Electronic Supplementary Information

Synthesis of 2D and 3D MOFs with tuneable Lewis acidity from preformed 1D hybrid sub-domains

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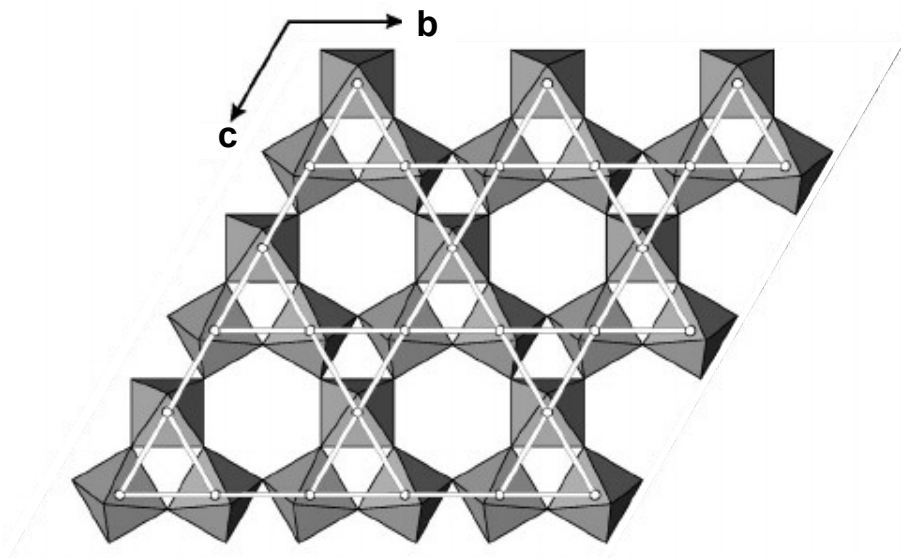
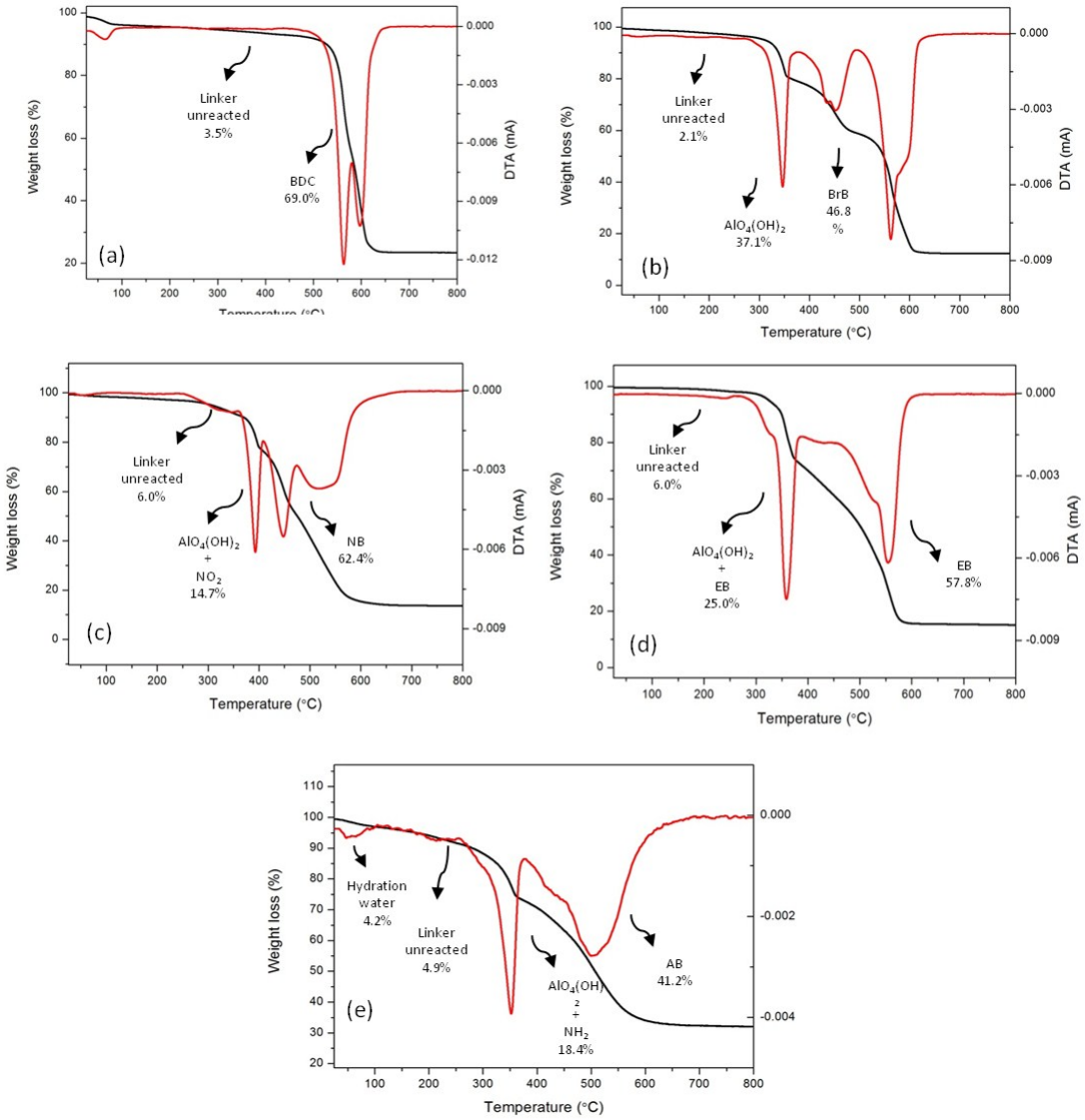


Figure S1. Representation of layers present in the solids L-MOF-EB and L-MOF-AB, based on associated aluminium octahedra following a Kagomé system. The organic spacers perpendicularly disposed to the layers were omitted for clarity. Image adapted from J. Frunzke *et al., J. Mater. Chem.,* 2001, **11**, 179-185.



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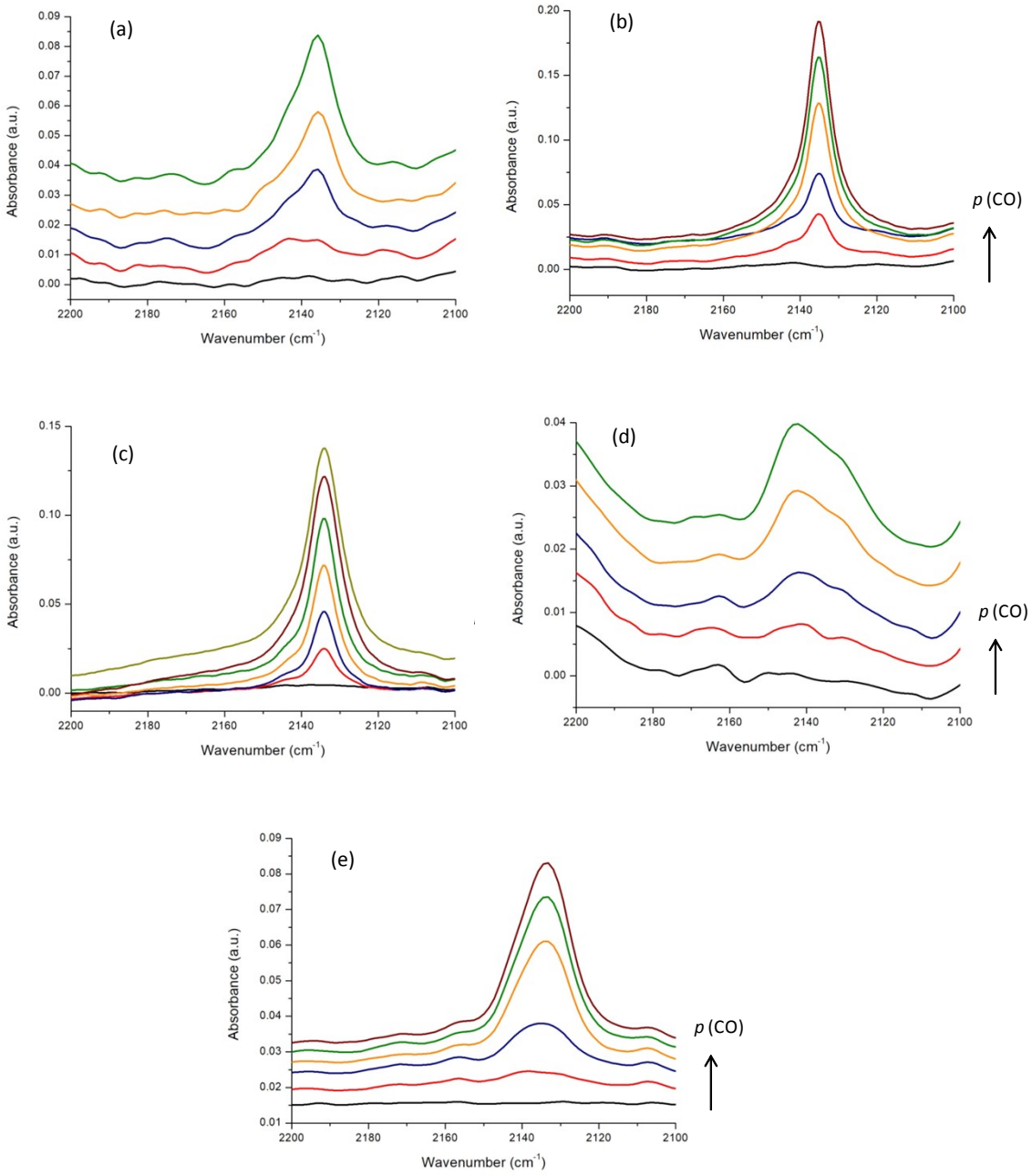

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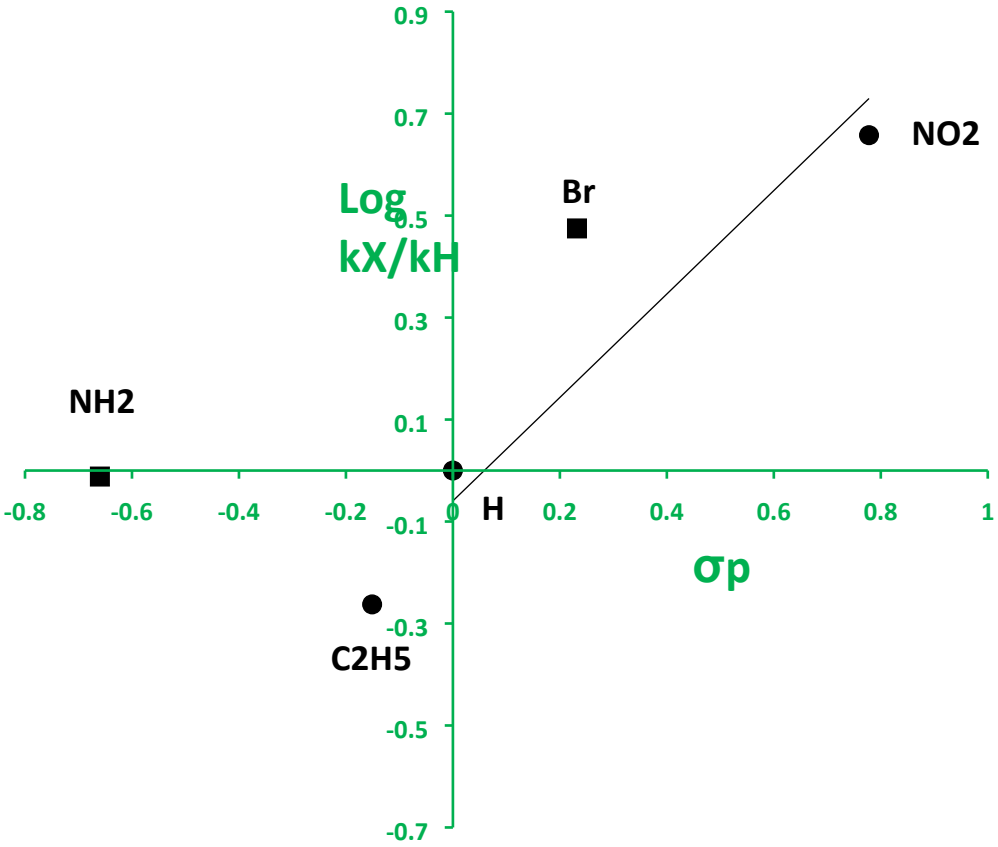

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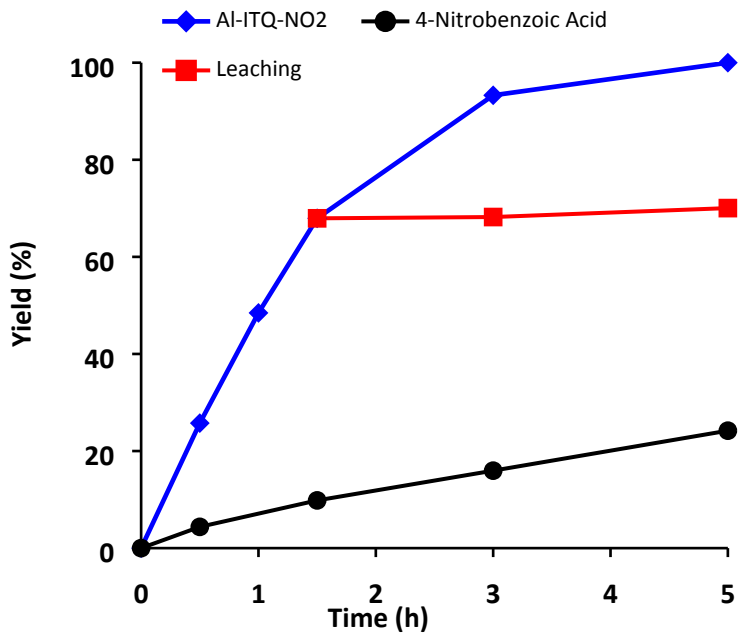


Figure S5. Kinetics for cyanohydrins production using Al-ITQ-NO_2 (0.5 mol% Al) and 4-nitrobenzoic acid (0.5 mol%) as catalysts. Test leaching was also represented.

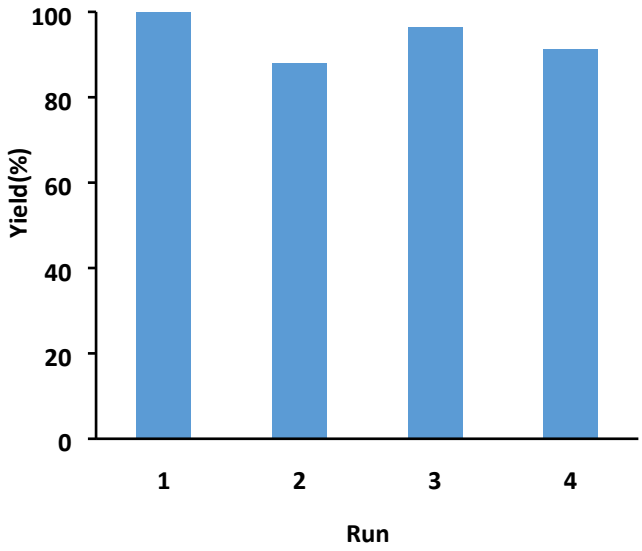


Figure S6. Yield for four consecutive uses for reaction of cyanosilylation of benzaldehyde at 5 h of reaction.

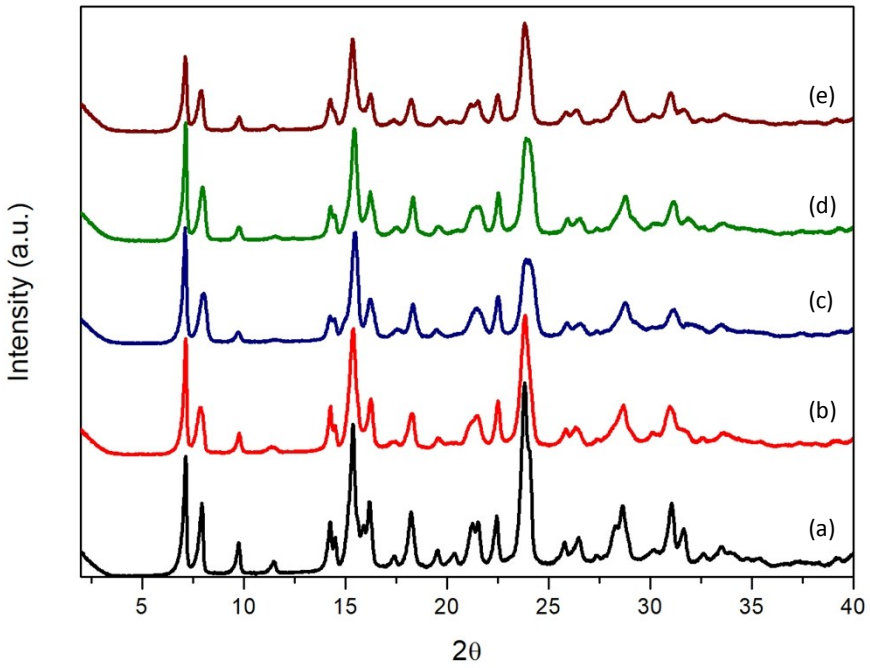
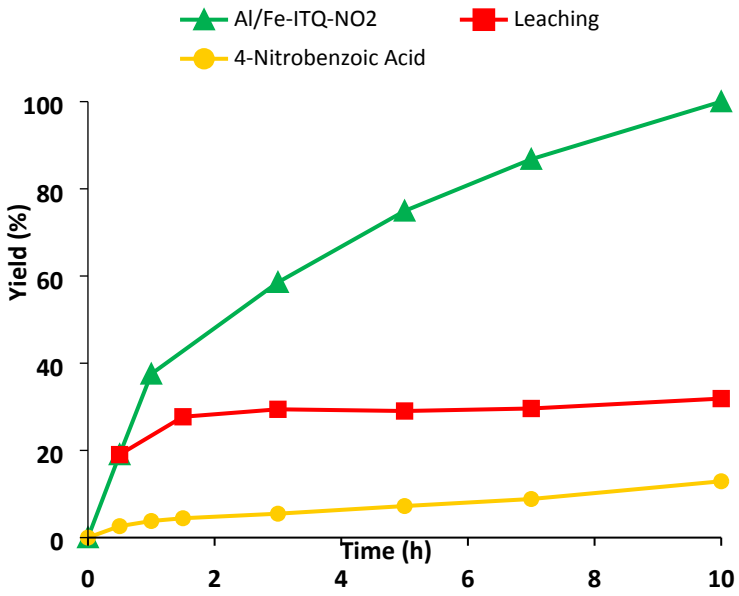


Figure S7. XRD patterns of Al-ITQ-NO_2 catalyst: (a) fresh, (b) first use, (c) second use, (d) third use and (e) fourth use.



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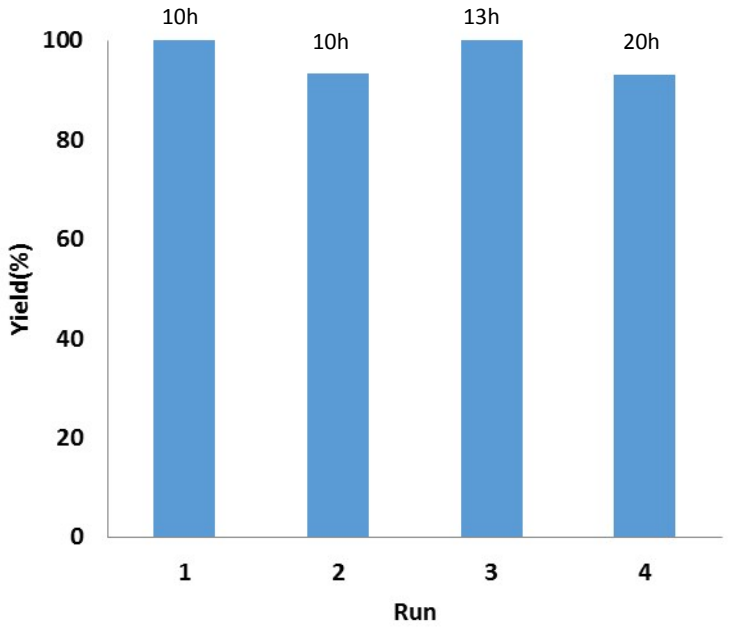

Figure S9. Yield for four consecutive uses for reaction of thiophenol oxidation.

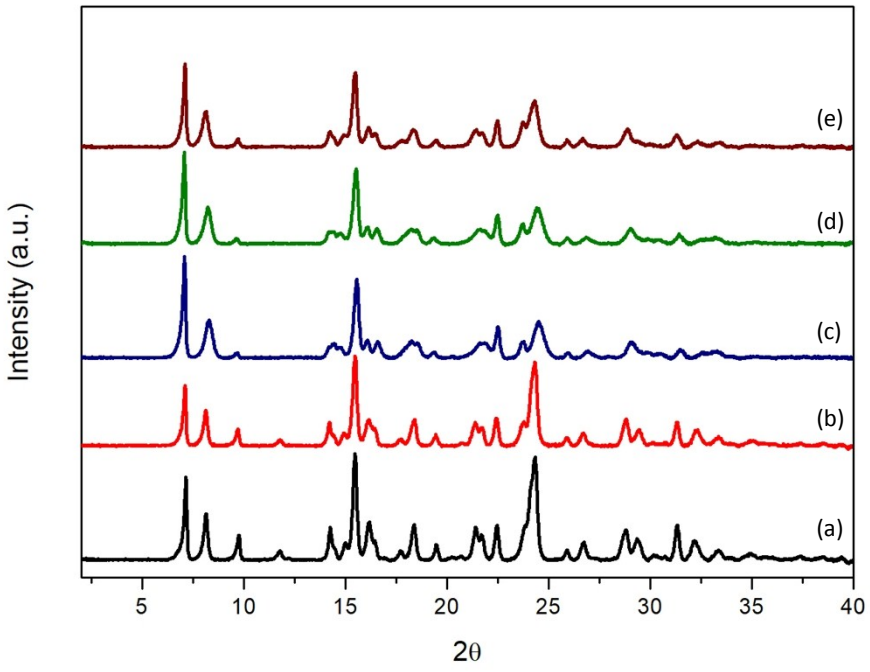

Figure S10. XRD patterns of Al/Fe-ITQ-NO_2 catalyst: (a) fresh, (b) first use, (c) second use, (d) third use and (e) fourth use.

Table S1. CO_2 uptake capacities of Al-MOF-type materials at 0ºC and 1 bar.

Samples	Adsorbed Volume (cm^3/g)
Al-ITQ-NO_2	24.3
Al/Fe-ITQ-NO_2	16.1
Al-ITQ-Br	14.7
L-MOF-EB	4.8
L-MOF-AB	6.3

Table S2. Yields and initial reaction rates for the cyanosilylation of aromatic aldehydes catalyzed by Al-ITQ-NO_2[a].

Substrate	Yield (%)	r_0 ($mol \cdot L^{-1} \cdot h^{-1}$)	TON	TOF (h^{-1}) [b]	TOF (h^{-1}) [c]
2-Napthaldehyde	90	3.5	180	179	134
4-Methylbenzaldehyde	99	2.9	200	148	154
4-Methoxybenzaldehyde	89	1.3	177	66	69

[a] Reaction conditions: Aldehydes (5 mmol), TMSCN (6 mmol), 0.5 mol %Al, at 30ºC, 5 h. [b] Calculated at initial rate. [c] Calculated at 0.5 h.

Table S3. Yields, TON and TOF values of different conventional MOFs for the preparation of cyanohydrins.

Samples	Catalyst loading (mol%)	Yield (%)	TON	TOF (h^{-1})[e]
MIL-47(V)[a] [1]	1	46	46	-
MIL-53(Al)[a] [1]	1	26	26	-
UiO66(Zr)[a] [1]	1	68	68	-
MIL-101(Cr)[a] [1]	1	96	96	541
In-MOF[a] [2]	1	72	72	204
In-MOF[a] [2]	0.1	80	800	1320
Zr-MCM-41[b] [3]	2	28	14	2
Zr-β[b] [3]	1	99	99	61
Cp-Zr-binol-SBA-15[b] [3]	2	95	48	0.7
Al-MCM-41[b] [4]	1	99	99	108
AlPO-5[b] [3]	10	0	-	-
H-Y[c] [4]	-	4	-	-
H-ZSM-5[c] [4]	-	0	-	-
Er-MCM-41[d] [5]	-	90	137	137[f]
Al-ITQ-NO_2[a]	1	97	97	210
Al-ITQ-NO_2[a]	0.1	92	920	405

[a] Reaction conditions: Benzaldehyde (1 mmol), TMSCN (1.2 mmol), 30ºC, 3 h. [b] Benzaldehyde (1 mmol), TMSCN (2 mmol), 40ºC, 20 h, CH_2Cl_2 (2.5 mL). [c] Benzaldehyde (1 mmol), TMSCN (5 mmol), 5 mg catalyst, 0ºC, 1 h, CH_2Cl_2. [d] Benzaldehyde (0.66 mmol), TMSCN (1.3 mmol), 10 mg catalyst, room temperature, 1 h. [e] Calculated at initial reaction rate. [f] Calculated at 1 h. In blue, hybrid catalyst synthesized in this study.

Table S4. Yields, TON and TOF values of MIL-101(Cr) with different mol% of active centres for the preparation of cyanohydrins.[a].

Samples	Catalysts (mol%)	Yield (%)	Time (h)	TON	TOF (h^{-1})		
					b	c	d
MIL-101(Cr)[6]	1.0	96	1.5	96	64	541	154
Al-ITQ-NO_2	1.0	97	3.0	97	32	210	105
MIL-101(Cr)[6]	0.55	96	2.5	174	69	382	187
Al-ITQ-NO_2	0.50	100	5.0	200	40	137	103
Al/Fe-ITQ-NO_2	0.50	98	5.0	196	39	410	242
MIL-101(Cr)[6]	0.25	95	5.0	380	76	360	240
MIL-101(Cr)[6]	0.15	95	8.0	633	79	300	210
Al-ITQ-NO_2	0.10	92	9.0	920	102	405	400

[a] Reaction conditions: Benzaldehyde (1 mmol), TMSCN (1.2 mmol), at 30ºC. [b] Calculated when the reaction was completed. [c] Calculated at initial rate. [d] Calculated at 0.5 h. In blue, hybrid catalysts synthesized in this study.

Table S5. Yields and initial reaction rates for the preparation of diphenyldisulfide[a].

Samples	Yield(%)	TON
Al/Fe-ITQ-NO_2	100	10
Al-ITQ-NO_2	33	3.3
MIL-53(Al)	11	1.1
MIL-53(Al)-NO_2	4	0.4
4-Nitrobenzoic Acid (10 mol%)	13	-
Blank	3	-
Fe(BTC)[b] [7]	64	2.5
MIL-100(Fe)[b] [7]	81	2.3

[a] Reaction conditions: Thiophenol (0.48 mmol), 10 mol %Fe, 70ºC, 10 h, acetonitrile (1 mL). [b] Thiophenol (0.250 mL), 9 mg Fe(BTC) or 10 mg MIL-100(Fe), 70ºC, 24 h, acetonitrile (5 mL)

References

[1] Z. Zhang, J. Chen, Z. Bao, G. Chang, H. Xing and Q. Ren, *RSC Adv*., 2015, **5**, 79355-79360.

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