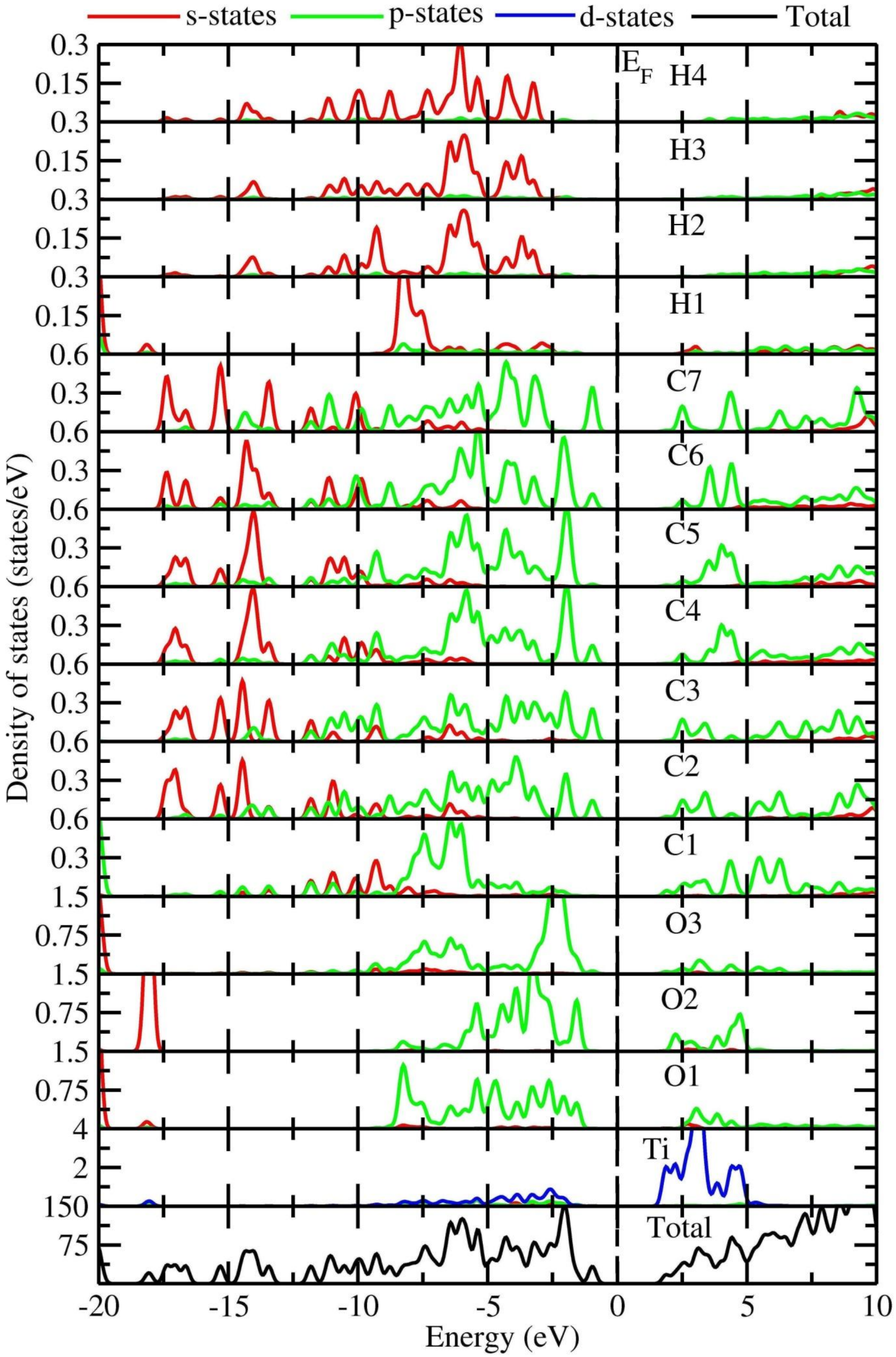


Figure S7. The calculated total density of states (TDOS) and partial density of states (PDOS) for Ti-UiO-68 in the face-centered cubic *F-43m* (no. 216) symmetry.

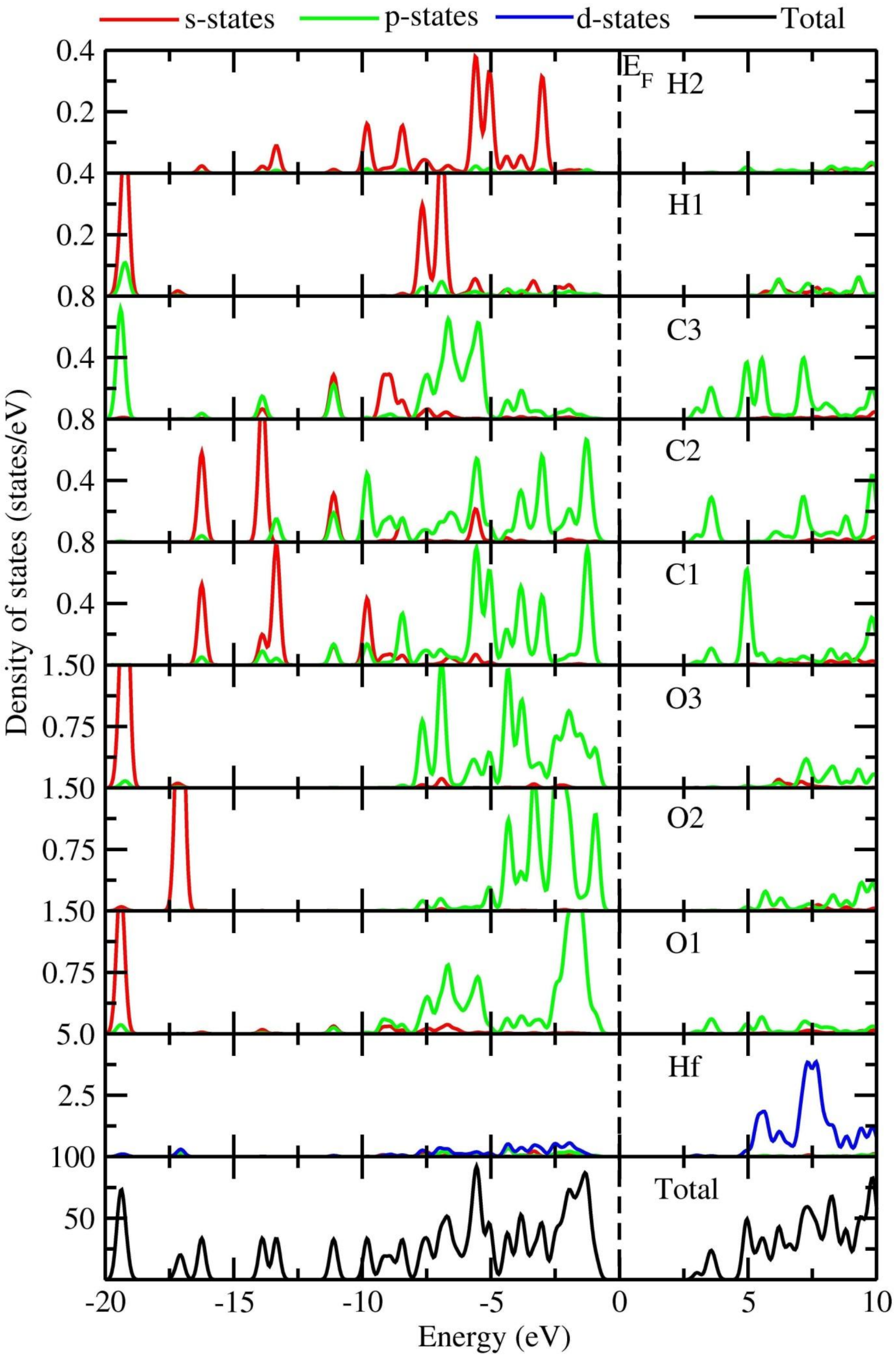


Figure S8. The calculated total density of states (TDOS) and partial density of states (PDOS) for Hf-UiO-66 in the face-centered cubic *F-43m* (no. 216) symmetry.

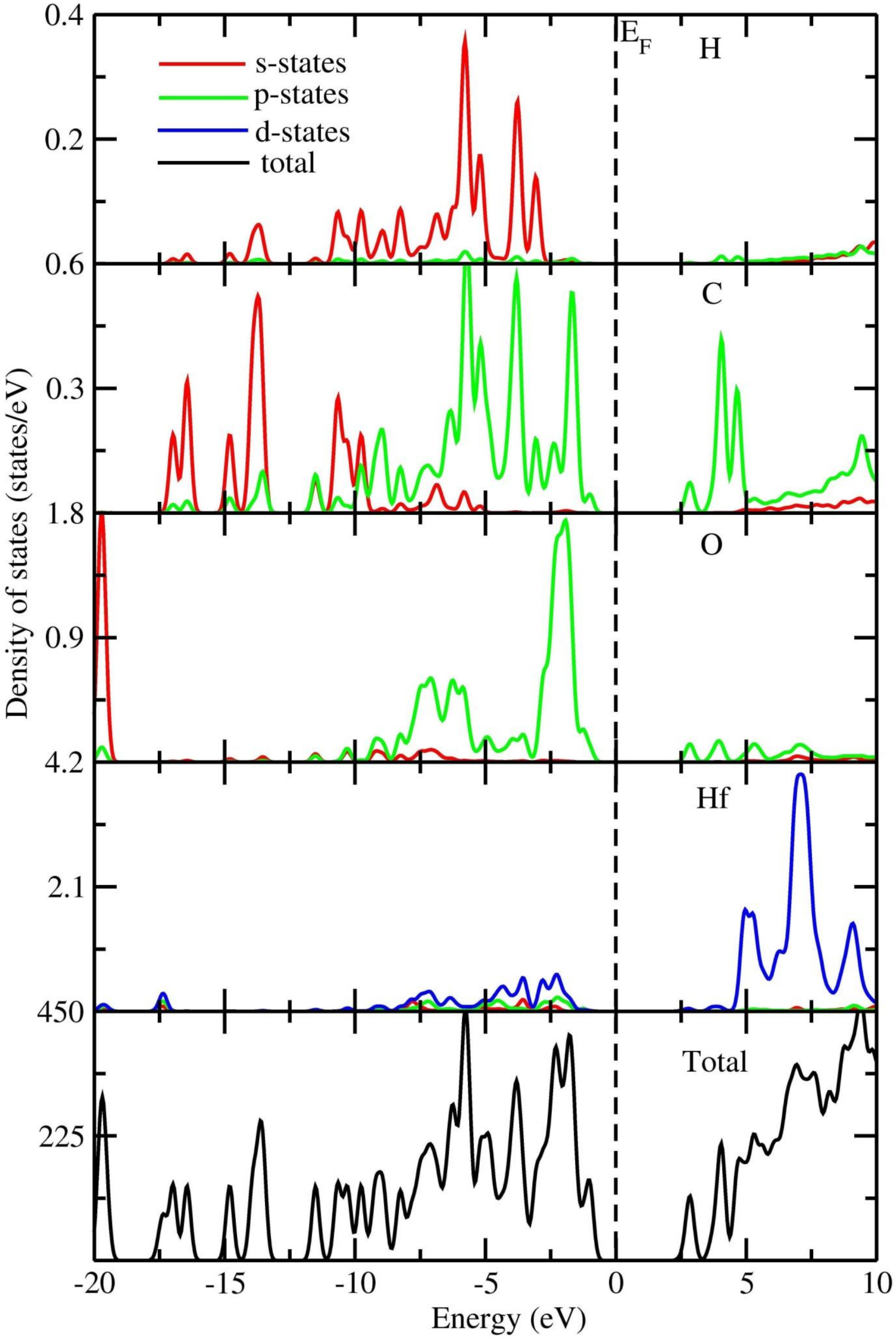


Figure S9. The calculated total density of states (TDOS) and partial density of states (PDOS) for Hf-UiO-67 in the simple cubic *P-43m* (no. 215) symmetry.

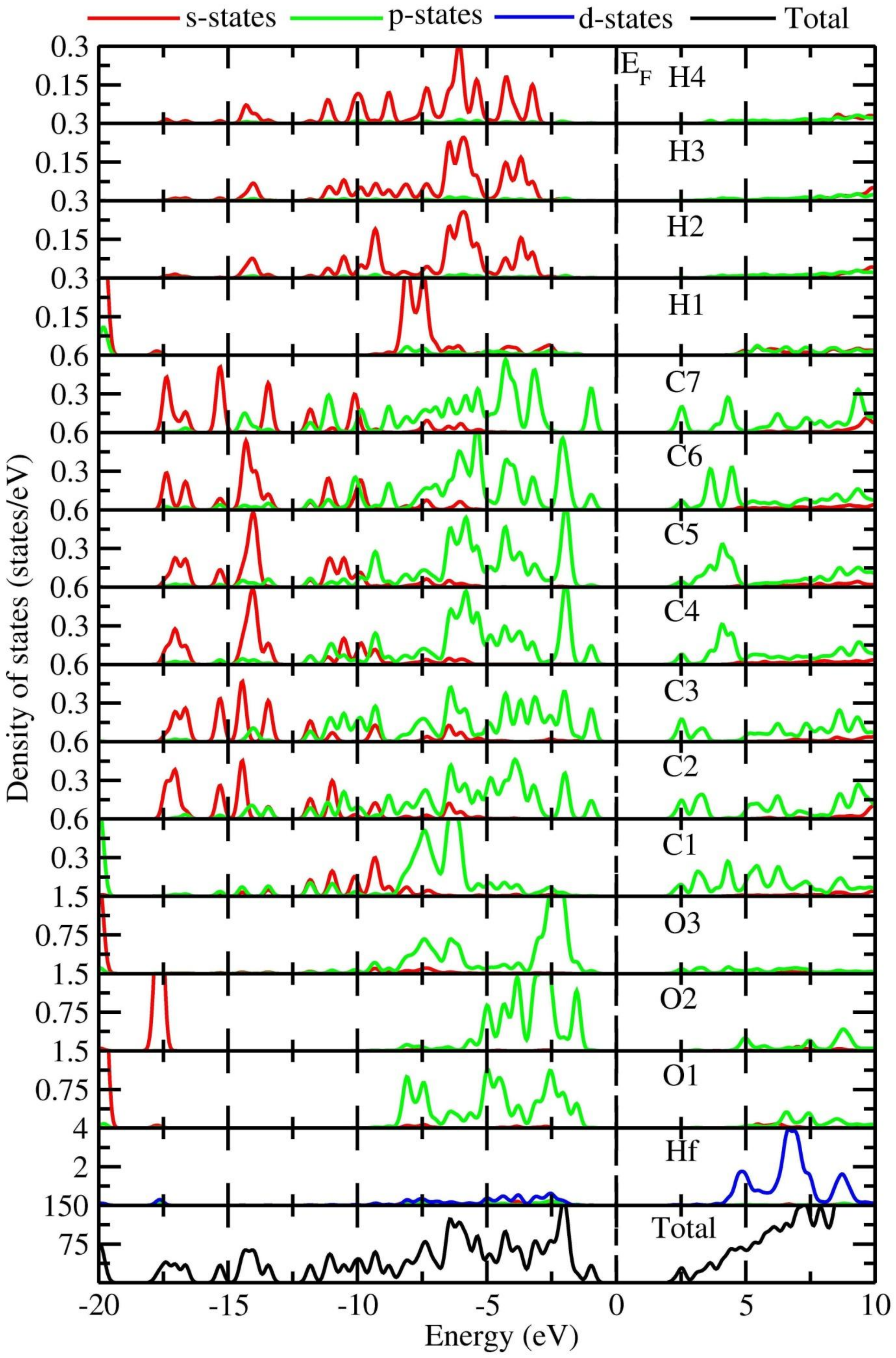
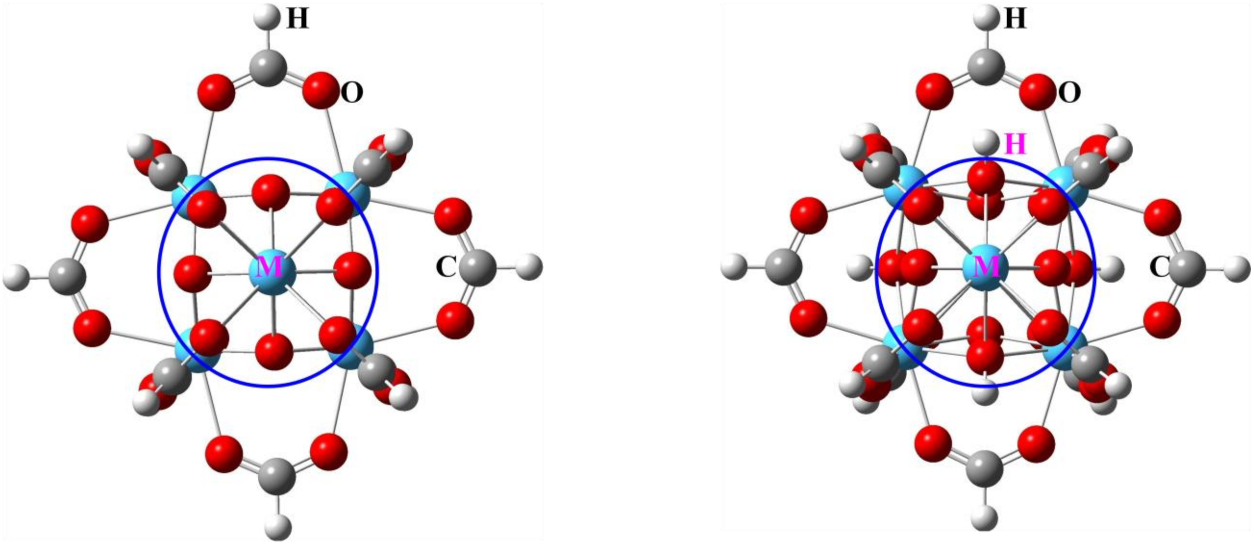
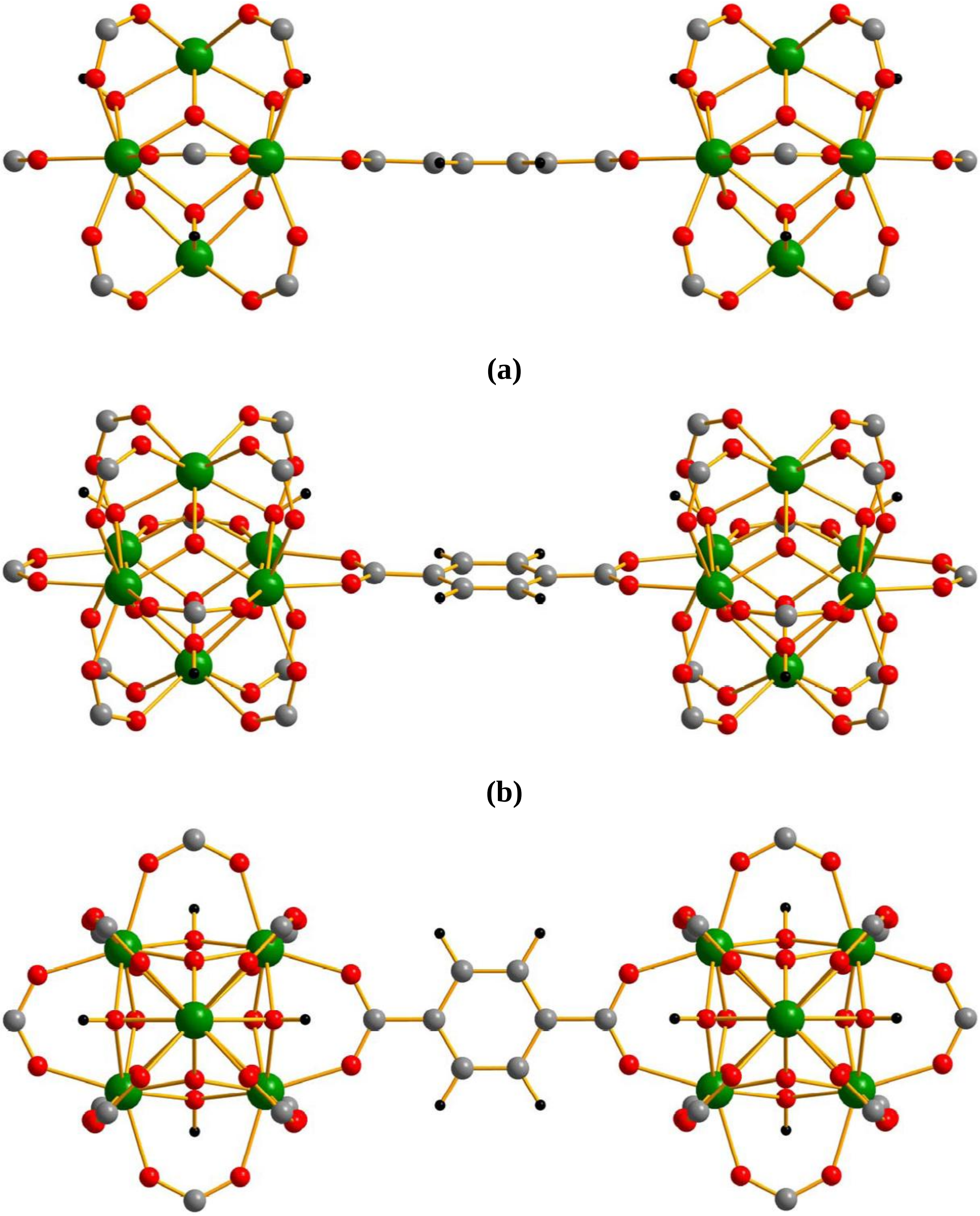


Figure S10. The calculated total density of states (TDOS) and partial density of states (PDOS) for Hf-UiO-68 in the face-centered cubic *F-43m* (no. 216) symmetry.



(a) $M_6O_8(HCO_2)_{12}^{4-}$ (b) $M_6O_4(OH)_4(HCO_2)_{12}$

Scheme S2. The comparison of the positions of the oxygen atoms with and without protons (H label in pink color in (b)) (oxygen with protons bulge out; whereas oxygen without protons are concave in) attached in two cluster models are shown in (a) $[M_6O_8(HCO_2)_{12}]^{4-}$ and (b) $M_6O_4(OH)_4(HCO_2)_{12}$ for the bulk frameworks of M-UiO-66 to -68, (M = Ti, Zr, and Hf). The blue circles highlight the different geometry for oxygen in (a) and (b). Note that both (a) and (b) are hypothetical clusters, but (b) is closer to the real system. O red, C gray, H white, metal atom M blue.

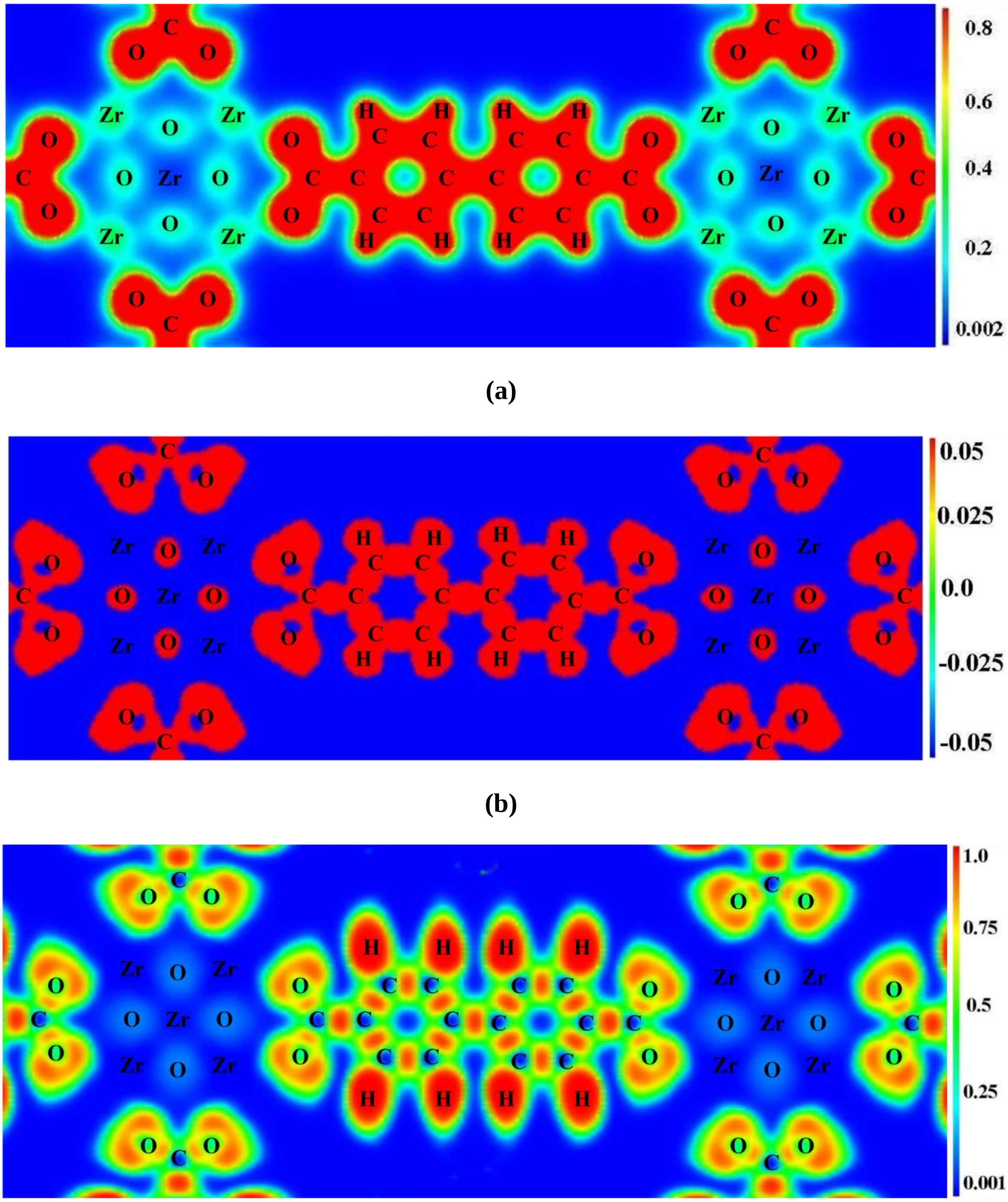


(a)

(b)

(c)

Scheme S3. Perspective plots of (a) side view, (b) tilted side view, (c) and top view of the UiO-66 framework, to improve understanding of the chemical bonding plots (the charge density, charge transfer, and electron localization function). From (a) to (c), one can see the distribution of different atoms in the same planes, relative positions, above or below the planes, and the different spatial positions in the frameworks. O red , C gray, H black, and Zr,Ti, Hf green.

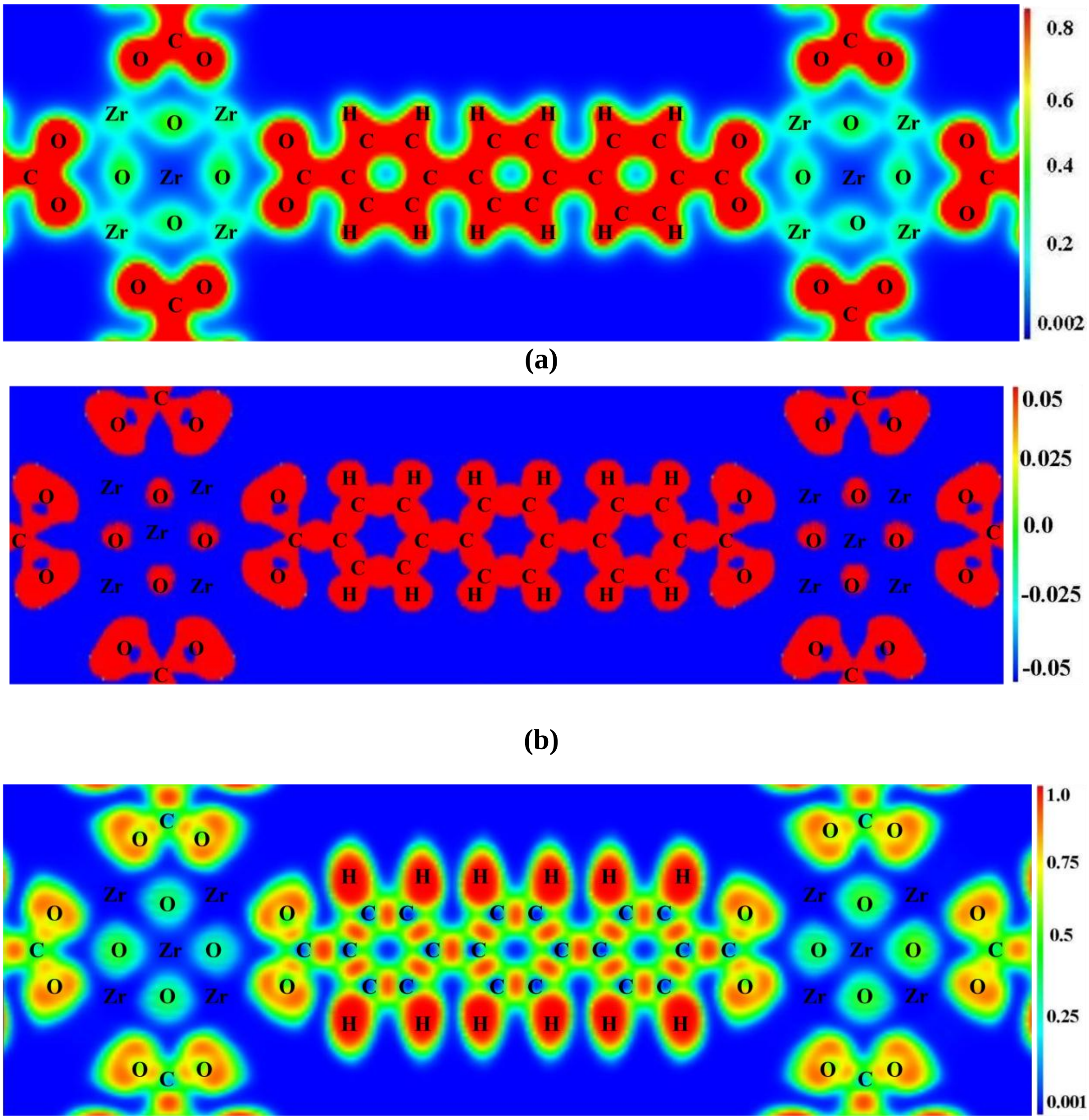


(a)

(b)

(c)

Figure S11. Calculated charge density (a), charge transfer (b) (in units of eÅ $^{-3}$), and electron localization function (c) plots for Zr-UiO-67 in the (110) plane.

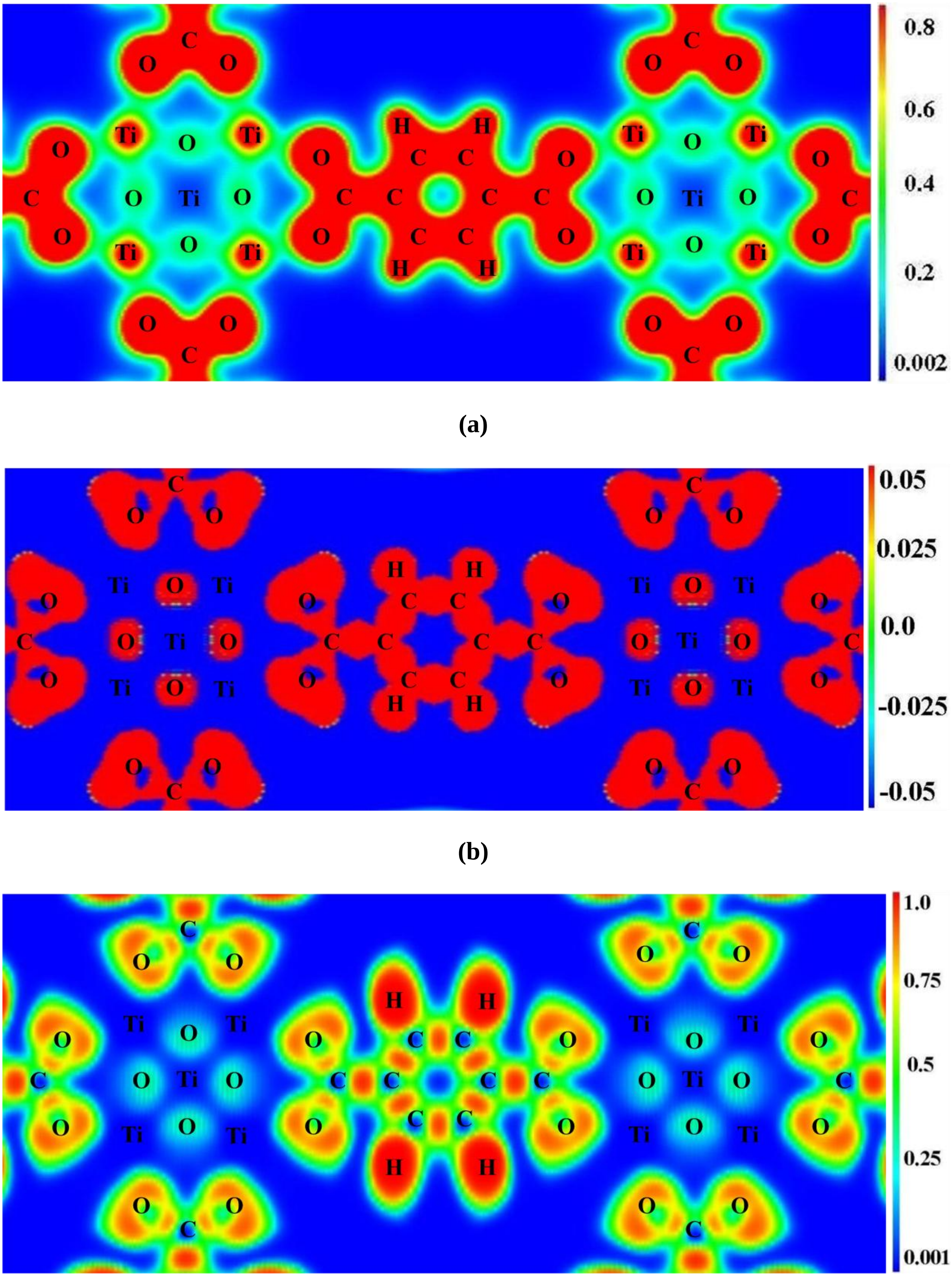


(a)

(b)

(c)

Figure S12. Calculated charge density (a), charge transfer (b) (in units of eÅ $^{-3}$), and electron localization function (c) plots for Zr-UiO-68 in the (110) plane.

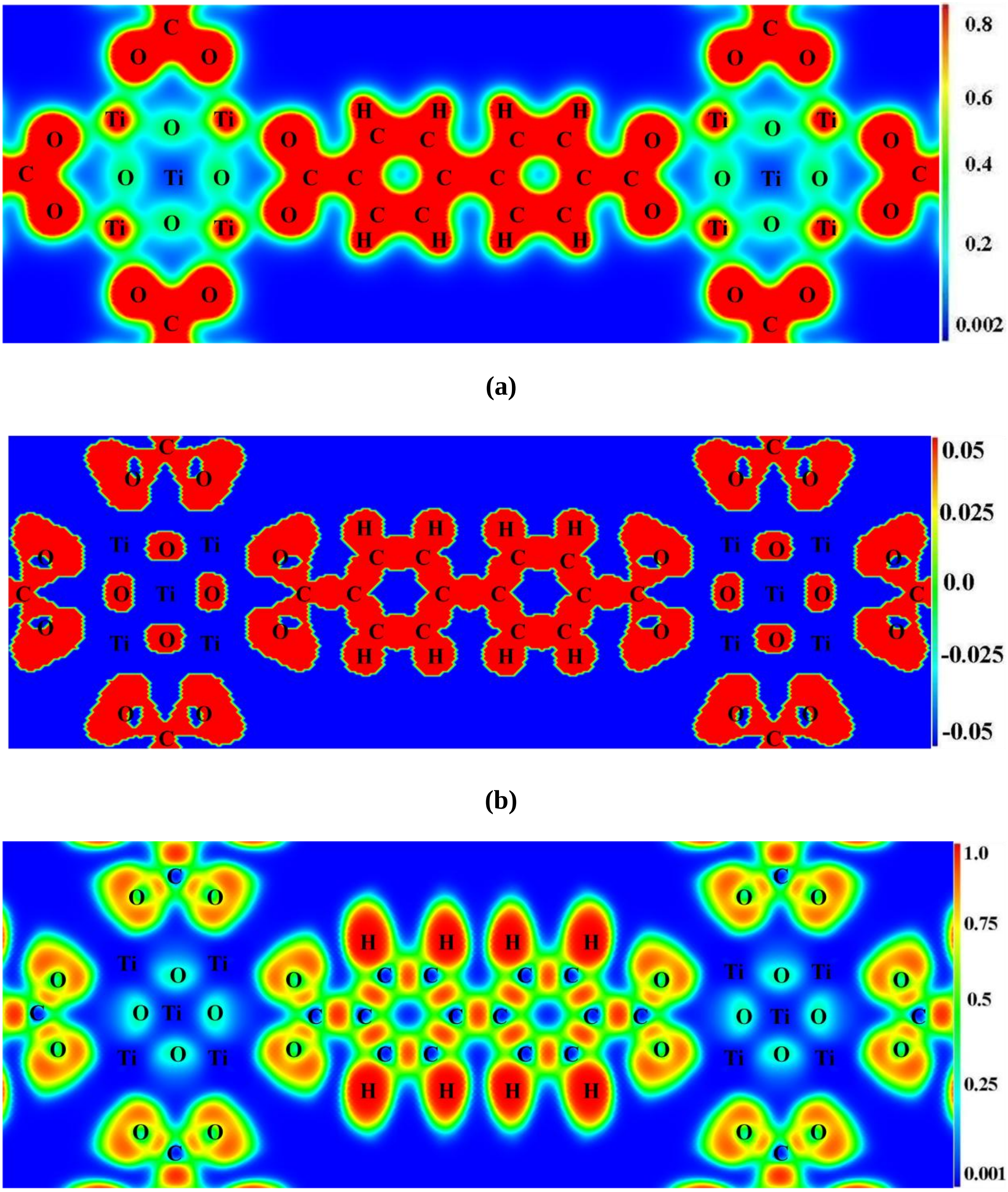


(a)

(b)

(c)

Figure S13. Calculated charge density (a), charge transfer (b) (in units of eÅ $^{-3}$), and electron localization function (c) plots for Ti-UiO-66 in the (110) plane.

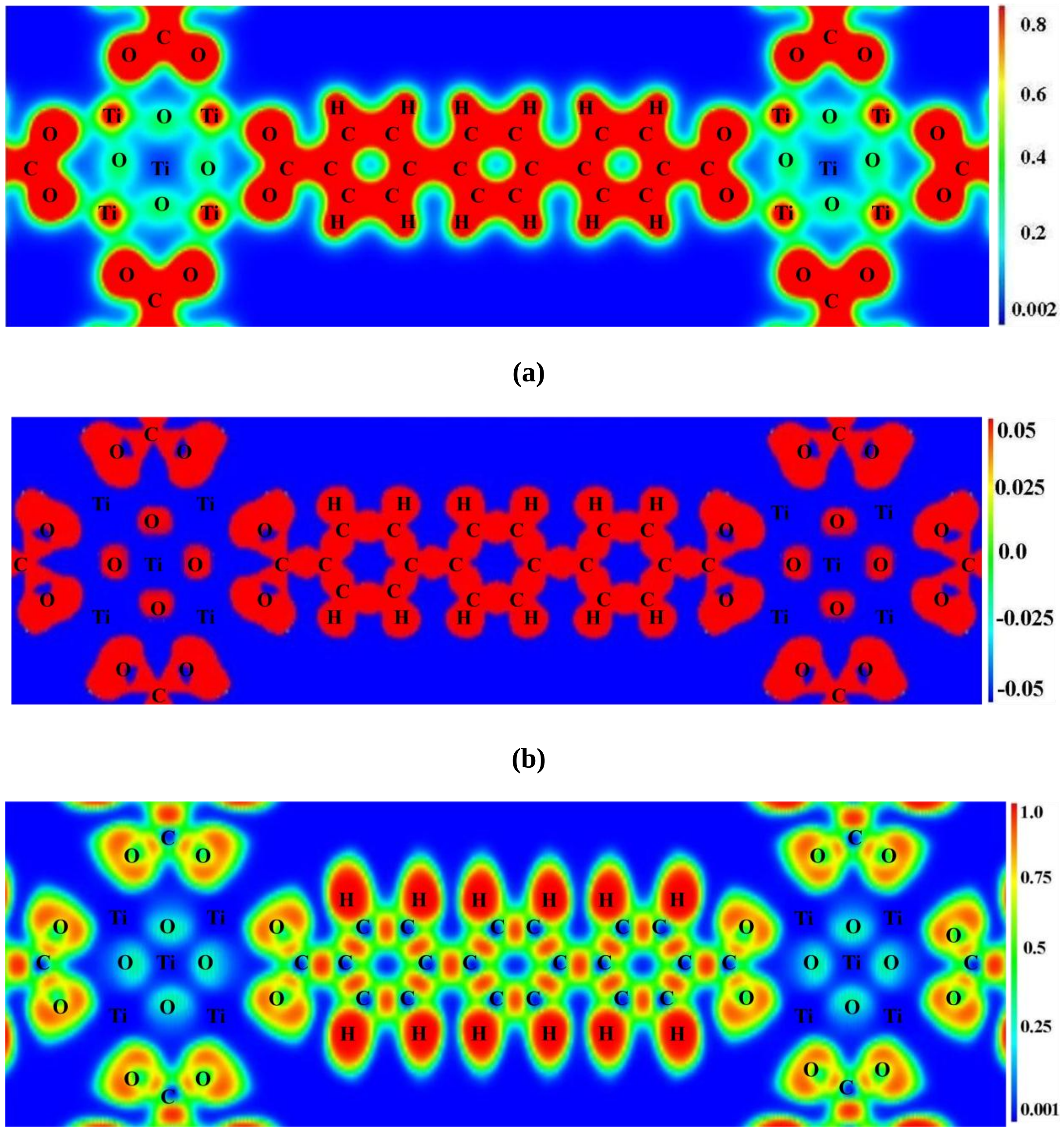


(a)

(b)

(c)

Figure S14. Calculated charge density (a), charge transfer (b) (in units of eÅ $^{-3}$), and electron localization function (c) plots for Ti-UiO-67 in the (110) plane.



(a)

(b)

(c)

Figure S15. Calculated charge density (a), charge transfer (b) (in units of eÅ $^{-3}$), and electron localization function (c) plots for Ti-UiO-68 in the (110) plane.

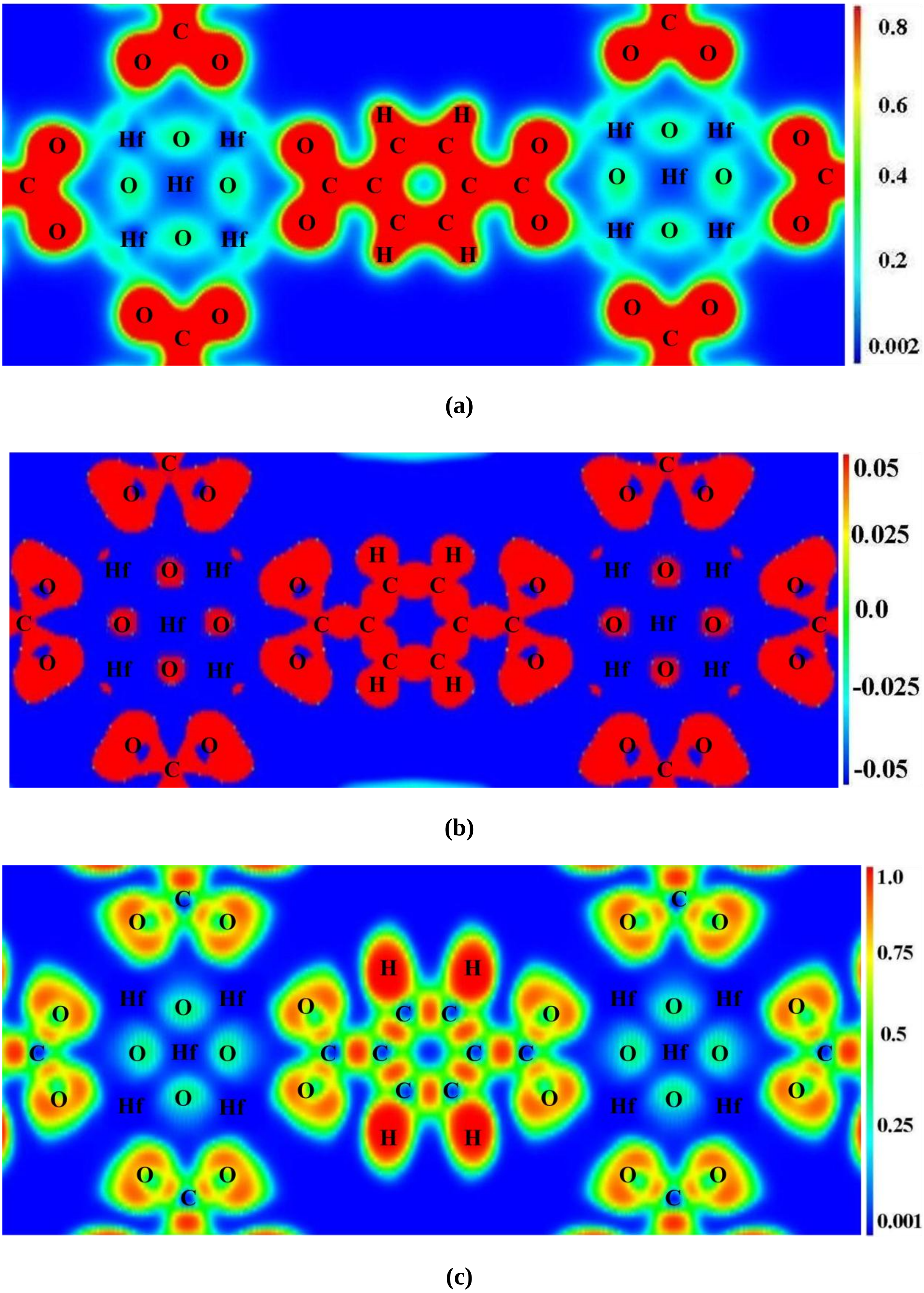
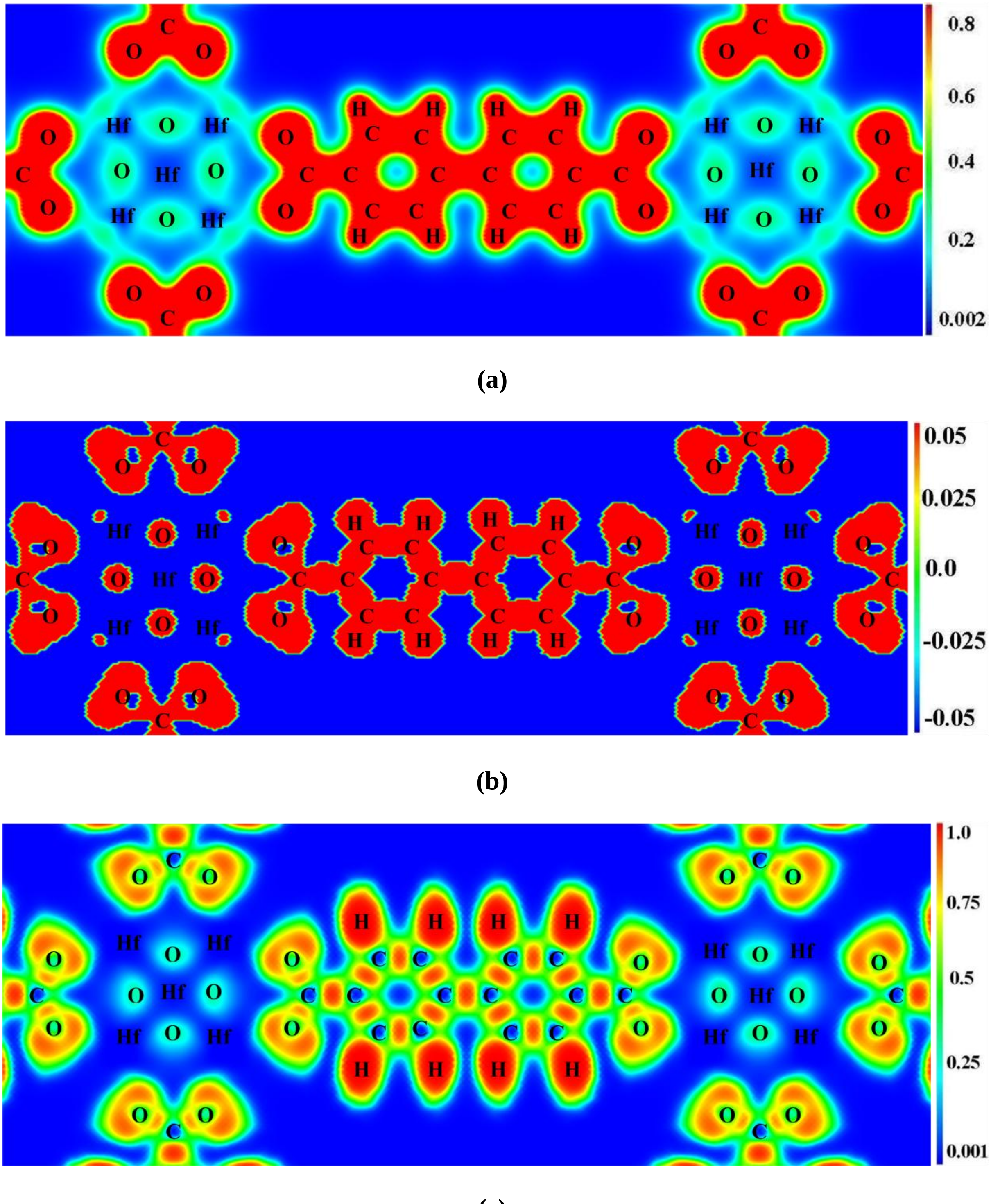


Figure S16. Calculated charge density (a), charge transfer (b) (in units of eÅ $^{-3}$), and electron localization function (c) plots for Hf-UiO-66 in the (110) plane.



(a)

(b)

(c)

Figure S17. Calculated charge density (a), charge transfer (b) (in units of eÅ $^{-3}$), and electron localization function (c) plots for Hf-UiO-67 in the (110) plane.

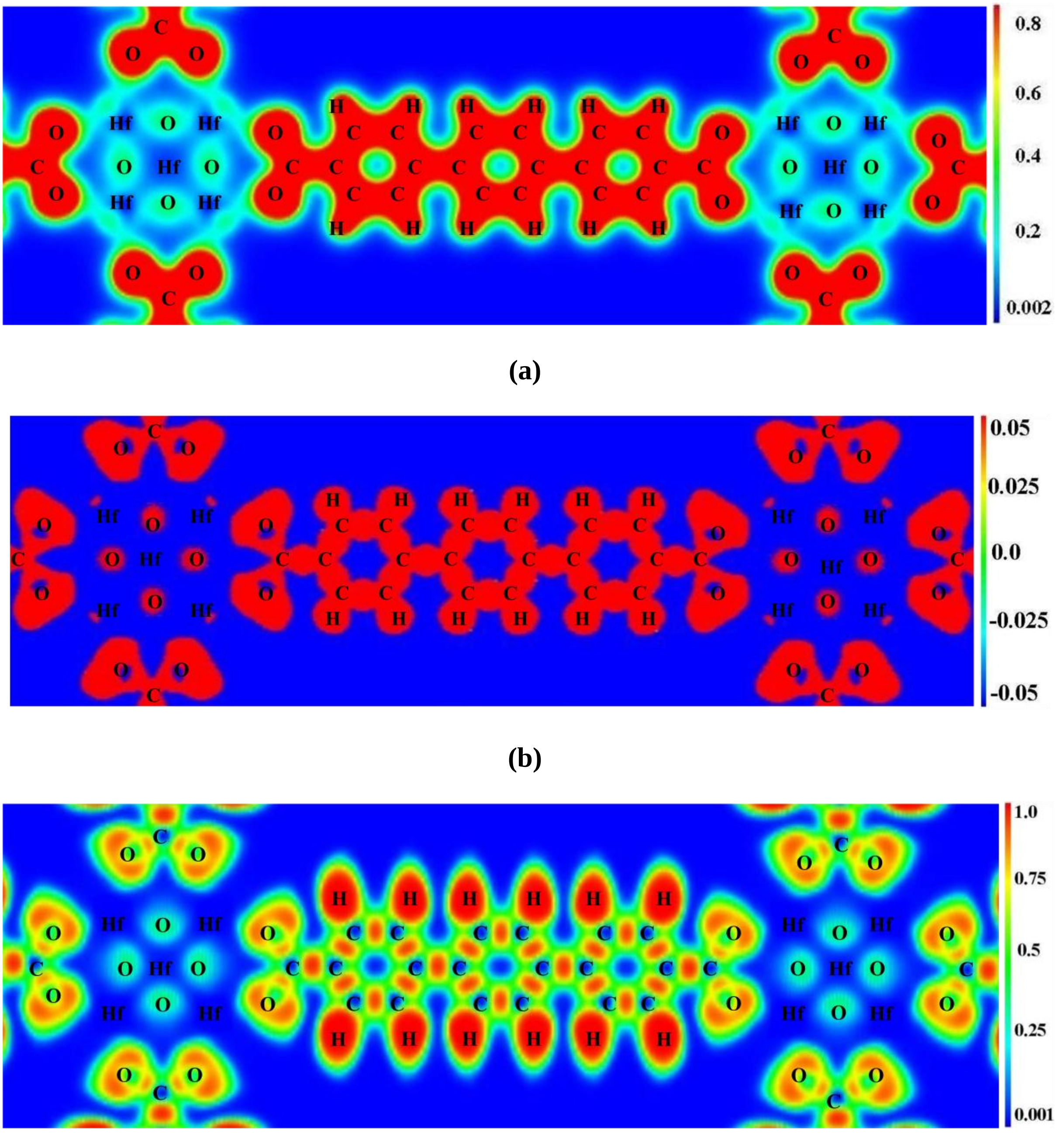


Figure S18. Calculated charge density (a), charge transfer (b) (in units of eÅ $^{-3}$), and electron localization function (c) plots for Hf-UiO-68 in the (110) plane.

Table S3. The calculated Hirshfeld charge (HC), Mulliken effective charge (MEC), bond overlap populations (BOP) (in |*e*|) for M-UiO-66 and -68 (M = Ti, Zr, and Hf). Note that the atomic labels M, O1, O2, O3, C1, C2, C3, C4, C5, C6, C7, H1, H2, H3, and H4 are numbered according to **Fig. 1**. We did not calculate the HC, MEC and BOP for UiO-67.

Materials	**Atomic sites**	**HC (|e|)**	**MEC (|*e*|)**	**BOP**
Ti-UiO-66	Ti	+0.53	+1.68	0.17-0.32 (Ti-O)
	O1	–0.18	–0.54	0.24 (O1-Ti)
	O2	–0.28	–0.61	0.32 (O2-Ti)
	O3	–0.22	–0.72	0.17 (O3-Ti)
	C1	–0.03	–0.27	1.08 (C1-C2)
				1.11 (C1-C1)
	C2	–0.01	–0.05	0.84 (C2-C3)
	C3	+0.19	+0.53	0.94 (C3-O1)
	H1	+0.14	+0.42	0.64 (H1-O3)
	H2	+0.05	+0.30	0.88 (H2-C1)
Zr-UiO-66	Zr	+0.65	+1.94	0.17-0.33 (Zr-O)
	O1	–0.20	–0.57	0.24 (O1-Zr)
	O2	–0.34	–0.73	0.33 (O2-Zr)
	O3	–0.25	–0.79	0.17 (O3-Zr)
	C1	–0.03	–0.26	1.08 (C1-C2)
				1.11 (C1-C1)
	C2	–0.01	–0.05	0.85 (C2-C3)
	C3	+0.20	+0.54	0.94 (C3-O1)
	H1	+0.15	+0.42	0.64 (H1-O3)
	H2	+0.05	+0.29	0.88 (H2-C1)
Hf-UiO-66	Hf	+0.65	+1.89	0.22-0.45 (Hf-O)
	O1	–0.19	–0.57	0.29 (O1-Hf)
	O2	–0.32	–0.69	0.45 (O2-Hf)
	O3	–0.25	–0.78	0.22 (O3-Hf)

	C1	–0.03	–0.26	1.09 (C1-C2)
				1.11 (C1-C1)
	C2	–0.01	–0.05	0.85 (C2-C3)
	C3	+0.19	+0.54	0.94 (C3-O1)
	H1	+0.14	+0.41	0.63 (H1-O3)
	H2	+0.05	+0.29	0.89 (H2-C1)
Ti-UiO-68	Ti	+0.52	+1.68	0.17-0.32 (Ti-O)
	O1	–0.22	–0.72	0.17 (O1-Ti)
	O2	–0.28	–0.61	0.32 (O2-Ti)
	O3	–0.18	–0.54	0.24 (O3-Ti)
	C1	+0.19	+0.52	0.93 (C1-O3)
				0.85 (C1-C3)
	C2	+0.01	–0.01	1.09 (C2-C4)
				0.92 (C2-C7)
	C3	–0.01	–0.06	1.08 (C3-C5)
	C4	–0.04	–0.27	1.13 (C4-C5)
	C5	–0.04	–0.26	0.88 (C5-H3)
	C6	–0.04	–0.26	1.14 (C6-C6)
	C7	0.00	–0.02	1.09 (C7-C6)
	H1	+0.14	+0.42	0.64 (H1-O1)
	H2	+0.04	+0.28	0.90 (H2-C4)
	H3	+0.05	+0.29	0.88 (H3-C5)
	H4	+0.04	+0.28	0.90 (H4-C6)
Zr-UiO-68	Zr	+0.64	+1.94	0.17-0.33 (Zr-O)
	O1	–0.25	–0.79	0.17 (O1-Zr)
	O2	–0.34	–0.73	0.33 (O2-Zr)
	O3	–0.20	–0.58	0.24 (O3-Zr)

	C1	+0.19	+0.54	0.93 (C1-O3)
				0.86 (C1-C3)
	C2	+0.01	–0.01	1.09 (C2-C4)
				0.92 (C2-C7)
	C3	–0.02	–0.06	1.08 (C3-C5)
	C4	–0.04	–0.27	1.13 (C4-C5)
	C5	–0.04	–0.26	0.89 (C5-H3)
	C6	–0.04	–0.26	1.14 (C6-C6)
	C7	0.00	–0.02	1.09 (C7-C6)
	H1	+0.14	+0.42	0.64 (H1-O1)
	H2	+0.04	+0.28	0.90 (H2-C4)
	H3	+0.05	+0.29	0.89 (H3-C5)
	H4	+0.04	+0.28	0.90 (H4-C6)
Hf-UiO-68	Hf	+0.62	+1.89	0.22-0.45 (Hf-O)
	O1	-0.24	–0.78	0.22 (O1-Hf)
	O2	–0.31	–0.69	0.45 (O2-Hf)
	O3	–0.20	–0.57	0.29 (O3-Hf)
	C1	+0.19	+0.54	0.93 (C1-O3)
				0.86 (C1-C3)
	C2	+0.01	–0.01	1.09 (C2-C4)
				0.92 (C2-C7)
	C3	–0.02	–0.06	1.08 (C3-C5)
	C4	–0.04	–0.27	1.13 (C4-C5)
	C5	–0.04	–0.26	0.89 (C5-H3)
	C6	–0.04	–0.26	1.14 (C6-C6)
	C7	0.00	–0.02	1.09 (C7-C6)
	H1	+0.14	+0.42	0.64 (H1-O1)

H2	+0.04	+0.28	0.90 (H2-C4)
H3	+0.05	+0.29	0.89 (H3-C5)
H4	+0.04	+0.28	0.90 (H4-C6)

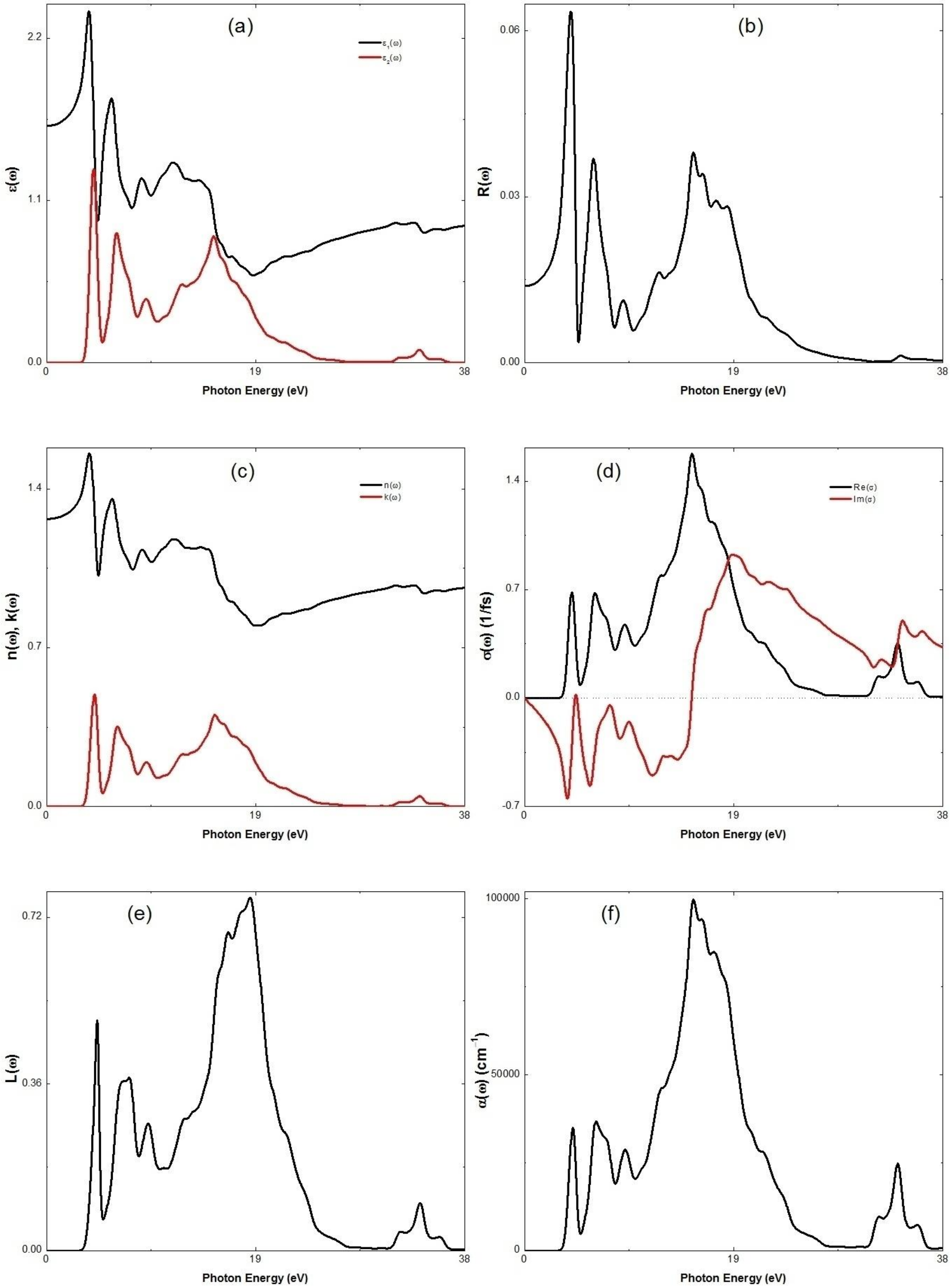


Figure S19. The calculated optical spectra for Zr-UiO-68: (a) dielectric function ε(ω); (b) reflectivity R(ω); (c) refractive index **n**(ω) and extinction coefficient **k**(ω); (d) optical conductivity σ(ω); (e) energy loss function L(ω); and (f) absorption coefficient α(ω) (cm^{-1}).

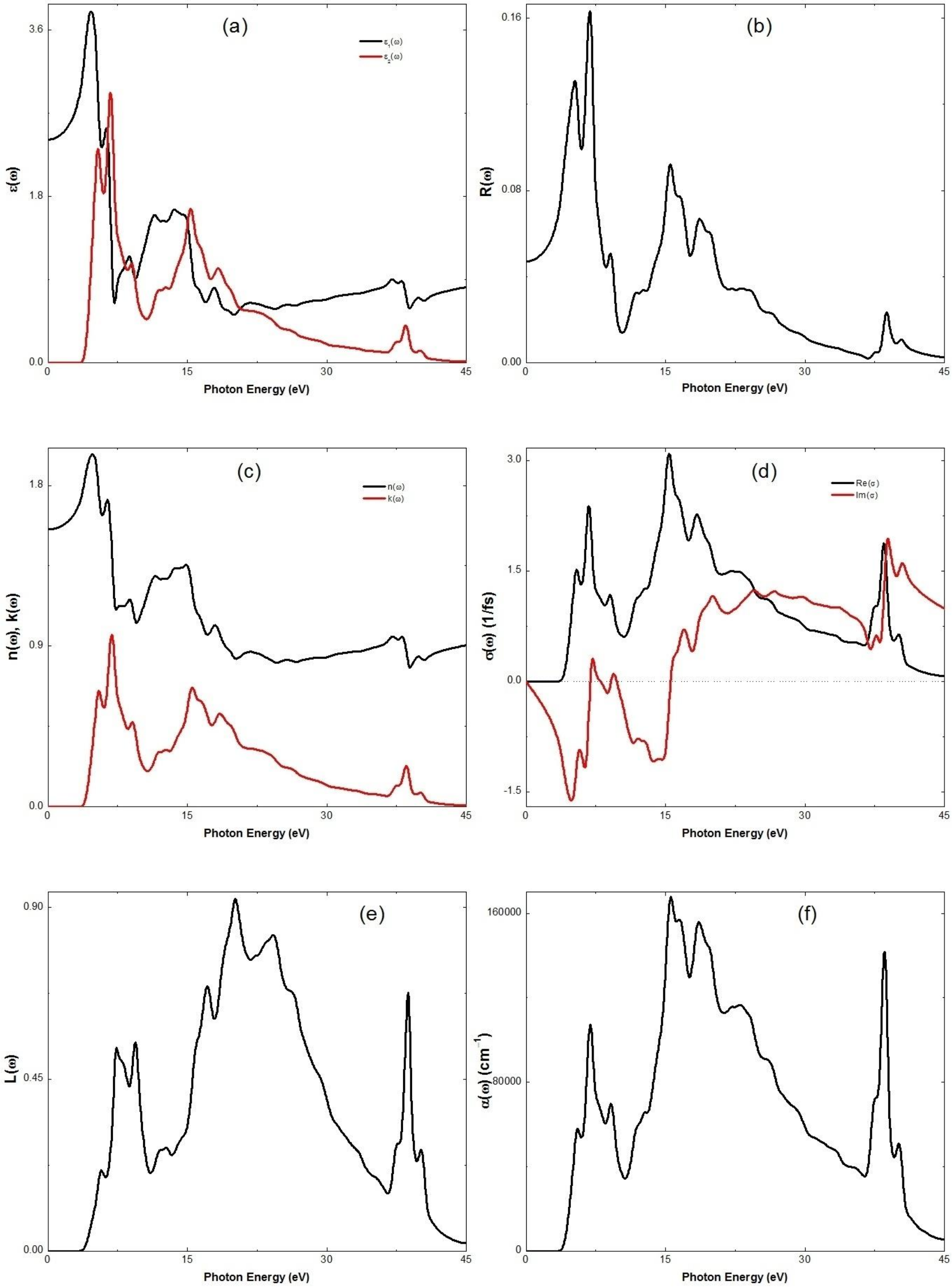


Figure S20. Calculated optical properties for Ti-UiO-66: (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), (f) absorption α(ω).

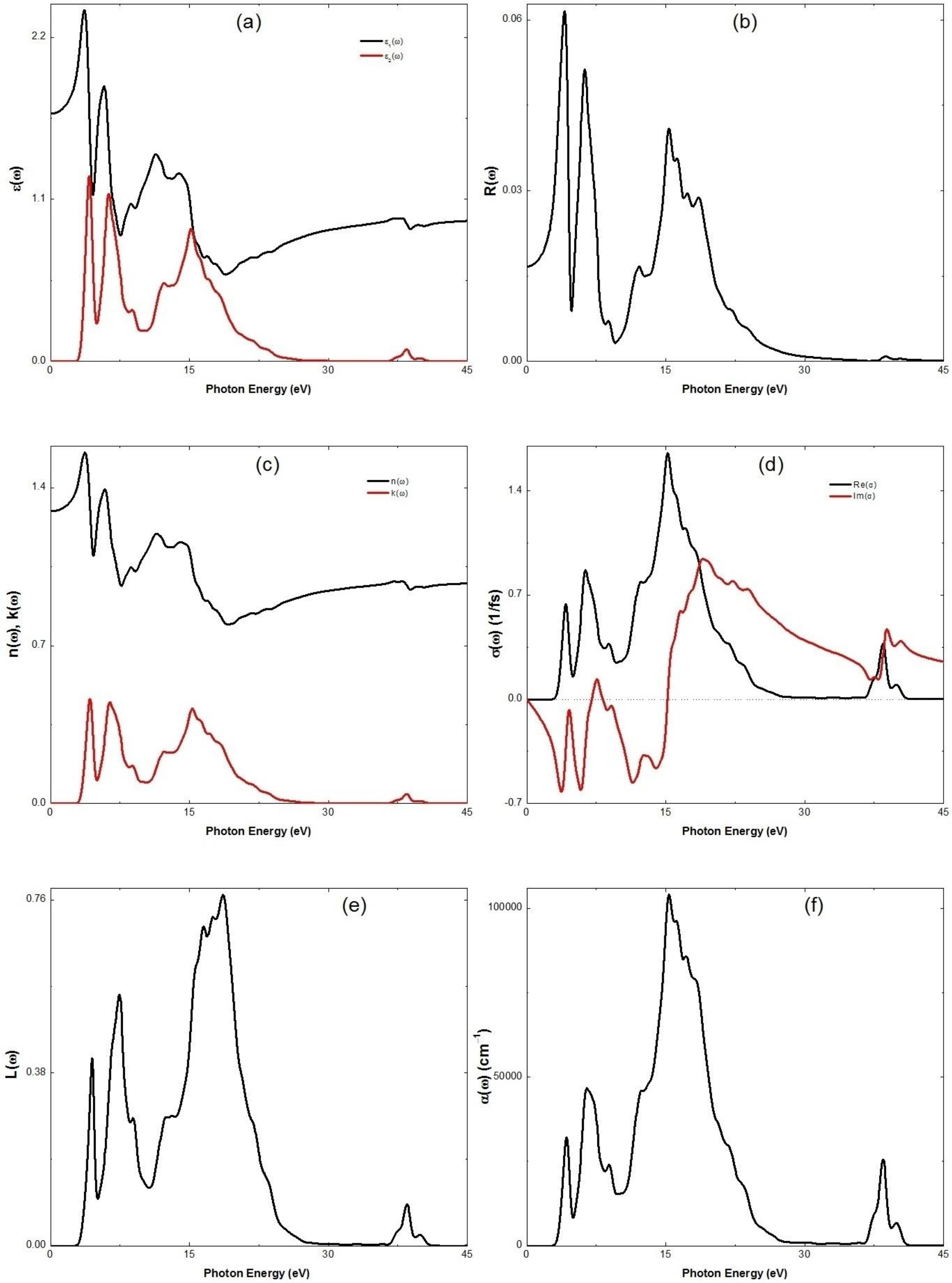


Figure S21. Calculated optical properties for Ti-UiO-68: (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), (f) absorption α(ω).

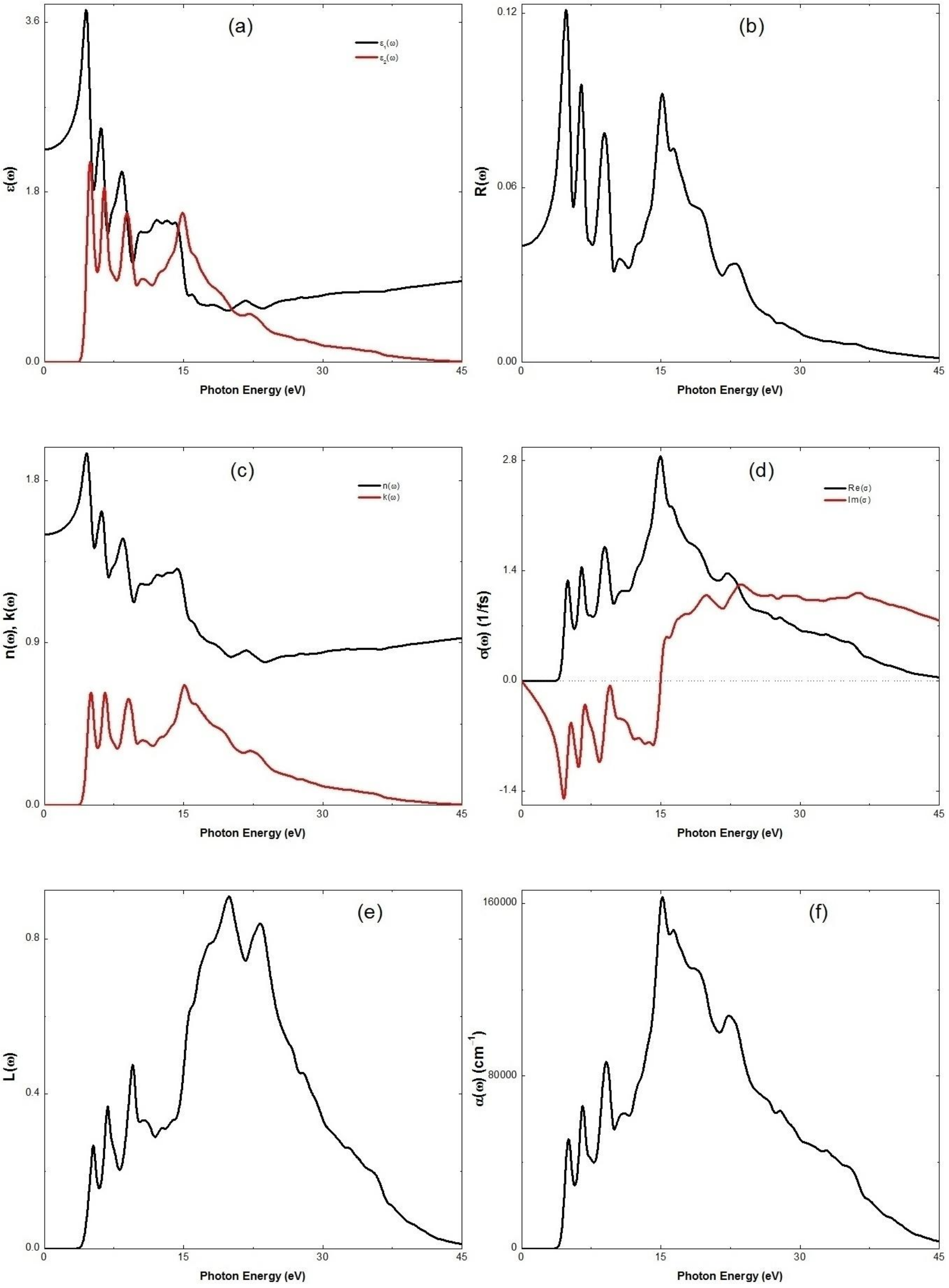


Figure S22. Calculated optical properties for Hf-UiO-66: (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), (f) absorption α(ω).

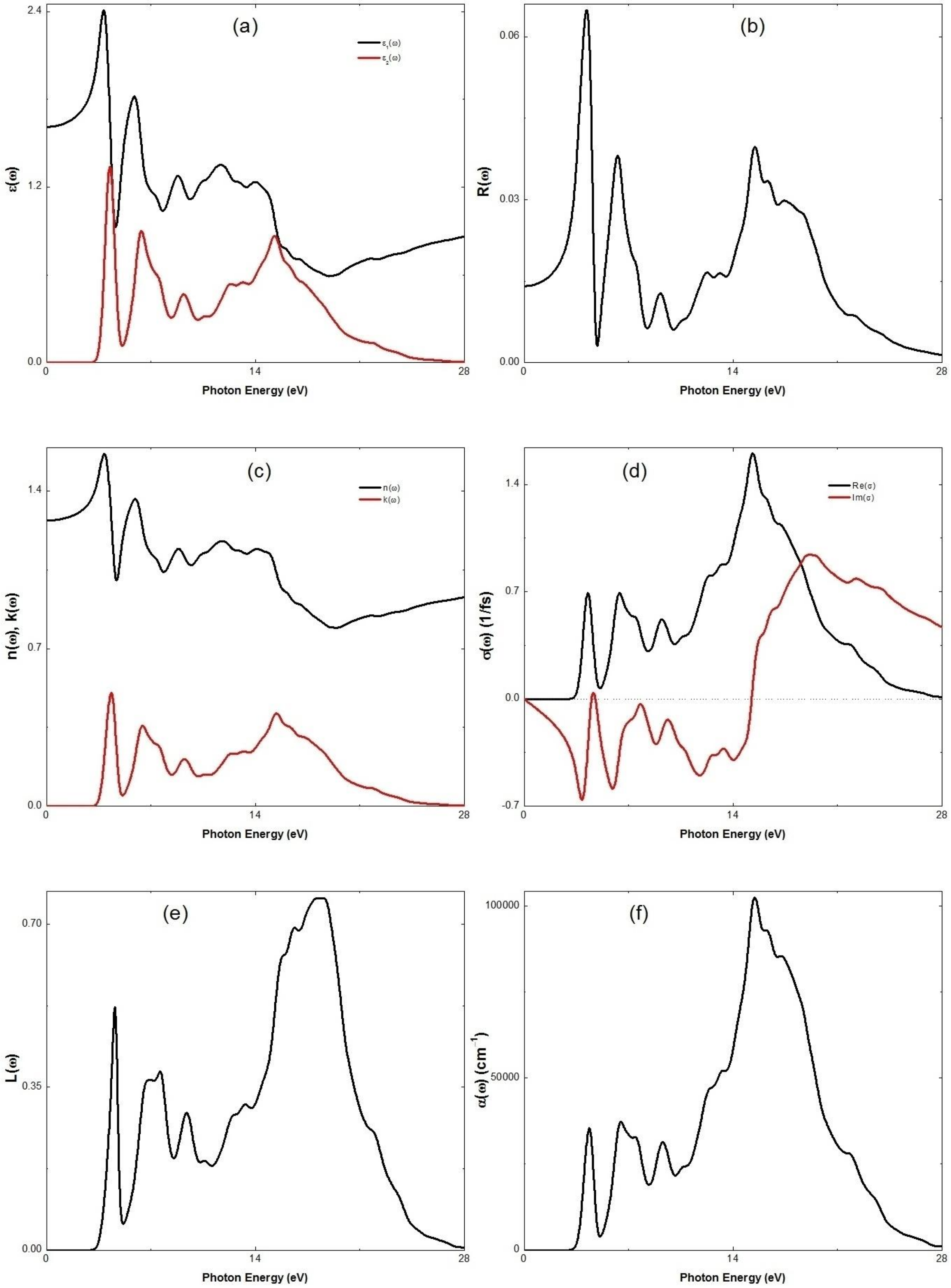


Figure S23. Calculated optical properties for Hf-UiO-68: (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), (f) absorption α(ω).

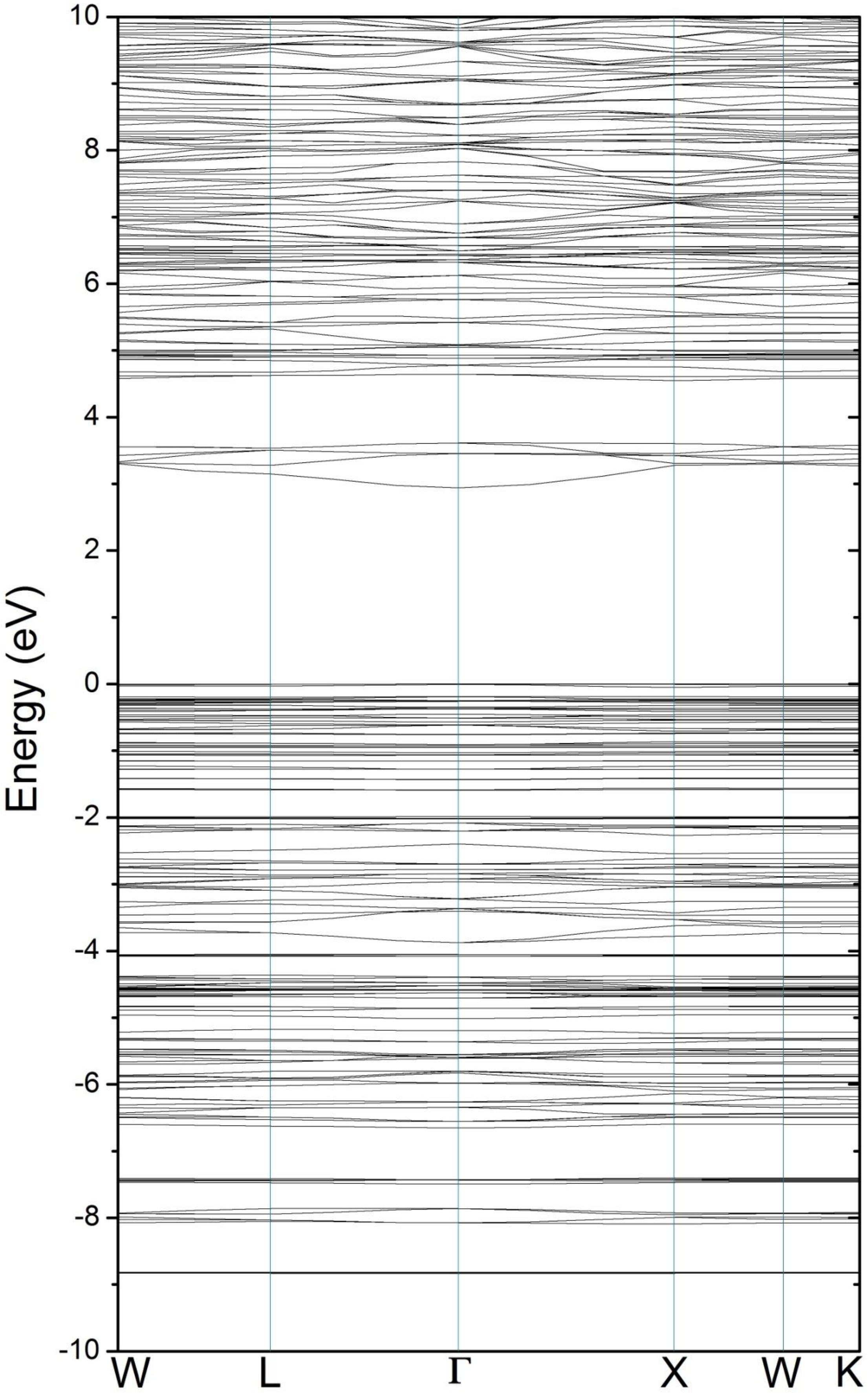


Figure S24. The calculated band structure of Zr-UiO-66. The Fermi level is set to zero.

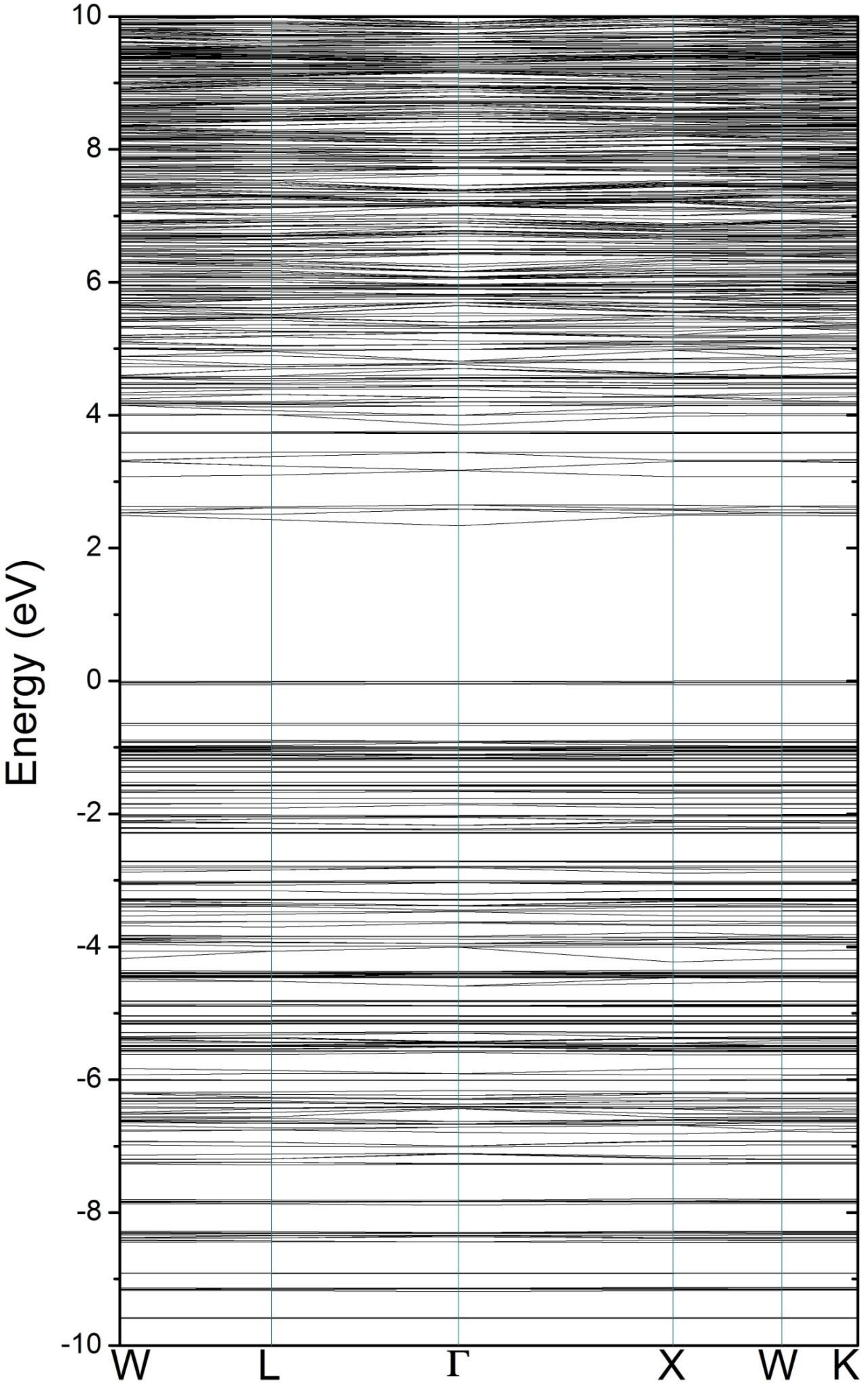


Figure S25. The calculated band structure of Zr-UiO-68. The Fermi level is set to zero.

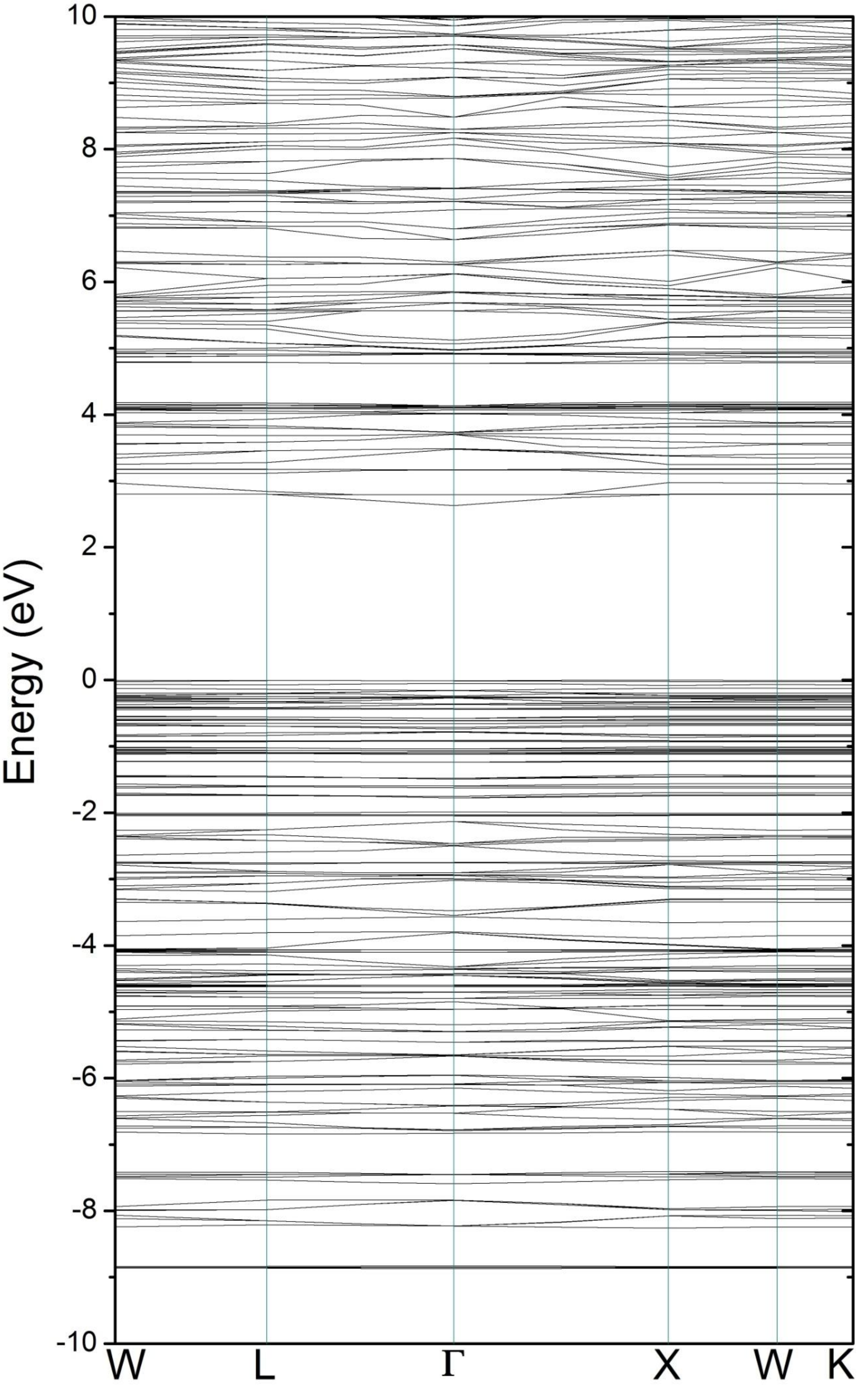


Figure S26. The calculated electronic band structure of Ti-UiO-66. The Fermi level is set to zero and placed in the valence band maximum.

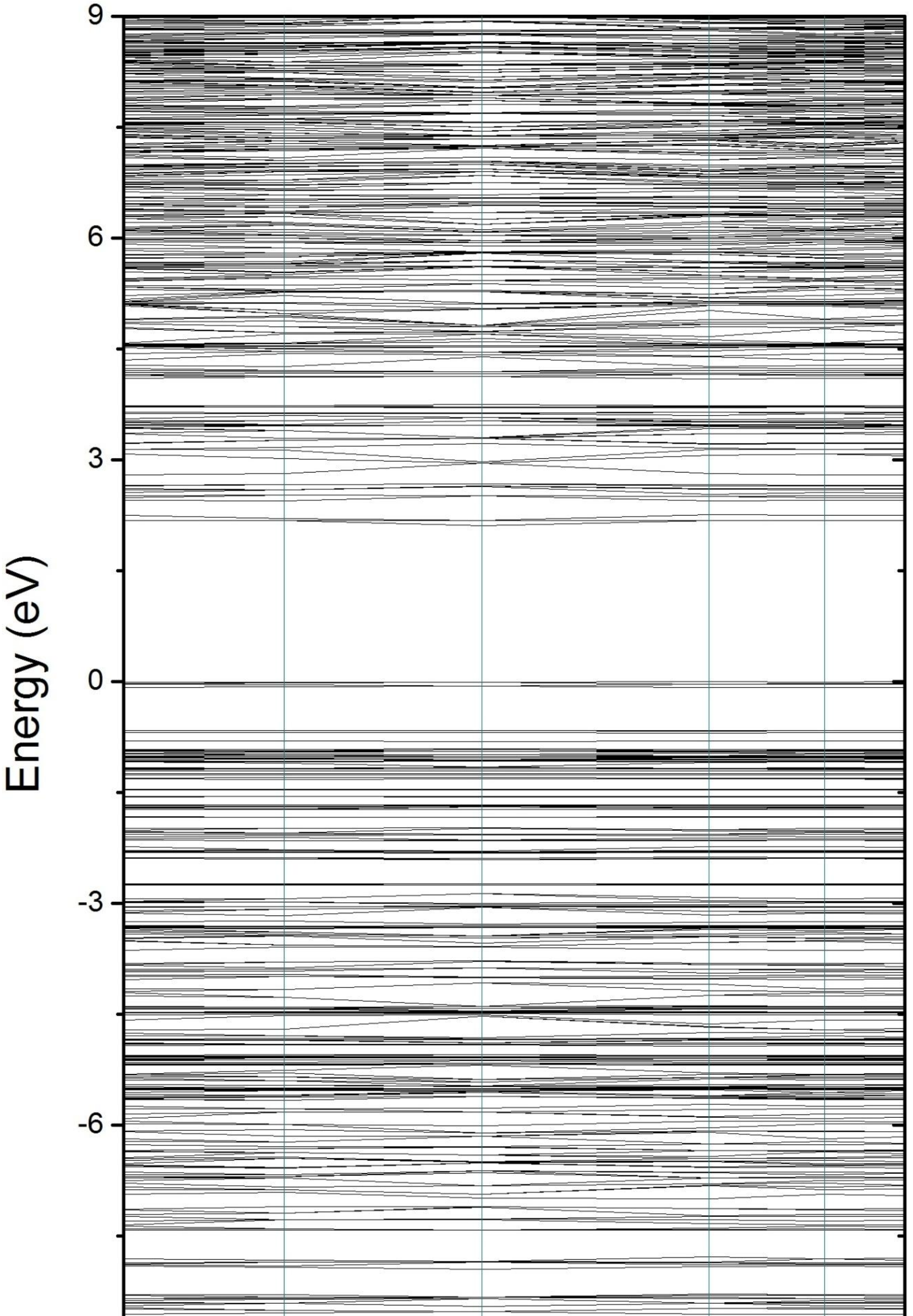


Figure S27. The calculated electronic band structure of Ti-UiO-68. The Fermi level is set to zero and placed in the valence band maximum.

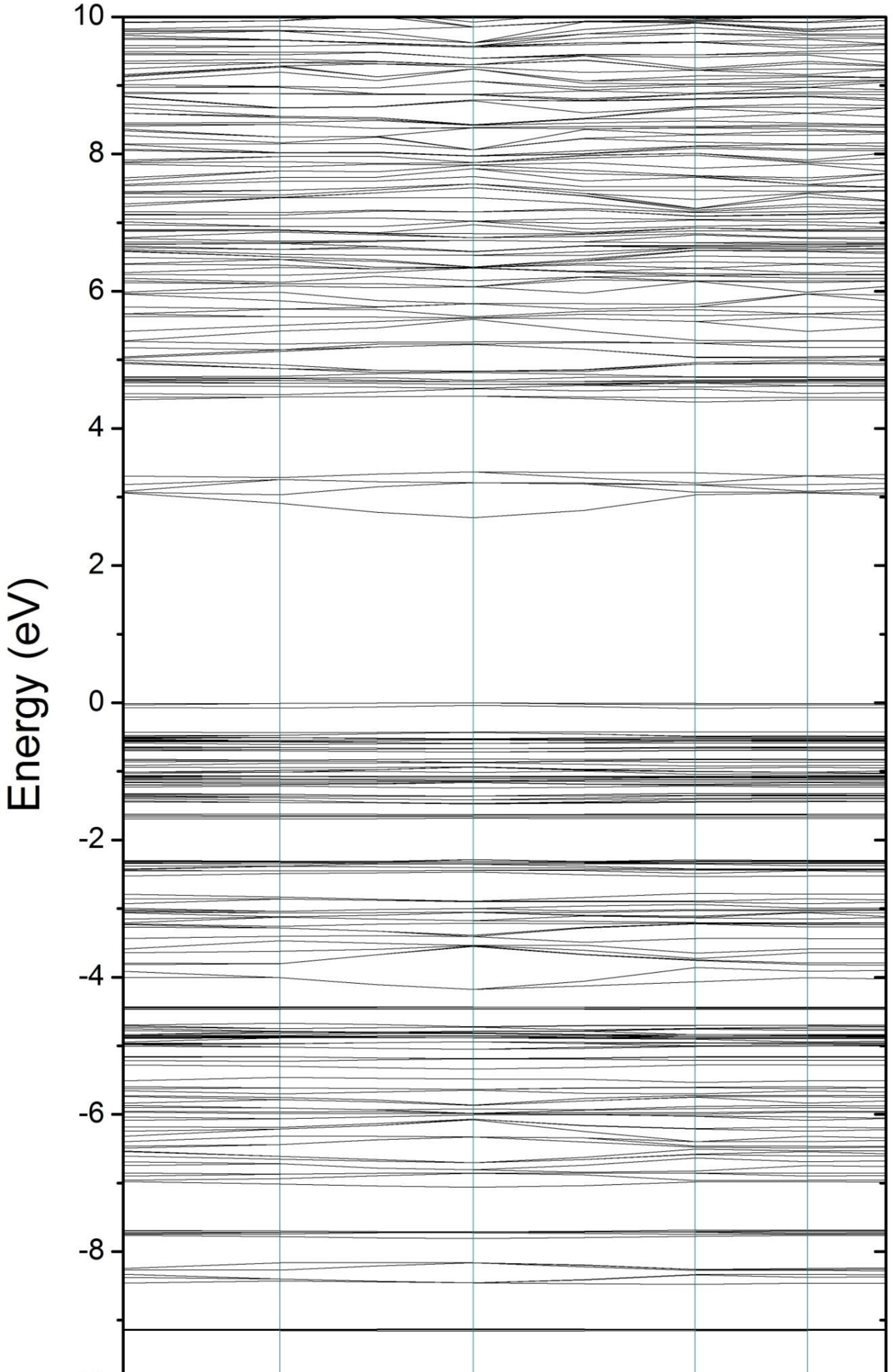


Figure S28. The calculated electronic band structure of Hf-UiO-66. The Fermi level is set to zero and placed in the valence band maximum.

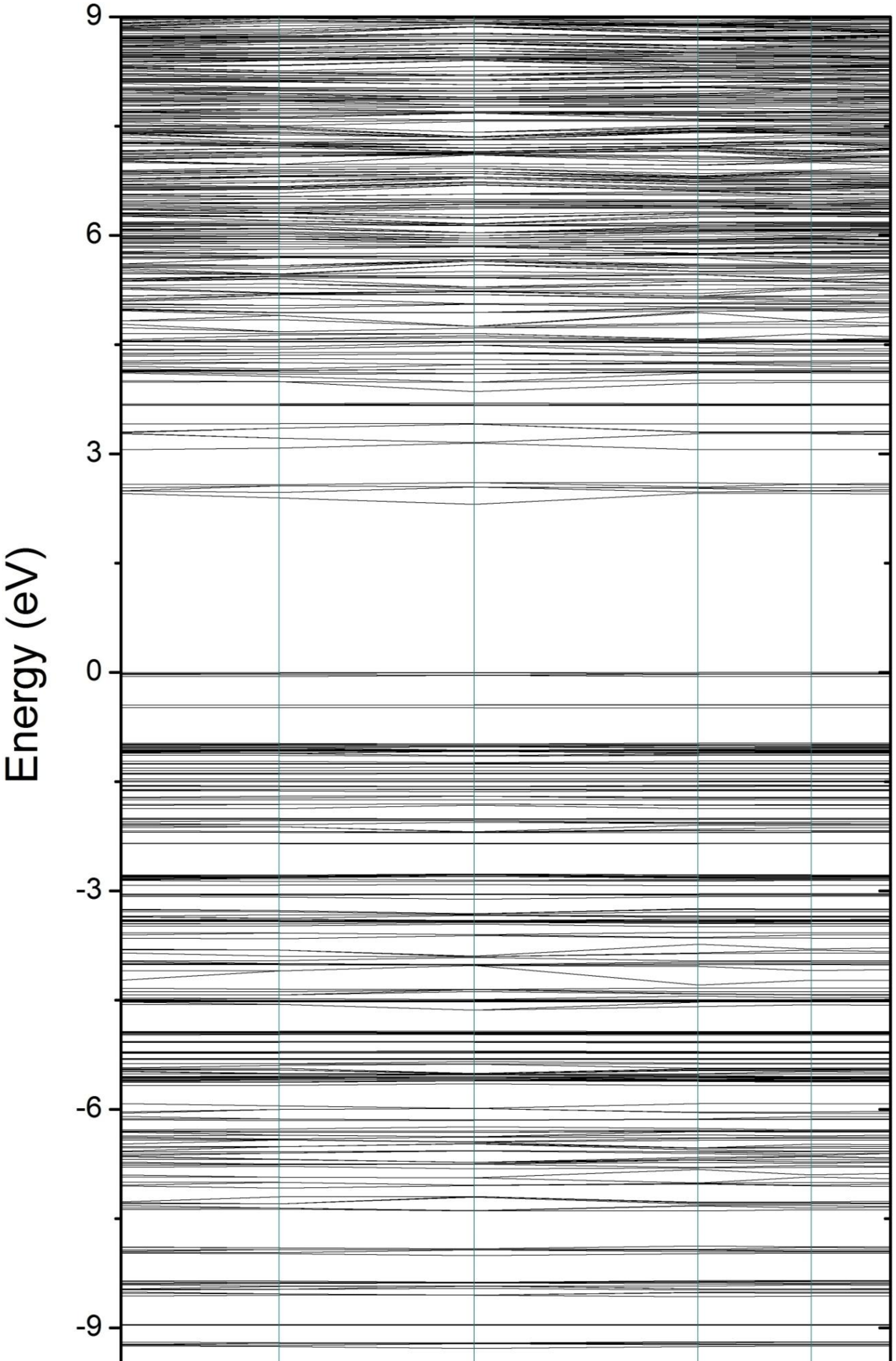


Figure S29. The calculated electronic band structure of Hf-UiO-68. The Fermi level is set to zero and placed in the valence band maximum.