Formation of intermediate band in isoreticular metal-organic framework-993 and its analogues

Supporting Information

Li-Ming Yang*[†], Ponniah Ravindran[‡], Ponniah Vajeeston[‡], and Mats Tilset*[†]

[†]*Center of Theoretical and Computational Chemistry, Department of Chemistry, University of Oslo, P.O.Box 1033 Blindern, N-0315 Oslo, Norway,* [‡]*Center for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, P.O.Box 1033 Blindern, N-0315 Oslo, Norway*

(E-mail of corresponding authors: mats.tilset@kjemi.uio.no and l.m.yang@kjemi.uio.no.; Fax: +47 22855441)

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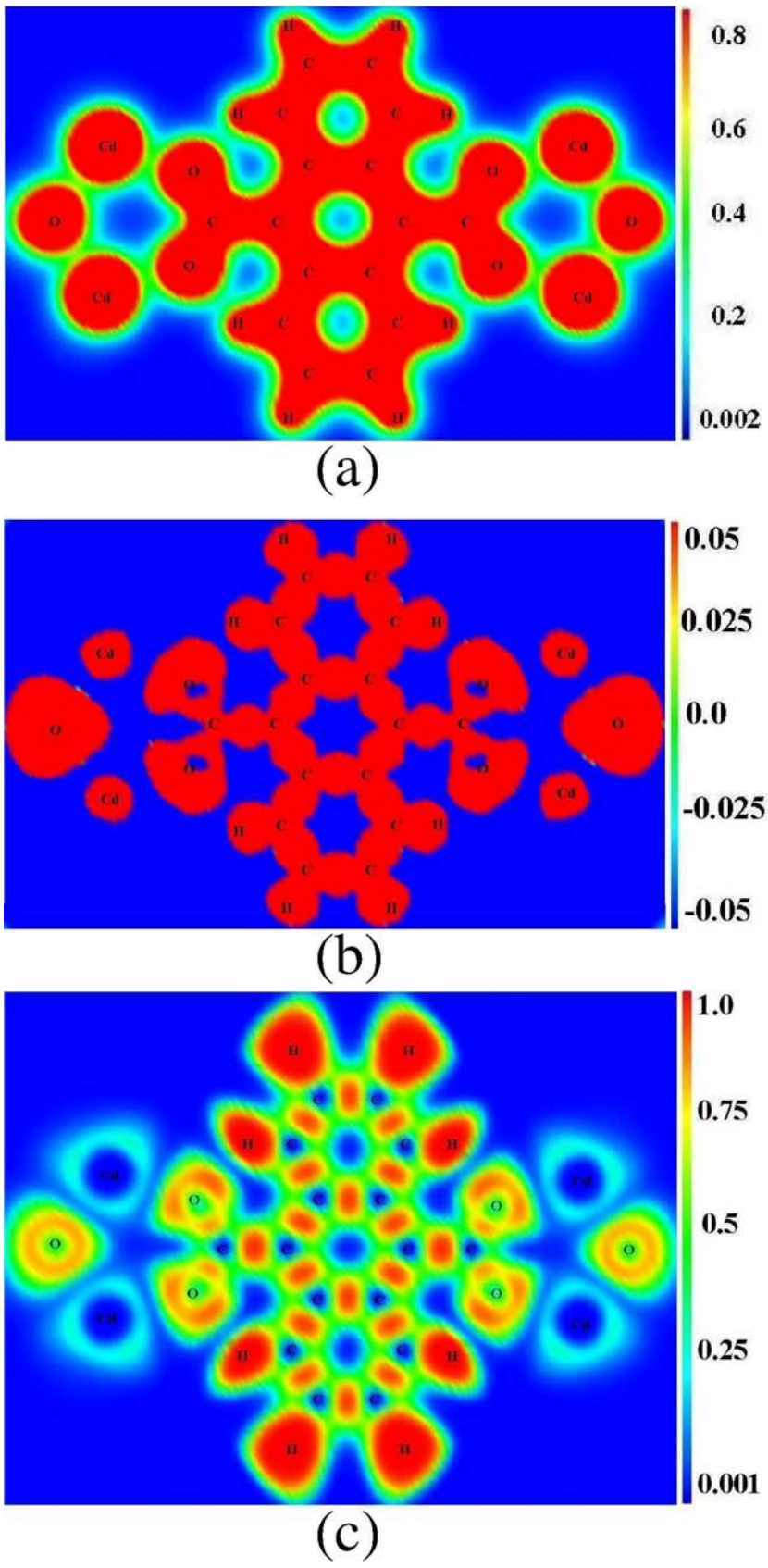

Figure S1. Calculated charge density (a), charge transfer (b), and electron localization function (c) plots for Cd-IRMOF-993 in the (110) plane.

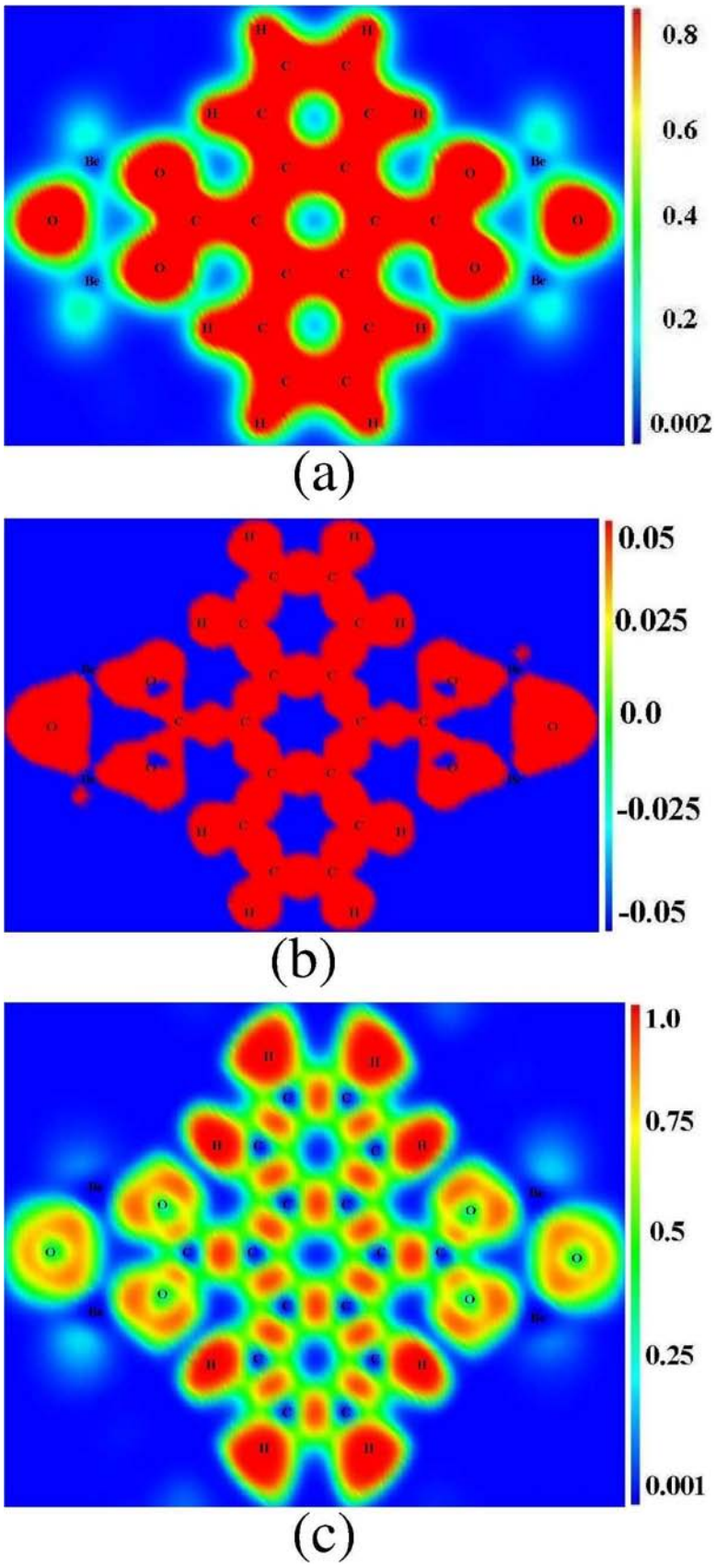

Figure S2. Calculated charge density (a), charge transfer (b), and electron localization function (c) plots for Be-IRMOF-993 in the (110) plane.

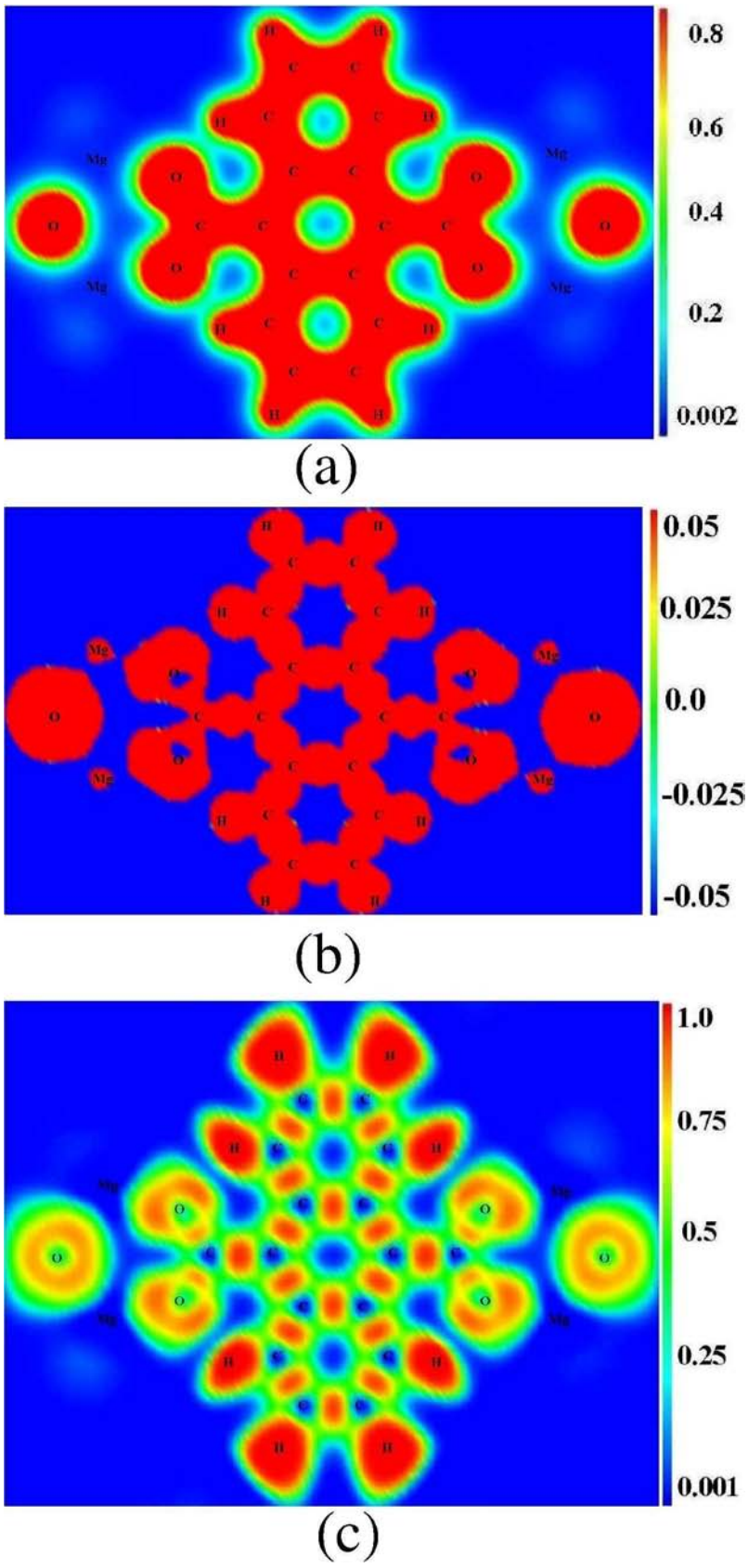

Figure S3. Calculated charge density (a), charge transfer (b), and electron localization function (c) plots for Mg-IRMOF-993 in the (110) plane.

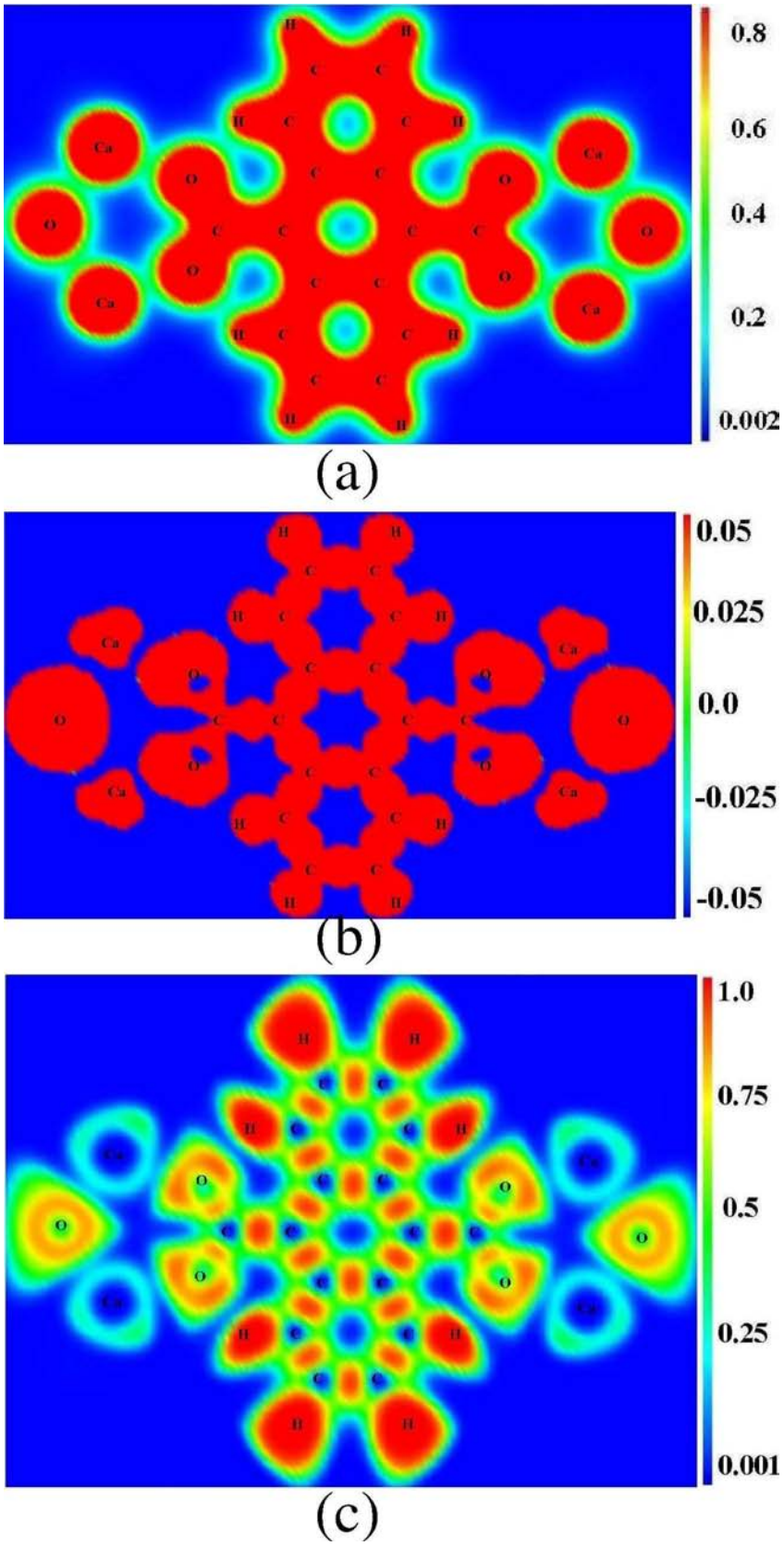

Figure S4. Calculated charge density (a), charge transfer (b), and electron localization function (c) plots for Ca-IRMOF-993 in the (110) plane.

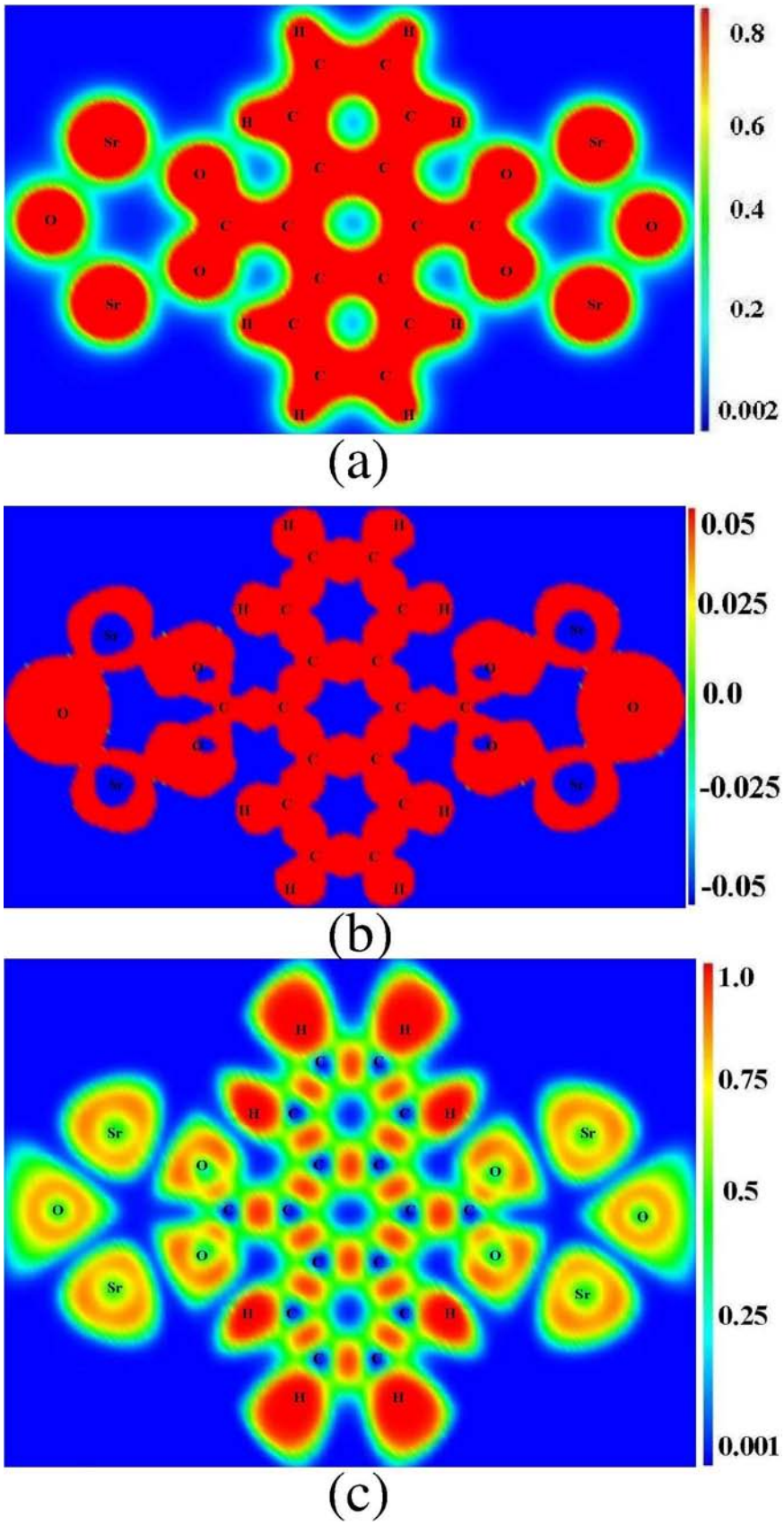

Figure S5. Calculated charge density (a), charge transfer (b), and electron localization function (c) plots for Sr-IRMOF-993 in the (110) plane.

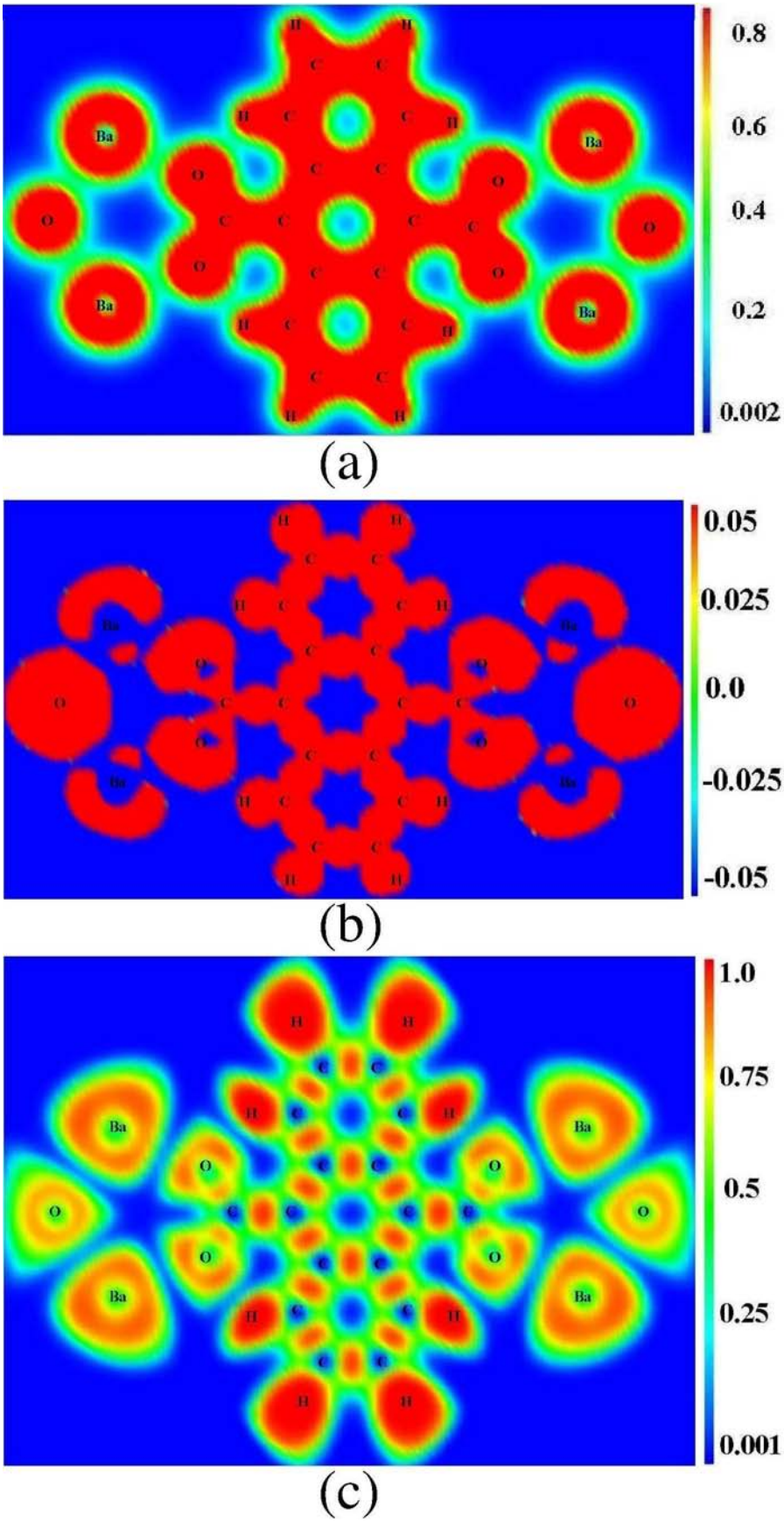

Figure S6. Calculated charge density (a), charge transfer (b), and electron localization function (c) plots for Ba-IRMOF-993 in the (110) plane.

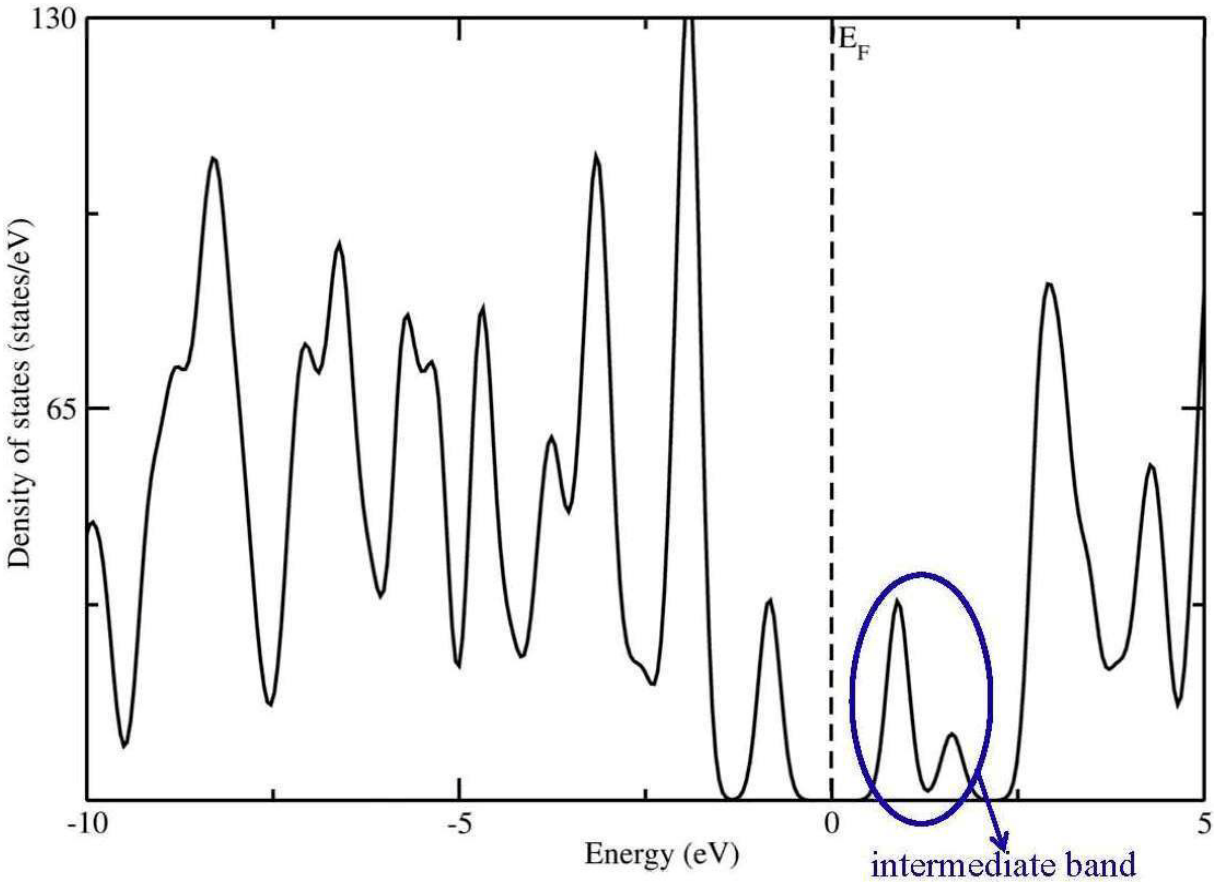

Figure S7. The calculated total density of states (TDOS) for Cd-IRMOF-993 in the cubic *Fm-3m* symmetry (no. 225)

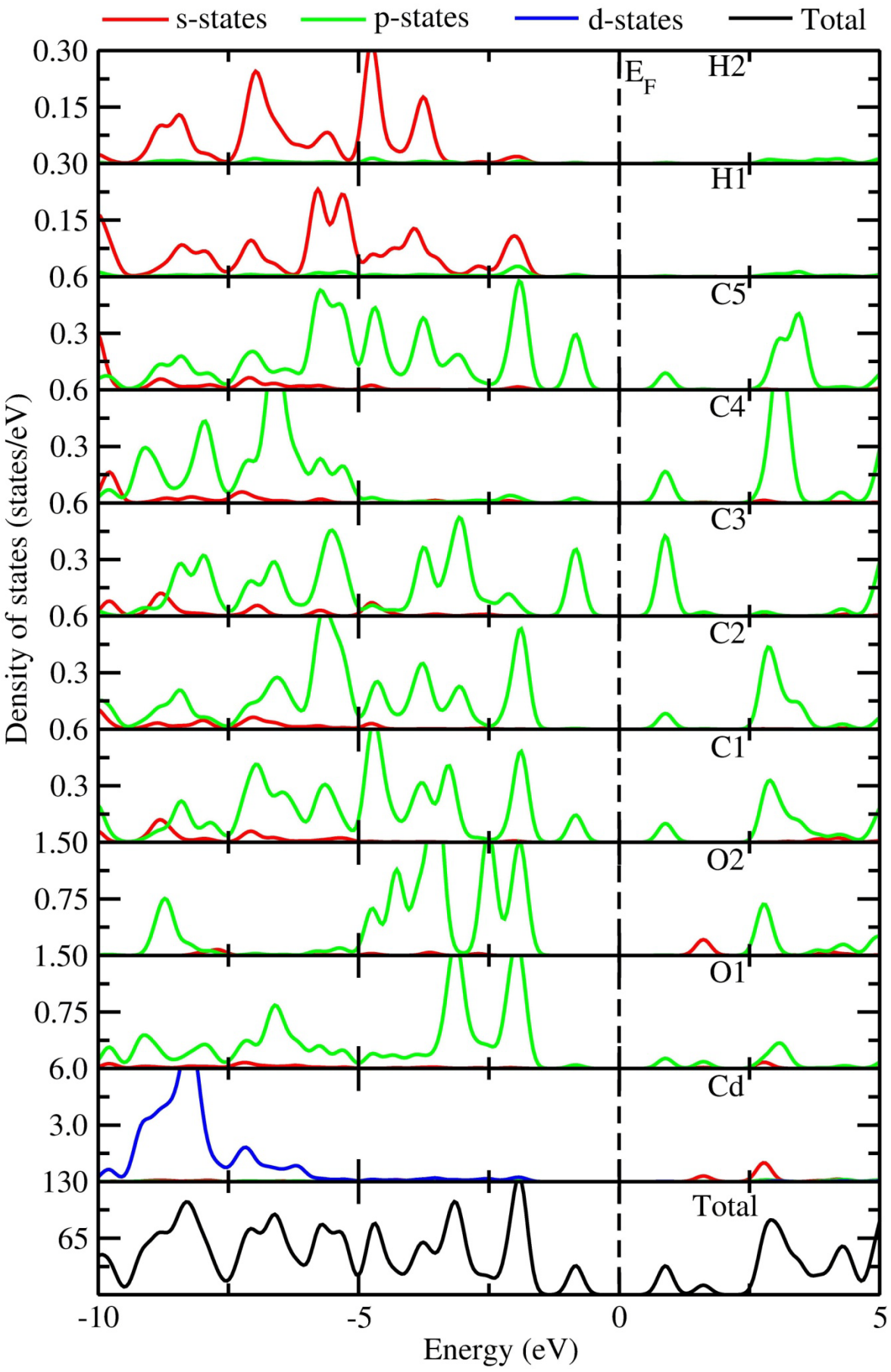

Figure S8. The calculated total density of states (TDOS) and partial density of states (PDOS) for Cd-IRMOF-993 in the cubic *Fm-3m* symmetry (no. 225)

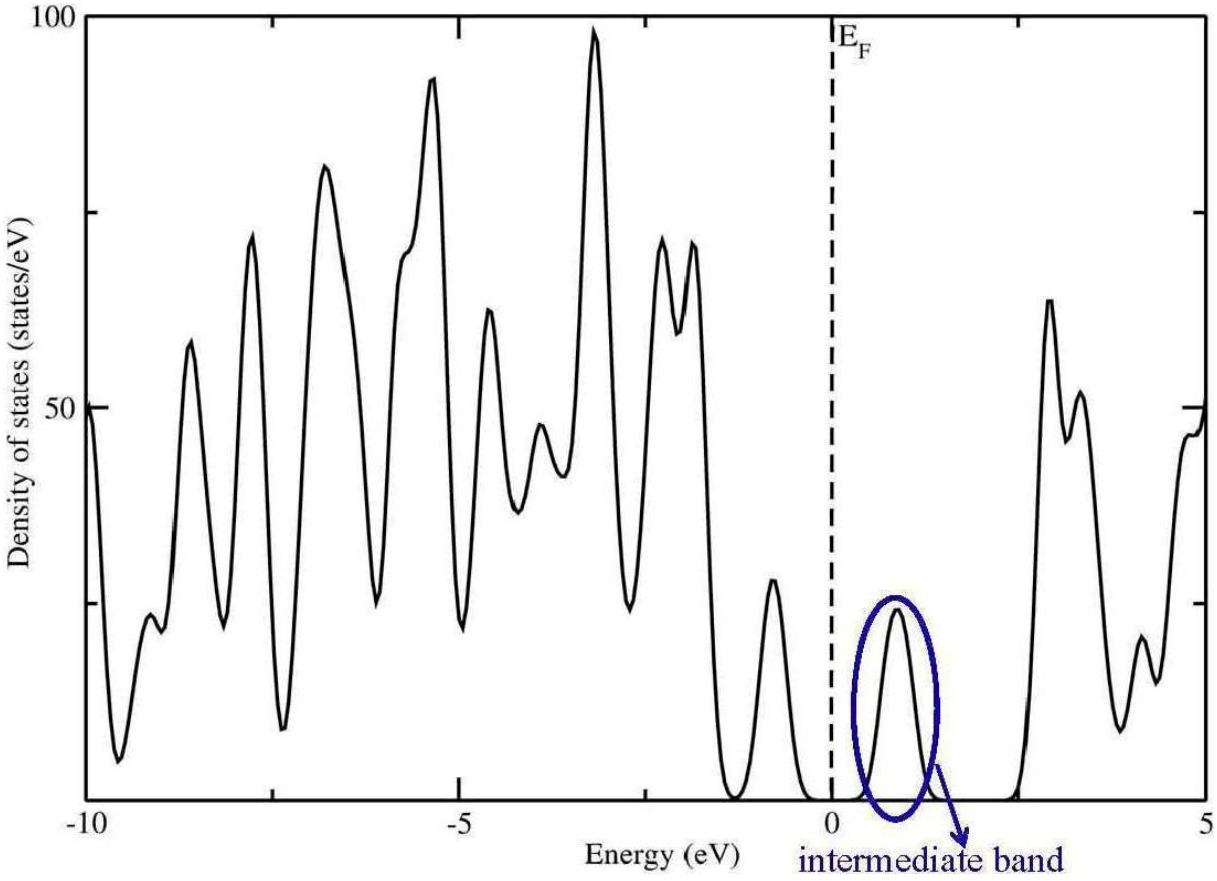

Figure S9. The calculated total density of states (TDOS) for Be-IRMOF-993 in the cubic *Fm-3m* symmetry (no. 225)

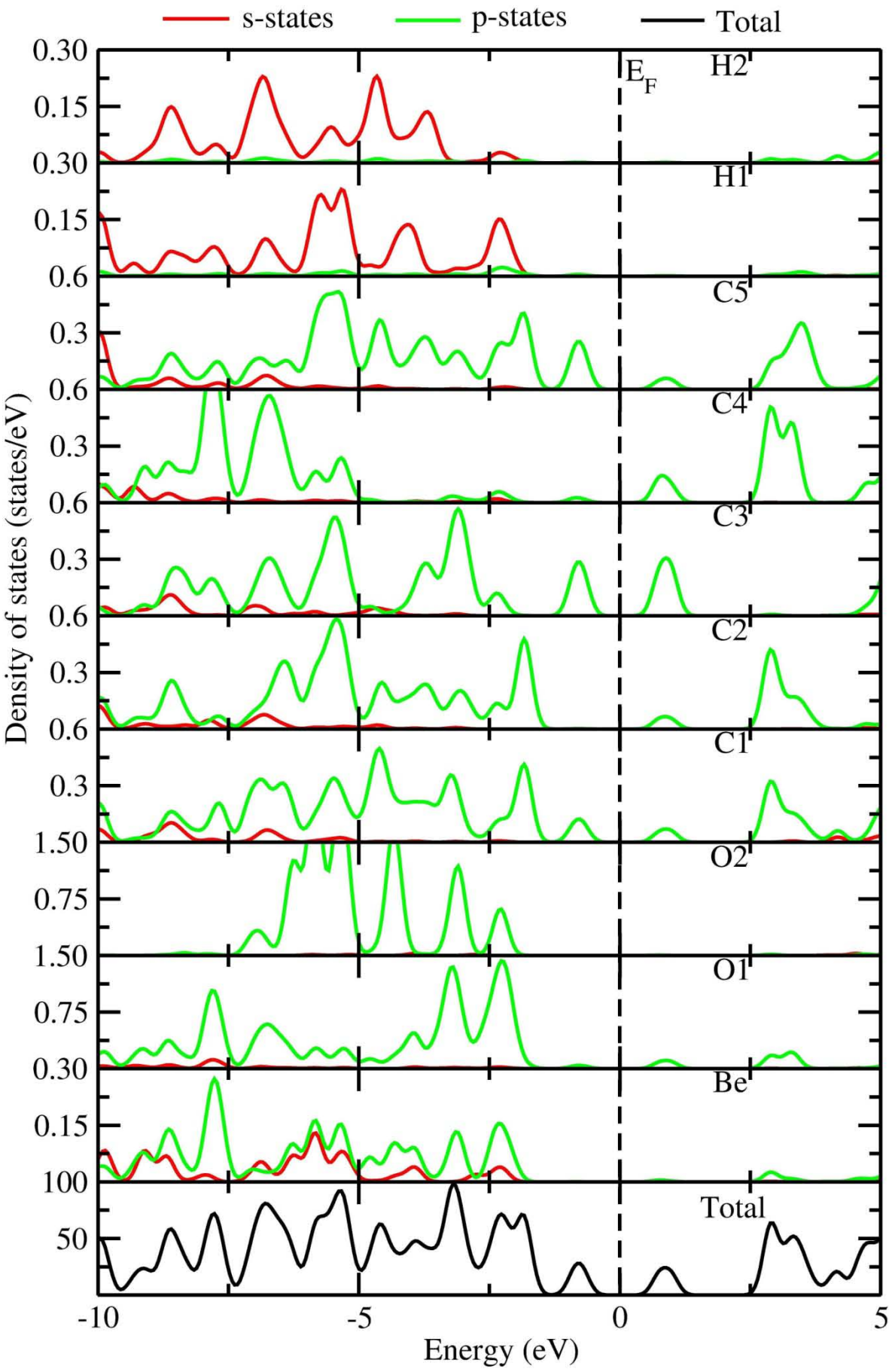

Figure S10. The calculated total density of states (TDOS) and partial density of states (PDOS) for Be-IRMOF-993 in the cubic *Fm-3m* symmetry (no. 225)

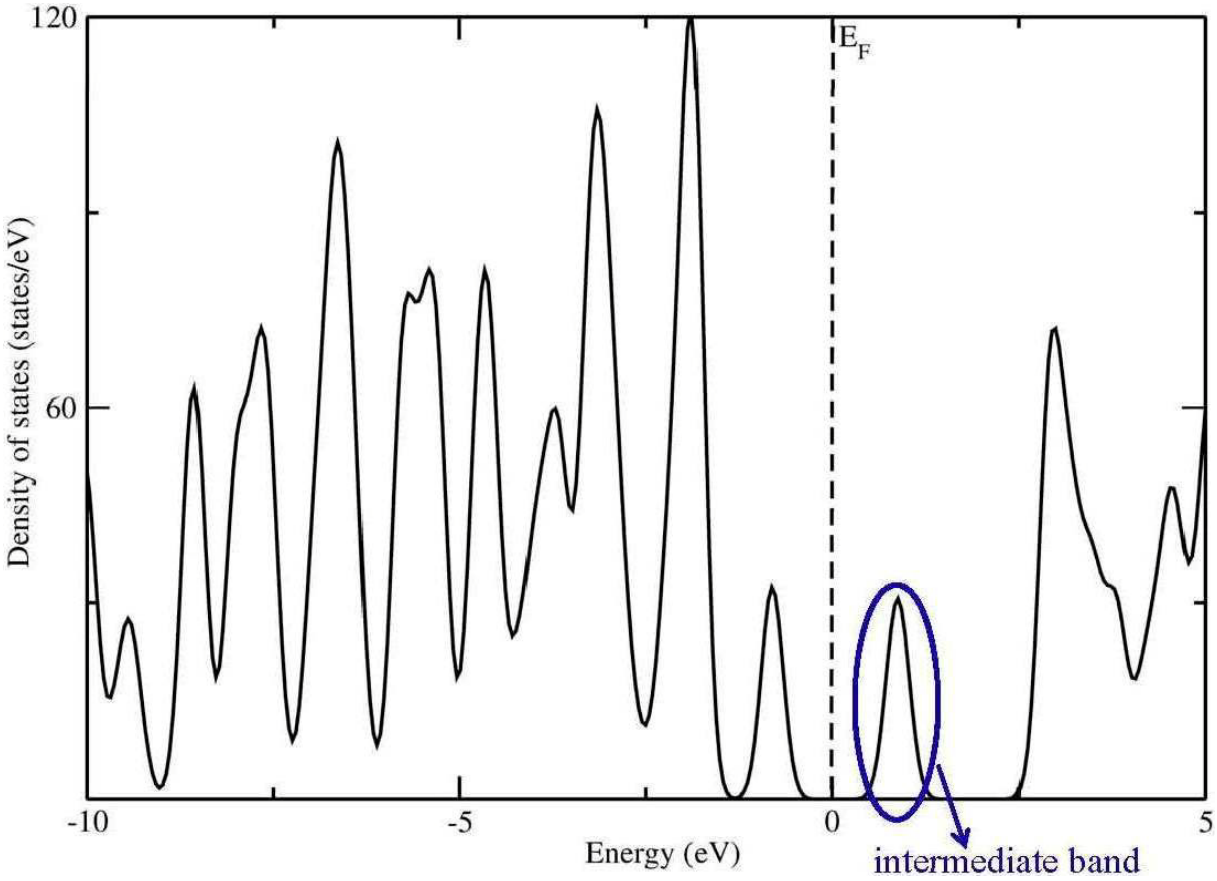

Figure S11. The calculated total density of states (TDOS) for Mg-IRMOF-993 in the cubic *Fm-3m* symmetry (no. 225)

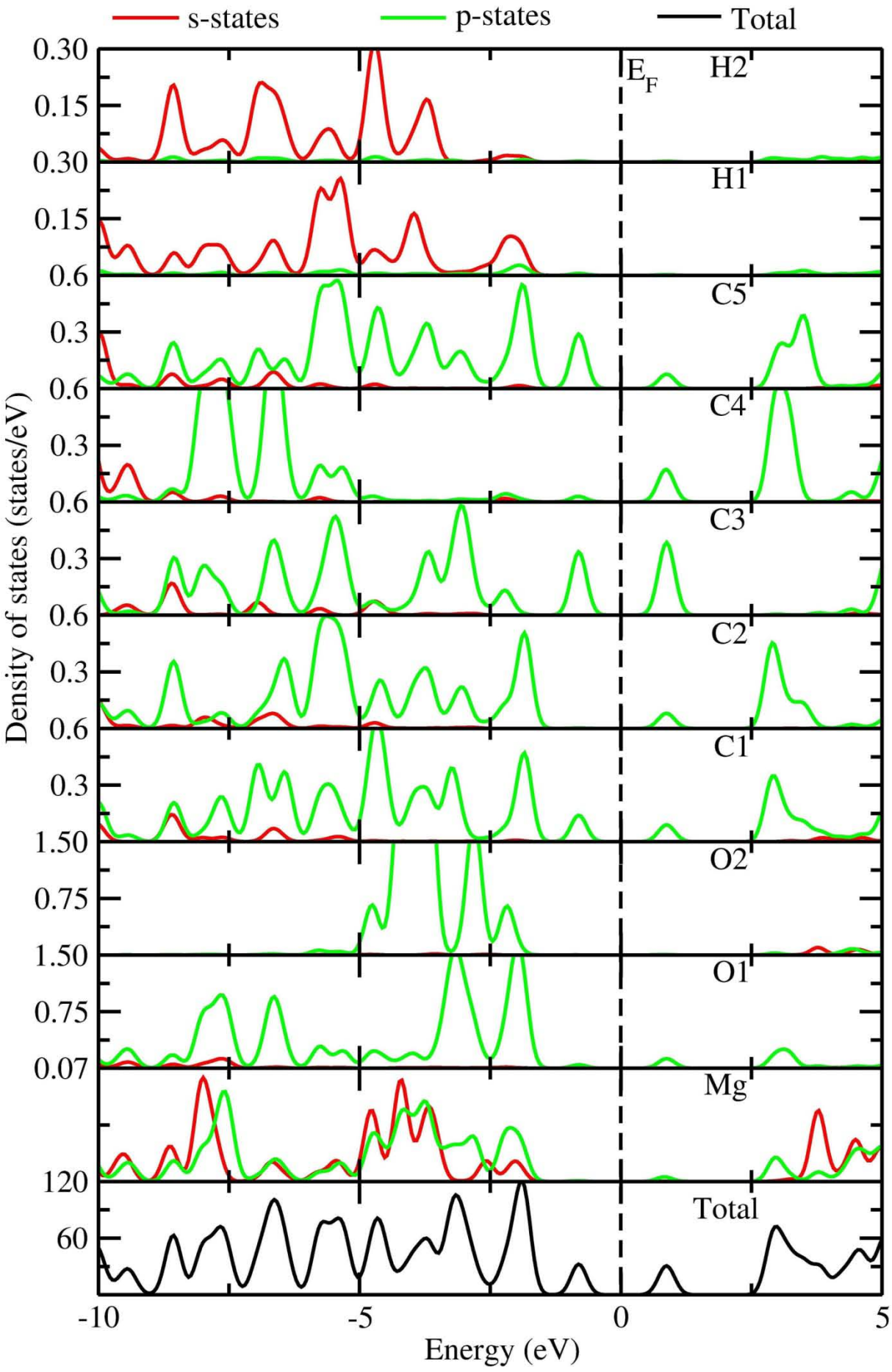

Figure S12. The calculated total density of states (TDOS) and partial density of states (PDOS) for Mg-IRMOF-993 in the cubic *Fm-3m* symmetry (no. 225)

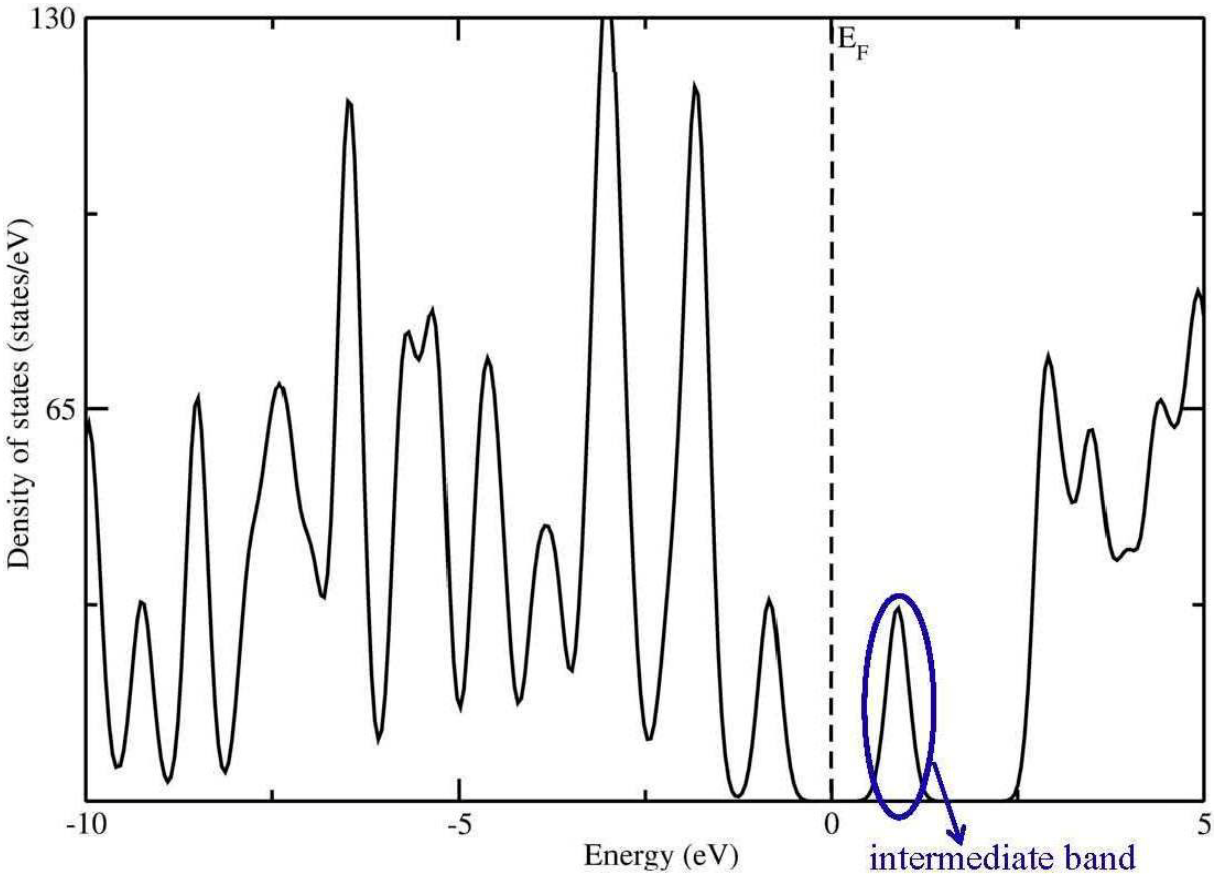

Figure S13. The calculated total density of states (TDOS) for Ca-IRMOF-993 in the cubic *Fm-3m* symmetry (no. 225)

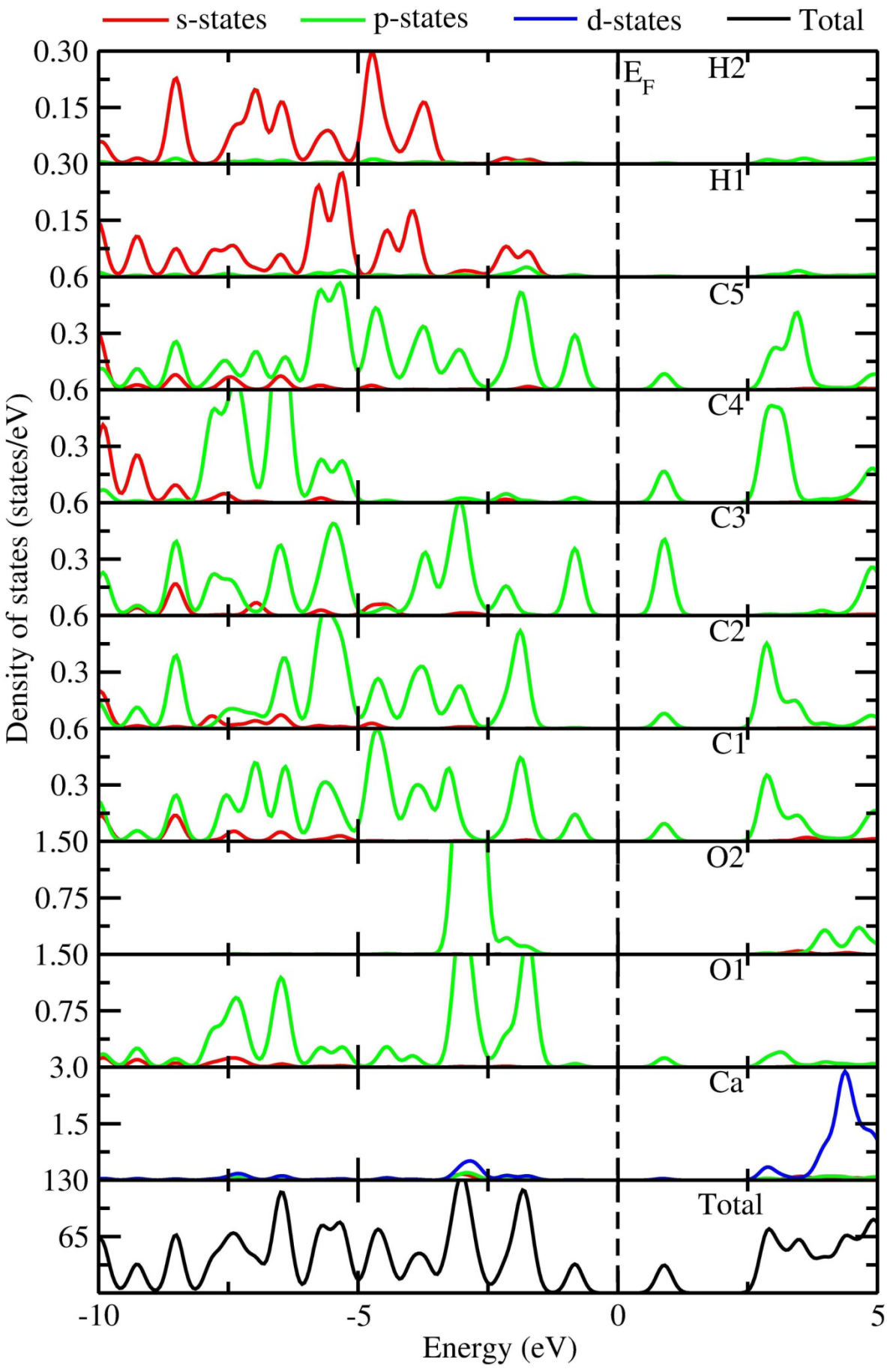

Figure S14. The calculated total density of states (TDOS) and partial density of states (PDOS) for Ca-IRMOF-993 in the cubic *Fm-3m* symmetry (no. 225)

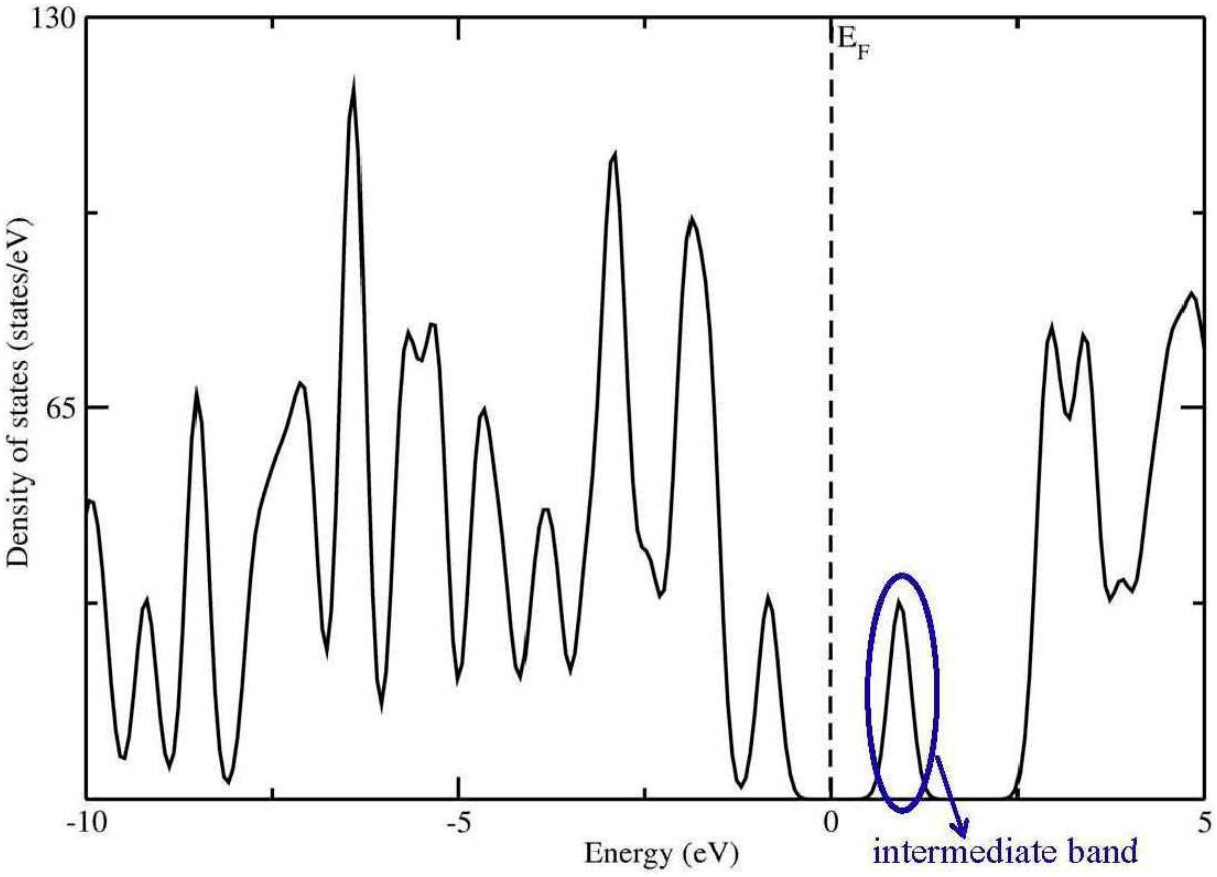

Figure S15. The calculated total density of states (TDOS) for Sr-IRMOF-993 in the cubic *Fm-3m* symmetry (no. 225)

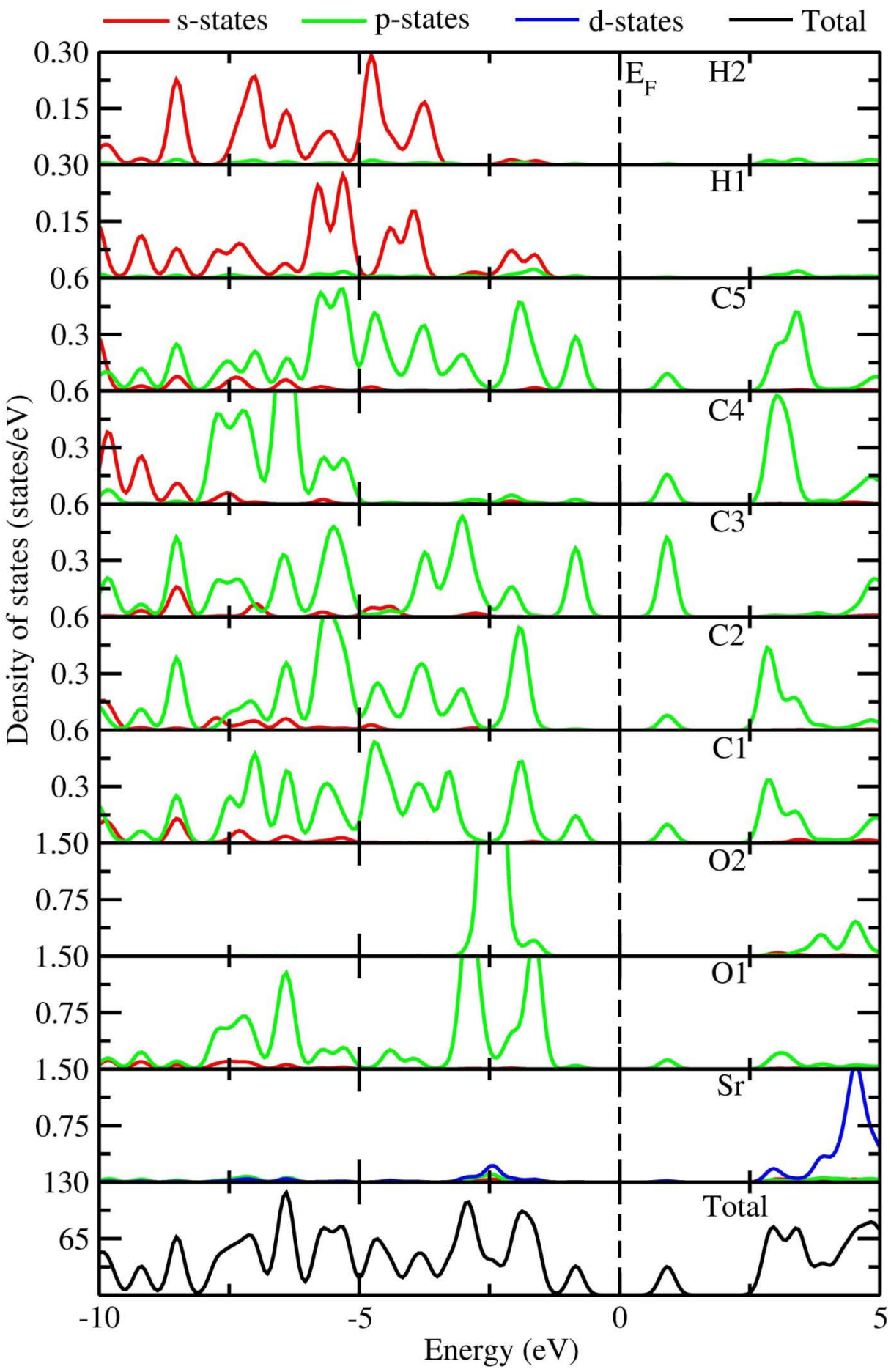

Figure S16. The calculated total density of states (TDOS) and partial density of states (PDOS) for Sr-IRMOF-993 in the cubic *Fm-3m* symmetry (no. 225)

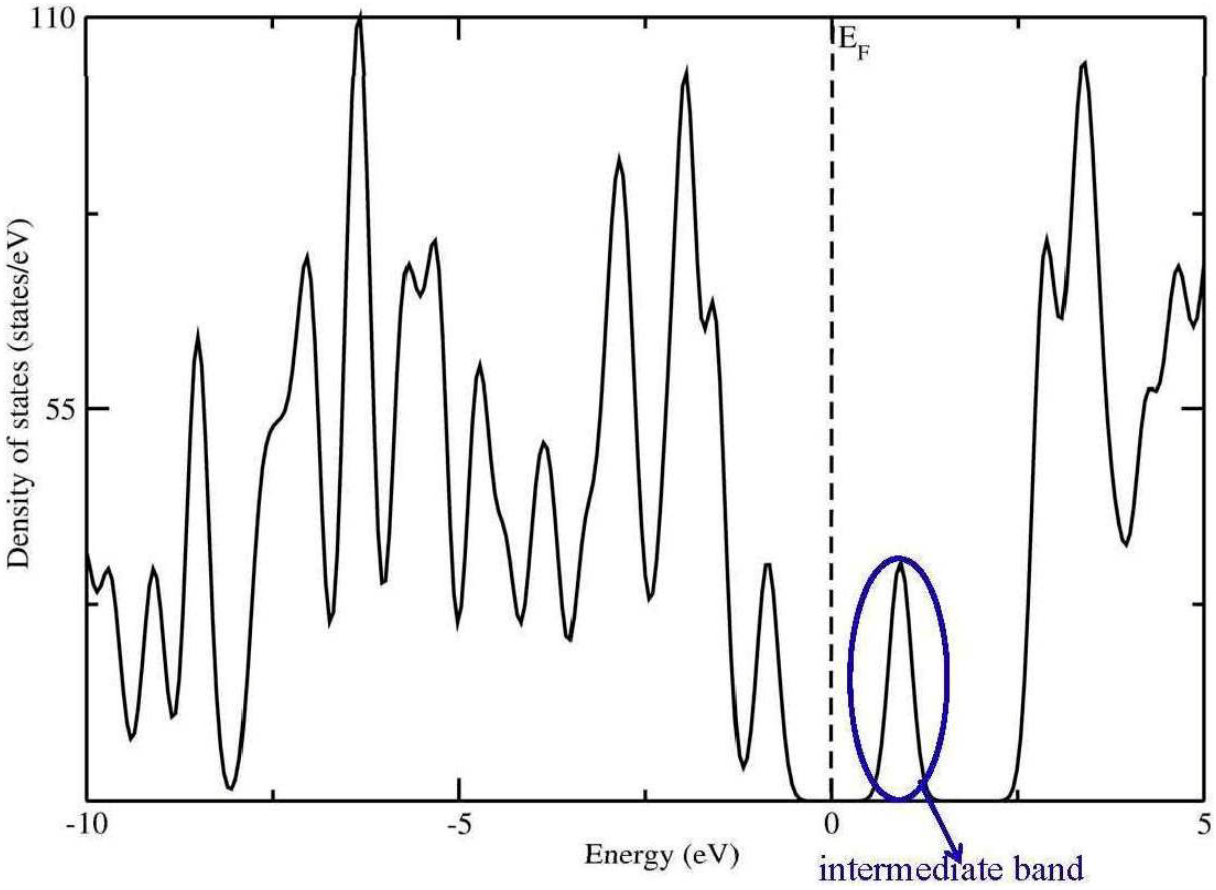

Figure S17. The calculated total density of states (TDOS) for Ba-IRMOF-993 in the cubic *Fm-3m* symmetry (no. 225)

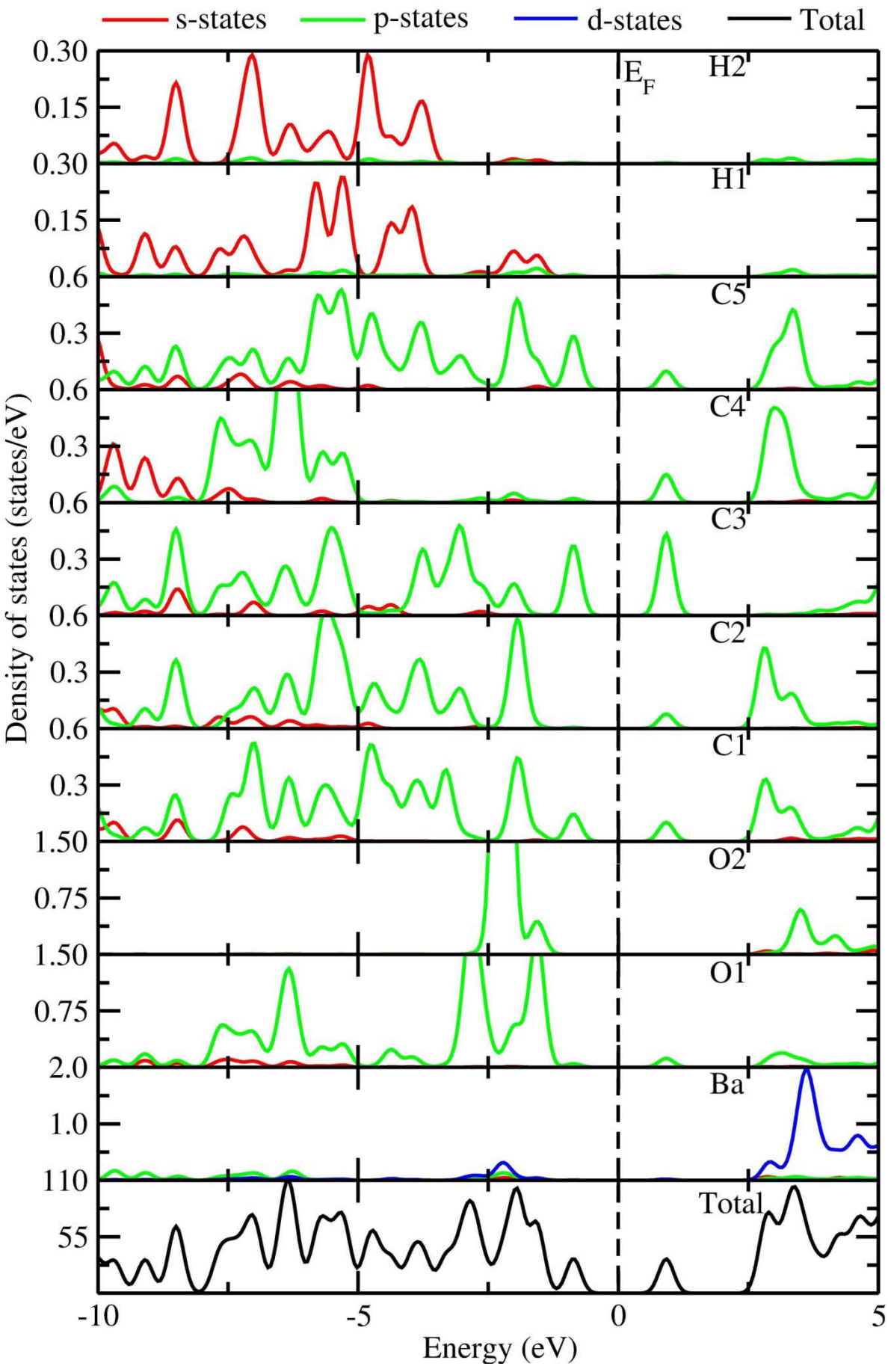

Figure S18. The calculated total density of states (TDOS) and partial density of states (PDOS) for Ba-IRMOF-993 in the cubic *Fm-3m* symmetry (no. 225)

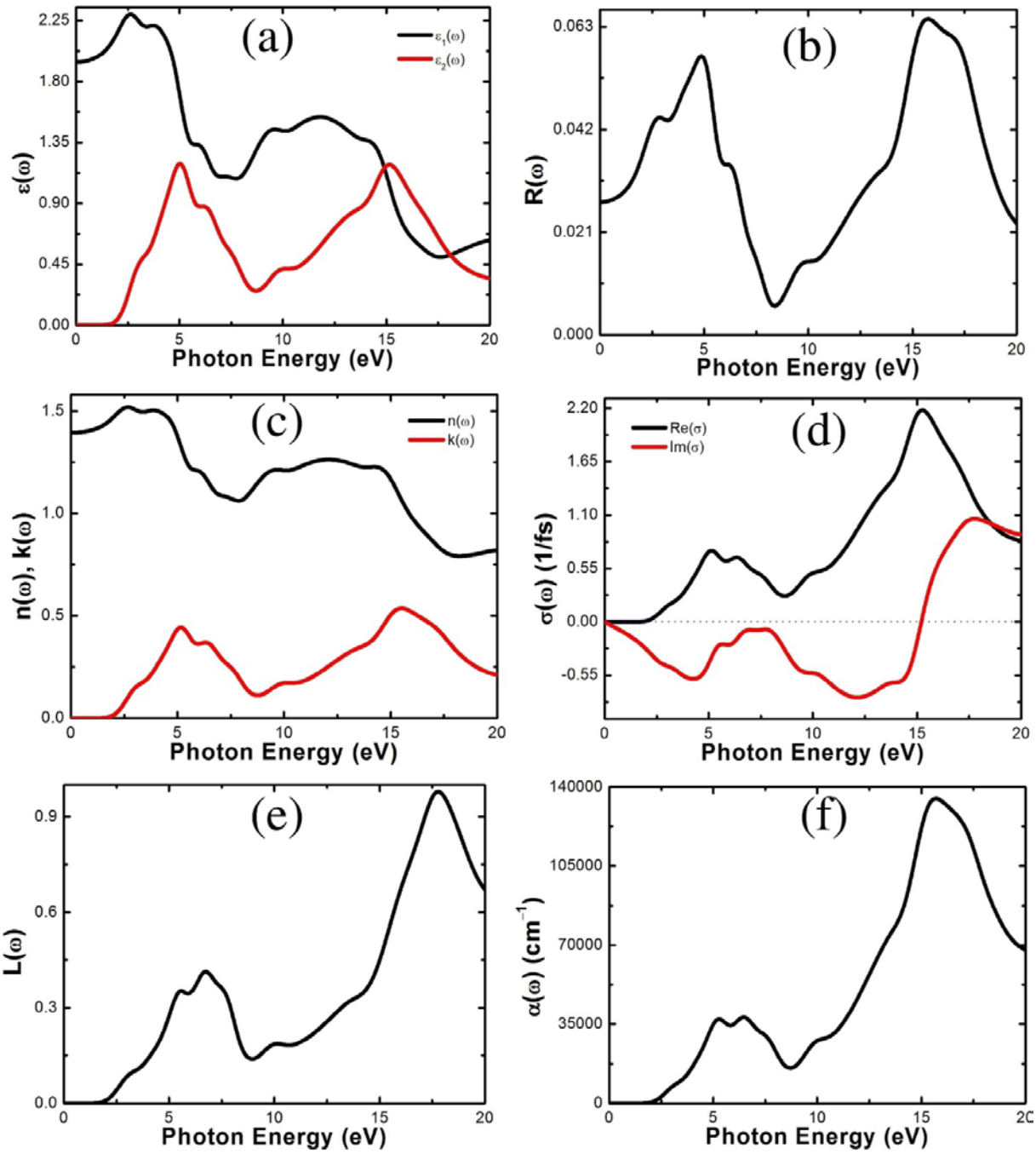

Figure S19. Calculated optical properties for Cd-IRMOF-993: (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), (f) absorption α(ω).

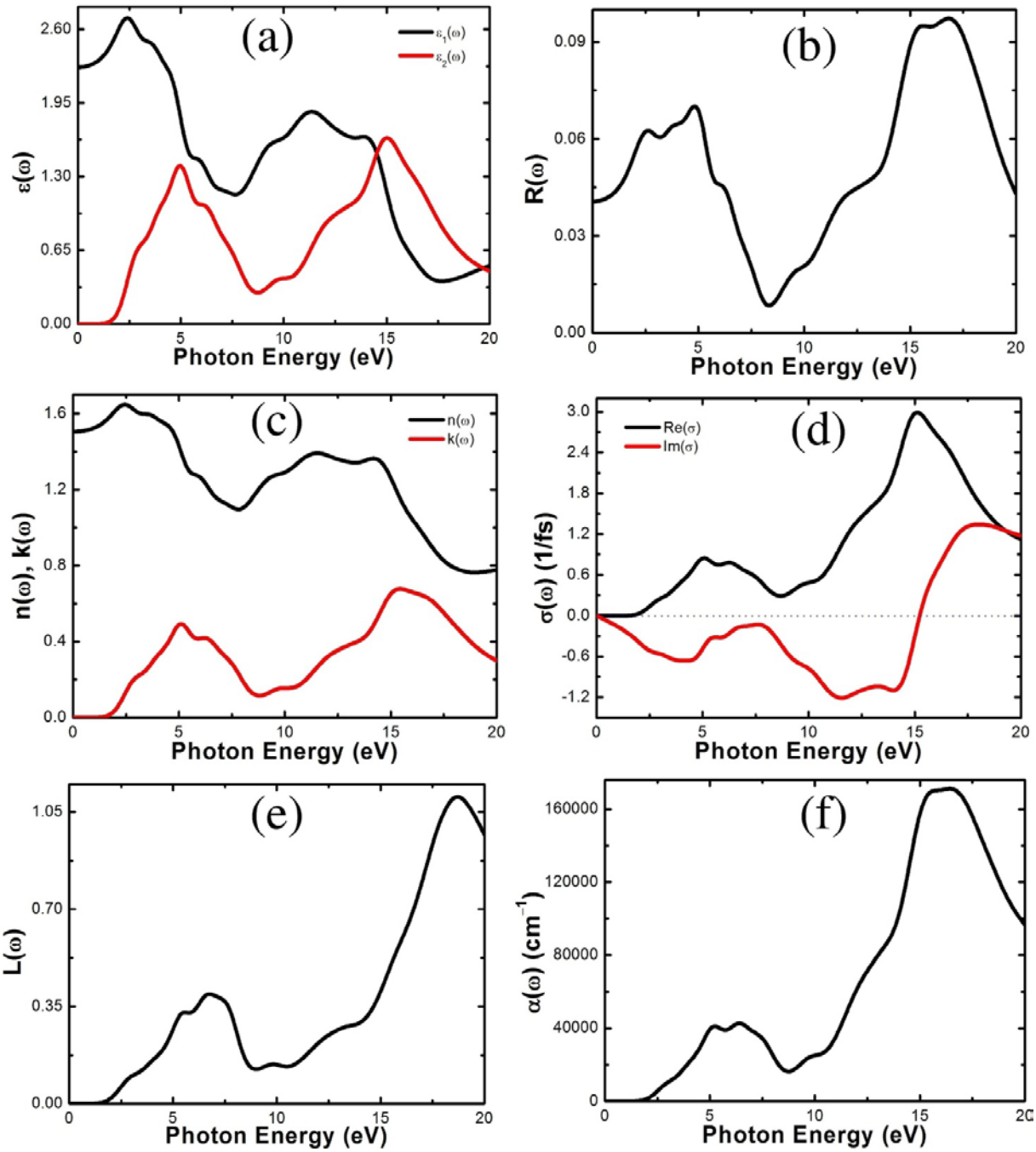

Figure S20. Calculated optical properties for Be-IRMOF-993: (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), (f) absorption α(ω).

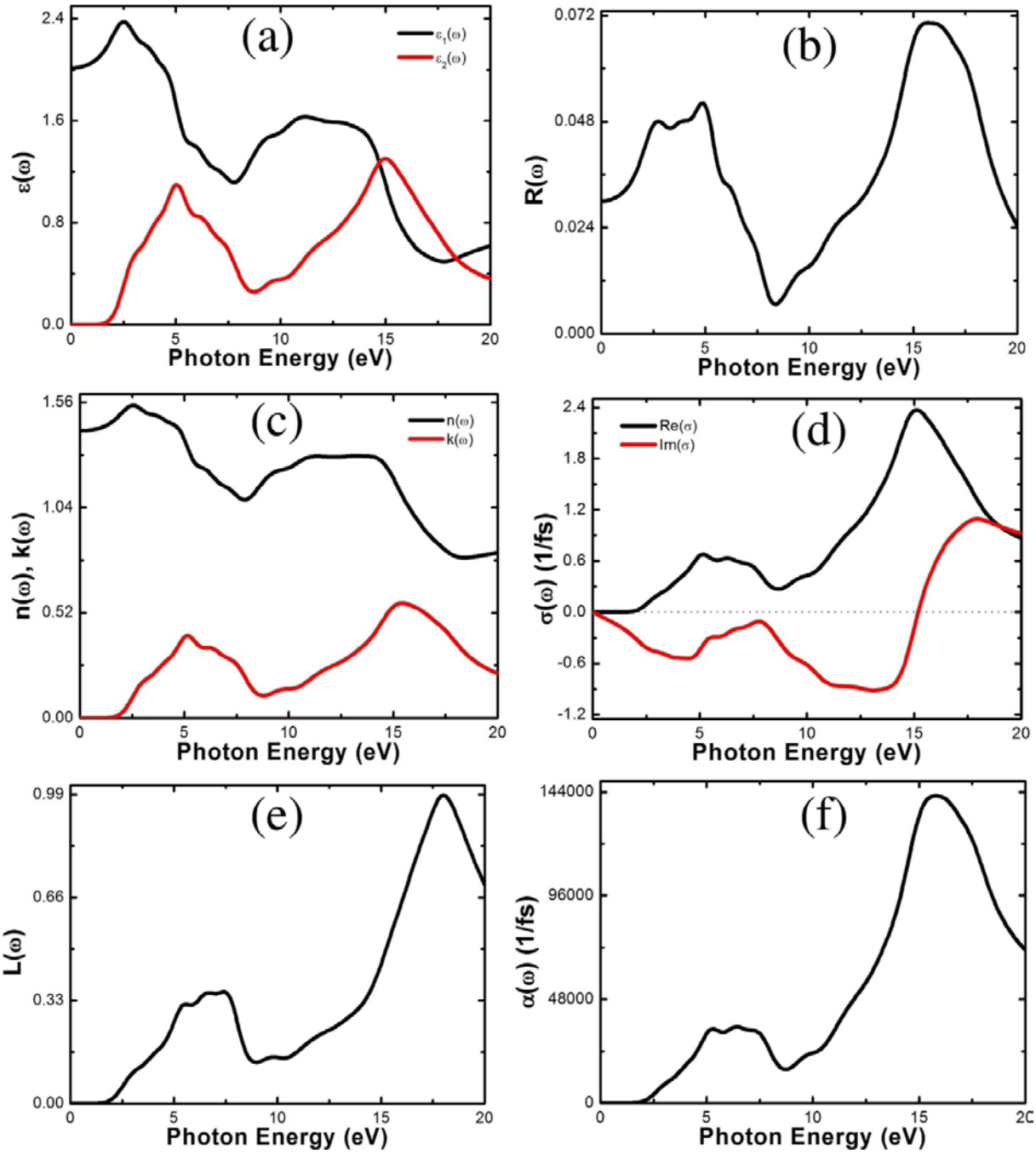

Figure S21. Calculated optical properties for Mg-IRMOF-993: (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), (f) absorption α(ω).

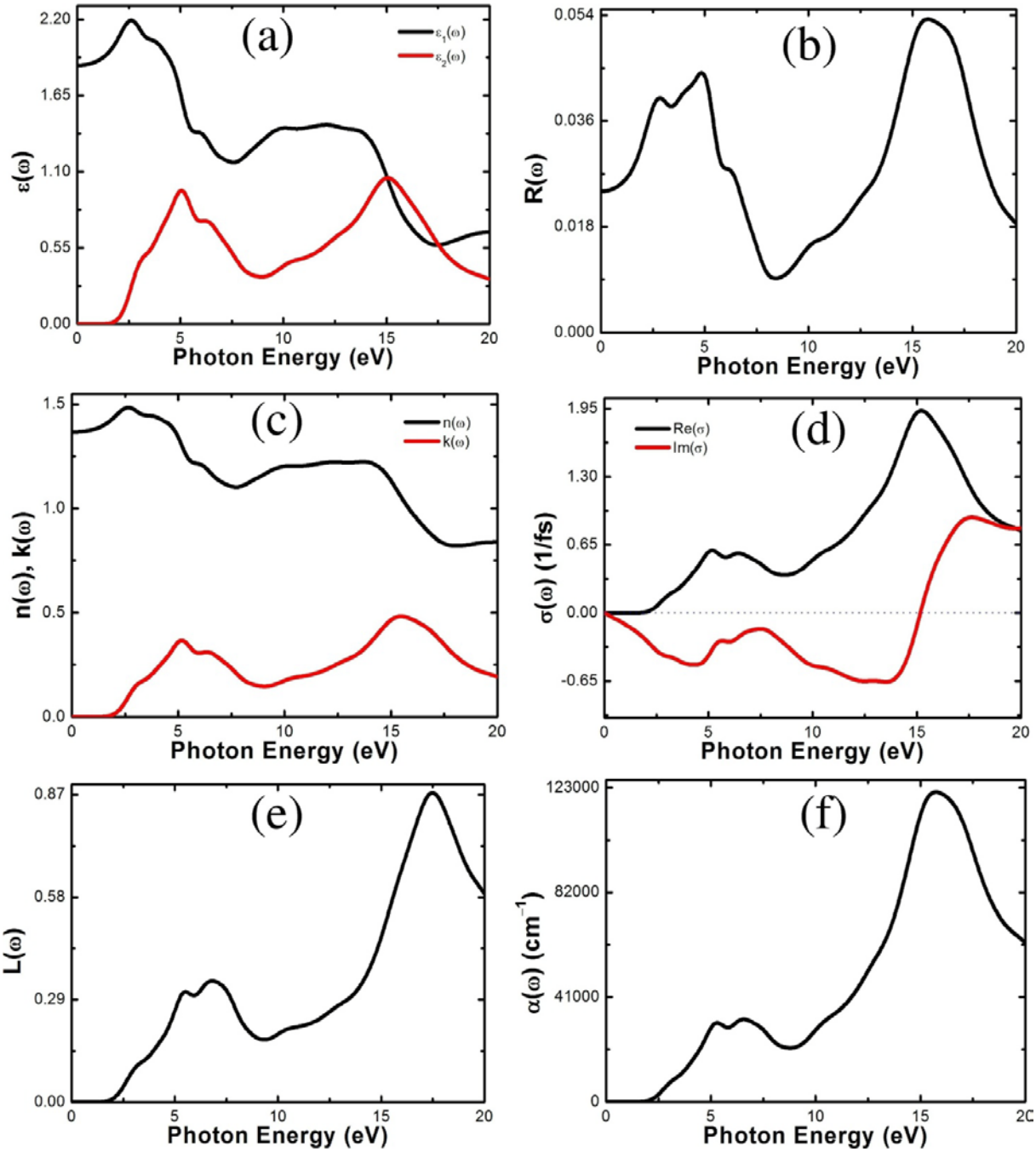

Figure S22. Calculated optical properties for Ca-IRMOF-993: (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), (f) absorption α(ω).

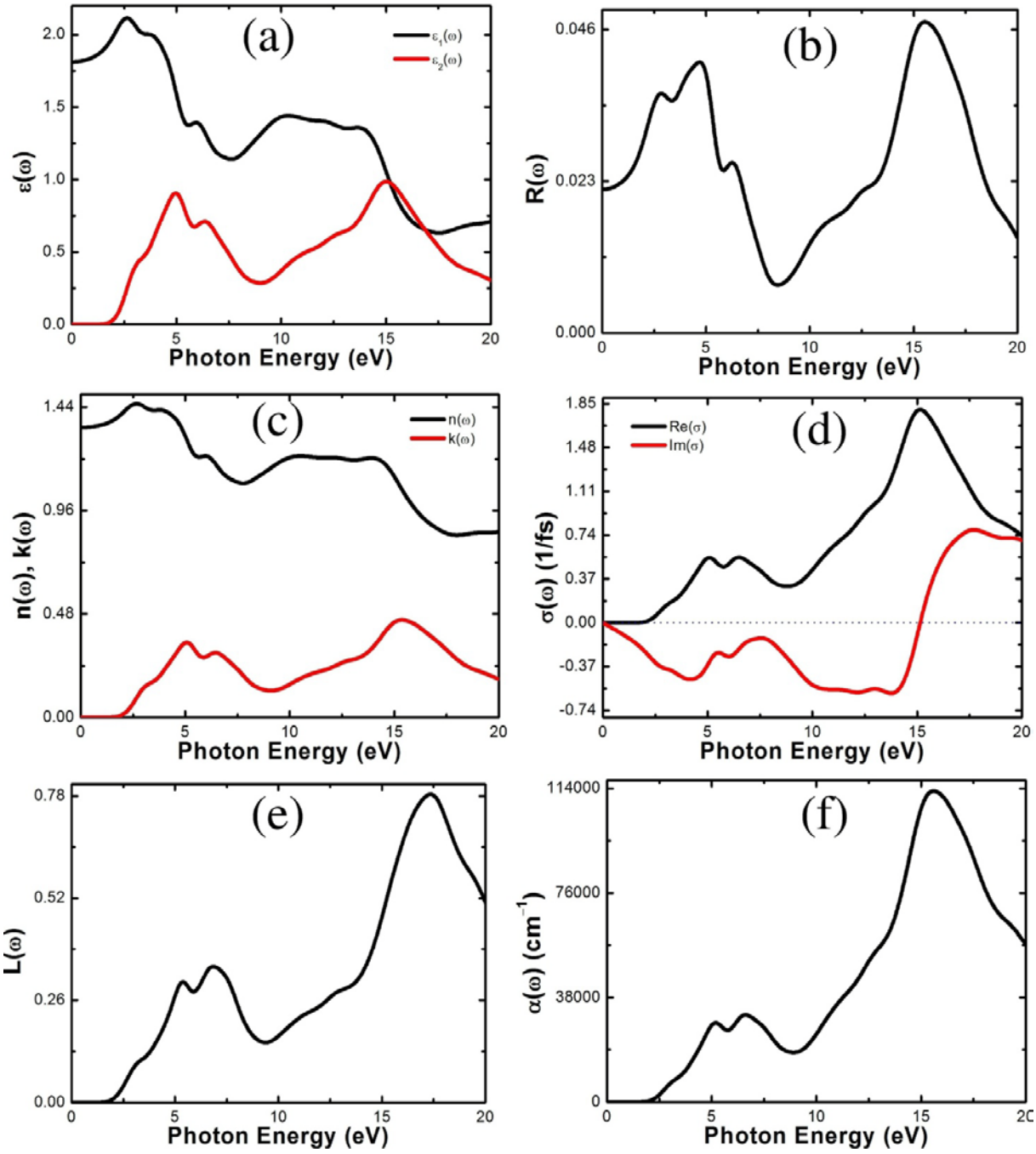

Figure S23. Calculated optical properties for Sr-IRMOF-993: (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), (f) absorption α(ω).

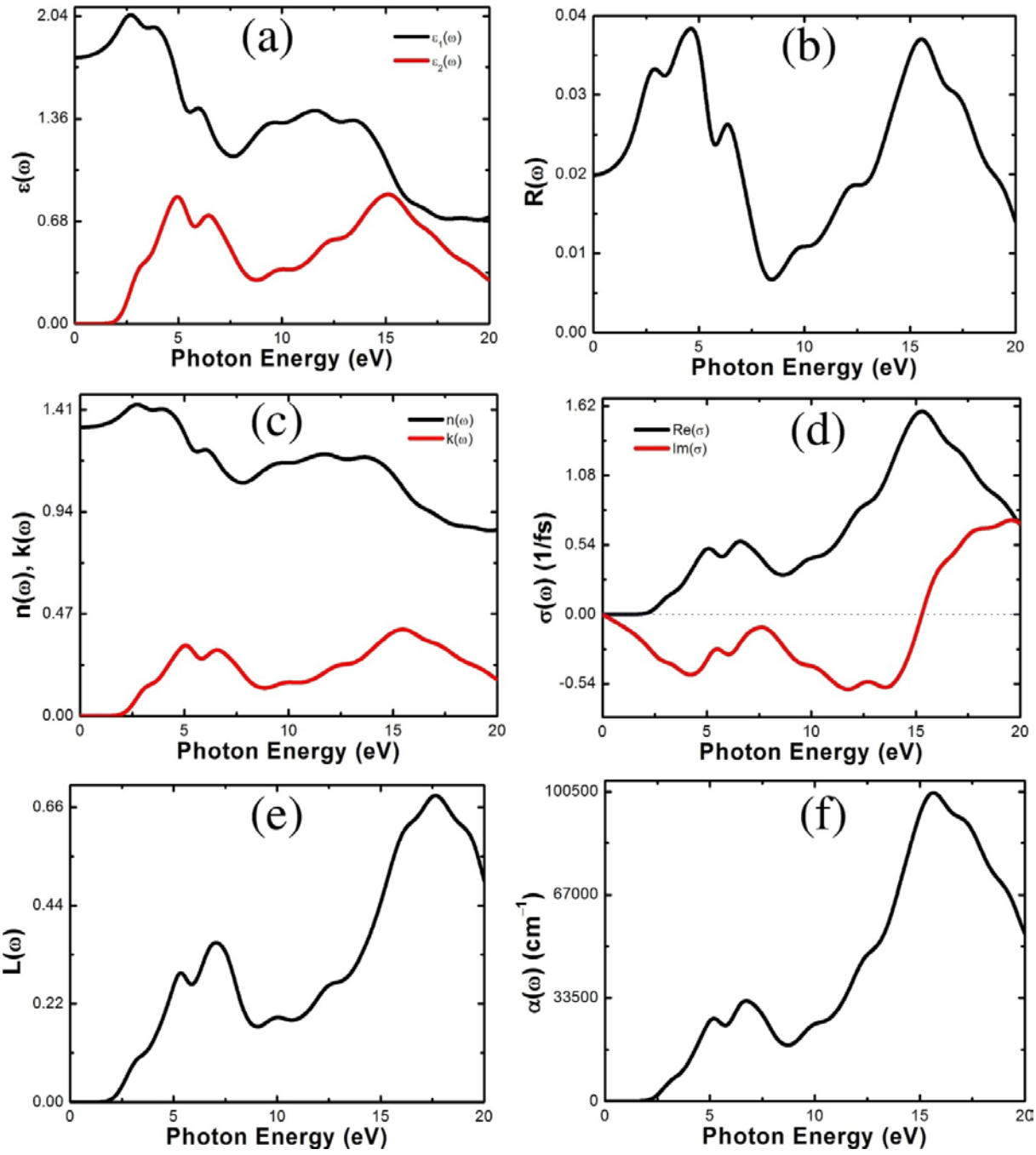

Figure S24. Calculated optical properties for Ba-IRMOF-993: (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), (f) absorption α(ω).

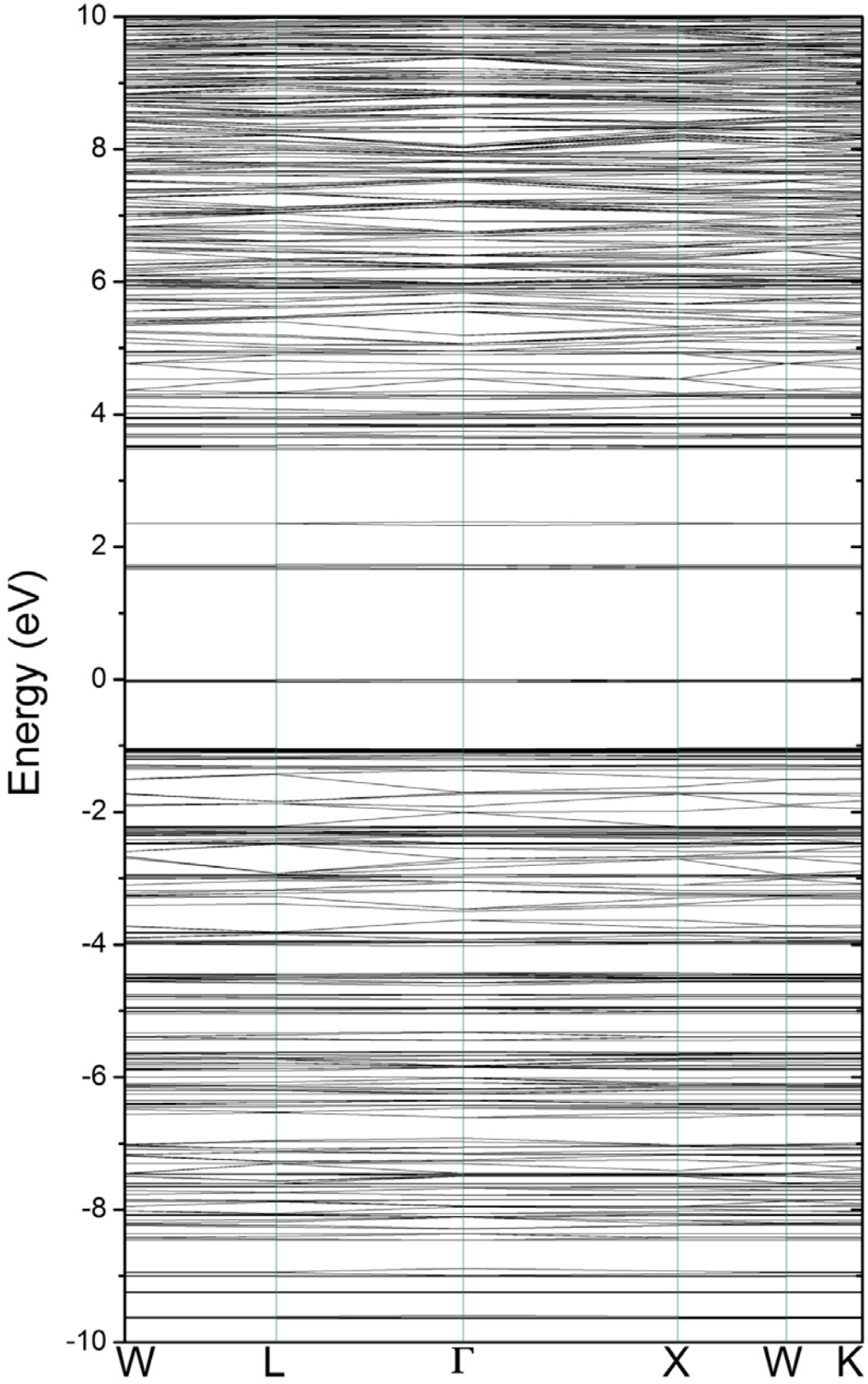

Figure S25. The electronic band structure of Cd-IRMOF-993. The Fermi level is set to zero and placed in the valence band maximum.

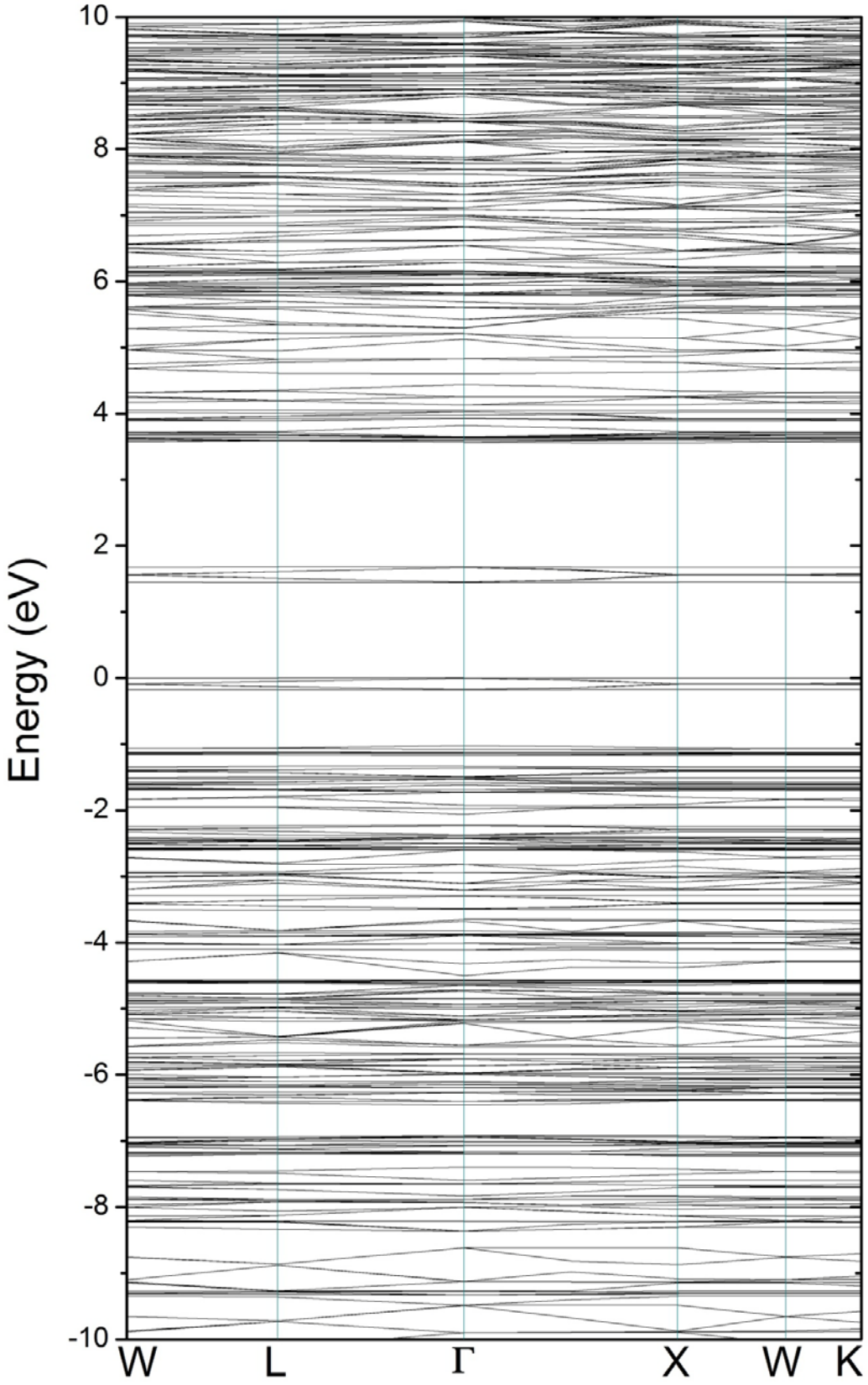

Figure S26. The electronic band structure of Be-IRMOF-993. The Fermi level is set to zero and placed in the valence band maximum.

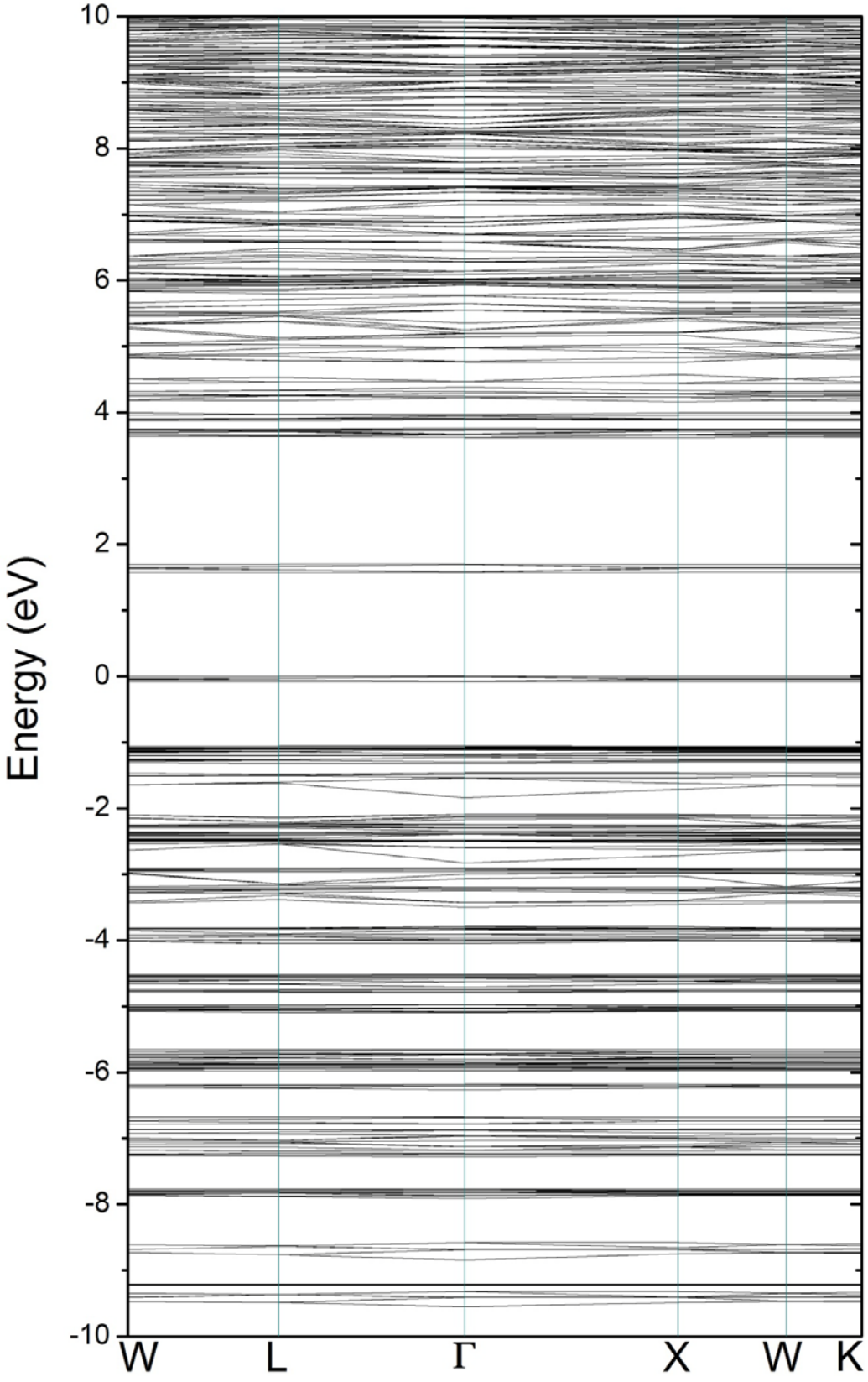

Figure S27. The electronic band structure of Mg-IRMOF-993. The Fermi level is set to zero and placed in the valence band maximum.

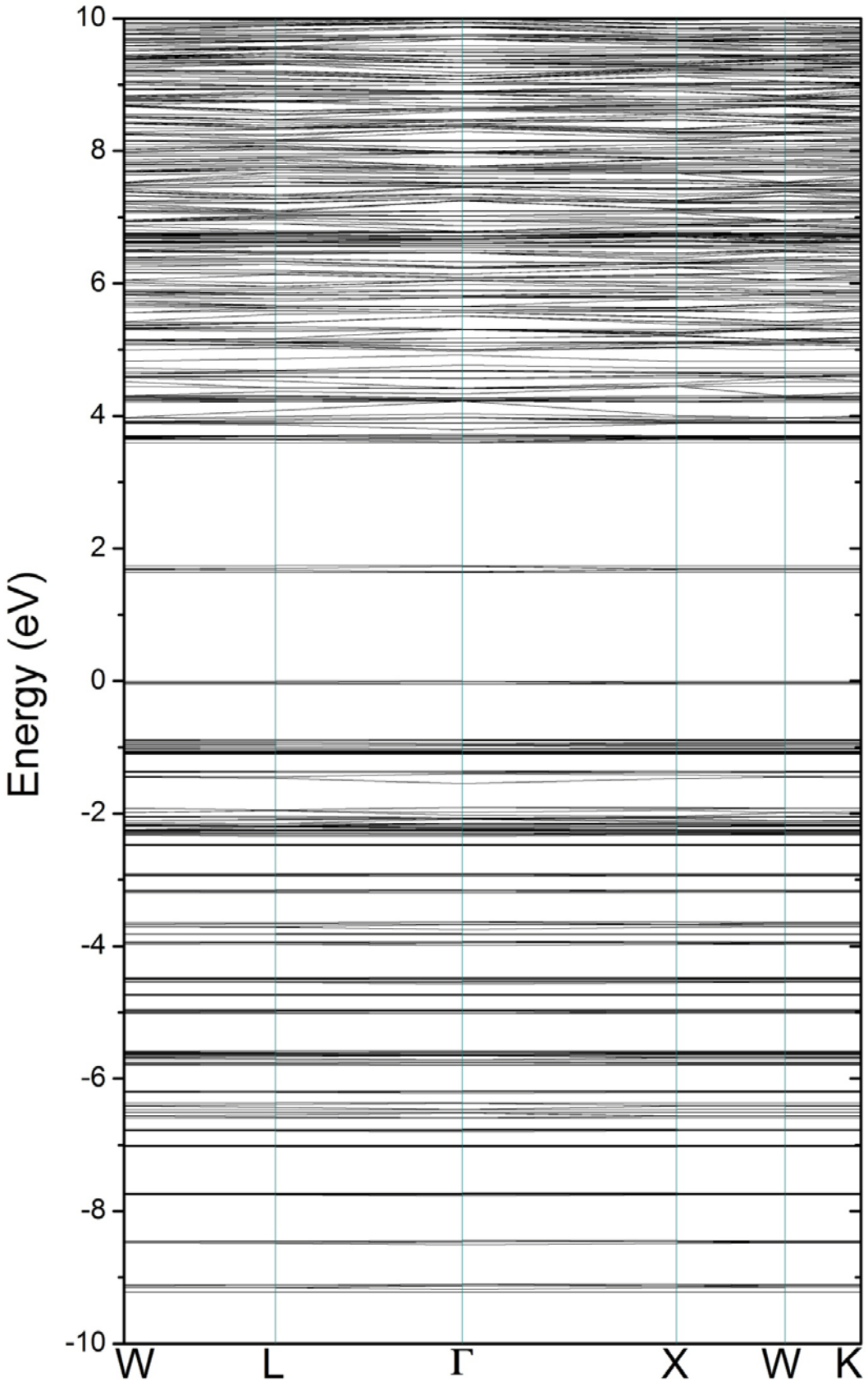

Figure S28. The electronic band structure of Ca-IRMOF-993. The Fermi level is set to zero and placed in the valence band maximum.

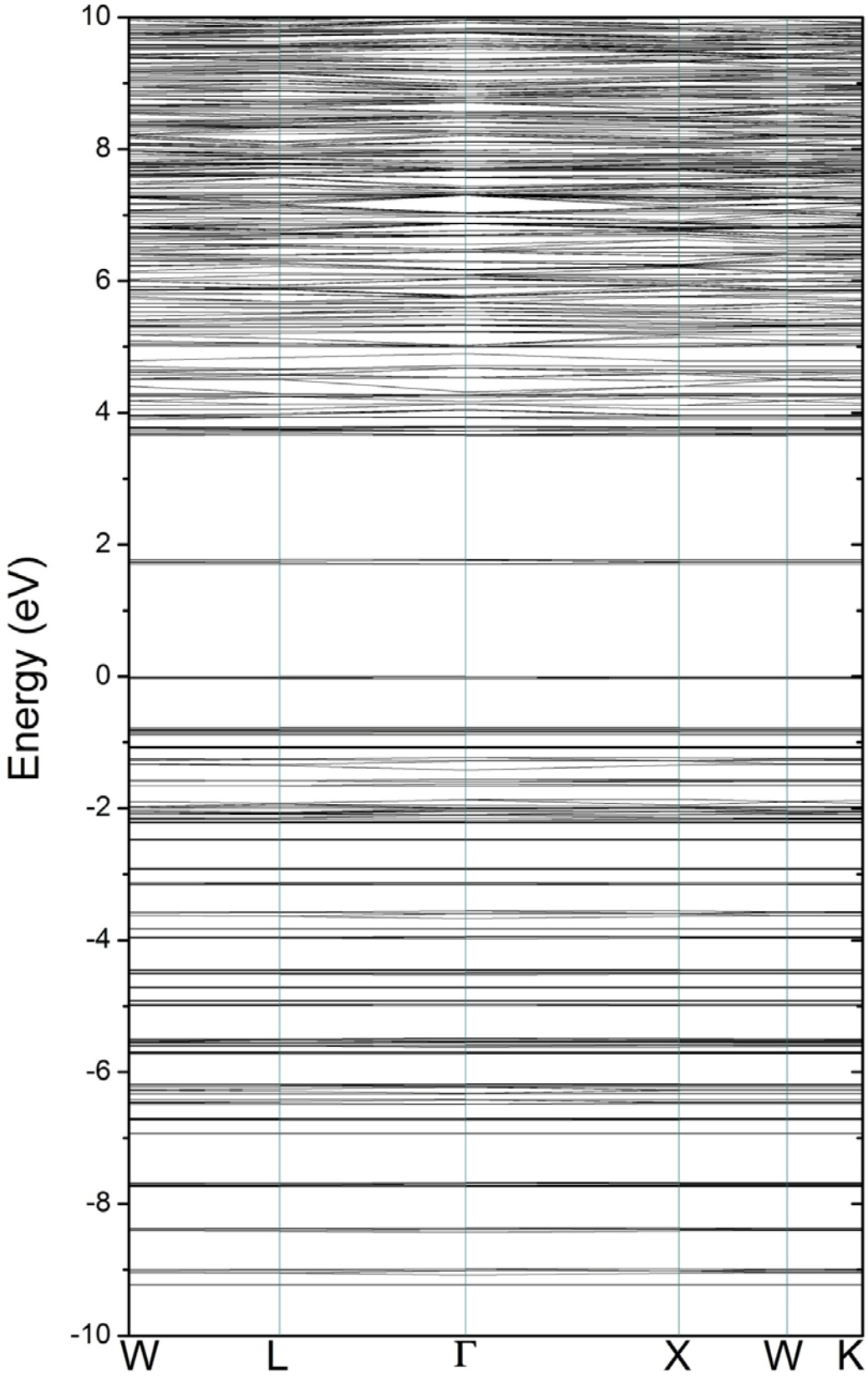

Figure S29. The electronic band structure of Sr-IRMOF-993. The Fermi level is set to zero and placed in the valence band maximum.

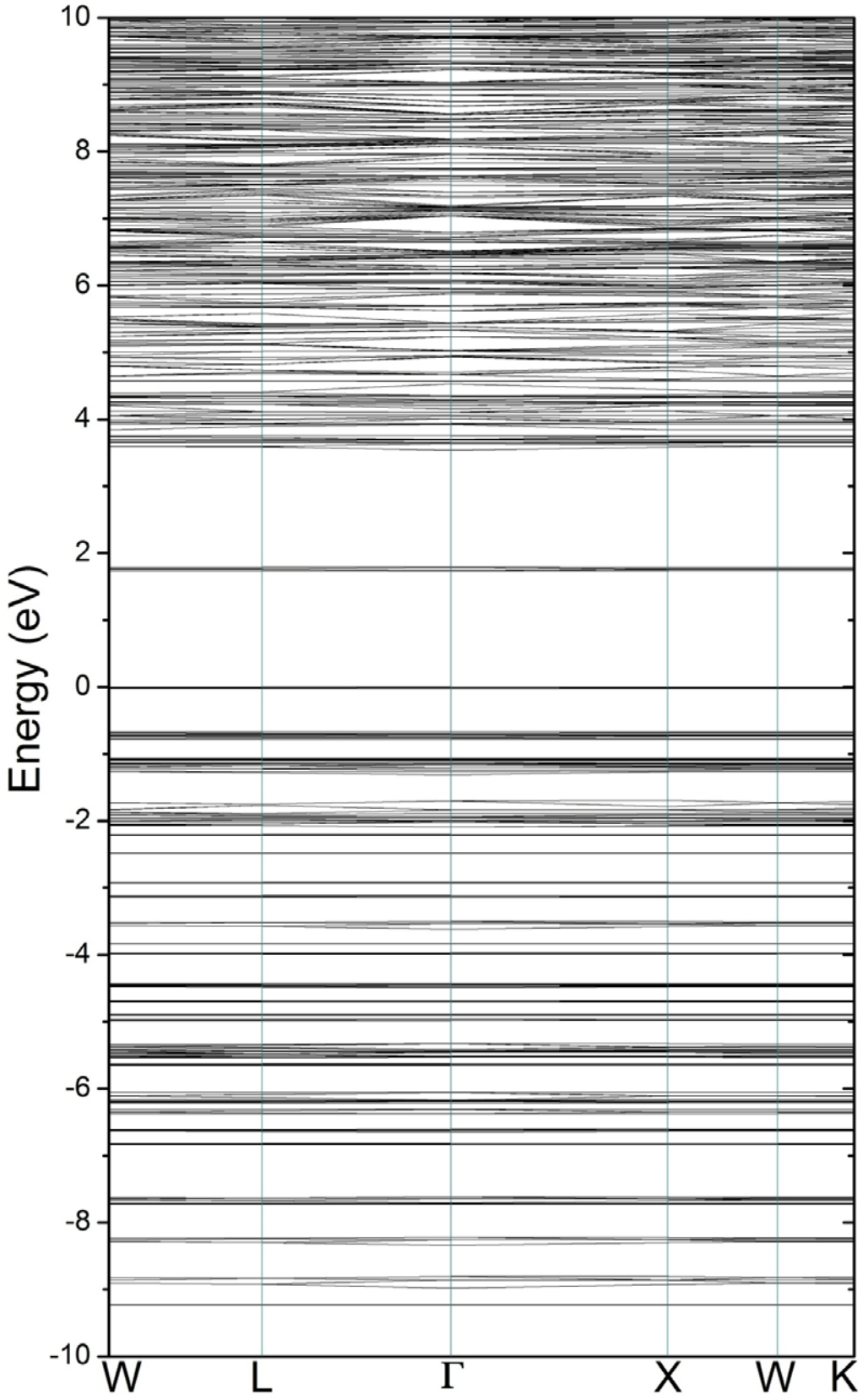

Figure S30. The electronic band structure of Ba-IRMOF-993. The Fermi level is set to zero and placed in the valence band maximum.

Table S1. Optimized bond distances (Å) and bond angles (°) for *M*-IRMOF-993 (*M* = Zn, Cd, Be, Mg, Ca, Sr, Ba) at their equilibrium volumes

M	C1-C1	C1-C5	C2-C2	C2-C3	C2-C5	C3-C4	C4-O1	*M*-O1	*M*-O2	C1-C5-C2	C2-C3-C2	O1-C4-O1	O1-*M*-O1	O1-*M*-O2
Zn	1.406	1.370	1.466	1.438	1.436	1.534	1.280	1.969	1.949	123.727	118.576	120.841	107.680	111.208
						<1.470>[a]	<1.312>[a]	<2.082>[a]	<2.060>[a]				<109>[a]	
Cd	1.406	1.370	1.467	1.437	1.436	1.541	1.278	2.200	2.161	123.872	118.448	121.496	110.804	108.103
Be	1.405	1.370	1.466	1.437	1.435	1.526	1.278	1.638	1.686	123.389	118.525	118.430	102.892	115.444
Mg	1.406	1.370	1.465	1.437	1.435	1.531	1.280	1.958	1.962	123.685	118.450	118.814	108.480	110.445
Ca	1.407	1.371	1.465	1.437	1.435	1.536	1.280	2.241	2.247	123.731	118.181	118.316	112.624	106.097
Sr	1.407	1.370	1.464	1.436	1.436	1.540	1.279	2.404	2.410	123.765	118.113	118.513	114.277	104.086
Ba	1.408	1.370	1.464	1.436	1.436	1.543	1.279	2.579	2.586	123.785	117.960	118.676	115.686	102.160

[a]The data in <> are from A. Kuc, A. Enyashin and G. Seifert, *J. Phys. Chem. B*, 2007, **111**, 8179-8186.

Table S2. The calculated Mulliken effective charge (MEC), bond overlap populations (BOP) and Bader charges (BC; given in terms of *e*) for Zn-IRMOF-993 and its analogues *M*-IRMOF-993 (*M* = Cd, Be, Mg, Ca, Sr, Ba). Note that the atomic labels of atoms are numbered according to Figure 1 in the manuscript.

Materials	Atomic site	MEC (*e*)	BOP	BC (*e*)
Zn-IRMOF-993	Zn	+1.40	0.27-0.30 (Zn-O)	+1.3937
	O1	-0.64	0.30 (O1-Zn)	-1.7678
	O2	-1.02	0.27 (O2-Zn)	-1.3402
	C1	-0.28	0.98 (C1-C1)	-0.0603
			1.16 (C1-C5)	
	C2	-0.01	1.02 (C2-C2)	+0.0063
			1.09 (C2-C3)	
			1.04 (C2-C5)	
	C3	-0.05	0.86 (C3-C4)	-0.0232
	C4	+0.61	0.90 (C4-O1)	+2.6838
	C5	-0.24		+0.1281
	H1	+0.25	0.94 (H1-C5)	-0.0031
	H2	+0.26	0.89 (H2-C1)	+0.0138
Cd-IRMOF-993	Cd	+1.37	0.22-0.24 (Cd-O)	+1.3286
	O1	-0.64	0.24 (O1-Cd)	-1.2091
	O2	-1.00	0.22 (O2-Cd)	-1.7695
	C1	-0.28	0.97 (C1-C1)	-0.0739
			1.16 (C1-C5)	
	C2	-0.01	1.02 (C2-C2)	+0.0234
			1.09 (C2-C3)	
			1.04 (C2-C5)	
	C3	-0.05	0.85 (C3-C4)	-0.0678
	C4	+0.62	0.90 (C4-O1)	+2.7390
	C5	-0.24		+0.1167
	H1	+0.25	0.94 (H1-C5)	-0.0044
	H2	+0.27	0.88 (H2-C1)	+0.0301
Be-IRMOF-993	Be	+1.14	0.37-0.39 (Be-O)	+2.0000
	O1	-0.62	0.39 (O1-Be)	-2.0189
	O2	-0.93	0.37 (O2-Be)	-1.9016
	C1	-0.25	0.99 (C1-C1)	-0.0422
			1.16 (C1-C5)	
	C2	0.00	1.02 (C2-C2)	-0.0026
			1.08 (C2-C3)	
			1.03 (C2-C5)	
	C3	-0.04	0.87 (C3-C4)	-0.0289
	C4	+0.60	0.91 (C4-O1)	+2.6534
	C5	-0.24		+0.1293
	H1	+0.28	0.92 (H1-C5)	+0.0168
	H2	+0.26	0.90 (H2-C1)	-0.0102
Mg-IRMOF-993	Mg	+1.69	0.24-0.25 (Mg-O)	+2.0000
	O1	-0.71	0.25 (O1-Mg)	-2.0045
	O2	-1.27	0.24 (O2-Mg)	-1.9040
	C1	-0.28	0.98 (C1-C1)	-0.0733
			1.16 (C1-C5)	
	C2	-0.01	1.02 (C2-C2)	-0.0003

			1.09 (C2-C3)	
			1.04 (C2-C5)	
	C3	-0.05	0.86 (C3-C4)	-0.0336
	C4	+0.60	0.91 (C4-O1)	+2.6731
	C5	-0.24		+0.1361
	H1	+0.24	0.95 (H1-C5)	+0.0096
	H2	+0.27	0.88 (H2-C1)	+0.0125
Ca-IRMOF-993	Ca	+1.37	0.15-0.18 (Ca-O)	+1.6213
	O1	-0.69	0.15 (O1-Ca)	-1.4988
	O2	-1.11	0.18 (O2-Ca)	-1.8320
	C1	-0.29	0.97 (C1-C1)	-0.0544
			1.15 (C1-C5)	
	C2	0.00	1.02 (C2-C2)	+0.0076
			1.08 (C2-C3)	
			1.03 (C2-C5)	
	C3	-0.05	0.84 (C3-C4)	-0.0251
	C4	+0.65	0.88 (C4-O1)	+2.7063
	C5	-0.26		+0.0993
	H1	+0.28	0.89 (H1-C5)	+0.0063
	H2	+0.29	0.87 (H2-C1)	+0.0170
Sr-IRMOF-993	Sr	+1.42	0.14-0.19 (Sr-O)	+1.6225
	O1	-0.69	0.14 (O1-Sr)	-1.4642
	O2	-1.09	0.19 (O2-Sr)	-1.8278
	C1	-0.29	0.97 (C1-C1)	-0.0171
			1.16 (C1-C5)	
	C2	-0.01	1.02 (C2-C2)	+0.0271
			1.09 (C2-C3)	
			1.03 (C2-C5)	
	C3	-0.05	0.84 (C3-C4)	-0.0622
	C4	+0.63	0.89 (C4-O1)	+2.7285
	C5	-0.25		+0.0784
	H1	+0.27	0.91 (H1-C5)	-0.0084
	H2	+0.29	0.87 (H2-C1)	-0.0042
Ba-IRMOF-993	Ba	+1.41	0.12-0.17 (Ba-O)	+1.6098
	O1	-0.68	0.12 (O1-Ba)	-1.4170
	O2	-1.05	0.17 (O2-Ba)	-1.8244
	C1	-0.29	0.97 (C1-C1)	+0.0052
			1.16 (C1-C5)	
	C2	-0.01	1.02 (C2-C2)	-0.0110
			1.09 (C2-C3)	
			1.03 (C2-C5)	
	C3	-0.05	0.83 (C3-C4)	-0.0026
	C4	+0.64	0.88 (C4-O1)	+2.6988
	C5	-0.25		+0.0588
	H1	+0.27	0.90 (H1-C5)	+0.0010
	H2	+0.29	0.86 (H2-C1)	+0.0038