Electronic Supplementary Material (ESI) for New Journal of Chemistry

Combinatorial Synthesis of Metal-Organic Frameworks libraries by Click-Chemistry

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Supporting Information

Chemicals

DMF, C_3H_7NO (Aldrich, 99.8%); dichloromethane, CH_2Cl_2 (Acros Organics, 99.99%); tetrahydrofuran, THF, C_4H_8O (Aldrich, 99%); methanol, MeOH, CH_4O (Sigma-Aldrich, 99 %); 2-aminoterephthalic acid, NH_2-bdc, $C_8H_7NO_4$ (Alfa Aesar, 99%); 1,4-diazabicyclo[2.2.2] octane, DABCO, $C_6H_{12}N_2$ (Aldrich, 98%); indium nitrate, $In(NO_3).4H_2O$ (Alfa Aesar, 99.99%); zinc nitrate, $Zn(NO_3)_2{\cdot}4H_2O$ (Merck, 98.5%); aluminium chloride, $AlCl_3.6H_2O$ (Sigma-Aldrich, 98%); iron chloride, $FeCl_3.6H_2O$ (Fluka, 97%); *tert*-butyl nitrite, tBuONO, $C_4H_9NO_2$ (Aldrich, 90%); trimethylsilyl azide, $TMSN_3$, $C_3H_9N_3Si$ (Aldrich, 99.5%); tetrakis(acetonitrile)copper(I) hexafluorophosphate, $Cu^I(CH_3CN)_4PF_6$ (Aldrich, n.c); phenylacetylene, C_8H_6 (Aldrich, 98%); diethylpropargylamine, $C_7H_{13}N$ (Fluka, 90%); 1-hexyne, C_6H_{10} (Aldrich, 97%); propargyl alcohol, C_3H_4O (Aldrich, 99%); propargylamine, C_3H_5N (Aldrich, 98%); propiolic acid, $C_3H_2O_2$ (Aldrich, 95%); deuterium chloride, DCl (Aldrich, 99% D); deuterated dimethyl sulfoxide, DMSO-d_6, C_2D_6OS (Eurisotop, 99.8% D); sodium deuteroxide, NaOD (Aldrich, 99% D); and hydrogen fluoride, HF (Merck, 40%).

DMOF-NH_2 (1)

^{1}H NMR 250 MHz, (DCl/D_2O/DMSO-d_6) δ: 3.52 (s, 6.68H, DABCO), 7.13 (d, 1H, J = 8.3Hz), 7.47 (s, 1H), 7.79 (d, 1H, J = 8.3Hz).BET surface area: 1320 $m^2.g^{-1}$

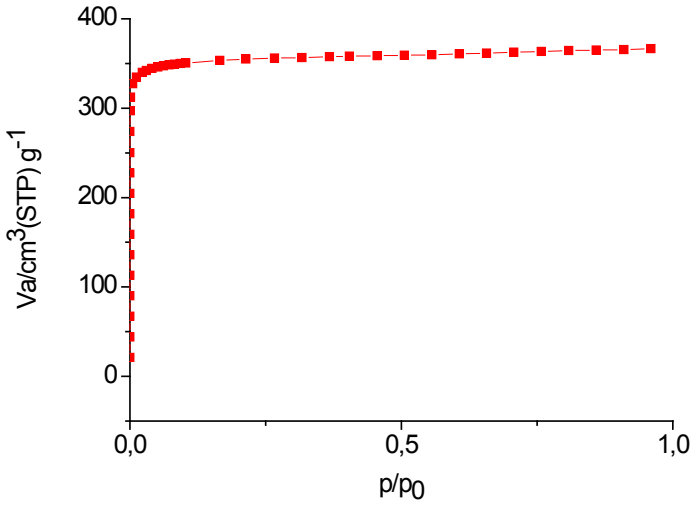

Figure S1. N_2 adsorption isotherms of DMOF-NH_2 (1)

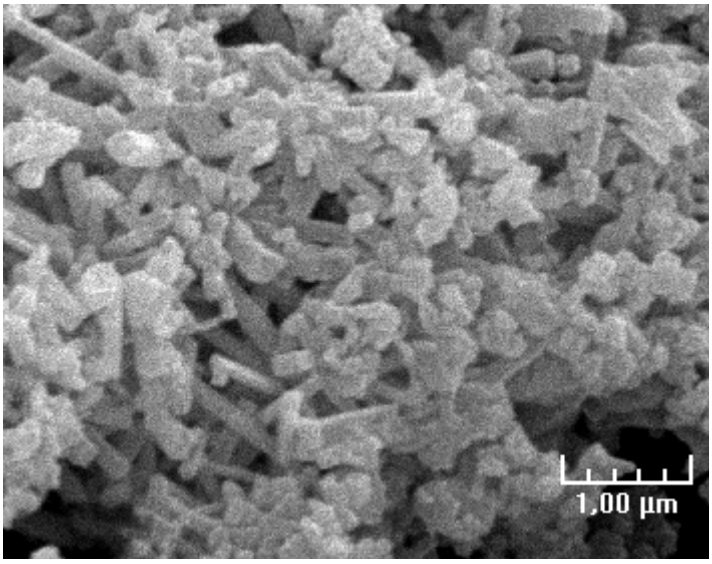

Figure S2. SEM photograph of DMOF-NH_2 (1)

MIL-68(In)-NH_2 (2)

^{1}H NMR 250 MHz, (DCl/D_2O/DMSO-d_6) δ: 7.15 (d, 1H, J = 8.3Hz), 7.44 (s, 1H), 7.80 (d, 1H, J = 8.3Hz). BET surface area: 1120 $m^2.g^{-1}$.

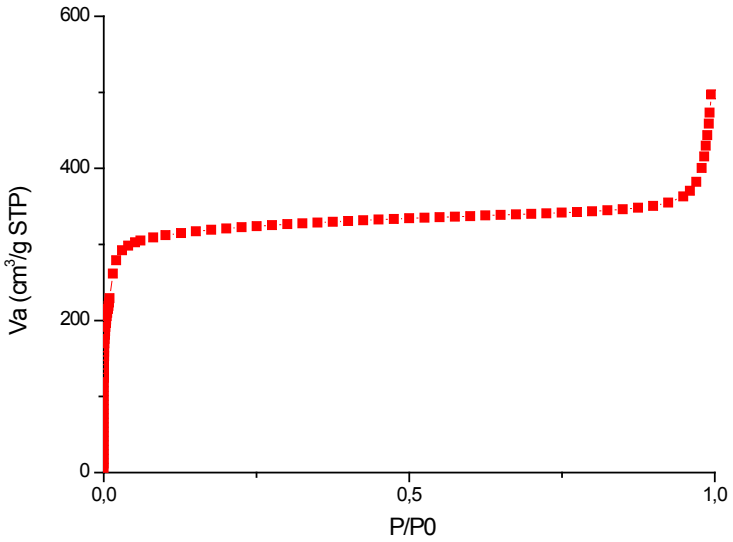

Figure S3. N_2 adsorption isotherms of MIL-68(In)-NH_2 (2)

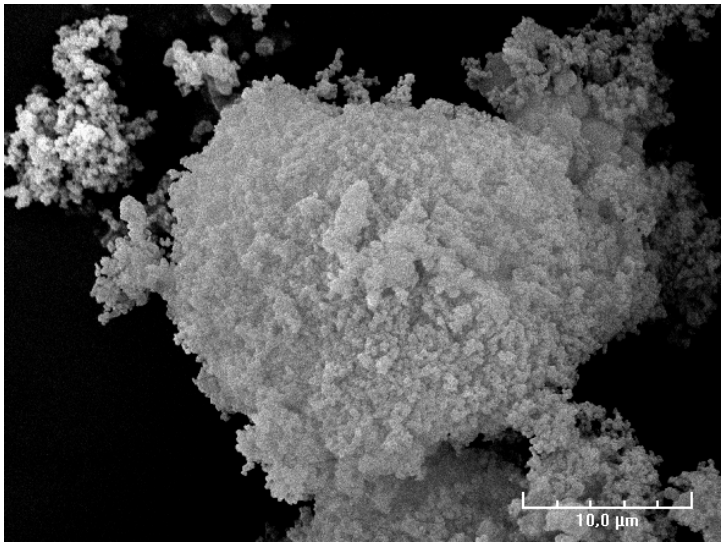

Figure S4. SEM picture of MIL-68(In)-NH_2 (2)

CAU-1 (3)

^{1}H NMR 250 MHz, (DCl/D_2O/DMSO-d_6) δ: 6,88 (d, 1H, J = 8 Hz); 7,03 (s, 1H); 7,6 (d, 1H, J = 8 Hz).

BET surface area: 1434 $m^2.g^{-1}$.

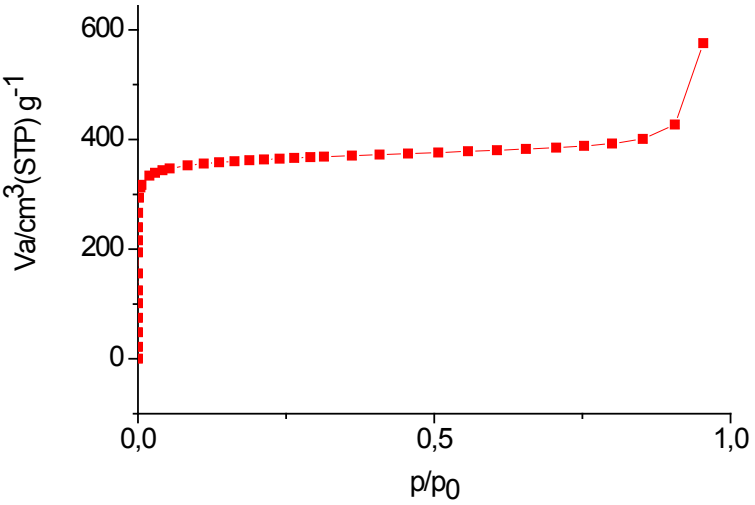

Figure S5. N_2 adsorption isotherms of CAU-1 (3)

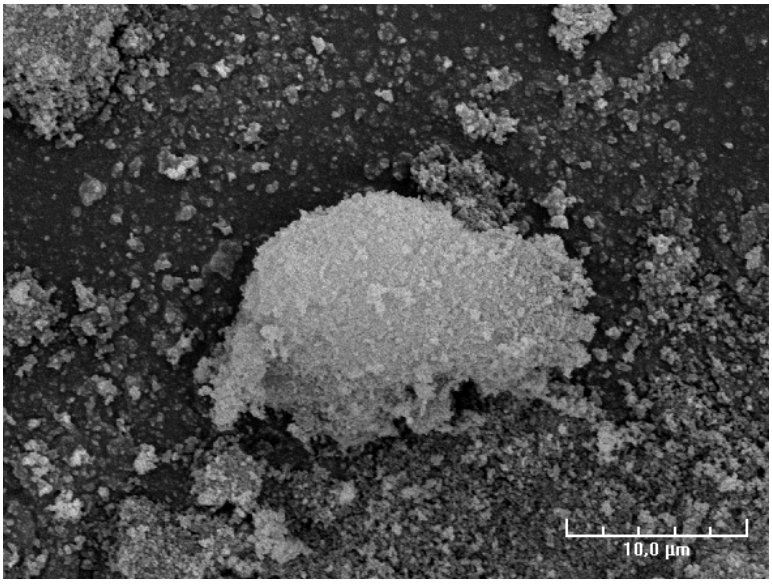

Figure S6. SEM photograph of CAU-1 (3)

MIL-53(Al)-NH_2 (4)

^{1}H NMR 250 MHz, (DCl/NaOD/D_2O/DMSO-d_6) δ: 7.15 (d, 1H, J = 8.3Hz), 7.44 (s, 1H), 7.80 (d, 1H, J = 8.3Hz).BET surface area: 1155 $m^2.g^{-1}$.

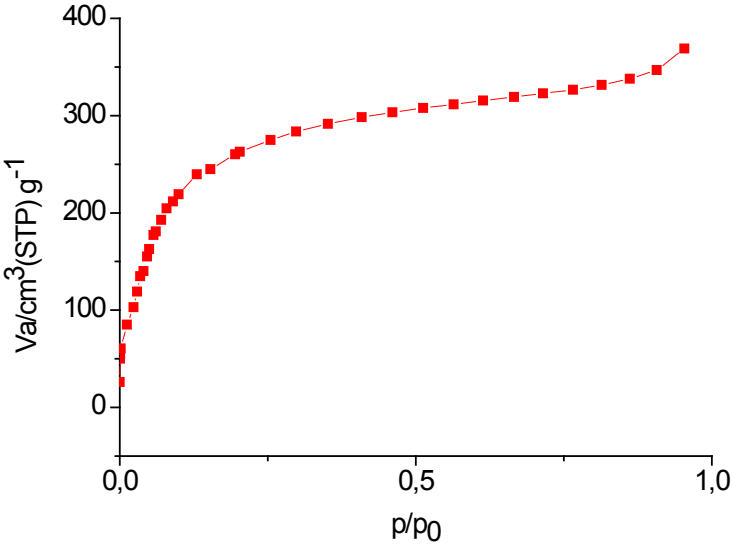

Figure S7. N_2 adsorption isotherms of MIL-53(Al)-NH_2 (4)

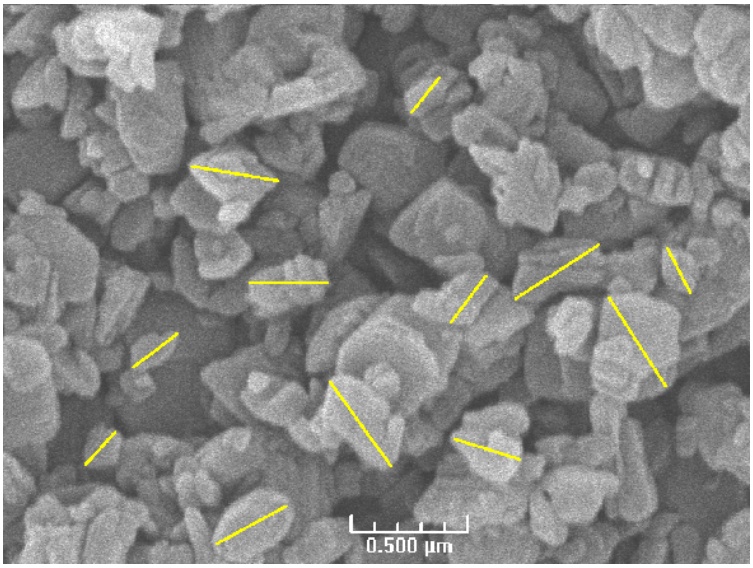

Figure S8. : SEM photograph of MIL-53(Al)-NH_2 (4)

MIL-101(Fe)-NH_2 (5)

^{1}H NMR 250 MHz, (DCl/D_2O/DMSO-d_6) δ: 7.32 (s, 1H); 7,63 (s, 1H); 7,86 (s, 1H).

BET surface area: 2436 $m^2.g^{-1}$ Porous volume: 1.12 $cm^3.g^{-1}$.

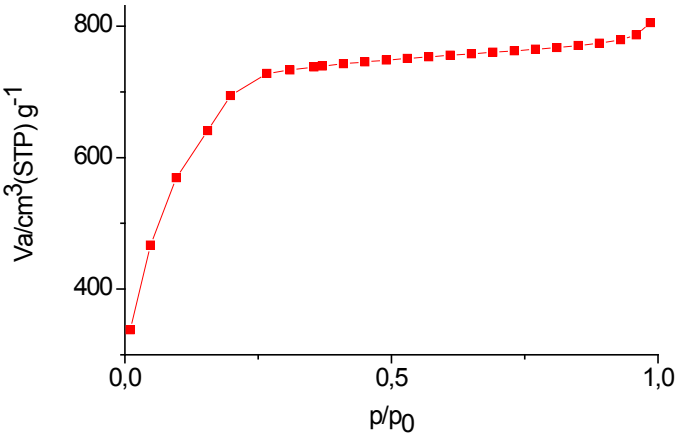

Figure S9. N_2 adsorption isotherms of MIL-101(Fe)-NH_2 (5)

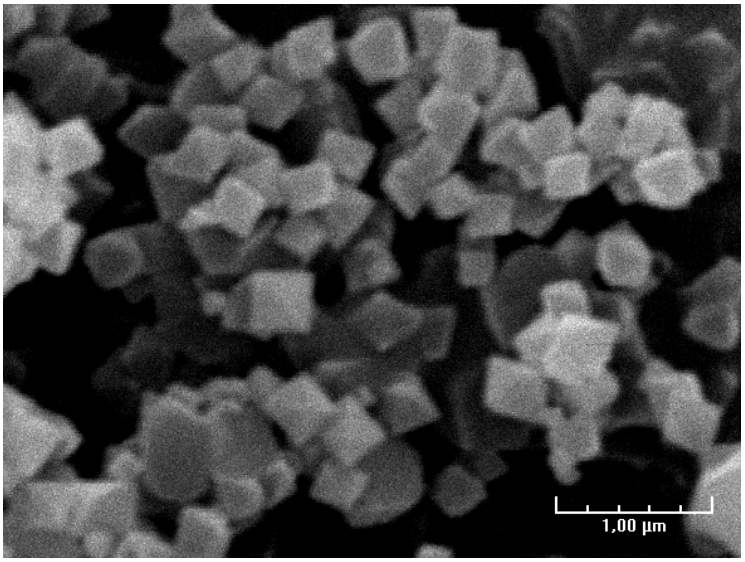

Figure S10. SEM photograph of MIL-101(Fe)-NH_2 (5)

Table S1. Experimental Conditions

	equiv of $-NH_2$	tBuONO $TMSN_3$	Cu^I (b)	Cu^I (c)	Cu^I (d)	Cu^I (e)	Cu^I (f)	Cu^I (g)
1	0.27 mmol	0.22 mL (1.84 mmol, 7 eq) 0.2 mL (1.51 mmol, 6 eq)	48 mg (0.13 mmol, 0.5 eq) 0.96 mL (8.8 mmol, 32 eq)	24 mg (0.06 mmol, 0.25 eq) 0.33 mL (2.3 mmol, 8.5 eq)	24 mg (0.06 mmol, 0.25 eq) 0.26 mL (2.3 mmol, 8.5 eq)	24 mg (0.06 mmol, 0.25 eq) 0.134 mL (2.3 mmol, 8.5 eq)	[b]	[a]
2	0.26 mmol	1.5 mL (12.5 mmol, 48 eq) 1.3 mL (9.88 mmol, 38 eq)	96 mg (0.26 mmol, 1 eq) 1.9 mL (17.6 mmol, 68 eq)	192 mg (0.52 mmol, 2 eq) 4.88mL (35.6 mmol, 136 eq)	144 mg (039 mmol, 1.5 eq) 2.02mL (17.6 mmol, 68 eq)	96 mg (0.26 mmol, 1eq) 1.54mL (26.6 mmol, 68 eq)	96 mg (0.26 mmol,1eq) 1.08mL (17.6 mmol, 51 eq)	96 mg (0.26 mmol, 1eq) 1.13mL (17.6 mmol, 68 eq)
3	0.3 mmol	0.74 mL (6.3 mmol, 21 eq) 0.65 mL (5 mmol, 17 eq)	55 mg (0.15 mmol, 0.5eq) 0.92 mL (8.4 mmol, 28 eq)	58 mg (0.15 mmol, 0.5eq) 1.18 ml (8.5 mmol, 28 eq)	55 mg (0.15 mmol, 0.5eq) 0.59 ml (5.1 mmol, 17 eq)	55 mg (0.15 mmol, 0.5eq) 0.3 ml (5.1 mmol, 17 eq)	55 mg (0.15 mmol, 0.5eq) 0.52 ml (8.4 mmol, 28 eq)	[a]
4	0.36 mmol	[c] 3.8 mL (32 mmol, 89 eq) 3.6 mL (28 mmol, 78 eq)	192 mg (0.52 mmol, 1.5eq) 2.7 mL (24.6 mmol, 68eq)	264 mg (0.71 mmol, 2eq) 3.3 mL (23 mmol, 68eq)	192 mg (0.52 mmol, 1.5eq) 2.8 mL (24.4 mmol, 68eq)	132 mg (0.36 mmol, 1eq) 1.2 mL (20.6 mmol, 57eq)	66mg (0.18 mmol, 0.5eq) 0.5 mL (8.1 mmol, 22eq)	[a]
5	0.3 mmol	0.3 mL (2.1 mmol, 7 eq) 0.27mL (1.8 mmol, 6 eq)	110 mg (0.3 mmol, 1 eq) 1.8 mL (16.8 mmol, 56 eq)	[a]	[a]	[a]	[a]	[a]

[a]: not performed; [b]: dissolution; [c]: performed in ethanol

Table S2. Comparison of the Lattice Parameters of Parent MOF and Modified Azide-MOF

	Parent MOF	MOF-N_3
DMOF-1	[4]quadratic system, *P4/m*, a= b = 10.929 Å, c=9.608 Å	quadratic system, *P4/m* a =b = 10.837 Å, c = 9.614 Å
MIL-68(In)	[5]orthorhombic system, *Cmcm* a = 21.7739 Å; b = 37.677 Å; c = 7.233 Å	orthorhombic system, *Cmcm* a = 21.804 Å; b = 37.517 Å; c = 7.207 Å
CAU-1	[6]quadratic system, *I4/mmm*, a = b = 18,3517 Å; c = 17,7772Å	quadratic system, *I4/mmm* , a = b = 18,384 Å; c = 17,803 Å
MIL-53(Al)	[7]Monoclinic system, *Cc*, a = 19.722 Å ; b = 7.692 Å; c = 6.578 Å	Monoclinic system, *Cc*, a = 19.892 Å ; b = 8.066 Å; c = 6.639 Å

The automatic indexing program DICVOL was used for the lattice parameters determination and the values of the lattice parameters were refined by Le Bail technique (full-pattern matching).

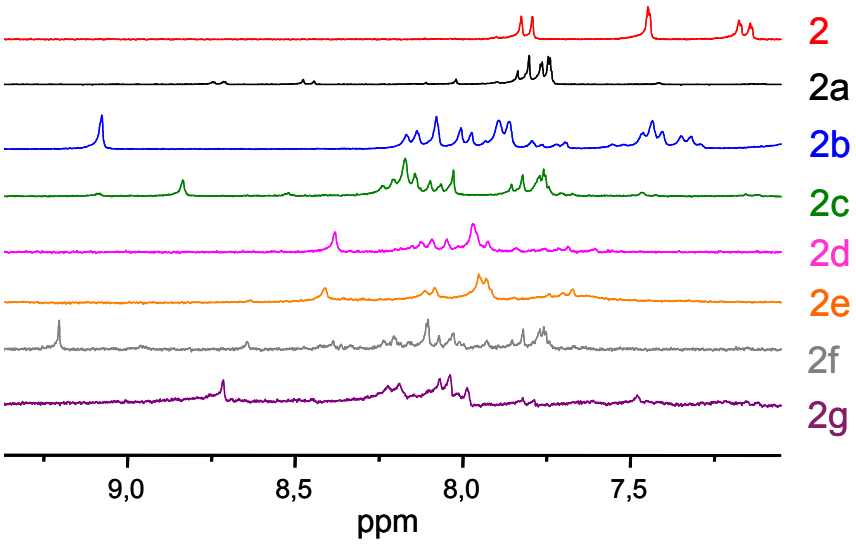

Figure S11. ^{1}H NMR of digested (2), (2a), (2b), (2c), (2d), (2e), (2f) and (2g)

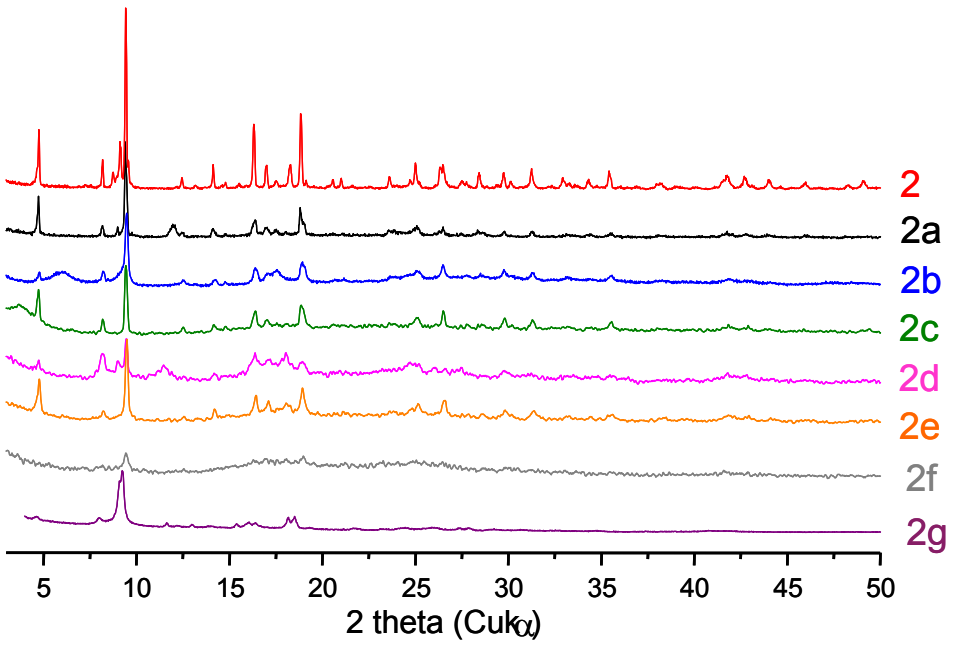

Figure S12. PXRD patterns of (2), (2a), (2b), (2c), (2d), (2e), (2f) and (2g)

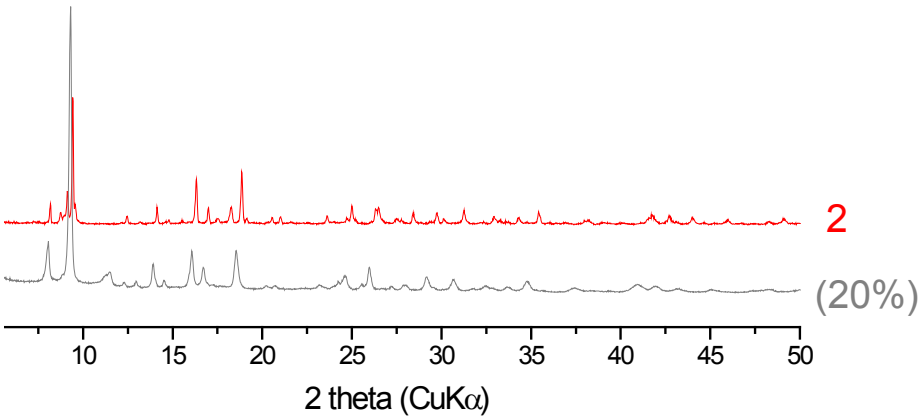

Figure S13. PXRD of MIL-68-In-NH2 and MIL-68-In containing 20% of (f)

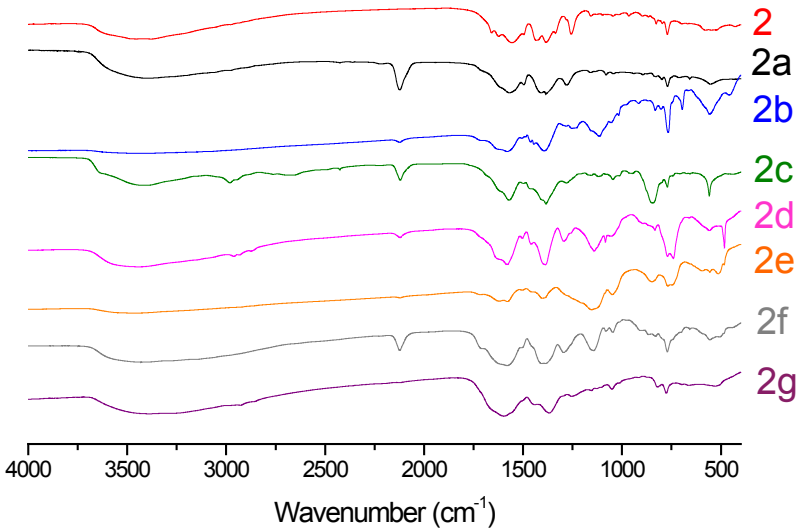

Figure S14. FTIR spectra of (2), (2a), (2b), (2c), (2d), (2e) (2f) and (2g)

Elemental analysis for (2f) (70%)

$[In(OH)(C_{11}H_5O_6N_3)_{0,7}(C_8H_3O_4N_3)_{0,3}]$

Calculated: In 22.69, C 26.28, H 1.87, N 8.29.

Found: In 26.4, C 22.09, H 1.85, N 6.10

Elemental analysis for (2c) (20%)

$[In(OH)(C_8H_3O_4N_3)_{0,8}(C_{15}H_{16}O_4N_4)_{0,2}]$

Calculated: In 31.97 , H 1.85, N 12.48.

Found: In 32.76, H 2.69, N 7.92

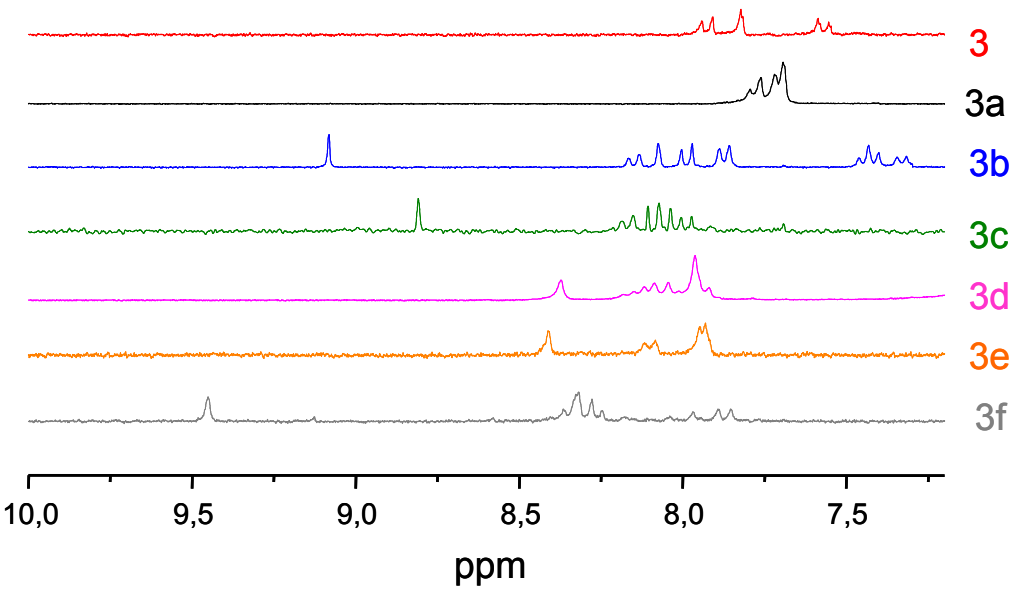

Figure S15. ^{1}H NMR of digested (3), (3a), (3b), (3c), (3d), (3e) and (3f)

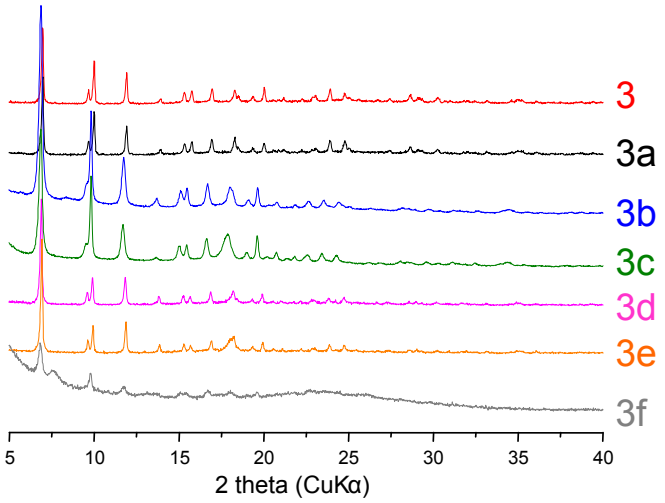

Figure S16. PXRD patterns of (3), (3a), (3b), (3c), (3d), (3e) and (3f)

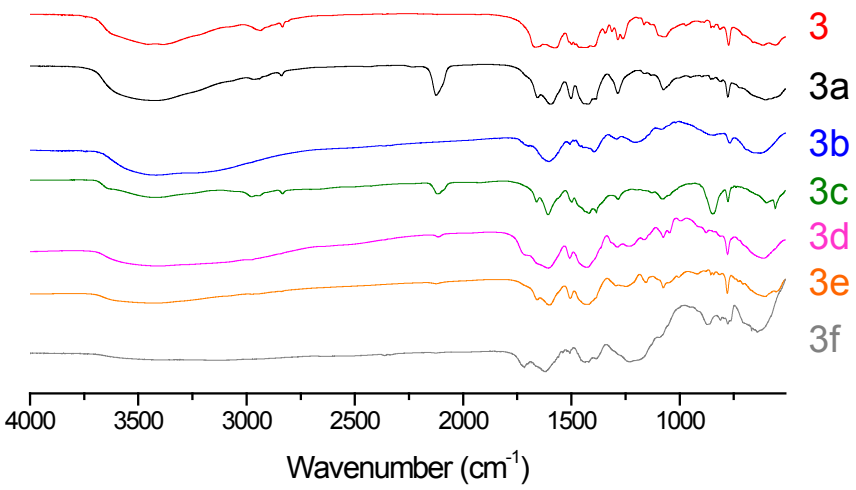

Figure S17. FTIR spectra of (3), (3a), (3b), (3c), (3d), (3e) and (3f)

Elemental analysis for (3b)(10%)

$[Al_4(OH)_2(OCH_3)_4(C_8H_3O_4N_3)_{2,7}(C_{16}H_9O_4N_3)_{0,3}]$

Calculated: Al 11.83, C 40.03, H 2.74

Found: Al 10.04, C 37, H 2.75

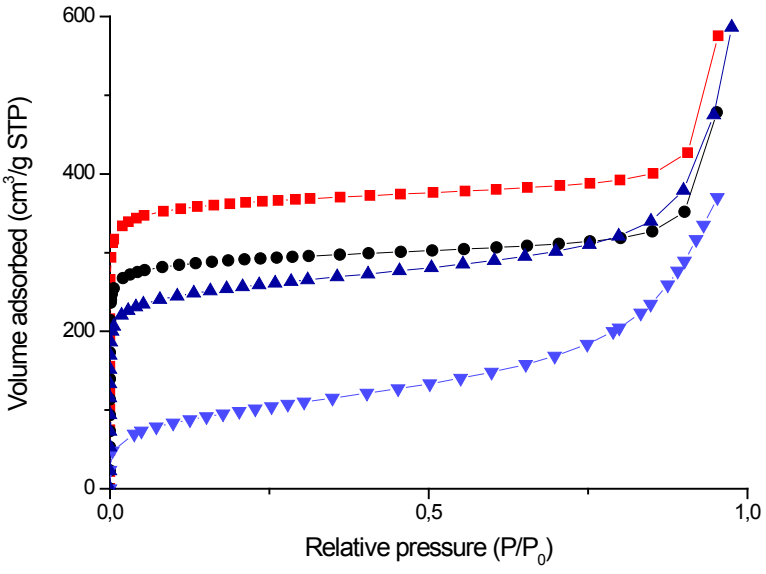

Figure S18. Effect of the degree of modification with phenylacetylene (b) on N_2 adsorption isotherms of CAU-1 (3) (■); at 0% (●), corresponding to (3a); at 20% (▲); and at 100% (▼)

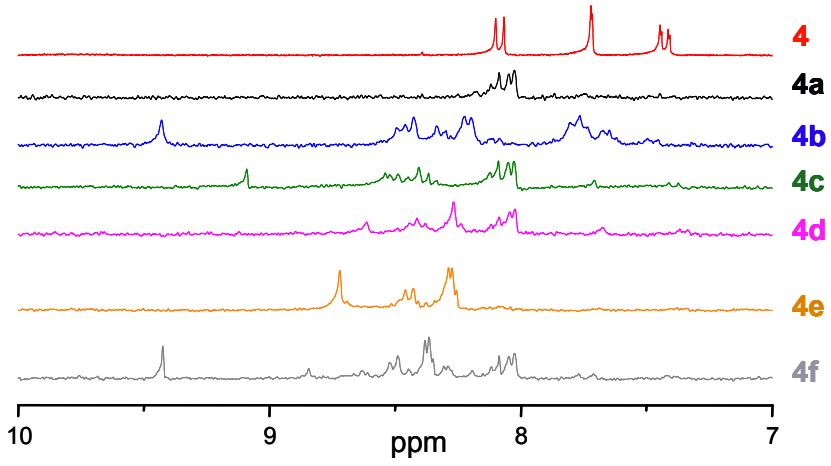

Figure S19. ^{1}H NMR of digested (4), (4a), (4b), (4c), (4d), (4e) and (4f)

It was found that the classic digestion method (dilute DCl/D_2O/DMSO-d_6 solution) was not appropriate due to the high chemical stability of MIL-53-Al derivates. Complete dissolution is obtained by using HF/DMSO-d_6 solution (Fig. 16, **4a**') [8]. For safety reasons, however, the use of HF solution is restricted in our laboratory and not allowed to be used routinely. As an alternative solution, we found that the use of DCl/D_2O/DMSO-d_6 followed by NaOD/D_2O/DMSO-d_6 allowed complete digestion of **(4a).** Also lower resolution and signal noise ratio are observed for ^{1}H NMR sample **(4a)**, this protocol allows the quantification of grafting rate (with a lower accuracy however).

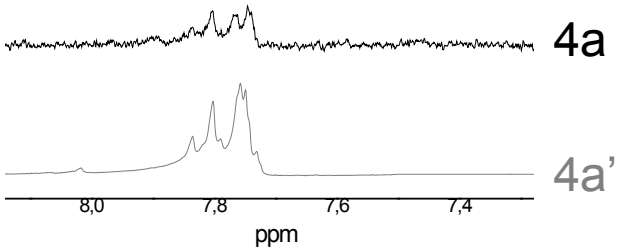

Figure S20. ^{1}H NMR of digested (4a) and (4a')

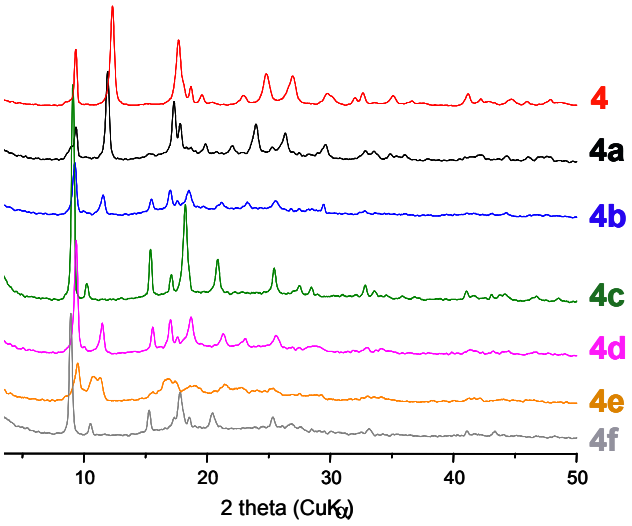

Figure S21. PXRD patterns of (4), (4a), (4b), (4c), (4d), (4e) and (4f)

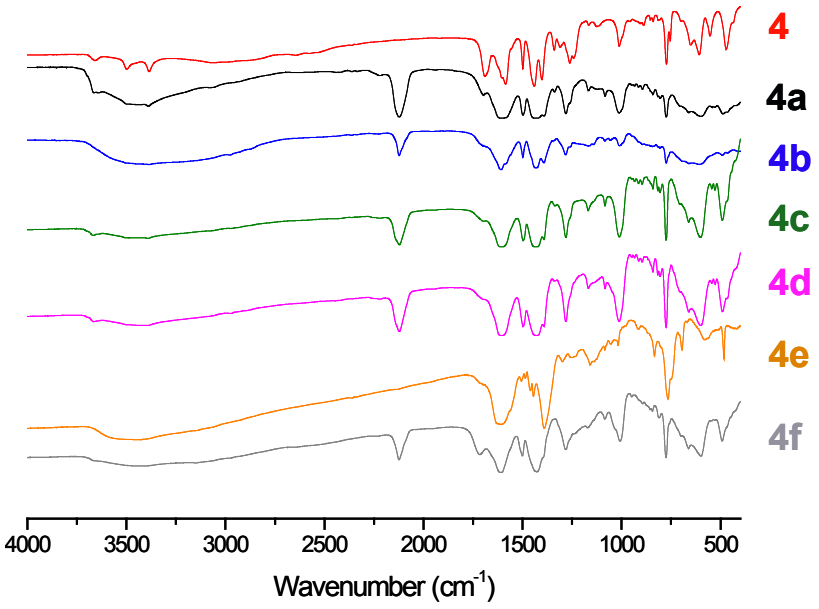

Figure S22. FTIR spectra of (4), (4a), (4b), (4c), (4d), (4e) and (4f)

Elemental analysis for (4e)

$[Al(OH)(C_{11}H_7O_5N_3)]$

Calculated: Al 8.78, H 2.60

Found: Al 10.89, H 2.52

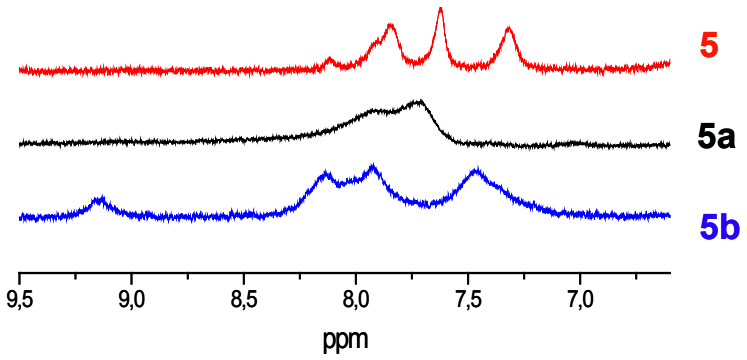

Figure S23. ^{1}H NMR of digested (5), (5a) and (5b)

^{1}H NMR spectra from digested MIL-101(Fe) were recorded according the same procedure (DCl/D_2O/DMSO-d_6 solution). Nevertheless, the obtention of very broad NMR peaks arises from the presence of paramagnetic iron species.

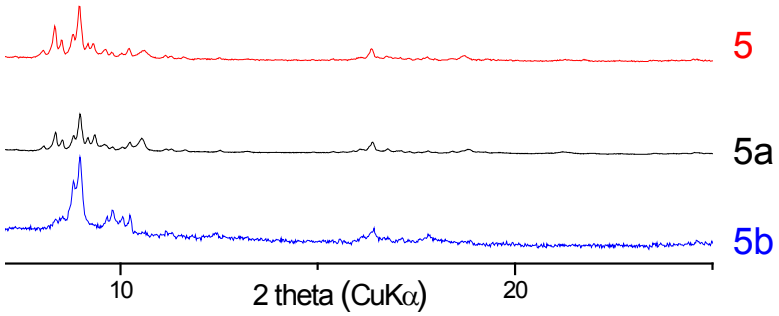

Figure S24. PXRD patterns of (5), (5a) and (5b)

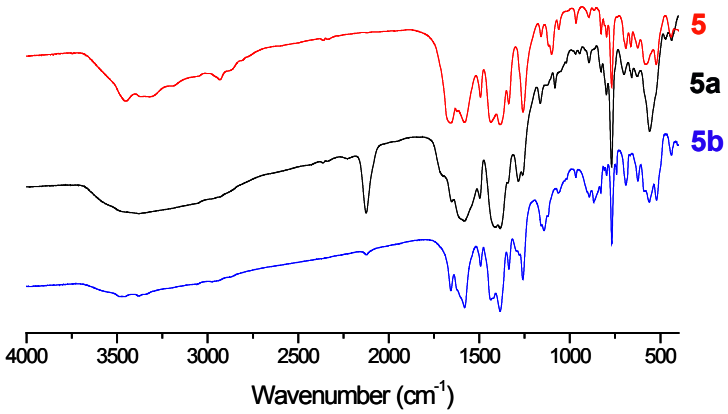

Figure S25. FTIR spectra of (5), (5a) and (5b)

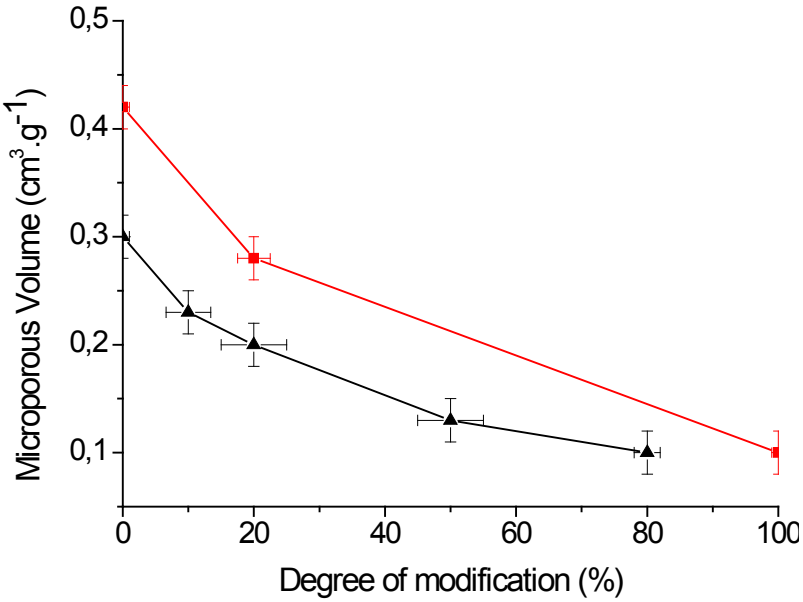

Figure S26. Effect of the degree of modification with phenylacetylene (b) on microporous volume of MIL-68(In)-N_3 (2a) (▲) and CAU-1-N_3 (3a) (■)

Table S3. Effect of the degree of modification with phenylacetylene (b) on apparent BET surface areas and microporous volume of MIL-68(In)-N_3 (2a) and CAU-1-N_3 (3a)

MOF	Degree of modification (%)	BET surface area ($cm^2.g^{-1}$)	microporous volume (cm^3.g-1)
MIL-68	0± 1%	800± 42	0.30± 0.02
	10± 3.4%	717± 40	0.23± 0.02
	20± 5%	571± 26	0.20± 0.01
	50 ± 5%	399± 18	0.13± 0.01
	80± 2%	360± 21	0.10±0.01
CAU-1	0± 1%	1147± 112	0.42± 0.03
	20± 2.5%	954± 46	0.28±0.02
	100± 1%	347± 24	0.10± 0.01

The apparent BET surface areas and the microporous volumes were obtained by N_2 adsorption at 77K.

Table S4. Experimental conditions of the control of the degree of modification with phenylacetylene (b) on MIL-68(In)-N_3 (2a) and CAU-1-N_3 (3a)

MOF-N_3	Degree of modification with **(b)**	$Cu(ACN)_4PF_6$	Phenylacetylene **(b)**
MIL-68 80 mg (0.21 mmol eq of $-N_3$)	10± 3.4%	24 mg (0.06 mmol, 0.3 eq)	0.48 mL (4.4 mmol, 21 eq)
	20± 5%	36 mg (0.1 mmol, 0.45 eq)	0.72 mL (6.6 mmol, 31.5 eq)
	50 ± 5%	48 mg (0.13 mmol, 0.6 eq)	0.96 mL (8.8 mmol, 42 eq)
	80± 2% **(2b)**	96 mg (0.26 mmol, 1.2eq)	1.9 mL (17.6 mmol, 84 eq)
CAU-1 (0.27 mmol eq of $-N_3$)	20± 2.5%	27 mg (0.074mmol, 0.27eq)	0.46 mL (4.2 mmol, 15.5 eq
	100± 1% **(3b)***	55 mg (0.15 mmol, 0.55eq)	0.92 mL (8.4 mmol, 31 eq

***(3b)** was stirred for 48 h instead of 24h.

References

[1] Z. Q. Wang, K. K. Tanabe, S. M. Cohen, *Inorg. Chem.* **2009**, *48*, 296-306.

[2] M. Savonnet, D. Bazer-Bachi, C. Pinel, V. Lecocq, N. Bats, D. Farrusseng, FR Patent 09/05.102, **2009**.

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