Understanding and Controlling the Dielectric Response of Metal–Organic Frameworks

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Supporting Information

Understanding and Controlling the Dielectric Response of Metal–Organic Frameworks

Matthew R. Ryder,[a] Lorenzo Donà,[b] Jenny G. Vitillo,[b] and Bartolomeo Civalleri*[b]

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S1. List of examined MOFs and additional computational details

MOF	Metal	Linker	Basis set					Shrink Factors	K points	Space Group	Laue Class
IRMOF-1 family			**Metal**	**Linker**							
IRMOF-1	Zn	BDC	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1		2 2	3	FM-3M	m-3m
IRMOF-1 IP	Zn	BDC	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1		2 2	4	R-3M	-3m
IRMOF-2-F	Zn	BDC-F	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1	F 6-31d1	2 2	4	R3	-3
IRMOF-2-F2	Zn	BDC-F2	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1	F 6-31d1	2 2	4	R-3	-3
IRMOF-2-F4	Zn	BDC-F4	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1	F 6-31d1	2 2	4	FM-3	-3m
IRMOF-2-Cl	Zn	BDC-Cl	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1	Cl 86-31d1	2 2	4	R3	-3
IRMOF-2-Br	Zn	BDC-Br	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1	821111s-6311p-5	2 2	4	R3	-3
IRMOF-2-Br2	Zn	BDC-Br2	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1	821111s-6311p-5	2 2	4	R-3	-3
IRMOF-3-NH2	Zn	BDC-NH2	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1	N 6-31d1	2 2	4	R3	-3
IRMOF-3-(NH2)2 (a)	Zn	BDC-(NH2)2 (a)	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1	N 6-31d1	2 2	3	F-43M	m-3m
IRMOF-3-(NH2)2 (b)	Zn	BDC-(NH2)2 (b)	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1	N 6-31d1	2 2	4	R-3	-3
IRMOF-3-(NH2)4	Zn	BDC-(NH2)4	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1	N 6-31d1	2 2	3	FM-3M	m-3m
IRMOF-1-NH2-NO2	Zn	BDC-NH2-NO2	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1	N 6-31d1	2 2	4	R3	-3
IRMOF-1-NO2	Zn	BDC-NO2	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1	N 6-31d1	2 2	4	R3	-3
IRMOF-8	Zn	2,6-NDC	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1		2 2	4	R-3	-3
IRMOF-9	Zn	BPDC	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1		2 2	8	PNNM	mmm
IRMOF-10	Zn	BPDC	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1		2 2	3	F432	m-3m
IRMOF-12	Zn	HPDC	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1		2 2	3	FM-3M	m-3m
IRMOF-14	Zn	PDC	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1		2 2	3	FM-3M	m-3m
IRMOF-18	Zn	TMBDC	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1		2 2	3	FM-3M	m-3m
Zr-based MOFs											
UiO-66	Zr	BDC	9s-7631sp-621d	C 6-31d1	O 8-411d1	H 3-1p1		2 2	3	F-43M	m-3m
UiO-66-F	Zr	BDC-F	9s-7631sp-621d	C 6-31d1	O 8-411d1	H 3-1p1	F 6-31d1	2 2	4	R3	-3
UiO-66-Br	Zr	BDC-Br	9s-7631sp-621d	C 6-31d1	O 8-411d1	H 3-1p1	821111s-6311p-5	2 2	4	R3	-3
UiO-66-NH2	Zr	BDC-NH2	9s-7631sp-621d	C 6-31d1	O 8-411d1	H 3-1p1	N 6-31d1	2 2	4	R3	-3
UiO-67	Zr	BPDC	9s-7631sp-621d	C 6-31d1	O 8-411d1	H 3-1p1		2 2	3	F23	m-3
UiO-67 dehydrox	Zr	BPDC	9s-7631sp-621d	C 6-31d1	O 8-411d1	H 3-1p1		2 2	4	R32	-3m
UiO-68	Zr	TPDC	9s-7631sp-621d	C 6-31d1	O 8-411d1	H 3-1p1		2 2	3	F-43M	m-3m
MIL-140-A	Zr	BDC	9s-7631sp-621d	C 6-31d1	O 8-411d1	H 3-1p1		2 2	6	C2/C	2/m
NU-1000	Zr	TBAPy	9s-7631sp-621d	C 6-31d1	O 8-411d1	H 3-1p1		1 1	1	P-6M2	6/mmm
DUT-122	Zr	FDC	9s-7631sp-621d	C 6-31d1	O 8-411d1	H 3-1p1		1 1	1	PA3	m-3
FJI-H6-OH	Zr	TBPP	9s-7631sp-621d	C 6-31d1	O 8-411d1	H 3-1p1	N 6-31d1	2 2	4	P23	m-3
MOF-74-M family											
MOF-74-Mg	Mg	DOBDC	POB-TZVP	C 6-31d1	O 8-411d1	H 3-1p1		2 2	4	R-3	-3
MOF-74-Mn	Mn	DOBDC	POB-TZVP	C 6-31d1	O 8-411d1	H 3-1p1		2 2	4	R-3	-3
MOF-74-Fe	Fe	DOBDC	POB-TZVP	C 6-31d1	O 8-411d1	H 3-1p1		2 2	4	R-3	-3
MOF-74-Co	Co	DOBDC	POB-TZVP	C 6-31d1	O 8-411d1	H 3-1p1		2 2	4	R-3	-3
MOF-74-Ni	Ni	DOBDC	POB-TZVP	C 6-31d1	O 8-411d1	H 3-1p1		2 2	4	R-3	-3
MOF-74-Zn	Zn	DOBDC	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1		2 2	4	R-3	-3
MIL-127-M family											
MIL-127-Al	Al	ABD	POB-TZVP	C 6-31d1	O 8-411d1	H 3-1p1	N 6-31d1	2 2	6	P-42C	4/mmm
MIL-127-Sc	Sc	ABD	POB-TZVP	C 6-31d1	O 8-411d1	H 3-1p1	N 6-31d1	2 2	6	P-42C	4/mmm
MIL-127-Cr	Cr	ABD	POB-TZVP	C 6-31d1	O 8-411d1	H 3-1p1	N 6-31d1	2 2	6	P-42C	4/mmm
MIL-127-Fe	Fe	ABD	POB-TZVP	C 6-31d1	O 8-411d1	H 3-1p1	N 6-31d1	2 2	6	P-42C	4/mmm
MIL-53 Narrow and Large Pore											
MIL-53 NP	Al	BDC	POB-TZVP	C 6-31d1	O 8-411d1	H 3-1p1		2 2	6	C2/C	2/m
MIL-53 LP	Al	BDC	POB-TZVP	C 6-31d1	O 8-411d1	H 3-1p1		2 2	5	IMMA	mmm
Other MOFs											
MIL-68-Ga	Ga	BDC	m-pVDZ-PP	C 6-31d1	O 8-411d1	H 3-1p1		2 2	6	CMCM	mmm
MIL-68-In	In	BDC	m-pVDZ-PP	C 6-31d1	O 8-411d1	H 3-1p1		2 2	6	CMCM	mmm
MIL-125	Ti	BDC	86s-411sp-31d	C 6-31d1	O 8-411d1	H 3-1p1		2 2	4	I4/MMM	4/mmm
HKUST-1	Cu	BTC	86s-411sp-31d	C 6-31d1	O 8-411d1	H 3-1p1		2 2	3	FM-3M	m-3m
HKUST-1-Zn	Zn	BTC	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1		2 2	3	FM-3M	m-3m
CPO-54-Zn	Zn	DH2PhDC	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1		2 2	4	P3221	-3m
medi-MOF-1	Zn	Curcumin	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1		2 2	4	P3221	-3m
Zn(OA)2	Zn	Oxalic Acid	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1		2 2	8	P21/n	2/m

Legend

BDC=1,4-benzenedicarboxylate
BDC-F=2-fluoro-1,4-benzenedicarboxylate
BDC-F2=2,5-difluoro-1,4-benzenedicarboxylate
BDC-F4=2,3,5,6-tetrafuoro-1,4-benzenedicarboxylate
BDC-Cl=2-chloro-1,4-benzenedicarboxylate
BDC-Br=2-bromo-1,4-benzenedicarboxylate
BDC-Br2=2,5-dibromo-1,4-benzenedicarboxylate
BDC-NH2=2-amino-1,4-benzenedicarboxylate
BDC-(NH2)2 (a)=2,6-diamino-1,4-benzenedicarboxylate
BDC-(NH2)2 (b)=2,5-diamino-1,4-benzenedicarboxylate
BDC-(NH2)4=2,3,5,6-tetraamino-1,4-benzenedicarboxylate
BDC-NH2-NO2=2-amino-5-nitro-1,4-benzenedicarboxylate
BDC-NO2=2-nitro-1,4-benzenedicarboxylate

2,6-NDC=2,6-naphthalenedicarboxylate
BPDC=biphenyl-4,4'-dicarboxylate
HPDC=4,5,9,10-tetrahydropyrene-2,7-dicarboxylate
PDC=2,7-pyrenedicarboxylate
TMBDC=2,3,5,6-tetramethyl-1,4-benzenedicarboxylate
TPDC=p-terphenyl-4,4''-dicarboxylate
TBAPy=1,3,6,8-tetrakis(p-benzoate) pyrene
FDC=9-fluoreneone-2,7-dicarboxylate
TBPP=4',4''',4''''',4'''''''-(porphyrin-5,10,15,20-tetrayl)tetrakis([1,1'-biphenyl]-4-carboxylate
DOBDC=2,5-dihydroxy-1,4-benzenedicarboxylate
ABD=3,3',5,5'- azobenzenetetracarboxylate
BTC=1,3,5-benzenetricarboxylate
DH2PhDC=3,3'-dihydroxy-[1,1'-biphenyl]-4,4'-dicarboxylate

S2. Comparison of band gap and dielectric properties of MOF-5 as computed with different HF/DFT hybrid functionals (global and range-separated hybrids)

The following basis sets were used: 86s-4111sp-31d-1f for Zn and 6-31G(d,p) for H, C and O.

Functional	%HF	Band Gap (eV)	Polarizability (Å^3)	Dielectric tensor
B1WC	16	4.80	888.6	1.374
B3LYP	20	5.07	868.2	1.365
B97H	21	5.17	864.1	1.364
PBE0	25	5.46	853.1	1.359
PBE0-13	33.3	6.05	829.3	1.349
HSE06	25 sr	4.73	-	-
HSEsol	25 sr	4.71	-	-
CAM-B3LYP	100 lr	7.68	819.8	1.345
LC-BLYP	100 lr	10.12	776.6	1.327

Results reported in the table above and in Figure S1 show that, not unexpectedly, the band gap of MOF-5 increases with the amount of HF exchange included in the hybrid functional. With long-range corrected functionals the band gap is predicted to be very large in agreement with the general trend observed for solids as reported Ref. [1]. For all methods, the computed band gap of MOF-5 is overestimated concerning the experimental value of 4.0 eV.[2] However, the polarizability and the dielectric tensor decrease with the HF exchange.

From the whole set of methods, the computed mean value for the dielectric tensor is 1.354, and the standard deviation is about 1.6%. Therefore, B3LYP represents a reasonable compromise among different hybrid functionals.

[1] P. Pernot, B. Civalleri, D. Presti and A. Savin *J. Phys. Chem. A* **119** (2015) 5288-5304.
[2] J. Gascon, M. D. Hernandez-Alonso, A. R. Almeida, G. P. van Klink, F. Kapteijn, G. Mul, *ChemSusChem* **1** (2008) 981-983.

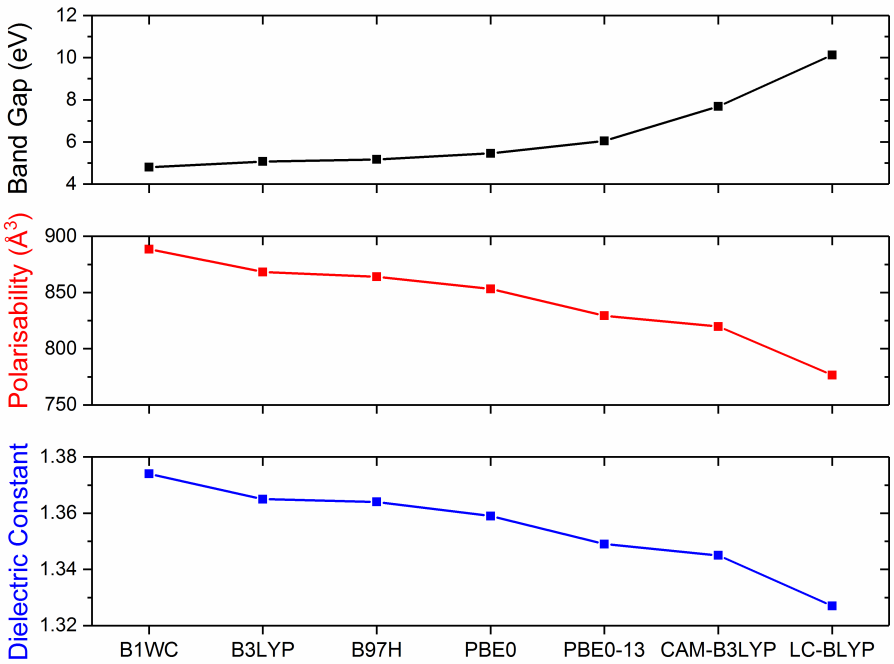

Figure S1. Dependence of the band gap, polarisability and dielectric constant of MOF-5 on the HF exchange included in the DFT method.

S3. Basis set dependence of the band gap and dielectric properties of MOF-5 and MOF-74-Mg as obtained with the B3LYP-D* functional

MOF-5 (Cubic – Fm3m)

Basis Set		Number of AO	Band Gap (eV)	Polarizability (Å^3)	Dielectric tensor	Volume (Å^3)	Density (g/cm^3)
Zn	H/C/O						
86s-4111sp-31d-1f	6-31G(d,p)	1564	5.07	868.2	1.365	17695.8	0.57
TZP	TZP	1856	5.07	885.7	1.372	17752.8	0.57
TZP	6-311G (2df,2pd)	2788	5.18	861.2	1.368	17445.0	0.58
86s-4111sp-31d-1f	6-311G (2df,2pd)	2860	5.16	904.3	1.384	17549.4	0.58
TZPP	TZPP	3016	5.10	949.8	1.398	17768.6	0.57
TZPP	QZVPP	3336	5.09	964.7	1.405	17749.7	0.57

MOF-74-Mg (Hexagonal – R-3)

Basis Set		Number of AO	Band Gap (eV)	Polarizability (Å^3)		Dielectric tensor		Volume (Å^3)	Density (g/cm^3)
Mg	H/C/O			XX	ZZ	XX	ZZ		
73211s-511p-1d	6-31G(d,p)	804	3.35	459.5	628.5	1.640	1.875	4012.2	0.90
8-511d1	6-311G (2df,2pd)	1452	3.36	471.6	627.5	1.664	1.883	3970.2	0.91
7321s-511p-1d	6-311G (2df,2pd)	1452	3.38	476.6	634.7	1.666	1.887	3999.5	0.90

Results in the tables above show that the basis set dependence of computed properties is small for both MOF-5 and MOF-74-Mg. Among them, only the polarisability appears to be slightly more influenced by the basis set size. As expected, the larger the basis set, the larger the polarisability. However, due to the inverse relation with the unit cell volume, the dielectric tensor only varies on the second decimal place with an increment from the smallest to the most extensive basis set of less than 3%.

S4. Computed data (B3LYP-D*) for the MOF structures investigated in present work: polarisability tensor, optimised primitive cell volume, and density

MOF	Metal	Linker	Polarizability tensor ($Å^3$)						Primitive cell Volume ($Å^3$)	Density ($g\ cm^{-3}$)
IRMOF-1 family			**XX**	**XY**	**XZ**	**YY**	**YZ**	**ZZ**		
IRMOF-1	Zn	BDC	868.2						4424.0	0.57
IRMOF-1 IP	Zn	BDC	1825.5					1795.8	4416.0	1.15
IRMOF-2-F	Zn	BDC-F	871.2	-6.3	-6.3	871.2	-6.3	871.2	4439.0	0.61
IRMOF-2-F2	Zn	BDC-F2	876.9	-11.5	-11.5	876.9	-11.5	876.9	4458.3	0.65
IRMOF-2-F4	Zn	BDC-F4	883.8						4519.1	0.72
IRMOF-2-Cl	Zn	BDC-Cl	947.3	-8.5	-8.5	947.3	-8.5	947.3	4392.5	0.65
IRMOF-2-Br	Zn	BDC-Br	999.3	-4.7	-4.6	999.3	-4.7	999.3	4354.5	0.76
IRMOF-2-Br2	Zn	BDC-Br2	1134.9	-27.6	-27.6	1134.9	-27.6	1134.9	4420.5	0.93
IRMOF-3-NH2	Zn	BDC-NH2	958.2	-5.6	-5.6	958.2	-5.6	958.2	4404.8	0.61
IRMOF-3-(NH2)2 (a)	Zn	BDC-(NH2)2 (a)	1031.1						4478.5	0.63
IRMOF-3-(NH2)2 (b)	Zn	BDC-(NH2)2 (b)	1064.0	-17.1	-17.0	1064.0	-17.1	1064.0	4402.1	0.64
IRMOF-3-(NH2)4	Zn	BDC-(NH2)4	1244.6						4553.1	0.69
IRMOF-1-NH2-NO2	Zn	BDC-NH2-NO2	1083.1	-56.3	-56.2	1083.1	-56.3	1083.1	4344.0	0.72
IRMOF-1-NO2	Zn	BDC-NO2	965.0	-12.1	-12.1	965.0	-12.1	965.0	4343.8	0.69
IRMOF-8	Zn	2,6-NDC	1162.4					1446.4	6911.4	0.44
IRMOF-9	Zn	BPDC	2676.4			2867.4		2991.3	10399.2	0.63
IRMOF-10	Zn	BPDC	1408.3						10377.1	0.32
IRMOF-12	Zn	HPDC	1721.4						10438.1	0.37
IRMOF-14	Zn	PDC	1831.5						10315.3	0.37
IRMOF-18	Zn	TMBDC	1175.2						4364.2	0.71
Zr-based MOFs										
UiO-66	Zr	BDC	1107.4						2296.5	1.20
UiO-66-F	Zr	BDC-F	1153.0					992.3	2267.5	1.27
UiO-66-Br	Zr	BDC-Br	1296.4					1163.5	2254.1	1.54
UiO-66-NH2	Zr	BDC-NH2	1262.5					1106.3	2246.2	1.26
UiO-67	Zr	BPDC	1672.9						4946.3	0.71
UiO-67 dehydrox	Zr	BPDC	1655.3	47.8	47.8	1655.3		1655.3	4880.7	0.71
UiO-68	Zr	TPDC	2382.0						9219.8	0.46
MIL-140-A	Zr	BDC	808.1	-108.6		831.5		643.1	1056.0	1.70
NU-1000	Zr	TBAPy	4811.9					6714.1	22996.9	0.47
DUT-122	Zr	FDC	7263.4						17982.9	0.84
FJI-H6-OH	Zr	TBPP	4300.6						16778.7	0.39
MOF-74-M family										
MOF-74-Mg	Mg	DOBDC	459.5					628.5	1337.4	0.90
MOF-74-Mn	Mn	DOBDC	578.3					757.6	1422.9	1.06
MOF-74-Fe	Fe	DOBDC	608.9					830.7	1370.3	1.11
MOF-74-Co	Co	DOBDC	615.1					824.6	1348.6	1.15
MOF-74-Ni	Ni	DOBDC	612.3					806.9	1308.3	1.18
MOF-74-Zn	Zn	DOBDC	541.1					719.8	1348.9	1.19
MIL-127-M family										
MIL-127-Al	Al	ABD	3903.9					3980.1	10043.1	0.86
MIL-127-Sc	Sc	ABD	4518.1					4522.6	11248.5	0.83
MIL-127-Cr	Cr	ABD	4701.0					4723.6	10514.4	0.91
MIL-127-Fe	Fe	ABD	4955.9					4983.2	10686.7	0.91
MIL-53 Narrow and Large Pore										
MIL-53 NP	Al	BDC	415.2		0.6	170.1		372.1	387.4	1.78
MIL-53 LP	Al	BDC	331.0			327.2		218.2	719.5	0.96
Other MOFs										
MIL-68-Ga	Ga	BDC	910.8			898.5		1045.8	2714.2	0.92
MIL-68-In	In	BDC	931.4			923.7		1044.9	3070.5	0.96
MIL-125	Ti	BDC	1318.4					1110.3	3253.8	0.80
HKUST-1	Cu	BTC	1483.0						4595.1	0.87
HKUST-1-Zn	Zn	BTC	1298.1						4776.5	0.84
CPO-54-Zn	Zn	DH2PhDC	827.8					974.2	2798.6	0.71
medi-MOF-1	Zn	Curcumin	3409.9					2432.2	7195.7	0.64
Zn(OA)2	Zn	Oxalic Acid	126.4		-29.2	114.5		166.6	142.9	3.53

S5. Computed data (B3LYP-D*) for the MOF structures investigated in present work: dielectric tensor, band gap, and porosity (calculated using Mercury 3.8)

MOF	Metal		Dielectric tensor						Band Gap	Porosity
IRMOF-1 family			**XX**	**XY**	**XZ**	**YY**	**YZ**	**ZZ**	**eV**	**%**
IRMOF-1	Zn	BDC	1.37						5.07	77.8
IRMOF-1 IP	Zn	BDC	1.77					1.76	4.86	50.6
IRMOF-2-F	Zn	BDC-F	1.37	0.00	0.00	1.37	0.00	1.37	4.75	76.7
IRMOF-2-F2	Zn	BDC-F2	1.37	0.00	0.00	1.37	0.00	1.37	4.44	75.7
IRMOF-2-F4	Zn	BDC-F4	1.36						4.25	76.5
IRMOF-2-Cl	Zn	BDC-Cl	1.40	0.00	0.00	1.40	0.00	1.40	4.68	73.6
IRMOF-2-Br	Zn	BDC-Br	1.43	0.00	0.00	1.43	0.00	1.43	4.56	72.4
IRMOF-2-Br2	Zn	BDC-Br2	1.48	-0.01	-0.01	1.48	-0.01	1.48	4.34	68.8
IRMOF-3-NH2	Zn	BDC-NH2	1.41	0.00	0.00	1.41	0.00	1.41	3.72	74.8
IRMOF-3-(NH2)2 (a)	Zn	BDC-(NH2)2 (a)	1.43						3.38	75.2
IRMOF-3-(NH2)2 (b)	Zn	BDC-(NH2)2 (b)	1.45	-0.01	-0.01	1.45	-0.01	1.45	2.97	72.6
IRMOF-3-(NH2)4	Zn	BDC-(NH2)4	1.51						2.07	72.8
IRMOF-1-NH2-NO2	Zn	BDC-NH2-NO2	1.46	-0.02	-0.02	1.46	-0.02	1.46	3.87	70.2
IRMOF-1-NO2	Zn	BDC-NO2	1.41	-0.01	-0.01	1.41	-0.01	1.41	4.82	72.0
IRMOF-8	Zn	2,6-NDC	1.31					1.39	4.05	80.7
IRMOF-9	Zn	BPDC	1.48			1.51		1.54	4.46	69.8
IRMOF-10	Zn	BPDC	1.25						4.51	85.4
IRMOF-12	Zn	HPDC	1.31						4.07	81.9
IRMOF-14	Zn	PDC	1.33						3.63	82.6
IRMOF-18	Zn	TMBDC	1.50						5.95	58.2
Zr-based MOFs										
UiO-66	Zr	BDC	1.90						4.56	48.0
UiO-66-F	Zr	BDC-F	1.95					1.81	4.08	43.7
UiO-66-Br	Zr	BDC-Br	2.07					1.96	4.05	37.5
UiO-66-NH2	Zr	BDC-NH2	2.05					1.92	3.11	41.1
UiO-67	Zr	BPDC	1.63						4.09	64.2
UiO-67 dehydrox	Zr	BPDC	1.63	0.02	0.02	1.63		1.63	4.03	68.3
UiO-68	Zr	TPDC	1.48						3.54	75.2
MIL-140-A	Zr	BDC	2.42	-0.19		2.47		2.13	4.32	20.5
NU-1000	Zr	TBAPy	1.39					1.54	2.90	78.8
DUT-122	Zr	FDC	1.75						3.64	58.7
FJI-H6-OH	Zr	TBPP	1.48						2.52	
MOF-74-M family										
MOF-74-Mg	Mg	DOBDC	1.64					1.88	3.35	58.9
MOF-74-Mn	Mn	DOBDC	1.76					1.99	3.24	59.5
MOF-74-Fe	Fe	DOBDC	1.83					2.13	2.83	59.5
MOF-74-Co	Co	DOBDC	1.85					2.14	2.98	58.5
MOF-74-Ni	Ni	DOBDC	1.87					2.15	2.85	59.1
MOF-74-Zn	Zn	DOBDC	1.75					1.99	3.47	59.8
MIL-127-M family										
MIL-127-Al	Al	ABD	1.72					1.74	2.97	59.6
MIL-127-Sc	Sc	ABD	1.75					1.75	3.31	62.3
MIL-127-Cr	Cr	ABD	1.83					1.83	2.90	61.0
MIL-127-Fe	Fe	ABD	1.86					1.87	2.45	61.0
MIL-53 Narrow and Large Pore										
MIL-53 NP	Al	BDC	3.00		0.00	1.82		2.79	3.53	0.0
MIL-53 LP	Al	BDC	1.86			1.85		1.56	4.85	49.0
Other MOFs										
MIL-68-Ga	Ga	BDC	1.62			1.62		1.72	4.83	53.6
MIL-68-In	In	BDC	1.56			1.56		1.63	5.01	52.6
MIL-125	Ti	BDC	1.75					1.64	4.35	62.5
HKUST-1	Cu	BTC	1.60							66.4
HKUST-1-Zn	Zn	BTC	1.51						5.44	67.7
CPO-54-Zn	Zn	DH2PhDC	1.55					1.65	4.00	72.4
medi-MOF-1	Zn	Curcumin	1.88					1.63	2.83	64.0
Zn(OA)2	Zn	Oxalic Acid	2.65		-0.38	2.49		3.17	5.54	0.0

S6. Electronic band structure and density of states (DOS) of MOF-74-Ni, UiO-66, and MIL-53-Al

MOF-74-Ni:

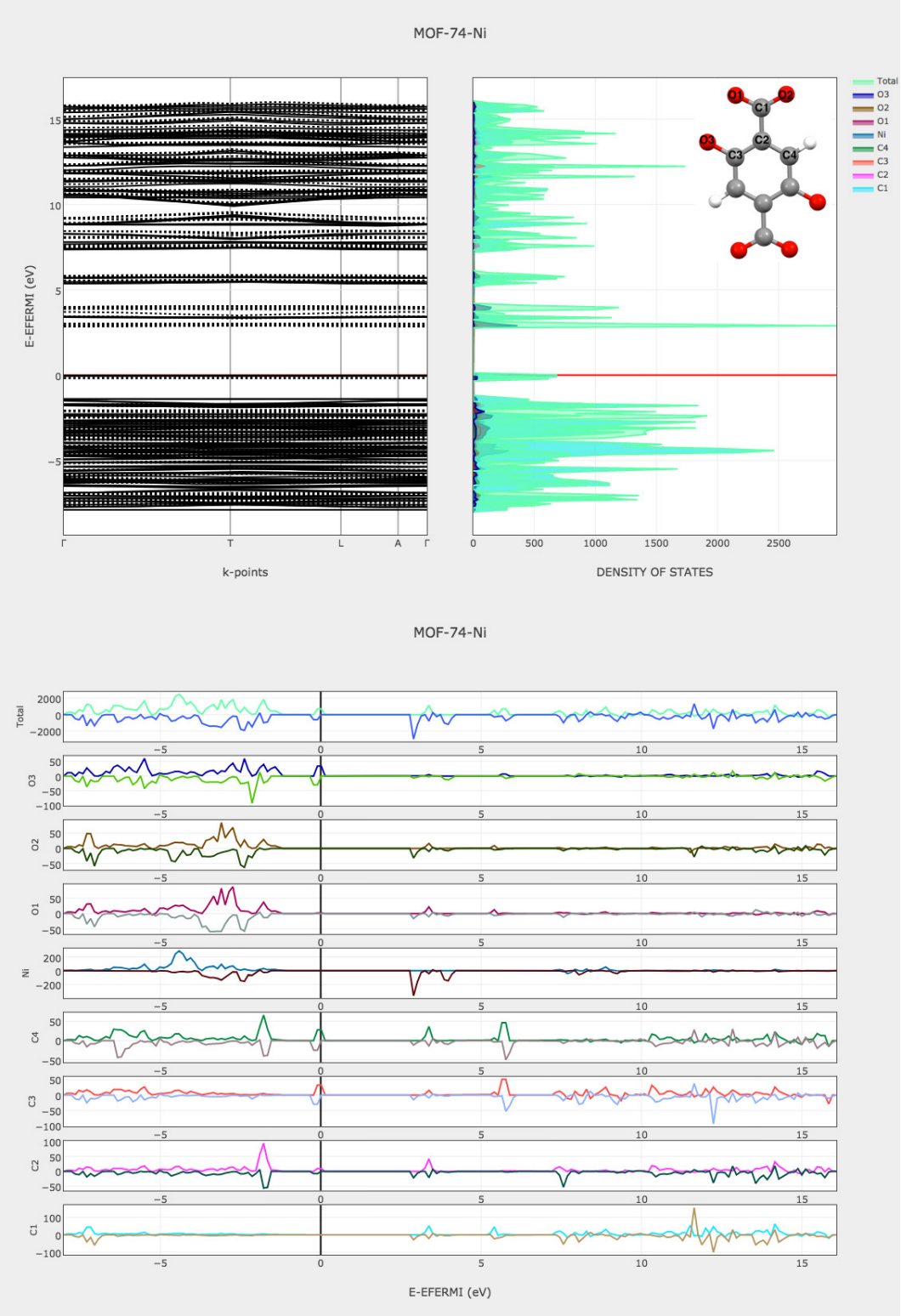

Figure S2. Electronic band structure and density of states (DOS) of MOF-74-Ni obtained using the B3LYP-D* functional. In the projected DOS, positive and negative values correspond to alpha and beta electrons, respectively.

UiO-66:

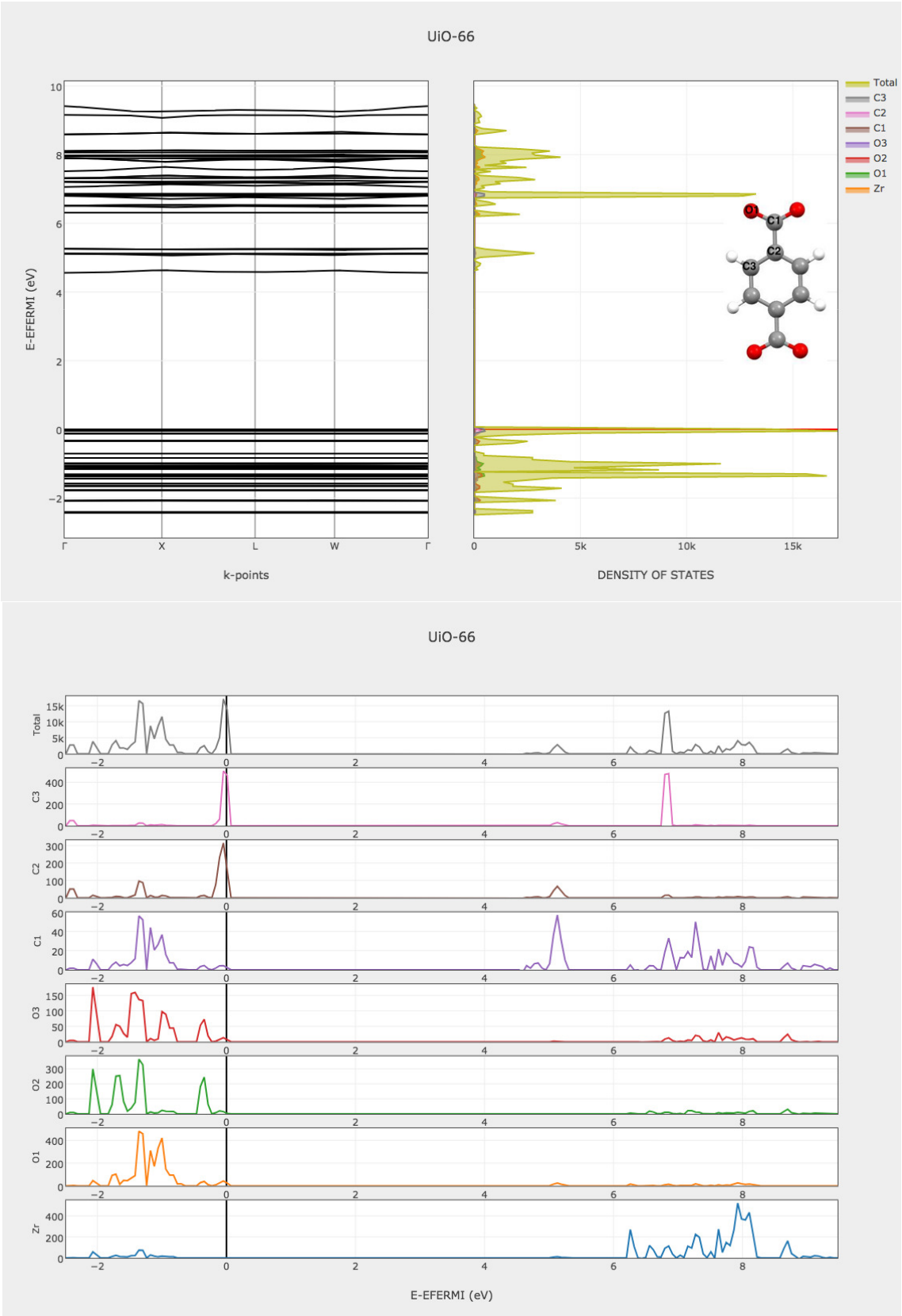

Figure S3. Electronic band structure and density of states (DOS) of UiO-66 obtained using the B3LYP-D* functional.

MIL-53 Large Pore:

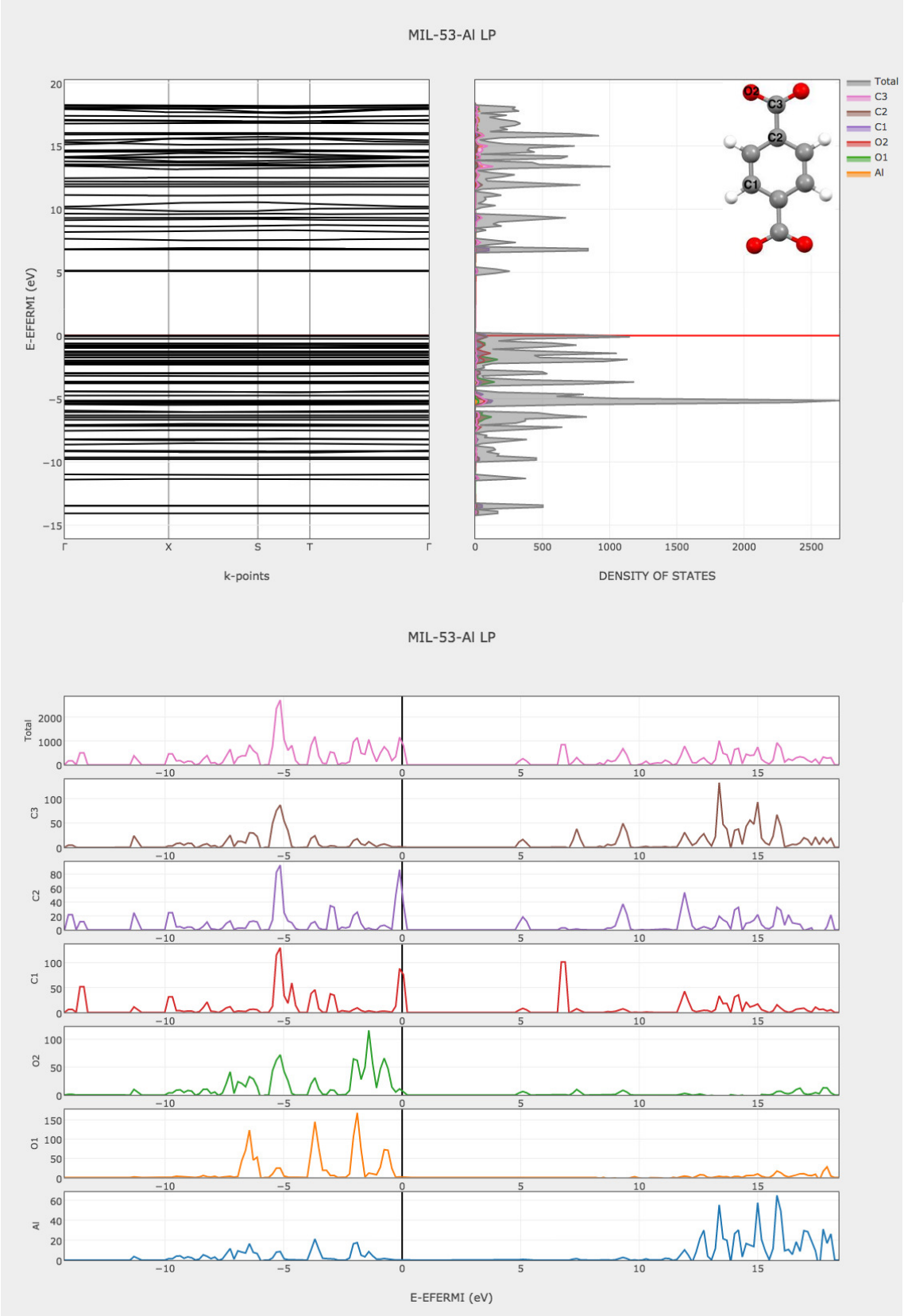

Figure S4. Electronic band structure and density of states (DOS) of MIL 53-Al (large pore) obtained using the B3LYP-D* functional.

MIL-53 Narrow Pore:

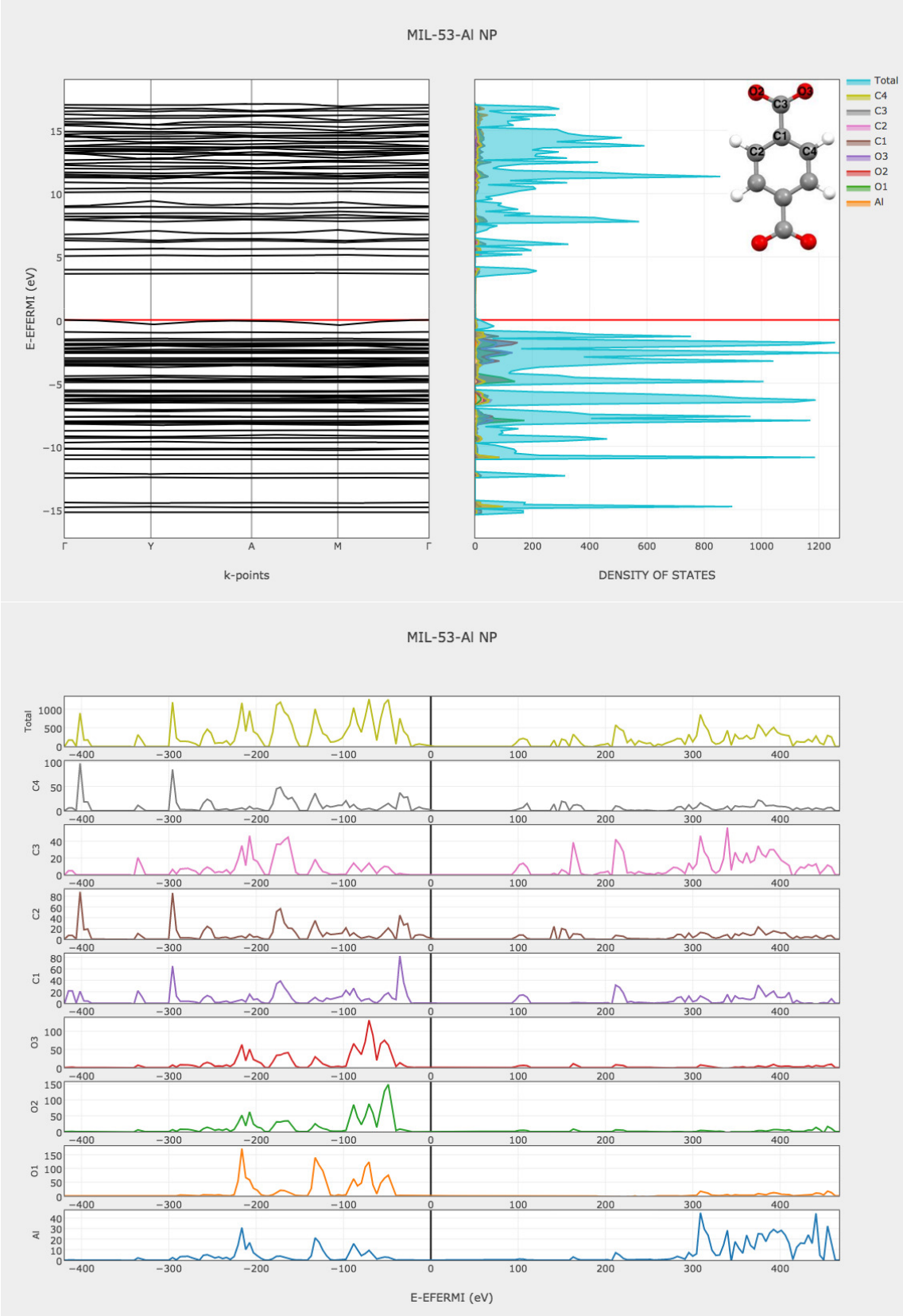

Figure S5. Electronic band structure and density of states (DOS) of MIL 53-Al (small pore) obtained using the B3LYP-D* functional.

S7. Voigt-Reuss-Hill averaged polycrystalline mechanical properties (in GPa) of UiO-66(OH) as obtained with the B3LYP-D* functional

C_{11}	C_{12}	C_{44}	Bulk Modulus	Shear Modulus	Young Modulus	Poisson Ratio	Ref.
59.7	29.3	20.0	39.4	17.9	46.7	0.30	Present work
59.4	31.9	17.6	41.0	-	-	-	(1)

(1) Hui Wu, Taner Yildirim, Wei Zhou "Exceptional Mechanical Stability of Highly Porous Zirconium Metal–Organic Framework UiO-66 and Its Important Implications" J. Phys. Chem. Lett. 2013, 4, 925–930

S8. Correlation between the static dielectric constant and the polarisability

Figure S6 reports the static dielectric constant as a function of the polarisability. It is shown that no obvious correlation can be identified between for the two quantities.

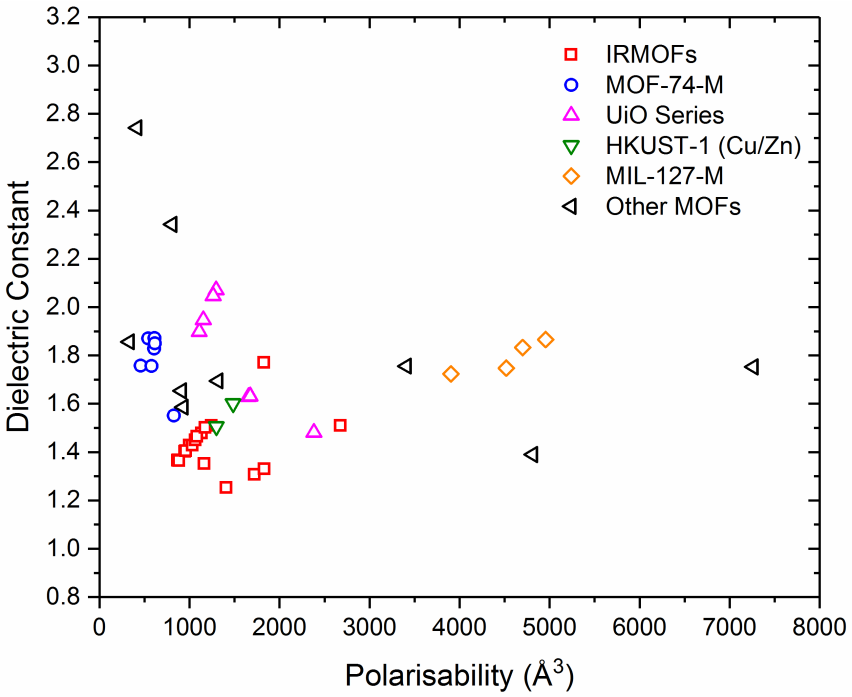

Figure S6. Correlation between the static dielectric constant and the polarisability obtained using the B3LYP-D* functional for the MOFs considered in this work. It is evident that the two quantities are not correlated.

S9. List of references for the MOF structures discussed

The geometries of the MOFs have been generated by starting from ones reported in the references listed below. For the series of MOFs, such as IRMOF-1, UiO-66, MOF-74-M, and MIL-127-M the initial structures were then modified to generate all the isoreticular series.

IRMOFs:
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Loredana Valenzano, Bartolomeo Civalleri, Sachin Chavan, Silvia Bordiga, Merete H. Nilsen, Søren Jakobsen, Karl Petter Lillerud, and Carlo Lamberti, *Chem. Mater.* **2011**, 23, 1700–1718.

Sachin Chavan, Jenny G. Vitillo, Diego Gianolio, Olena Zavorotynska, Bartolomeo Civalleri, Soren Jakobsen, Merete H. Nilsen, Loredana Valenzano, Carlo Lamberti, Karl Petter Lillerud, Silvia Bordiga, *Phys. Chem. Chem. Phys.* **2012**, 14, 1614-1626

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Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, 127, 1504–1518.
Dietzel, P. D. C.; Panella, B.; Hirscher, M.; Blom, R.; Fjellvag, H. *Chem. Commun.* **2006**, 959–961.

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A. M. Walker, B. Civalleri, B. Slater, C. Mellot-Draznieks, F. Corà, C. M. Zicovich-Wilson, G. Roman-Perez, J. M. Soler, Julian D. Gale *Angew. Chem. Int. Ed.* **2010**, 49, 7501 –7503

MIL-127-M:
Youssef Belmabkhout, Renjith S. Pillai, Dalal Alezi, Osama Shekhah, Prashant M. Bhatt, Zhijie Chen, Karim Adil, Sebastien Vaesen, Guy De Weireld, Maolin Pang, Mikhail Suetin, Amy J. Cairns, Vera

Solovyeva, Aleksander Shkurenko, Omar El Tall, Guillaume Maurin and Mohamed Eddaoudi*, J. Mater. Chem. A* **2017**,5, 3293-3303.

HKUST-1:

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MIL-68-M:

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M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez and G. Férey, *J. Am. Chem. Soc.*, **2009**, 131, 10857–10859

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