Supplementary Information for

IM-19: a new flexible microporous gallium based-MOF framework with pressure- and temperature-dependent openings

Gérald Chaplais,* Angélique Simon-Masseron, Florence Porcher, Claude Lecomte, Delphine Bazer-Bachi, Nicolas Bats and Joël Patarin

Syntheses

IM-19 ps or $Ga(OH)(O_2CC_6H_4CO_2)\cdot 0.75\ HO_2CC_6H_4CO_2H$ was hydrothermally prepared from a mixture $Ga(NO_3)_3\cdot x\ H_2O$ (Strem Chemicals, 99.99 %), 1,4-benzenedicarboxylic acid (H_2BDC, Fluka, 99 %), hydrofluoric acid (Prolabo, 40 %) and distilled water in the 1: 2: 1: 100 molar ratio (by assuming x=0). The mixture was heated at 220°C for 3 days in a Teflon®-lined stainless steel autoclave. The solid was filtered, washed with hot DMF (in order to remove the unreacted molecules of H_2BDC), ethanol and dried at room temperature (yield based on Ga and H_2BDC: 48.4 and 42.4 %, respectively). Elemental analysis (in wt %): C, 44.9 % (44.8 % calc.); H, 2.6 % (2.6 % calc.); Ga, 19.0 % (18.6 % calc.).

The investigation of a HF-free route has been fruitful with molar composition 1: 1: 100 at 160°C for 1 day (yield based on Ga and H_2BDC: 44.5 and 77.9 %, respectively). The recovering of the compound follows the same procedure detailed above. Higher temperatures lead to the formation of the by-product Ga(O)(OH). Elemental analysis (in wt %): C, 44.4 % (44.8 % calc.); H, 2.7 % (2.6 % calc.); Ga, 18.8 % (18.6 % calc.).

IM-19 dmf was produced from IM-19 ps by solvothermal treatment with DMF (weight ratio: 75) in a Teflon®-lined stainless steel autoclave at 160°C for 6 days. The solid was recovered by filtration, washed with DMF and dried at room temperature. The formula determined from TG analysis for IM-19 dmf is: $Ga(OH)(O_2CC_6H_4CO_2)\cdot 0.85\ (CH_3)_2NCOH$.

IM-19 h was obtained by thermal treatment in air of IM-19 dmf at 220°C for 1 day. After cooling down to ambient temperature, a white crystalline powder was recovered. Elemental analysis (in wt %): C, 35.2 % (35.7 % calc.); H, 2.7 % (2.6 % calc.); Ga, 25.8 % (25.9 % calc.). The following formula for IM-19 h: $Ga(OH)(O_2CC_6H_4CO_2)\cdot H_2O$ is in good agreement with the analysis.

Thermal analyses

Thermogravimetric analysis experiments were performed under air until 800°C (rate of 5°C/min) using a Setaram Labsys apparatus.

The thermogram of **IM-19 ps** (Fig. S1) shows two distinct weigh losses assigned to the departure of H_2BDC molecules occluded in the channels (29.6 % exp. vs 33.2 % calc.), and the combustion of organic moieties from the framework (40.4 % exp. vs 41.9 % calc.) causing the collapsing of the structure and leading to the formation of Ga_2O_3, identified by XRD measurement.

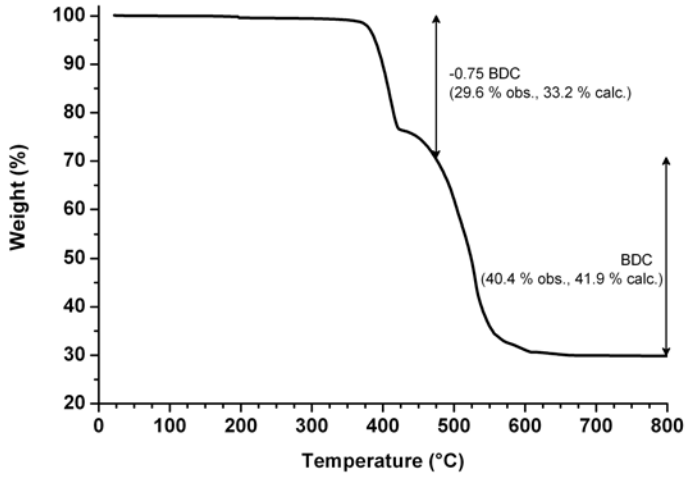

Figure S1 Thermogravimetric curve for **IM-19 ps**.

The thermogram of **IM-19 dmf** (Fig. S2) exhibits two distinct weigh losses corresponding to the departure of DMF molecules occluded in the channels (19.9 % exp. vs 19.9 % calc.), and the combustion of organic moieties from the framework (45.2 % exp. vs 50.2 % calc.). Ga_2O_3, identified by XRD measurement, is produced at higher temperatures.

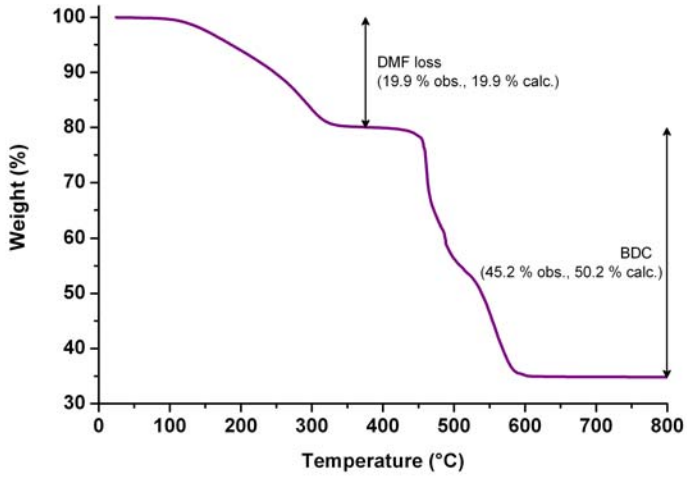

Figure S2 Thermogravimetric curve for **IM-19 dmf**.

The thermogram of **IM-19 h** (Fig. S3) presents two distinct weigh losses corresponding to the removal of water molecules occluded in the channels (6.6 % exp. vs 6.7 % calc.), and the combustion of organic moieties from the framework (55.7 % exp. vs 58.4 % calc.). At higher temperatures, Ga_2O_3 is identified by XRD measurement.

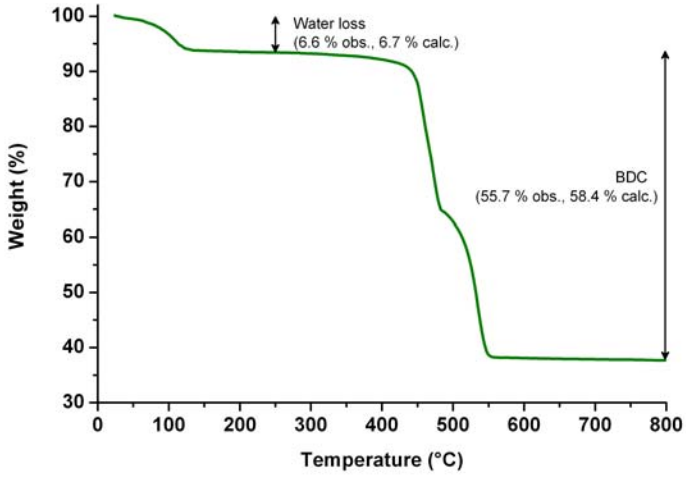

Figure S3 Thermogravimetric curve for **IM-19 h**.

Crystallographic data

Table S1 Unit-cell parameters of IM-19 and related M(OH)(BDC) materials (where M=Al, Cr, Fe, V, In) with H_2BDC, DMF and H_2O as guest molecules and guest-free.

Guest	M	Name	System	Unit-cell parameters				Space group	*d*/*D*	*α* (°)	Ref.
				a (Å)	*b* (Å)	*c* (Å)	*β* (°)				
H_2BDC	Ga	IM-19 ps	orthorhombic	17.4370(2)	6.7475(4)	12.1541(4)		*Pnma*	0.697[a]	34.9	This work
	Ga	F-free	orthorhombic	17.525(4)	6.7216(16)	11.893(3)		*Pnma*	0.679[a]	34.2	[1]
	Ga	F-containing	orthorhombic	17.410(3)	6.7444(10)	12.1646(17)		*Pnma*	0.699[a]	35.0	[1]
	Al	MIL-53(Al) as	orthorhombic	17.129(2)	6.628(1)	12.182(1)		*Pnma*	0.711[a]	35.4	[2]
			orthorhombic	17.019(4)	6.584(2)	12.262(3)		*Pnma*	0.720[a]	35.8	[1]
	Cr	MIL-53(Cr) as	orthorhombic	17.340(1)	6.822(1)	12.178(1)		*Pnma*	0.702[a]	35.1	[3]
	V	MIL-47 as	orthorhombic	17.519(1)	6.8750(4)	12.1680(8)		*Pnma*	0.695[a]	34.8	[4]
	In		monoclinic	18.228(3)	11.970(2)	34.062(6)	122.4(1)	*P21/c*	0.657[b]	33.3	[5]
DMF	Ga	IM-19 dmf	monoclinic	6.7120(4)	11.2486(11)	17.9650(16)	91.975(7)	*I2/a*[g]	0.627[c]	32.1	This work
	Fe	MIL-53(Fe),dmf	monoclinic	19.068(2)	11.2869(9)	6.8685(6)	108.925(6)	*C2/c*	0.626[d]	32.0	[6]
H_2O	Ga	IM-19 h	monoclinic	19.1866(26)	7.6278(13)	6.6688(7)	95.858(10)	-	0.400[d]	21.8	This work
	Al	MIL-53(Al) lt	monoclinic	19.513(2)	7.612(1)	6.576(1)	104.24(1)	*Cc*	0.402[d]	21.9	[2]
	Cr	MIL-53(Cr) lt	monoclinic	19.685(4)	7.849(1)	6.782(1)	104.90(1)	*C2/c*	0.413[d]	22.4	[7]
	Fe	MIL-53(Fe) lt	monoclinic	19.3197(2)	15.0362(2)	6.83508(6)	96.305(1)	*C2/c*	0.392[e]	21.4	[8]
-	Ga	IM-19 p1	monoclinic	19.3021(33)	7.1577(15)	6.7156(16)	95.133(18)	-	0.372[d]	20.4	This work
	Ga	IM-19 p2	orthorhombic	16.7338(31)	13.2824(26)	6.7413(9)		-	0.794[b]	38.4	This work
	Al	MIL-53(Al) ht	orthorhombic	6.608(1)	16.675(3)	12.813(2)		*Imma*	0.768[f]	37.5	[2]
	Cr	MIL-53(Cr) ht	orthorhombic	6.812(1)	16.733(1)	13.038(1)		*Imma*	0.779[f]	37.9	[3]
			orthorhombic	16.733(1)	13.038(1)	6.812(1)		*Imcm*	0.779[b]	37.9	[7]
	Fe	MIL-53(Fe) ht	monoclinic	21.2693(3)	6.7589(1)	6.8838(2)	114.625(2)	*C2/c*	0.350[d]	19.3	[8]
	V	MIL-47	orthorhombic	6.818(1)	16.143(3)	13.939(2)		*Pnma*	0.863[f]	40.8	[4]

[a] $d/D=c/a$. [b] $d/D=b/a$. [c] $d/D=b/(c.\sin(\beta))$. [d] $d/D=b/(a.\sin(\beta))$. [e] $d/D=(b/2)/(a.\sin(\beta))$. [f] $d/D=c/b$. [g] Conventional space group: *C2/c*.

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