Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

--Supporting Information--

Optical Absorption Properties of Metal-Organic Frameworks: Solid State versus Molecular Perspective

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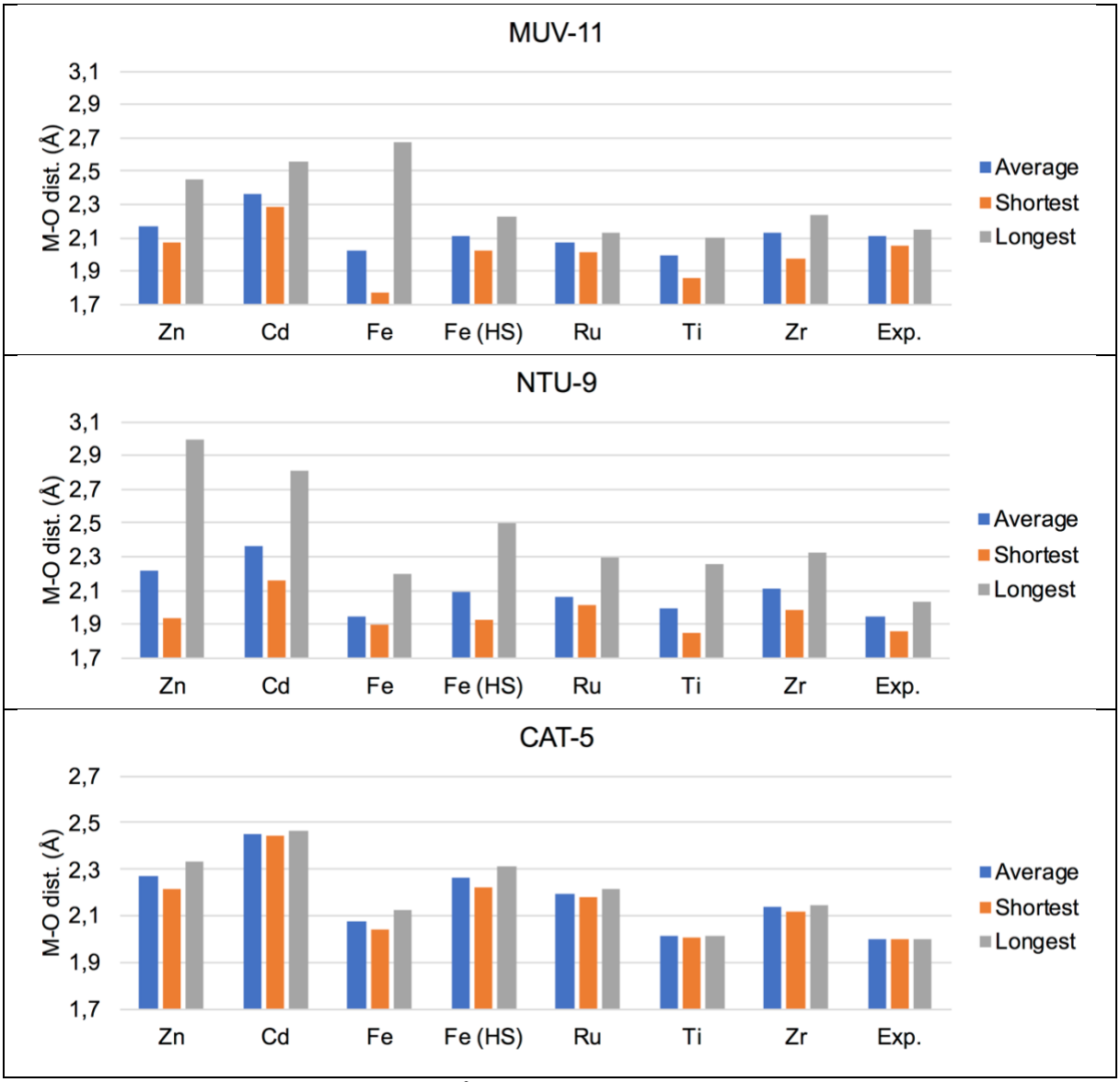


Figure S1. Metal-oxygen distances in Å of the optimized MOF crystals, MUV-11, NTU-9 and CAT-5 with the 6 metals considered Zn(II), Cd(II), Fe(II), Ru(II), Ti(IV) and Zr(IV). The values of the experimentally reported structure with Ti(IV) are also given. The blue, orange and grey values correspond to the average, shortest and largest M-O distances. Raw data in Table S2.

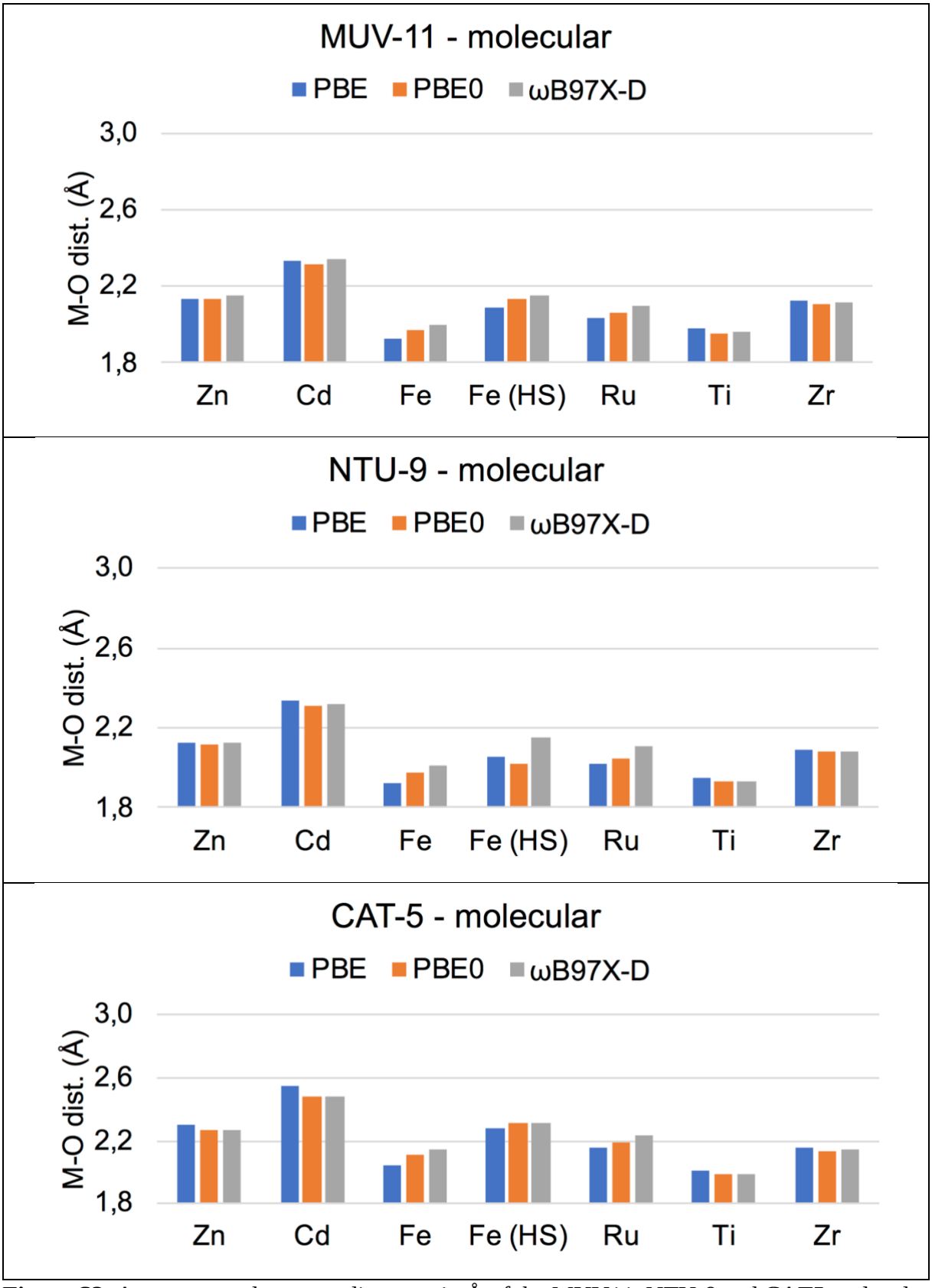


Figure S2. Average metal-oxygen distances in Å of the MUV11, NTU-9 and CAT5 molecular compounds with Zn(II), Cd(II), Fe(II), Ru(II), Ti(IV) and Zr(IV) transition metals optimized at the PBE and PBE0 level with D3BJ, and with ωB97X-D functional. Raw data in Table S3.

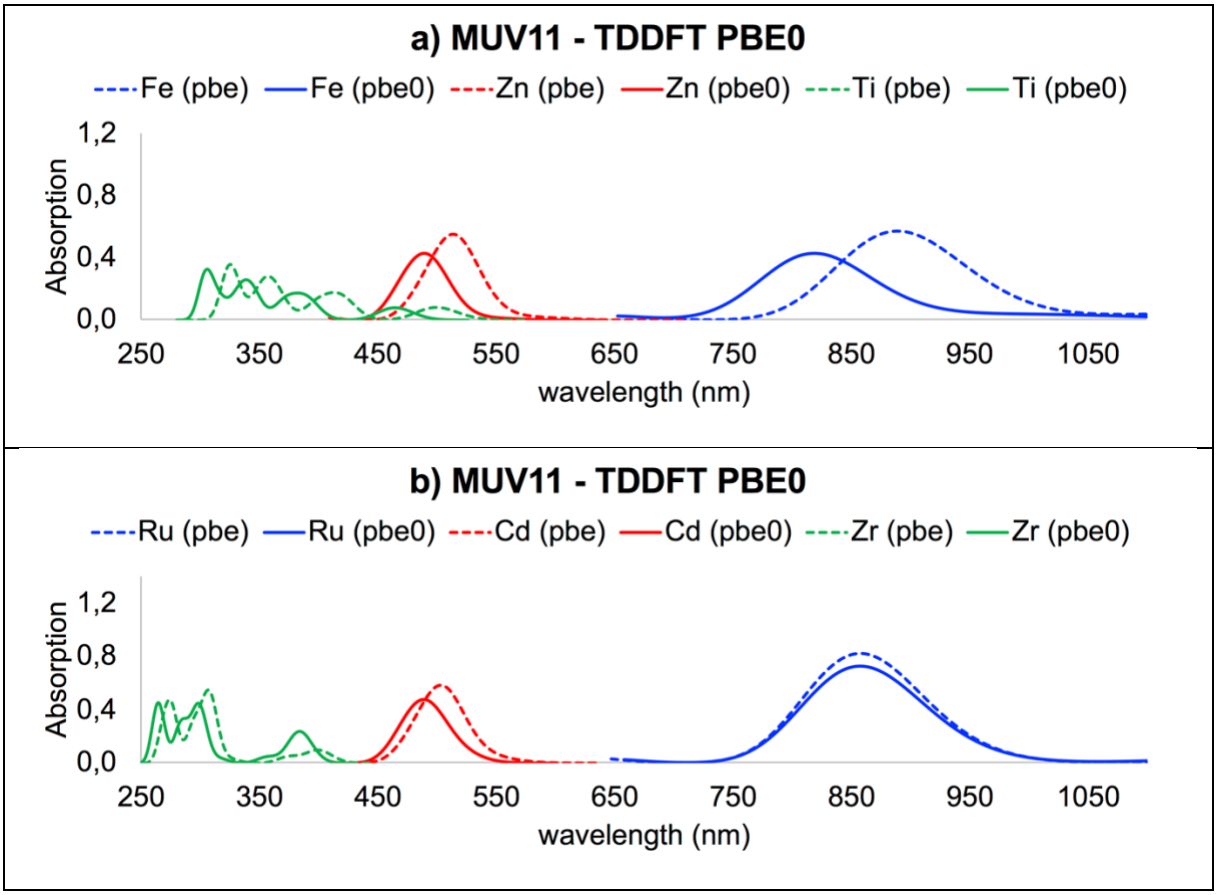


Figure S3. LR-TDDFT optical absorption spectra of a) 1rt-row and b) 2nd-row M-MUV-11 compounds with PBE0 at the PBE-D3BJ (dashed lines) and PBE0-D3BJ minima (thin lines).

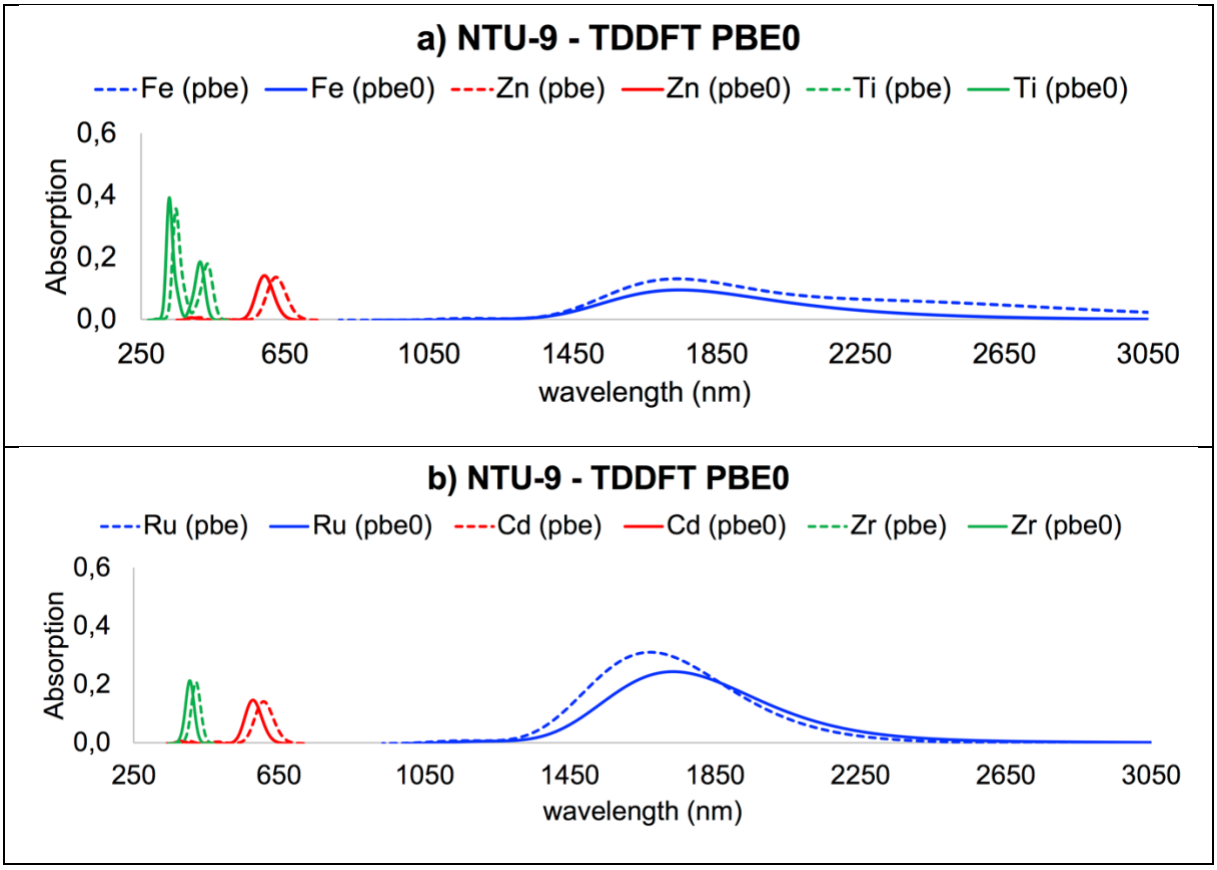


Figure S4. LR-TDDFT optical absorption spectra of a) 1rt-row and b) 2nd-row M-NTU-9 compounds with PBE0 at the PBE-D3BJ (dashed lines) and PBE0-D3BJ minima (thin lines).

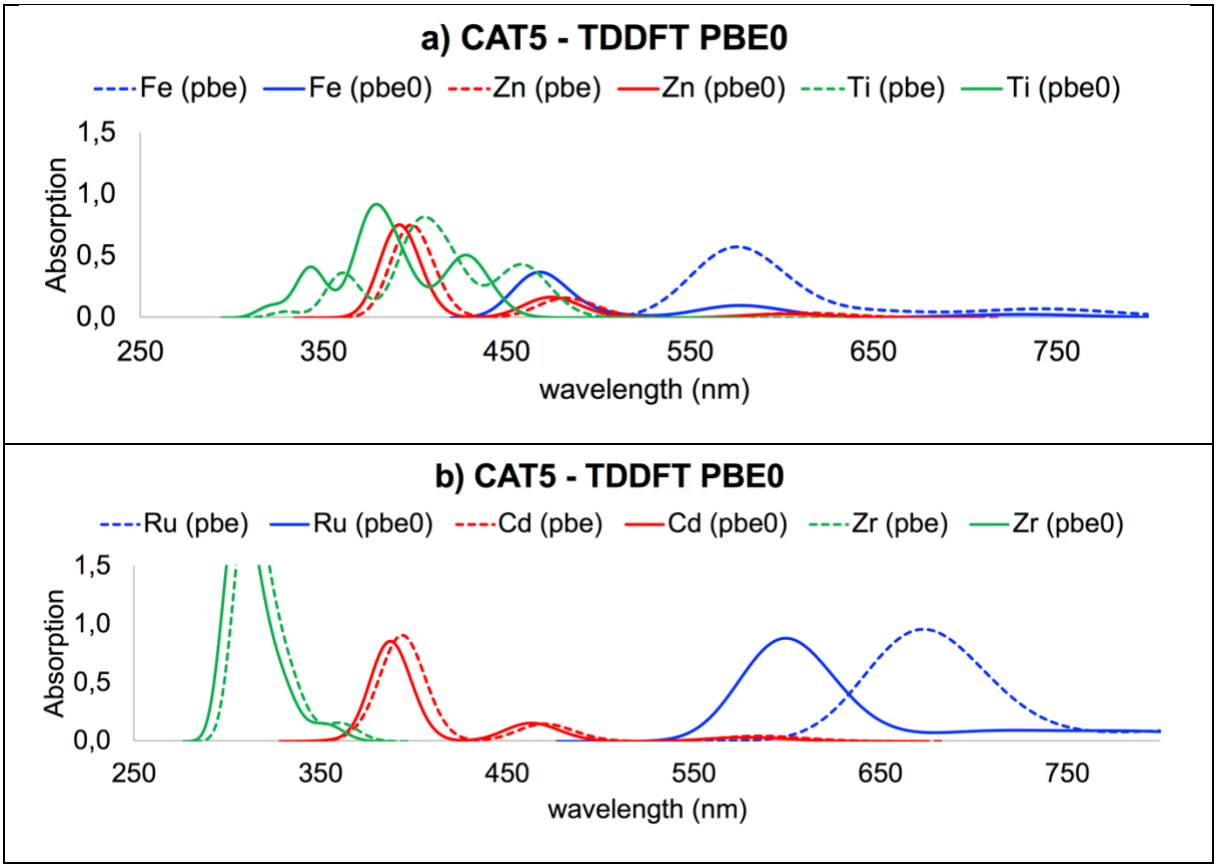


Figure S5. LR-TDDFT optical absorption spectra of a) 1rt-row and b) 2nd-row M-CAT5 compounds with PBE0 at the PBE-D3BJ (dashed lines) and PBE0-D3BJ minima (thin lines).

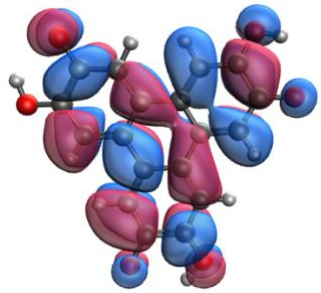
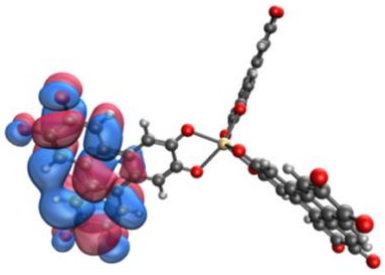
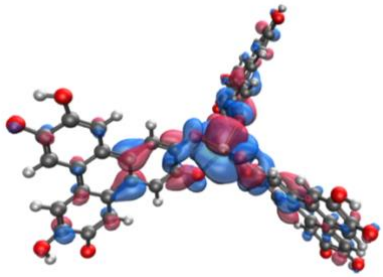
a) CAT-5 ligand	b) Cd(II)-CAT-5 TMC	c) Ti(IV)-CAT-5 TMC
		

Figure S6. LUMO of a) CAT-5 ligand, b) Cd(II)-CAT-5 and c) Ti(IV)-CAT-5 TMC computed with PBE0 at the PBE-D3BJ optimized geometries.

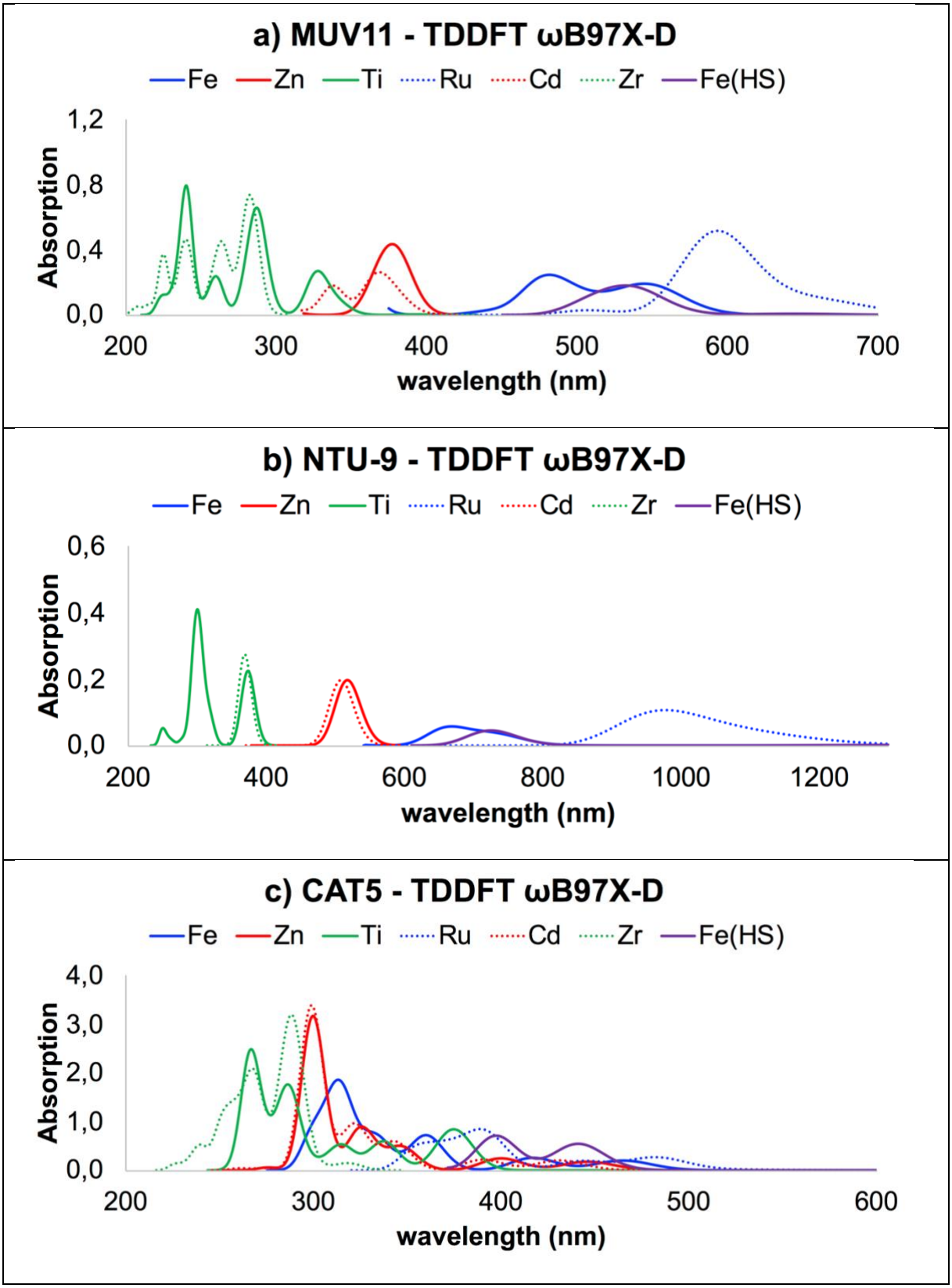


Figure S7. LR-TDDFT absorption spectra computed with ωB97X-D functional for (a) MUV-11, (b) NTU-9 and (c) CAT-5 TMCs. The absorption intensity of Fe(HS) is shown x3 to make it visible. Thin/dashed lines are used for 1rt/2nd row TMCs.

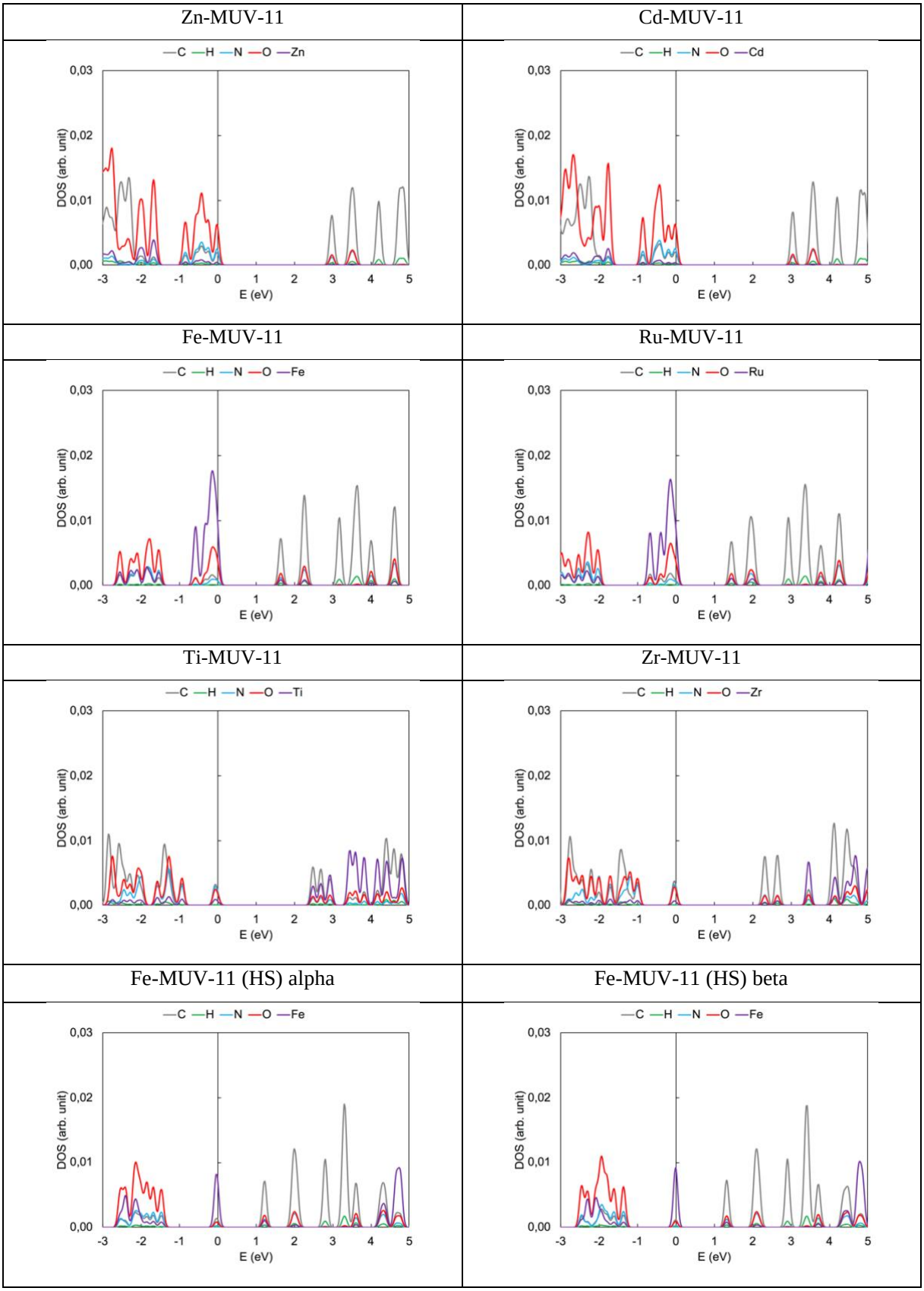


Figure S8. Projected Density of States of the 6 M-MUV-11 crystal structures computed with PBE0 at the PBE-D3BJ minima.

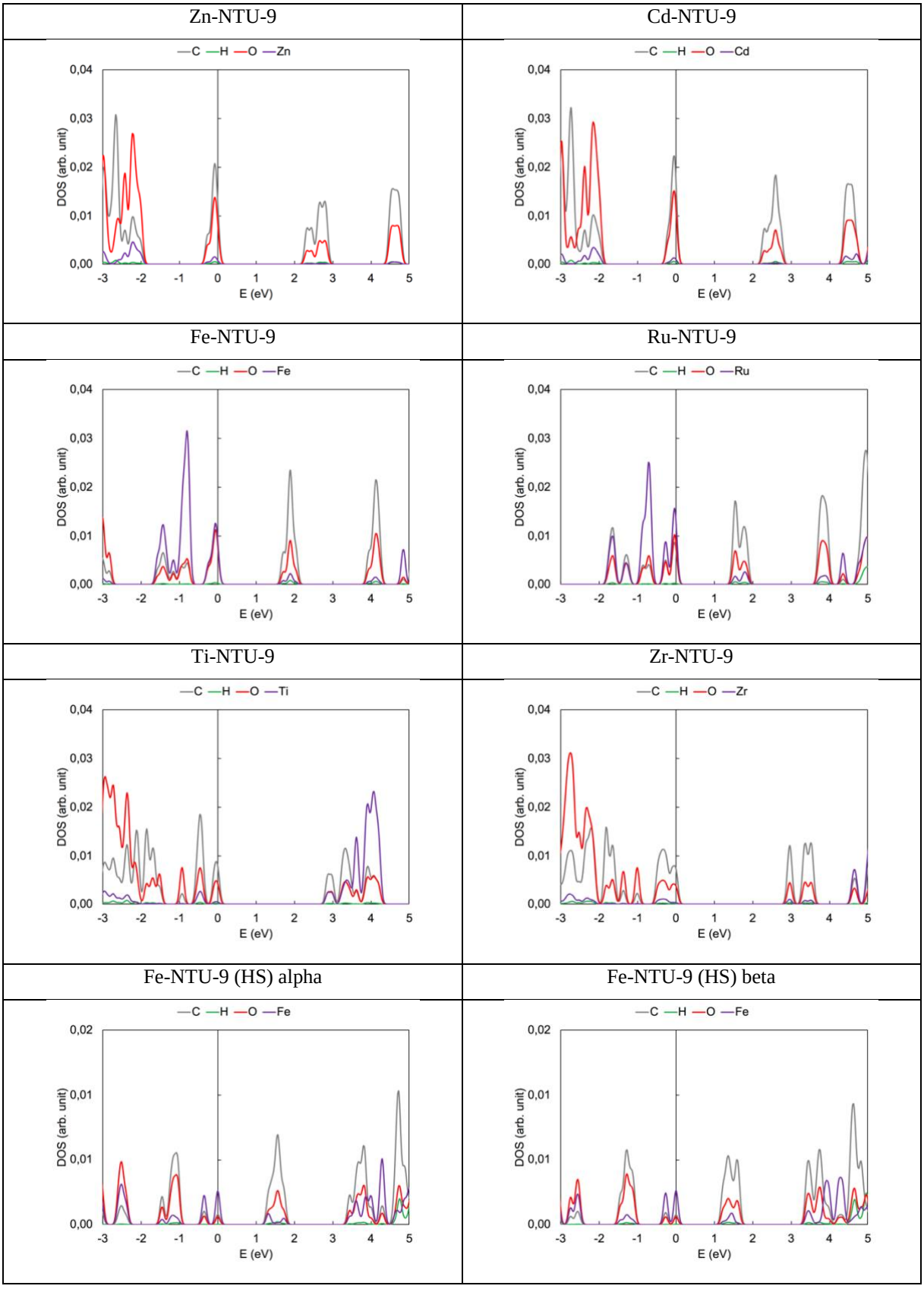


Figure S9. Projected Density of States of the 6 M-NTU-9 crystal structures computed with PBE0 at the PBE-D3BJ minima.

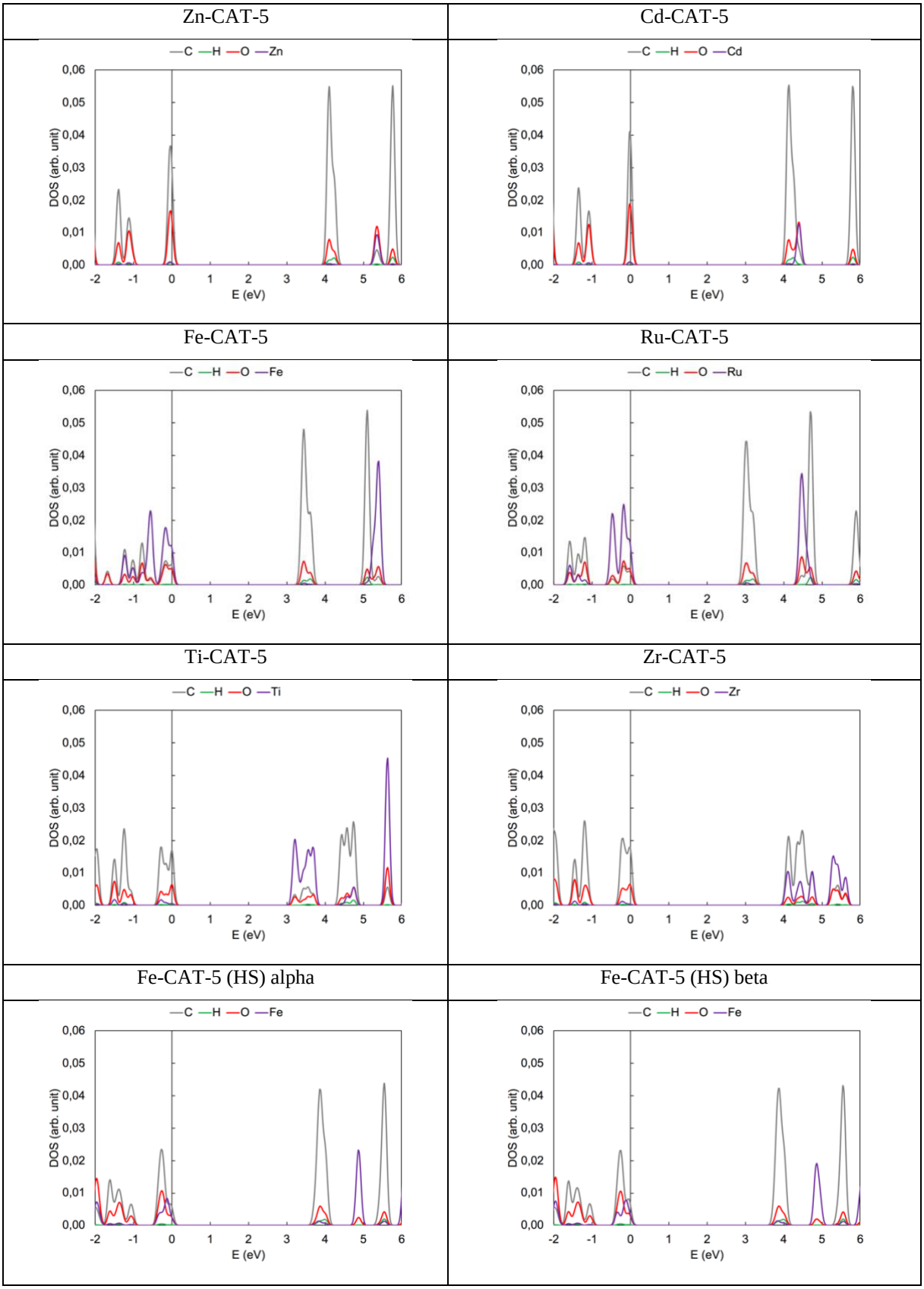


Figure S10. Projected Density of States of the 6 M-CAT-5 crystal structures computed with PBE0 at the PBE-D3BJ minima.

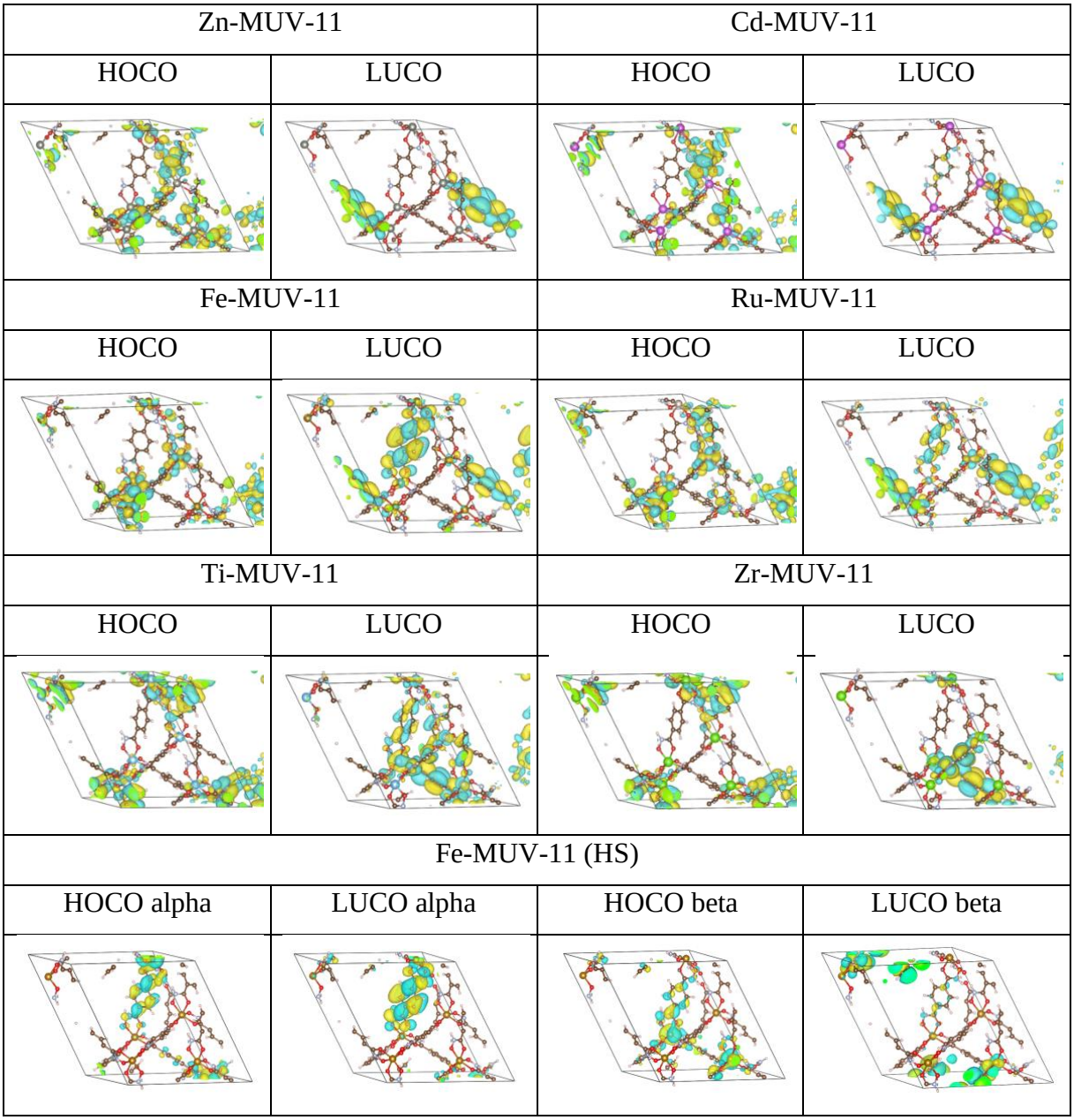


Figure S11. Highest Occupied Crystal Orbital (HOCO) and Lowest Unoccupied Crystal Orbital (LUCO) of the 6 M-MUV-11 crystal structures computed with PBE0 at the PBE-D3BJ minima.

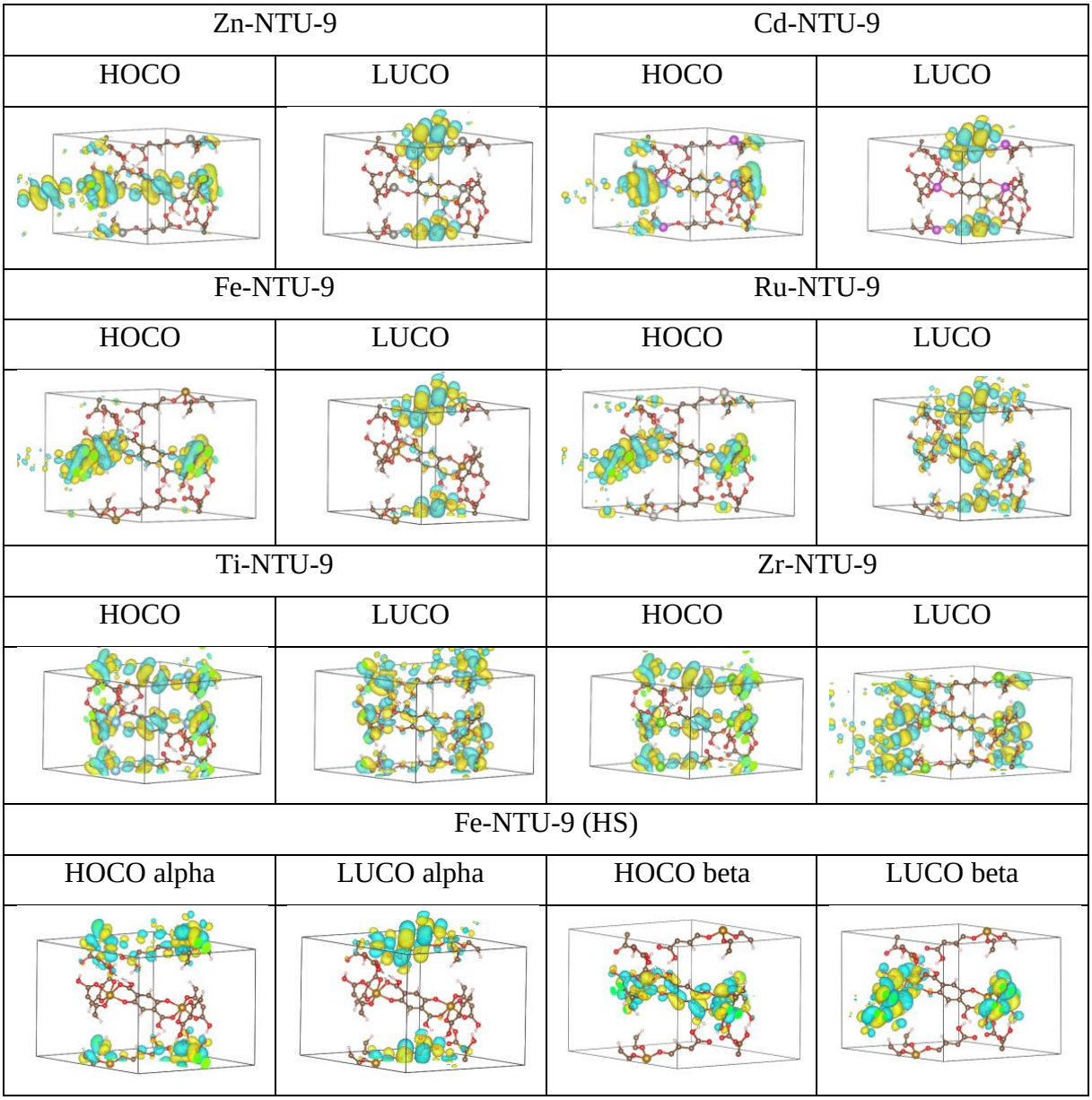


Figure S12. Highest Occupied Crystal Orbital (HOCO) and Lowest Unoccupied Crystal Orbital (LUCO) of the 6 M-NTU-9 crystal structures computed with PBE0 at the PBE-D3BJ minima.

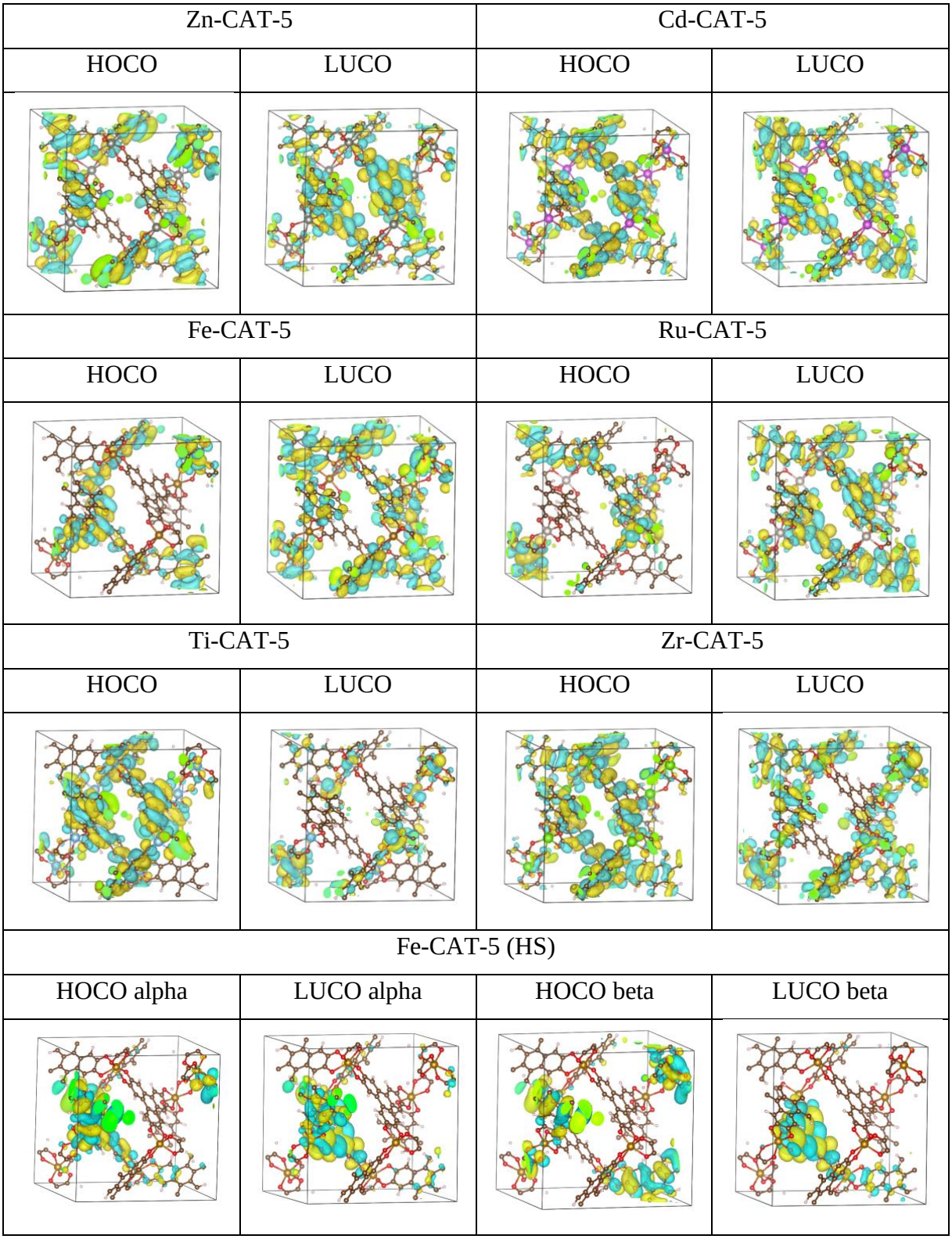


Figure S13. Highest Occupied Crystal Orbital (HOCO) and Lowest Unoccupied Crystal Orbital (LUCO) of the 6 M-CAT-5 crystal structures computed with PBE0 at the PBE-D3BJ minima.

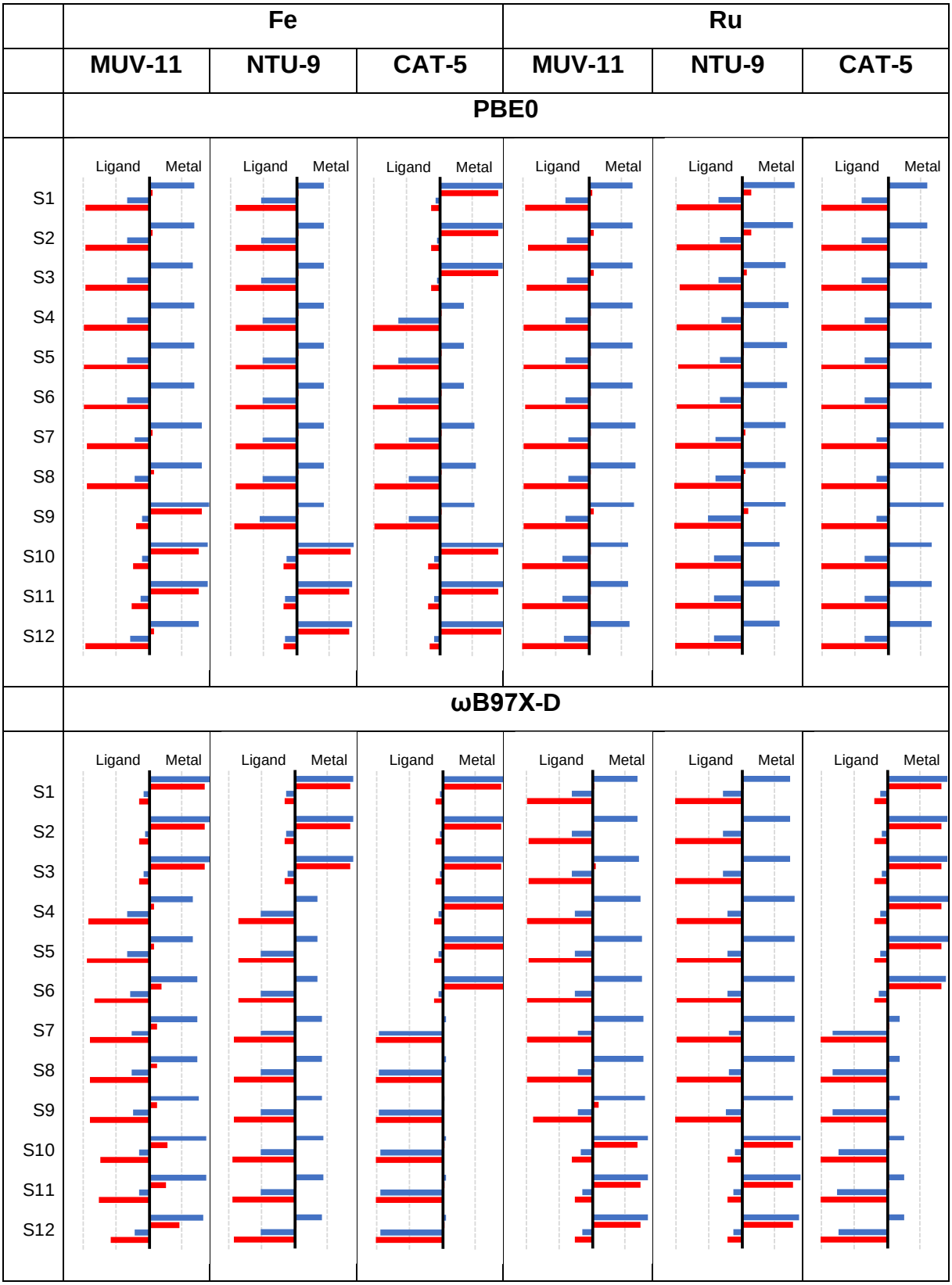


Figure S14. TDDFT/TDA excited state characterization of the lowest 12 excitations computed with PBE0 and ωB97X-D for the Fe- and Ru- MUV11, NTU-9 and CAT5 TMCs. The left side of each graph represents the ligand (L) and the right the metal (M). Blue: hole, red: electron.

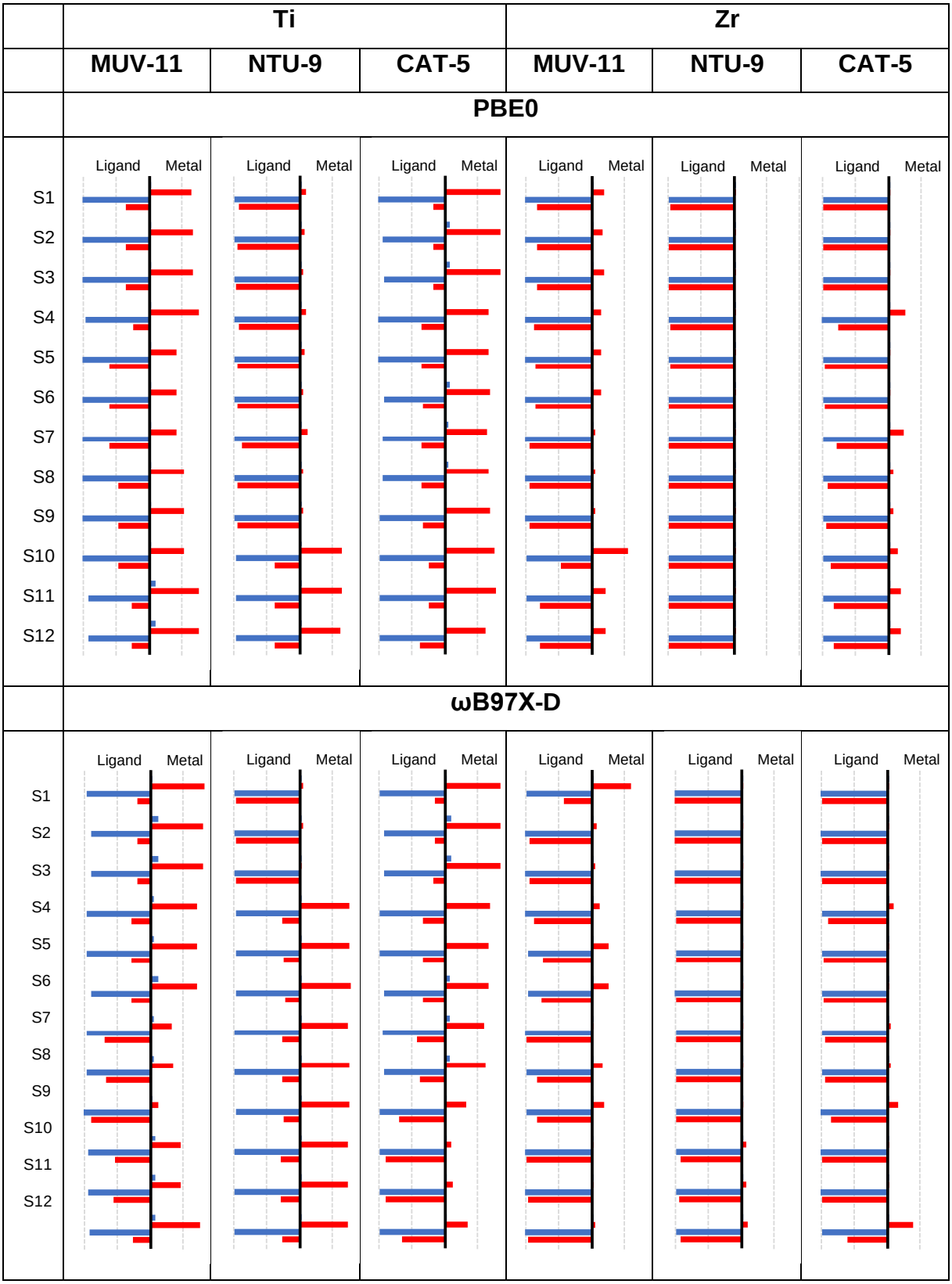


Figure S15. TDDFT/TDA excited state characterization of the lowest 12 excitations computed with PBE0 and ωB97X-D for the Ti- and Zr- MUV11, NTU-9 and CAT5 TMCs. The left side of each graph represents the ligand (L) and the right the metal (M). Blue: hole, red: electron.

Table S1. Optimized cell parameters in Å and degrees of the optimized MOF crystals, MUV11, NTU-9 and CAT-5, with the 6 metals considered Zn(II), Cd(II), Fe(II), Ru(II), Ti(IV) and Zr(IV). The values of the experimentally reported structure with Ti(IV) are given.

MUV11	a	b	c	alpha	beta	gamma
Zn	18.90400	18.79945	11.95816	89.80	89.91	120.43
Cd	19.43500	19.40192	12.00512	89.75	90.06	119.98
Fe	18.02200	18.10519	11.90483	90.20	90.46	120.16
Fe (HS)	18.72200	18.68622	11.94816	90.21	89.71	119.52
Ru	18.50500	18.46811	11.91033	89.77	90.43	120.09
Ti	18.19200	18.17136	11.45000	89.99	90.02	120.06
Zr	18.58300	18.60635	11.59411	90.00	90.22	119.84
Ti (exp)	18.12300	18.12300	11.22380	90.00	90.00	120.00

NTU-9	a	b	c	alpha	beta	gamma
Zn	15.05600	15.65045	12.59428	89.75	90.38	120.25
Cd	15.78500	16.16929	12.35471	89.41	90.15	119.96
Fe	14.29600	14.82967	13.95662	91.21	90.11	120.67
Fe (HS)	14.90100	15.54270	13.97024	90.85	90.54	120.61
Ru	14.70300	15.14185	13.83942	90.91	90.30	120.46
Ti	14.83700	14.93173	11.67876	89.01	90.55	120.18
Zr	15.30700	15.46295	11.51185	88.17	90.87	120.00
Ti (exp)	14.62000	14.62000	11.69800	90.00	90.00	120.00

CAT5	a	b	c	alpha	beta	gamma
Zn	19.15500	19.15501	19.15501	89.96	89.96	89.96
Cd	19.65700	19.65700	19.65700	90.01	90.01	90.01
Fe	18.62600	18.60101	18.60101	89.94	90.01	89.95
Fe (HS)	19.18500	19.16203	19.22710	89.91	89.85	89.91
Ru	19.65700	19.65700	19.65700	90.01	90.01	90.01
Ti	18.50000	18.50000	18.50000	90.00	90.00	90.00
Zr	18.85700	18.85714	18.85727	90.22	90.22	90.22
Ti (exp)	17.99600	17.99600	17.99600	90.00	90.00	90.00

Table S2. Average, shortest and longest metal-oxygen distances in Å of the optimized MOF crystals, MUV11, NTU-9 and CAT-5 with the 6 metals considered Zn(II), Cd(II), Fe(II), Ru(II), Ti(IV) and Zr(IV). The values of the experimentally reported structure with Ti(IV) are given.

	MUV11			NTU-9			CAT5		
	average	shortest	longest	average	shortest	longest	average	shortest	longest
Zn	2.172306	2.075957	2.452666	2.217043	1.932831	2.990241	2.273242	2.215319	2.331721
Cd	2.362807	2.284979	2.555457	2.368656	2.155981	2.810680	2.453025	2.443474	2.462438
Fe	2.027627	1.771818	2.670474	1.948255	1.895481	2.195401	2.075246	2.041437	2.123203
Fe (HS)	2.116186	2.026753	2.229403	2.092706	1.927299	2.495402	2.266335	2.219367	2.316062
Ru	2.069521	2.017996	2.126797	2.059316	2.013406	2.295637	2.195523	2.177860	2.215923
Ti	1.994368	1.861534	2.105540	1.994066	1.847911	2.252464	2.012852	2.009504	2.016215
Zr	2.126570	1.980123	2.241510	2.106937	1.981394	2.328418	2.136564	2.121325	2.145481
Ti (exp)	2.111763	2.050734	2.153916	1.946904	1.858001	2.035786	1.998993	1.998812	1.999173

Table S3. Average metal-oxygen distances in Å of the optimized molecular compounds, MUV11, NTU-9 and CAT-5, with the 6 metals considered Zn(II), Cd(II), Fe(II), Ru(II), Ti(IV) and Zr(IV). The values of the experimentally reported structure with Ti(IV) are given.

	PBE			PBE0			wB97XD		
	MUV11	NTU-9	CAT5	MUV11	NTU-9	CAT5	MUV11	NTU-9	CAT5
Zn	2.134131	2.128759	2.303190	2.131694	2.114513	2.267154	2.149269	2.123704	2.265171
Cd	2.334645	2.333032	2.552110	2.314884	2.311827	2.485654	2.347958	2.317896	2.483936
Fe	1.924541	1.921967	2.040936	1.972066	1.975946	2.115113	2.001983	2.009607	2.141840
Fe (HS)	2.087537	2.053273	2.280937	2.131803	2.019652	2.308084	2.155321	2.154328	2.264992
Ru	2.038561	2.022521	2.157307	2.059317	2.044714	2.186067	2.101681	2.105727	2.235797
Ti	1.982390	1.953780	2.014648	1.958079	1.930231	1.984839	1.963033	1.933171	1.985156
Zr	2.125418	2.093281	2.153249	2.109284	2.077949	2.134519	2.114598	2.084081	2.138462
Ti (exp)	2.111763	1.946904	1.998993	2.111763	1.946904	1.998993	2.111763	1.946904	1.998993

Table S4. PBE0 band gap given in eV computed for the MOF crystal structures at their optimized PBE-D3BJ geometry.

PBE0 band gap (eV)	MUV11	NTU-9	CAT5
Zn	2.951086	2.321971	4.089157
Cd	3.034832	2.297877	4.119200
Fe	1.631787	1.708889	3.403463
Fe (HS)*	1.257262	1.273947	3.730586
Ru	1.422960	1.506926	2.972636
Ti	2.475784	2.866689	3.199537
Zr	2.301077	2.938501	4.071384

* average between the alpha and beta band gap

Table S5. Computed fundamental gap given in eV of the 18 MOF-based molecular compounds a) with PBE0 method at PBE-D3BJ optimized geometries, b) with PBE0 method at PBE0-D3BJ optimized geometries and c) with wb97xD method at wb97xD optimized geometries.

a) PBE0 gap (eV) At PBE-D3BJ geo.	MUV11	NTU-9	CAT5
Zn	2.318377	2.560827	2.691712
Cd	2.730624	2.625862	2.767631
Fe	1.768715	1.046263	1.783137
Fe (HS)*	1.231842	0.407621	2.405180
Ru	1.565721	1.056875	1.463952
Ti	2.863686	3.464777	3.273211
Zr	3.531716	3.550219	4.085187

b) PBE0 gap (eV) At PBE0-D3BJ geo.	MUV11	NTU-9	CAT5
Zn	2.736338	2.677562	2.733617
Cd	2.865318	2.737427	2.804910
Fe	1.939328	1.247080	2.235384
Fe (HS)*	1.577422	0.434860	2.737427
Ru	1.661504	1.042998	1.672932
Ti	3.058516	3.609267	3.463688
Zr	3.687907	3.682737	4.153487

c) wb97xD gap (eV) At wb97xD geo.	MUV11	NTU-9	CAT5
Zn	6.035128	5.948597	5.720569
Cd	6.073767	6.013903	5.789140
Fe	5.100158	4.591584	5.438390
Fe (HS)*	4.947232	4.386141	5.745058
Ru	4.632673	3.908316	4.940973
Ti	6.625606	6.944247	6.687920
Zr	7.237310	7.039486	7.292004

* beta band gap