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Understanding and Controlling the Dielectric Response of Metal-Organic Frameworks

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(Article begins on next page)

CHEMPLUSCHEM

Supporting Information

Understanding and Controlling the Dielectric Response of Metal–Organic Frameworks

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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-CI	86s-4111sp-31d-1f	C 6-31d1	O 8-411d1	H 3-1p1	Cl 86-31d1	22	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	22	4	R3	-3
IRMOF-2-Br2	Zn	BDC-Br2	86s-4111sn-31d-1f	C 6-31d1	0 8-411d1	H 3-1n1	821111s-6311n-5	22	4	R-3	-3
IRMOF-3-NH2	2 7n	BDC-NH2	86s-4111sp-31d-1f	C 6-31d1	0 8-411d1	H 3-1n1	N 6-31d1	22	4	R3	-3
IRMOF-3-(NH2)2 (a)	2n 7n	BDC-(NH2)2 (a)	86s-4111sp-31d-1f	C 6-31d1	0 8-411d1	H 3-1n1	N 6-31d1	22	3	F-43M	m-3m
	211 7n		86c 4111cp 21d 1f	C 6 21d1	0 8 41141	L 2 1n1	N 6 21d1	22	1	1-4-5101	2
	20		805-41115p-510-11	C 6-3101	0 8-41101	п 5-1р1	N 0-5101	22	4	R-5	-5
	20		805-41115p-510-11	C 6-3101	0 8-41101	п 5-1р1	N 0-5101	22	5	FIVI-SIVI	111-5111
IRIVIOF-1-NHZ-NUZ	Zn	BDC-INHZ-NOZ	865-41115p-310-1f	C 6-3101	0 8-41101	H 3-101	N 6-3101	22	4	K3	-3
IRMOF-1-NO2	Zn	BDC-NO2	865-4111sp-31d-1f	C 6-31d1	08-41101	H 3-1p1	N 6-3101	22	4	R3	-3
IRMOF-8	Zn	2,6-NDC	86s-4111sp-31d-1f	C 6-31d1	0 8-411d1	H 3-1p1		22	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		22	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	22	4	R3	-3
UiO-66-NH2	Zr	BDC-NH2	9s-7631sp-621d	C 6-31d1	O 8-411d1	H 3-1p1	N 6-31d1	22	4	R3	-3
UiO-67	Zr	BPDC	9s-7631sp-621d	C 6-31d1	O 8-411d1	H 3-1p1		22	3	F23	m-3
UiO-67 dehvdrox	Zr	BPDC	9s-7631sp-621d	C 6-31d1	0 8-411d1	H 3-1p1		2.2	4	R32	-3m
UiO-68	Zr	TPDC	9s-7631sp-621d	C 6-31d1	0 8-411d1	H 3-1p1		2.2	3	F-43M	m-3m
MII-140-A	 7r	BDC	9s-7631sp-621d	C 6-31d1	0 8-411d1	H 3-1n1		22	6	C2/C	2/m
NU-1000	21 7r	TRAPV	9s=7631sp=621d	C 6-31d1	0 8-411d1	H 3-1n1		11	1	P=6M2	6/mmm
DUT-122	21 7r	EDC	9s-7631sp-621d	C 6-31d1	0.8-41141	H 2_1n1		11	1	DV3	m_3
FJI-H6-OH	Zr	ТВРР	9s-7631sp-621d	C 6-31d1	0 8-411d1 0 8-411d1	H 3-1p1	N 6-31d1	2 2	4	P23	m-3
MOF-74-INI family											
MOF-74-Mg	IVIg	DOBDC	POB-TZVP	C 6-31d1	08-41101	H 3-1p1		22	4	K-3	-3
MOF-74-Mn	Mn	DOBDC	POB-TZVP	C 6-31d1	0 8-411d1	H 3-1p1		2.2	4	R-3	-3
MOF-74-Fe	Fe	DOBDC	POB-TZVP	C 6-31d1	0 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	AI	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	0 8-411d1	H 3-1p1	N 6-31d1	2 2	6	P-42C	4/mmm
MIL-53 Narrow and La	arge 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	AI	BDC	POB-TZVP	C 6-31d1	0 8-411d1	H 3-1p1		2 2	5	IMMA	mmm
Other MOEs											
	6.	DDC	m n\/07 00	C 6 2141	00/11/4	L 2 1-1		2.2	F	CNACNA	
	Ga	BUC	m-pvDZ-PP	C C 21-11	0 8 41101	п 5-1р1		22	o c	CIVICIVI	mm
IVIIL-08-III	in 	BDC	m-pvDZ-PP	C 0-3101	0 8-41101	н з-1р1		22	0		mmm
IVIIL-125	11	BDC	865-4115p-31d	C 6-3101	0 8-411d1	н з-1р1		22	4		4/mmm
HKUSI-1	Cu	BIC	865-4115p-31d	C 6-3101	0 8-411d1	н з-1р1		22	3	FIVI-3IVI	m-3m
HKUSI-1-ZN	Zn	BIC	865-4111sp-31d-1f	C 6-31d1	U 8-411d1	н з-1р1		22	3	FM-3M	m-3m
CPO-54-Zn	Zn	DH2PhDC	865-4111sp-31d-1f	C 6-31d1	U 8-411d1	н 3-1р1		2.2	4	P3221	-3m
medi-MOF-1	Zn	Curcumin	865-4111sp-31d-1f	C 6-31d1	O 8-411d1	Н 3-1р1		22	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

2,6-NDC=2,6-naphthalenedicarboxylate BDC=1,4-benzenedicarboxylate BDC-F=2-fluoro-1,4-benzenedicarboxylate BDC-F2=2,5-difluoro-1,4-benzenedicarboxylate BPDC=biphenyl-4,4'-dicarboxylate HPDC=4,5,9,10-tetrahydropyrene-2,7-dicarboxylate BDC-F4=2,3,5,6-tetrafuoro-1,4-benzenedicarboxylate PDC=2,7-pyrenedicarboxylate BDC-Cl=2-chloro-1,4-benzenedicarboxylate 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 ${\tt BDC-Br=2-bromo-1,4-benzenedicarboxylate}$ 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 TBPP=4',4"",4""",4""",4"""-(porphyrin-5,10,15,20-tetrayl)tetrakis([1,1'-biphenyl]-4-carboxylate BDC-(NH2)2 (b)=2,5-diamino-1,4-benzenedicarboxylate DOBDC=2,5-dihydroxy-1,4-benzenedicarboxylate BDC-(NH2)4=2,3,5,6-tetraamino-1,4-benzenedicarboxylate ABD=3,3',5,5'- azobenzenetetracarboxylate BTC=1,3,5-benzenetricarboxylate DH2PhDC=3,3'-dihydroxy-[1,1'-biphenyl]-4,4'-dicarboxylate BDC-NH2-NO2=2-amino-5-nitro-1,4-benzenedicarboxylate BDC-NO2=2-nitro-1,4-benzenedicarboxylate

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

Functional	%HF	Band Gap (eV)	Polarizability (ų)	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

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

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.

[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.

^[1] P. Pernot, B. Civalleri, D. Presti and A. Savin *J. Phys. Chem. A* **119** (2015) 5288-5304.

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

Ba	Basis Set Num			Polarizability	Dielectric	Volume	Density
Zn	H/C/O	of AO	Gap (eV)	(Å ³)	tensor	(Å ³)	(g/cm^3)
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-5 (Cubic – Fm3m)

MOF-74-Mg (Hexagonal – R-3)

Basis Set		Number Band		Polariza	ability	Diele	ectric	Volume	Density										
Mg	H/C/0	of AO	Gap (eV)	(Å3)		(Å3)		(ų)		(ų)		(ų)		tensor		tensor		(Å3)	(g/cm ³)
				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						Primitive cell	Density
			(Å ³)						Volume	(g cm ⁻³)
IRMOF-1 family			xx	xv	X7	vv	¥7	77	(Å ³)	10 - 7
	7n	BDC	868.2	~	~~				(~) 4424 0	0.57
	211 7n	BDC	1925 5					1705 8	4424.0	1 15
	211 7n		071 0	6.2	6.2	071 2	6.2	071 0	4410.0	0.61
	Z11 Zie	BDC-F	871.2	-0.5	-0.5	071.2	-0.3	071.2	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-CI	Zn	BDC-CI	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	 7n	BPDC	1408 3			200711		200210	10377 1	0.32
	211 7n	HPDC	1721 /						10/38 1	0.32
	211 7n	DDC	1721.4 1921 E						10438.1	0.37
IRIVIOF-14	20	PDC	1831.5						10315.5	0.37
IRMOF-18	Zn	IMBDC	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 dehvdrox	Zr	BPDC	1655.3	47.8	47.8	1655.3		1655.3	4880.7	0.71
UiO-68	- 7r	TPDC	2382.0						9219.8	0.46
MII -140-A	 7r	BDC	808 1	-108.6		831 5		643 1	1056.0	1 70
	21 7r	TRADY	1211 0	-100.0		051.5		671/1	22006.0	0.47
NU-1000	21 7r		7262 /					0714.1	17082.0	0.47
FJI-H6-OH	Zr	ТВРР	4300.6						16778.7	0.84
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										
	A I		2002.0					2020 1	10042.1	0.96
	Ai Ca	ADD	3903.9					4522.0	11240 5	0.80
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 L	arge Pore	2								
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
MII -68-In	In	BDC	931 4			923.7		1044 9	3070 5	0.96
MII-125	ті	RDC	1218 /			525.7		1110 2	3253.5	0.20
	C	BTC	1/02 0					1110.3	1505 1	0.00
	20 70	DIC	1200 1						4535.1 1776 F	0.07
	Z11 7		1290.1					074.2	4//0.5	0.84
	Zn Zu		827.8					9/4.2	2/98.0	0.71
meai-MOF-1	Zn -	Curcumin	3409.9		a c a			2432.2	/195.7	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	01	Dielectric tensor			U		5	Band Gap	Porosity
IRMOF-1 family			xx	хү	xz	YY	ΥZ	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-CI	1.40	0.00	0.00	1.40	0.00	1.40	4.68	73.6
IRMOF-2-Br	<u>_</u> 7n	BDC-Br	1 43	0.00	0.00	1 43	0.00	1 43	4 56	72.4
IRMOF-2-Br2	<u>_</u> 7n	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	<u>_</u> 7n	BPDC	1.25			1.01		1.0 .	4.51	85.4
IRMOF-12	<u>_</u> 7n	HPDC	1.31						4.07	81.9
IRMOF-14	<u>_</u> 7n	PDC	1.33						3.63	82.6
IRMOF-18	<u>_</u> 7n	TMBDC	1.50						5.95	58.2
	2	Interest	1.50						5.55	50.2
Zr-based MOFs	7.		1.00						4.50	40.0
	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	0.00	0.00	4.60		1.60	4.09	64.2
UIO-67 dehydrox	Zr	BPDC	1.63	0.02	0.02	1.63		1.63	4.03	68.3
	Zr	TPDC	1.48			o 47			3.54	/5.2
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	/8.8
DUT-122	Zr	FDC	1.75						3.64	58.7
FЛ-H0-OH	Zr	IBPP	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	AI	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 L	arge Pore	2								
MIL-53 NP	AI	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 MOEs										
MIL-68-Ga	63	BDC	1.67			1 62		1 72	4 83	53.6
MIL-00-0a	Ud In	BDC	1.02			1.02		1.72	4.03 5.01	55.0 57.6
MIL-00-III	111 T:		1.30			1.20		1 64	2.UI	52.0 67 E
	 	DUC	1.75					1.04	4.33	02.5 66 A
	Cu 7n	DIC	1.00						E //	00.4 677
CDO-54-7p	211 7n		1.51					1 65	J.44 4 00	07.7 72 /
medi_MOE_1	211 7n	Curcumin	1.33					1 60 1 60	4.00 ว ๑ ว	72.4 61 0
7n(OA)2	211		1.00		0.20	2 40		1.03 2 4 7	2.03 E F 4	04.0
211(UA)2	Zn	Oxalic Acid	2.65		-0.38	z.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.





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

C11	C ₁₂	<i>C</i> 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.

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