Ca-Triazine Phosphonate Metal-Organic Framework as Fungicide Active Packaging

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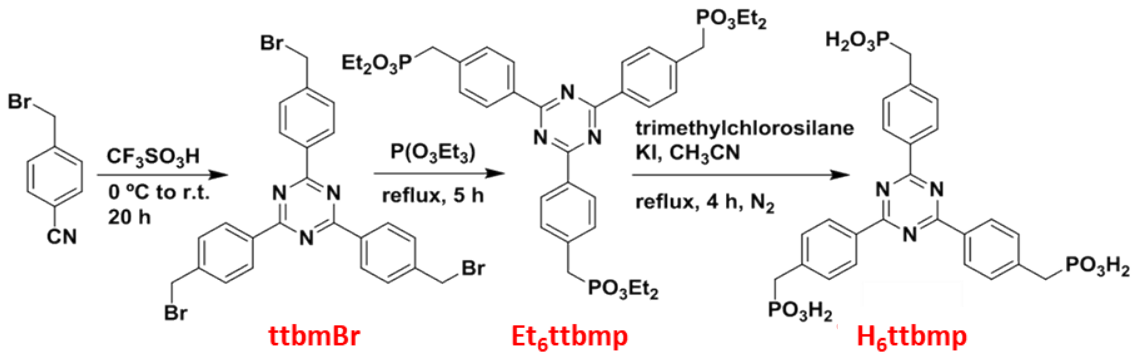
Electronic Supporting Information

SI_1. Synthesis of the organic linker and identification by UV-Vis.

The lab-made 2,4,6-tris[4-(phosphonomethyl)phenyl]1,3,5-triazine (H_6ttbmp) linker was synthesised following the this scheme:



Scheme S1. Synthetic route towards the preparation of H_6ttbmp.

The synthetic route toward H_6ttbmp is quite similar, with some modifications, to that previously reported by Taddei et al.[1]

Synthesis of 2,4,6-tris[4-(bromomethyl)phenyl]-1,3,5-triazine (ttbmBr).

To a 25 mL round-bottom flak 4-bromomethyl benzonitrile (0.500 g, 9.88 mmol, TCI, >98%, MW= 196.05 g mol^{-1}) is transferred and kept at 0 °C (ice bath). Then, trifluoromethanesulfonic acid (5 mL) is progressively added under N_2 atmosphere and the flask is capped, sealed, and kept at room temperature for 20 h, under constant magnetic stirring. The resulting orange mixture is poured into ice (or we can add ice directly inside of the flask), leading to the formation of a white solid, and neutralised with ammonium hydroxide (J. T. Baker, 25%). The desired compound is recovered by filtration, washed with water and acetone, and dried at 60 °C. Yield = 96%.

Synthesis of Synthesis of 2,4,6-tris[4-(diethylphosphonomethyl)phenyl]-1,3,5-triazine (Et_6ttbmp).

A reactive mixture composed of Triaz-Br (0.480 g, 0.816 mmol) and triethyl phosphite (5 mL, Sigma Aldrich, 98%) is prepared in a 100 mL round-bottom flask, purged with N2 and refluxed for 5 h, under constant magnetic stirring. Cooling to room temperature, some crystallization of a white solid is observed. Petroleum ether is added and the mixture is stirred for 1 h. The resulting solid is recovered by filtration, washed with petroleum ether, and dried at 60 °C. Yield = 97%.

Synthesis of 2,4,6-tris[4-(phosphonomethyl)phenyl]-1,3,5-triazine (H_6ttbmp).

Triaz-PO_3Et_2 (0.5513g, 0.726 mmol) is introduced in a 50 mL round-bottom flask, capped with a septum, and purged with a N_2 flow. Then, anhydrous acetonitrile (10 mL, ACROS Organics, 99.9%), trimethylchlorosilane (~1.0 mL, 7.879 mmol, ACROS Organics, 98%), and after removing the septum, potassium iodide (1.308 g, 7.879 mmol,

Sigma Aldrich, >99%) are added. The resulting reaction mixture was refluxed for 4 h, under N_2 and constant magnetic stirring. After reacting, it is added MeOH (~10 mL), and the mixture is filtered (to remove the byproduct KCl and some excess KI). The liquid phase is evaporated under a vacuum and the obtained residue is treated with distilled water to hydrolyze the trimethylsilyl ester. Then, NaOH is added until the complete dissolution of phosphonic acid, and the mixture is washed with dichloromethane to remove the trimethylsilanol. The water phase is recovered and acidified with a concentrated solution of HCl (J. T. Baker, 37%) until pH becomes sufficiently acidic to precipitate the desired phosphonic acid linker. Finally, the solid is recovered by filtration, washed with diethyl ether, and dried at 80 °C. Yield = 90%.

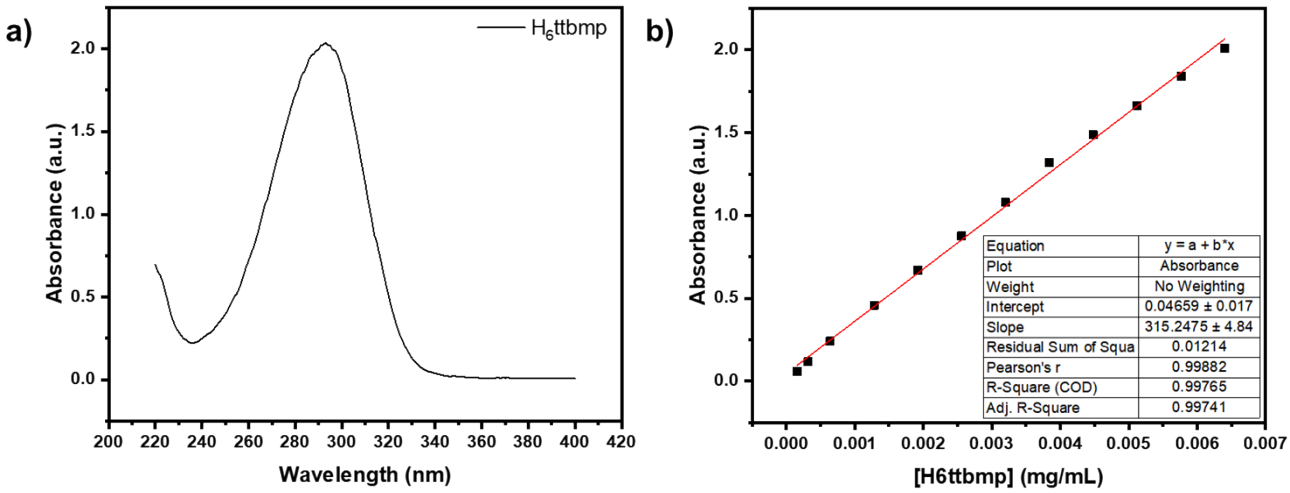


Figure S1. (a) UV-Vis spectrum and (b) standard calibration curve of H_6ttbmp linker.

SI_2. Crystallographic studies

Table S1. Crystallographic data and structure refinement details for IEF-32.

Compound	**IEF-32**
Empirical formula	$C_{24}H_{18}CaN_3O_9P_3$
Formula weight	625.40
CCDC number	2471077
Temperature/K	200.00
Crystal system	monoclinic
Space group	C2/c
a/Å	30.884(11)
b/Å	5.7014(14)
c/Å	33.916(10)
α/°	90
β/°	100.251(12)
γ/°	90
Volume/Å^3	5877(3)
Z	8
ρ_{calc}g/cm^3	1.414
μ/mm^{-1}	0.430
F(000)	2560.0
Crystal size/mm^3	0.24 × 0.18 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.134 to 34.618
Index ranges	-25 ≤ h ≤ 25, -4 ≤ k ≤ 4, -28 ≤ l ≤ 28
Reflections collected	32052
Independent reflections/R_{int}	1794 [R_{int} = 0.1564, R_{sigma} = 0.0495]
Data/restraints/parameters	1794/108/359
Goodness-of-fit on F^2	1.115
Final R indexes [I>=2σ (I)]	R_1 = 0.0963, wR_2 = 0.2574
Final R indexes [all data]	R_1 = 0.1057, wR_2 = 0.2688
Largest diff. peak/hole / e Å^{-3}	1.40/-0.43

Table S2. Bond lengths for IEF-32.

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ca1	O11[2]	2.402(9)	P3	O33	1.487(10)	C10	C11	1.38(2)
Ca1	O12[3]	2.407(9)	P3	C24	1.772(16)	C10	C15	1.39(2)
Ca1	O12[4]	2.382(9)	N1	C1	1.335(18)	C11	C12	1.37(2)
Ca1	O21[5]	2.818(11)	N1	C17	1.340(18)	C12	C13	1.37(2)
Ca1	O22[5]	2.486(10)	N2	C9	1.338(18)	C13	C14	1.39(2)
Ca1	O23	2.219(9)	N2	C17	1.326(19)	C13	C16	1.49(2)
Ca1	O33[6]	2.410(10)	N3	C1	1.352(18)	C14	C15	1.42(2)
P1	O11	1.505(10)	N3	C9	1.322(19)	C17	C18	1.45(2)
P1	O12	1.507(10)	C1	C2	1.47(2)	C18	C19	1.39(2)
P1	O13	1.568(10)	C2	C3	1.384(19)	C18	C23	1.36(2)
P1	C8	1.795(15)	C2	C7	1.40(2)	C19	C20	1.38(2)
P2	O21	1.582(10)	C3	C4	1.393(19)	C20	C21	1.36(2)
P2	O22	1.517(10)	C4	C5	1.39(2)	C21	C22	1.35(2)
P2	O23	1.489(10)	C5	C6	1.40(2)	C21	C24	1.53(2)
P2	C16	1.764(15)	C5	C8	1.512(19)	C22	C23	1.42(2)
P3	O31	1.573(11)	C6	C7	1.340(19)	C1	C2	1.47(2)
P3	O32	1.544(11)	C9	C10	1.48(2)			

[1]1-X,-1-Y,1-Z; [2]-1/2+X,-3/2+Y,+Z; [3]3/2-X,3/2-Y,1-Z; [4]-1/2+X,-5/2+Y,+Z; [5]+X,-1+Y,+Z; [6]1-X,-2+Y,1/2-Z

Table S3. Bond angels for IEF-32

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O11[3]	Ca1	Ca1[2]	82.7(2)	O12	P1	O13	107.9(5)
O11[3]	Ca1	P1[4]	90.3(2)	O12	P1	C8	107.4(6)
O11[3]	Ca1	P1[1]	82.0(2)	O13	P1	C8	103.7(6)
O11[3]	Ca1	P1[3]	19.3(2)	O21	P2	C16	107.8(7)
O11[3]	Ca1	P2[5]	163.6(2)	O22	P2	O21	103.4(6)
O11[3]	Ca1	O12[1]	81.4(3)	O22	P2	C16	110.8(7)
O11[3]	Ca1	O21[5]	151.3(3)	O23	P2	O21	109.7(6)
O11[3]	Ca1	O22[5]	151.0(3)	O23	P2	O22	118.0(6)
O11[3]	Ca1	O33[6]	77.5(3)	O23	P2	C16	106.7(6)
O12[1]	Ca1	Ca1[2]	38.4(2)	O31	P3	C24	111.5(7)
O12[4]	Ca1	O11[3]	87.3(3)	O32	P3	O31	106.8(6)
O12[4]	Ca1	O12[1]	77.2(3)	O32	P3	C24	106.4(7)
O12[4]	Ca1	O21[5]	79.0(3)	O33	P3	O31	110.4(6)
O12[1]	Ca1	O21[5]	71.2(3)	O33	P3	O32	113.3(7)
O12[4]	Ca1	O22[5]	87.9(3)	O33	P3	C24	108.4(7)
O12[1]	Ca1	O22[5]	125.1(3)	P1	O11	Ca1[8]	129.0(5)

O12[4]	Ca1	O33[6]	114.4(3)	Ca1[7]	O12	Ca1[1]	102.8(3)
O12[1]	Ca1	O33[6]	155.1(3)	P1	O12	Ca1[1]	128.7(5)
O22[5]	Ca1	O21[5]	54.1(3)	P1	O12	Ca1[7]	128.5(5)
O23	Ca1	O11[3]	90.5(3)	P2	O21	Ca1[9]	91.4(5)
O23	Ca1	O12[1]	87.6(3)	P2	O22	Ca1[9]	106.8(5)
O23	Ca1	O12[4]	164.8(4)	P2	O23	Ca1	167.4(6)
O23	Ca1	O21[5]	96.3(3)	P3	O33	Ca1[10]	134.3(6)
O23	Ca1	O22[5]	101.1(3)	C1	N1	C17	116.1(13)
O23	Ca1	O33[6]	79.7(4)	C17	N2	C9	116.2(14)
O33[6]	Ca1	O21[5]	131.1(3)	C9	N3	C1	115.5(14)
O33[6]	Ca1	O22[5]	78.6(3)	N1	C1	N3	123.7(14)
O11	P1	O12	117.6(5)	N1	C1	C2	119.6(13)
O11	P1	O13	108.7(5)	N3	C1	C2	116.6(14)
O11	P1	C8	110.6(6)	C3	C2	C1	121.0(14)
C10	C15	C14	118.7(16)	C3	C2	C7	118.7(14)
C13	C16	P2	119.3(10)	C7	C2	C1	120.2(14)
N1	C17	C18	117.7(14)	C2	C3	C4	119.7(14)
N2	C17	N1	123.7(15)	C5	C4	C3	121.2(14)
N2	C17	C18	118.5(15)	C4	C5	C6	117.7(13)
C19	C18	C17	119.2(18)	C4	C5	C8	122.2(13)
C23	C18	C17	124.3(19)	C6	C5	C8	120.0(13)
C23	C18	C19	116.4(16)	C7	C6	C5	121.2(14)
C20	C19	C18	121.9(17)	C6	C7	C2	121.5(14)
C21	C20	C19	121.1(17)	C5	C8	P1	114.1(10)
C20	C21	C24	123(2)	N2	C9	C10	118.1(14)
C22	C21	C20	118.5(17)	N3	C9	N2	124.6(15)
C22	C21	C24	119(2)	N3	C9	C10	117.3(14)
C21	C22	C23	121.0(17)	C11	C10	C9	121.3(14)
C18	C23	C22	121.1(17)	C11	C10	C15	120.0(14)
C21	C24	P3	116.7(11)	C15	C10	C9	118.6(14)
C12	C13	C14	116.9(15)	C12	C11	C10	118.8(15)
C12	C13	C16	124.5(15)	C13	C12	C11	124.0(16)
C14	C13	C16	118.4(15)	C13	C14	C15	121.4(15)

[1]3/2-X,3/2-Y,1-Z; [2]1-X,-1-Y,1-Z; [3]-1/2+X,-3/2+Y,+Z; [4]-1/2+X,-5/2+Y,+Z; [5]+X,-1+Y,+Z; [6]1-X,-2+Y,1/2-Z; [7]1/2+X,5/2+Y,+Z; [8]1/2+X,3/2+Y,+Z; [9]+X,1+Y,+Z; [10]1-X,2+Y,1/2-Z

SI_3. Optimization of the synthetic conditions

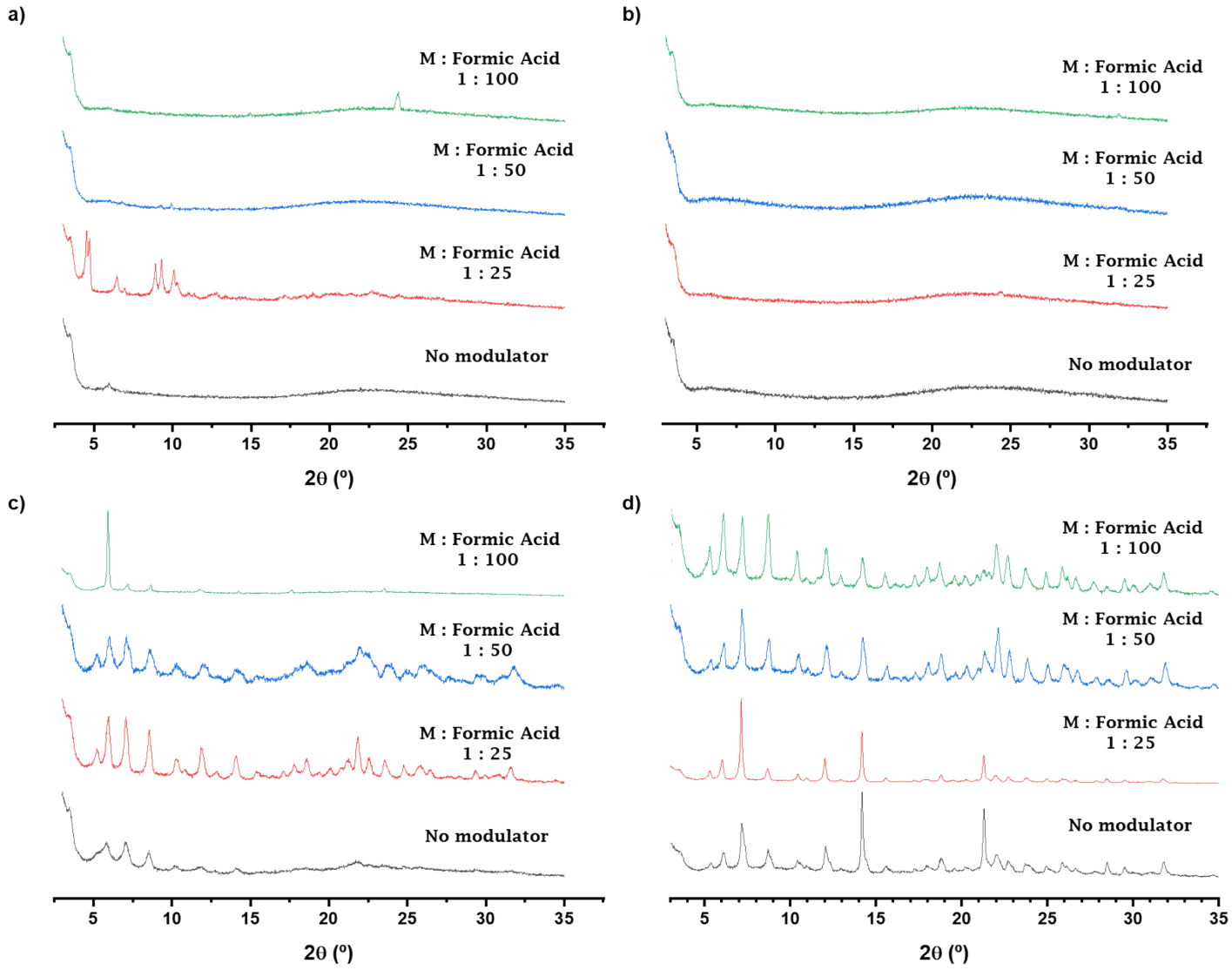


Figure S2. PXRD diffractograms employing Et_6ttbmp as linker (L) at (a, b) 120 °C and (c, d) 150 °C, and employing (a, c) $Ca(NO_3)_2{\cdot}4H_2O$ and (b, d) $CaCl_2{\cdot}2H_2O$ as metal precursor (M) for optimizing IEF-32(Ca) using the solvothermal high-throughput method. *Common conditions: [M] = 0.03 M, L/M = 0.5, H_2O:MeOH (2:1, %v/v ratio), t = 64 h, and 8h up/down Tª ramp of 0.27 °C/min*

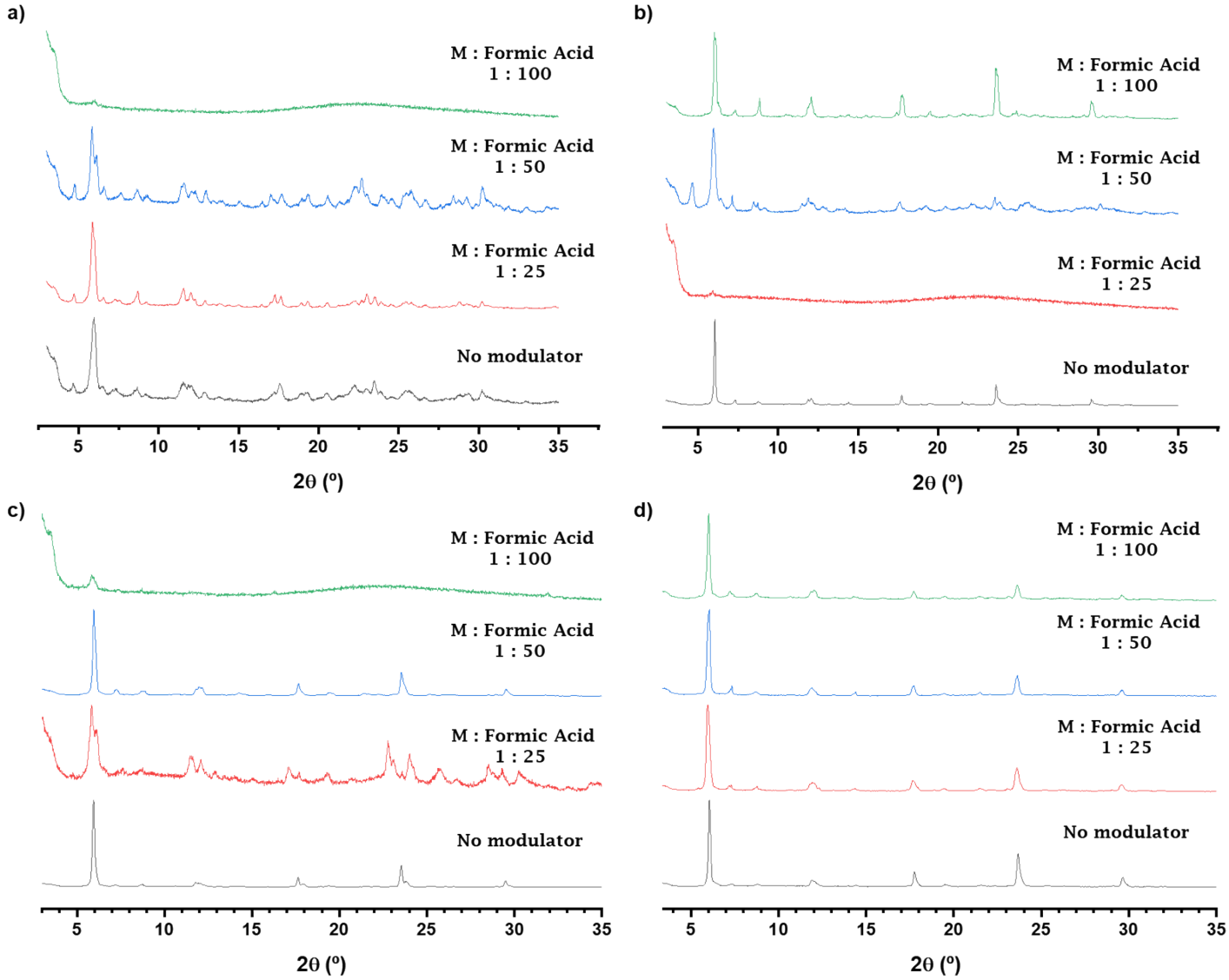


Figure S3. PXRD diffractograms employing H_6ttbmp as linker (L) at (a, b) 120 °C and (c, d) 150 °C, and employing (a, c) $Ca(NO_3)_2{\cdot}4H_2O$ and (b, d) $CaCl_2{\cdot}2H_2O$ as metal precursor (M) for optimizing IEF-32(Ca) using the solvothermal high-throughput method. *Common conditions: [M] = 0.03 M, L/M = 0.5, H_2O:MeOH (2:1, %v/v ratio), t = 64 h, and 8h up/down Tª ramp of 0.27 °C/min*

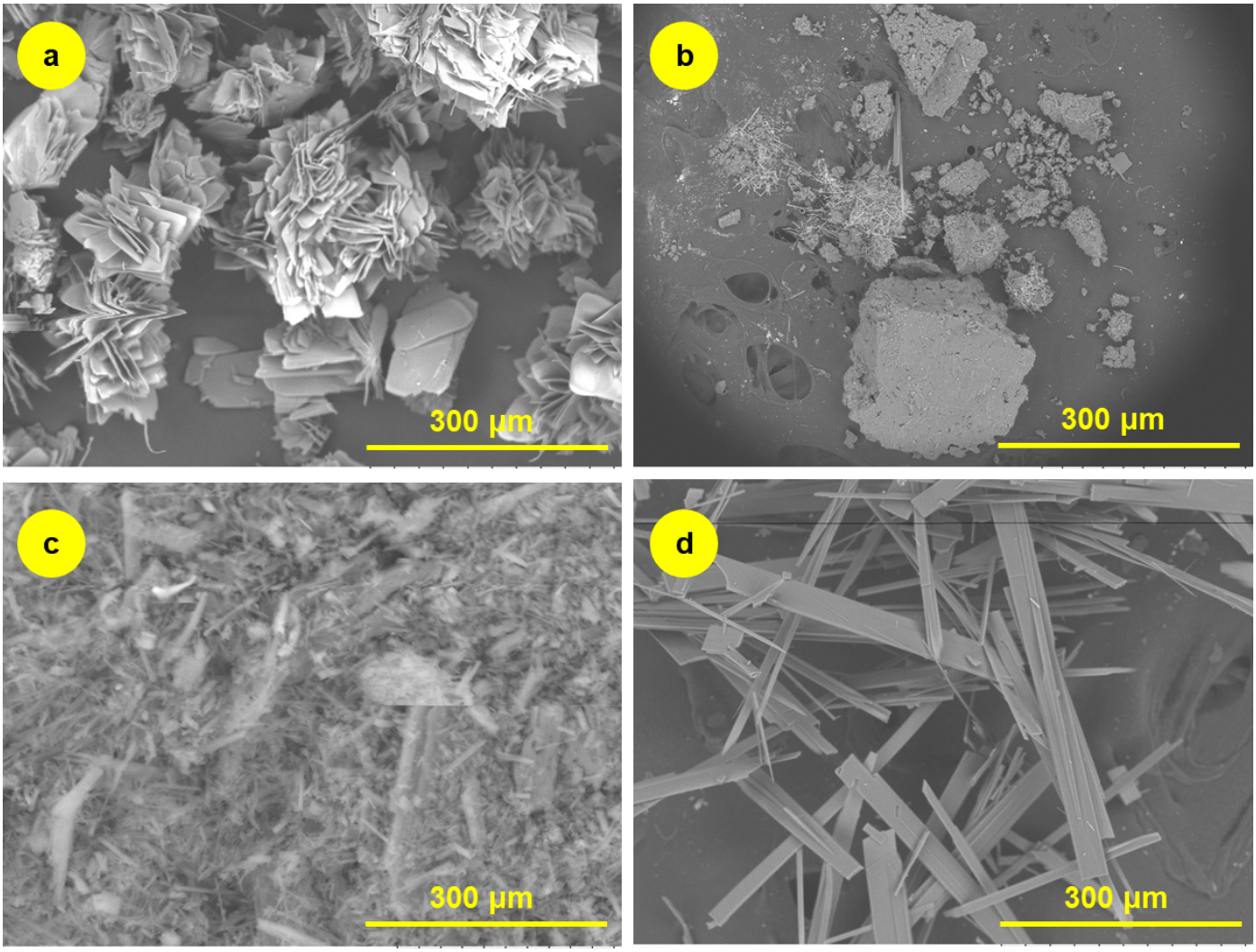


Figure S4. SEM images of (a) unknown phase, poorly crystallised IEF-32 using (b) Et_6ttbmp as linker (L), (c) $Ca(NO_3)_2{\cdot}4H_2O$ as metal precursor (M), and (d) pure and well-crystallised IEF-32 when using $CaCl_2{\cdot}2H_2O$ and H_6ttbmp at 150 ºC obtained by solvothermal high-throughput method. *Common conditions: [M] = 0.03 M, L/M = 0.5, H_2O:MeOH (2:1, %v/v ratio), t = 64 h, and 8h up/down Tª ramp of 0.27 °C/min*

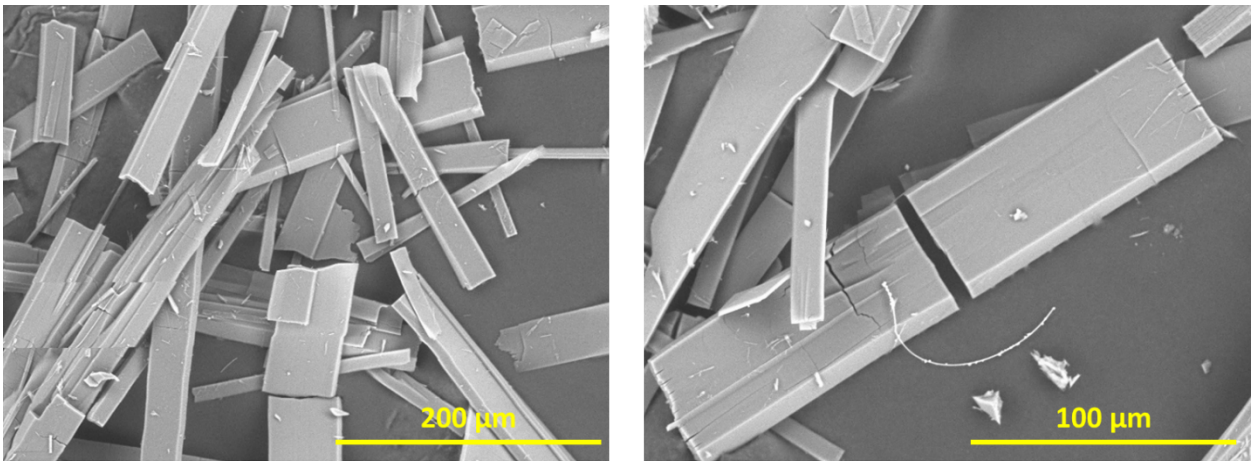


Figure S5. SEM images of the scaled-up IEF-32 obtained by conventional solvothermal synthesis.

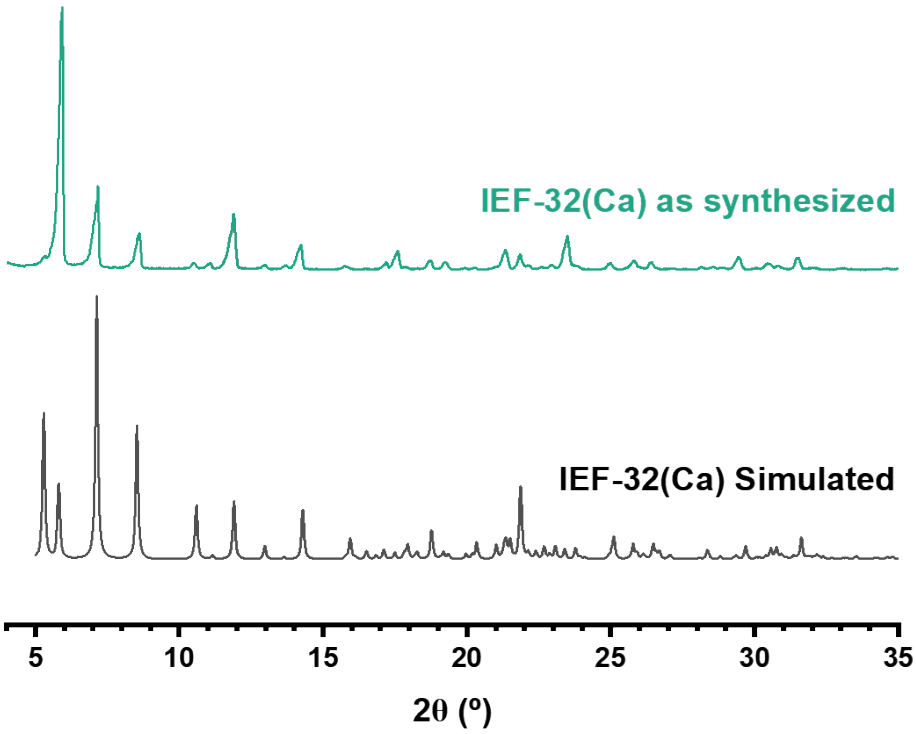


Figure S6. Simulated and experimental PXRD patterns of IEF-32.

SI_4. General characterization

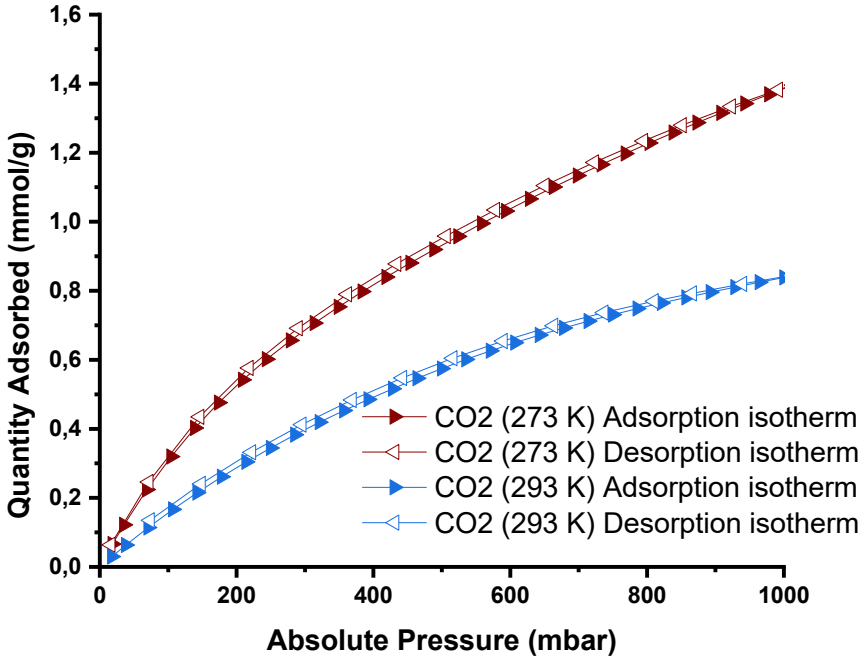


Figure S7. CO_2 adsorption isotherms for IEF-32 at 1 bar and 273 K (red) and 293 K (blue).

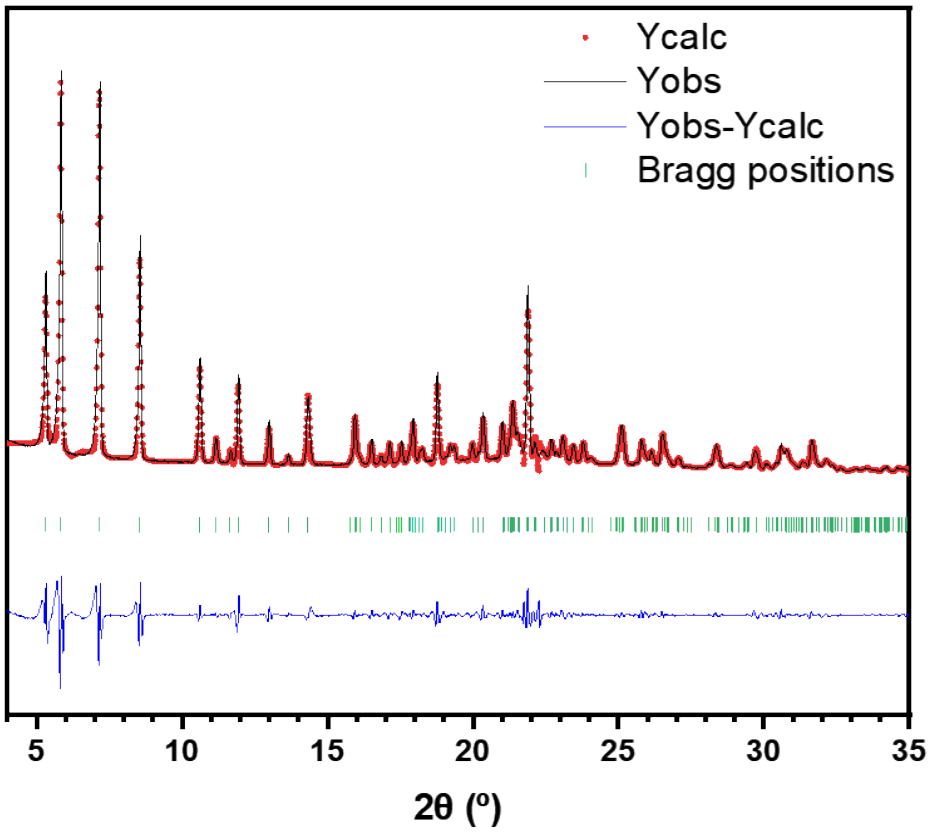


Figure S8. Le Bail intensity extraction of IEF-32 (Rf-factor = 0.4068; GOF = 0.0827; λ = 1.54056 Å)

Table S4. Structural parameters of IEF-32 obtained by SC-XRD and by Le Bail refinement.

	IEF-32	
	SC-XRD	**PXRD**
Space Group	C2/c	C2/c
a (Å)	30.884(11)	30.8215
b (Å)	5.7014(14)	5.7046
c (Å)	33.916(10)	33.8520
α (°)	90	90
β (°)	100.251	100.178
γ (°)	90	90
Volume (Å³)	5876.56	5858.35

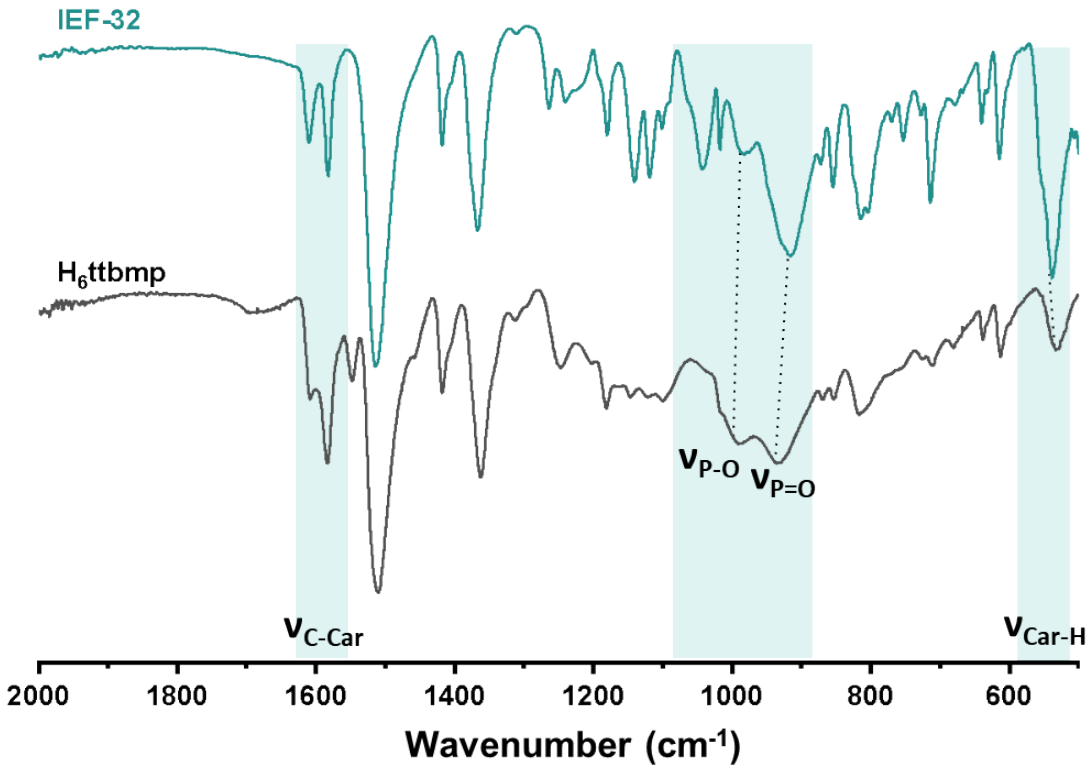


Figure S9. FTIR-ATR spectra of H_6ttbmp and IEF-32 from 2000 cm^{-1} to 500 cm^{-1} highlighting the shifting of the bands.

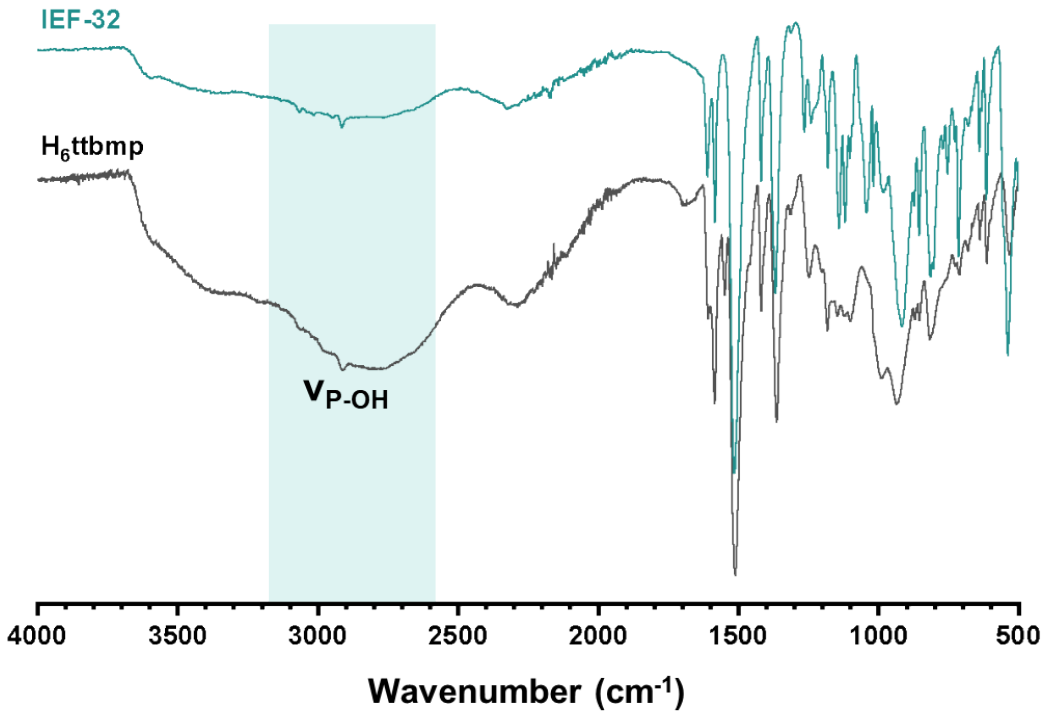


Figure S10. FTIR-ATR spectra of H_6ttbmp and IEF-32 from 4000 cm^{-1} to 500 cm^{-1}.

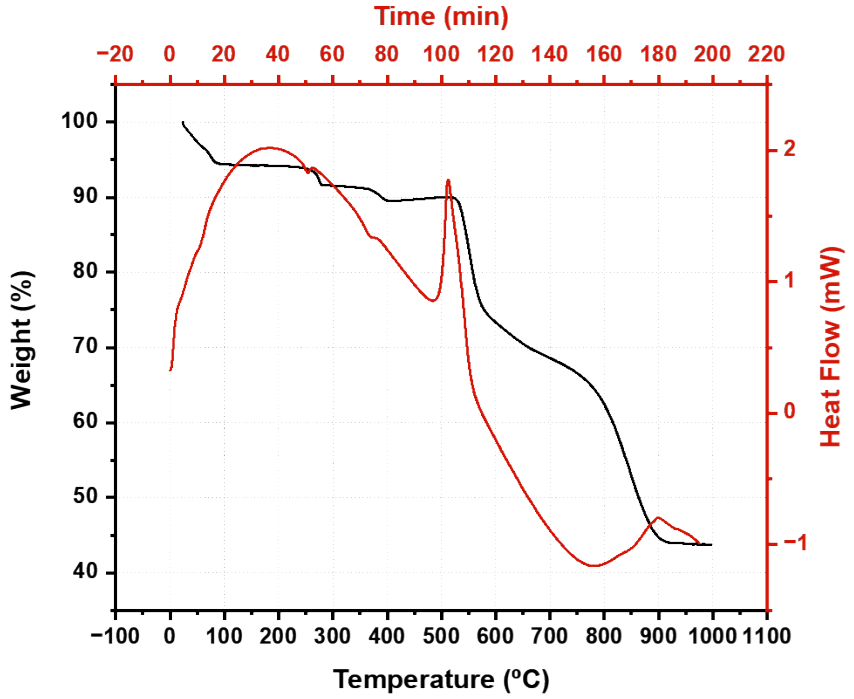


Figure S11. TGA curve of IEF-32 under air. Note that since vitrification limited PXRD identification, β-tricalcium phosphate (β-TCP; $Ca_3(PO_4)_2$) was assumed as thermal residue, equilibrating the final combustion reaction with P_2O_5. Combustion reaction: $3C_{24}H_{21}CaN_3O_9P_3$ (IEF-32) ⟶ $Ca_3(PO_4)_2$ + 3.5 P_2O_5; $\%Total_{Oxide}$ = $([(1)\times M_w(Ca_3(PO_4)_2)+(3.5)\times M_w(P_2O_5)]/[(3)\times M_w(\text{IEF-32})])\times 100$

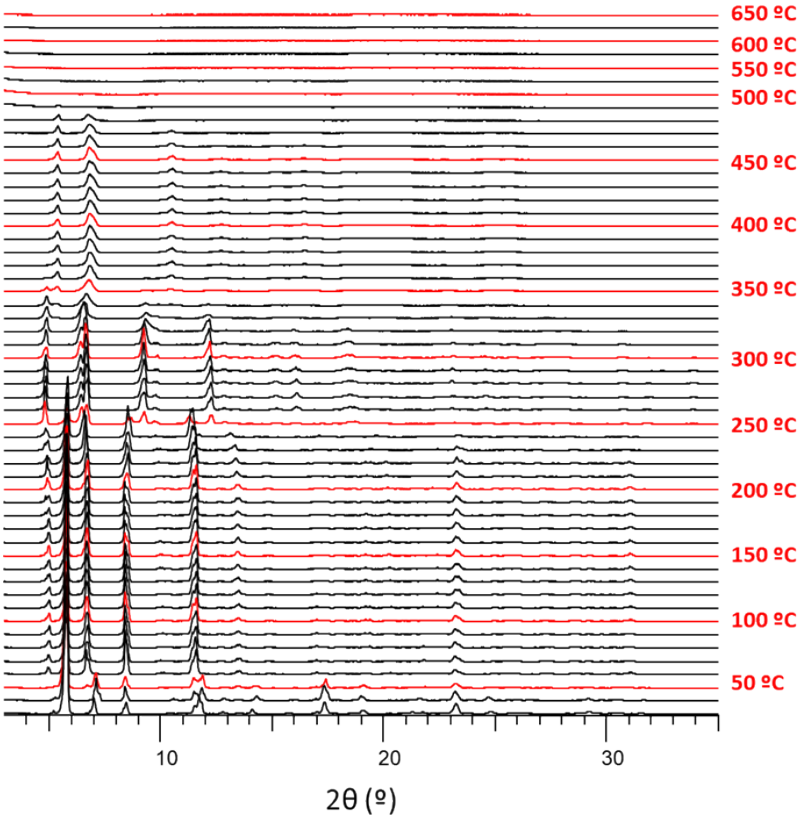


Figure S12. VT-PXRD of the IEF-32 under air from 30 to 650 °C.

SI_5. Chemical stability

Each test has been performed suspending 10 mg of as-synthesised material in 2 mL of different solvents (THF, tetrahydrofuran; MeCN, acetonitrile; DMF, *N*,*N*'-dimethylformamide; DMSO, dimethylsulfoxide; hexane; toluene; octane; $MeCl_2$, dichloromethane; MeOH, methanol; and MilliQ water) for 24 h under stirring (400 rpm). Afterwards. the solid was centrifuged (13000 rpm, 3 min) and dried in air at room temperature before PXRD acquisition.

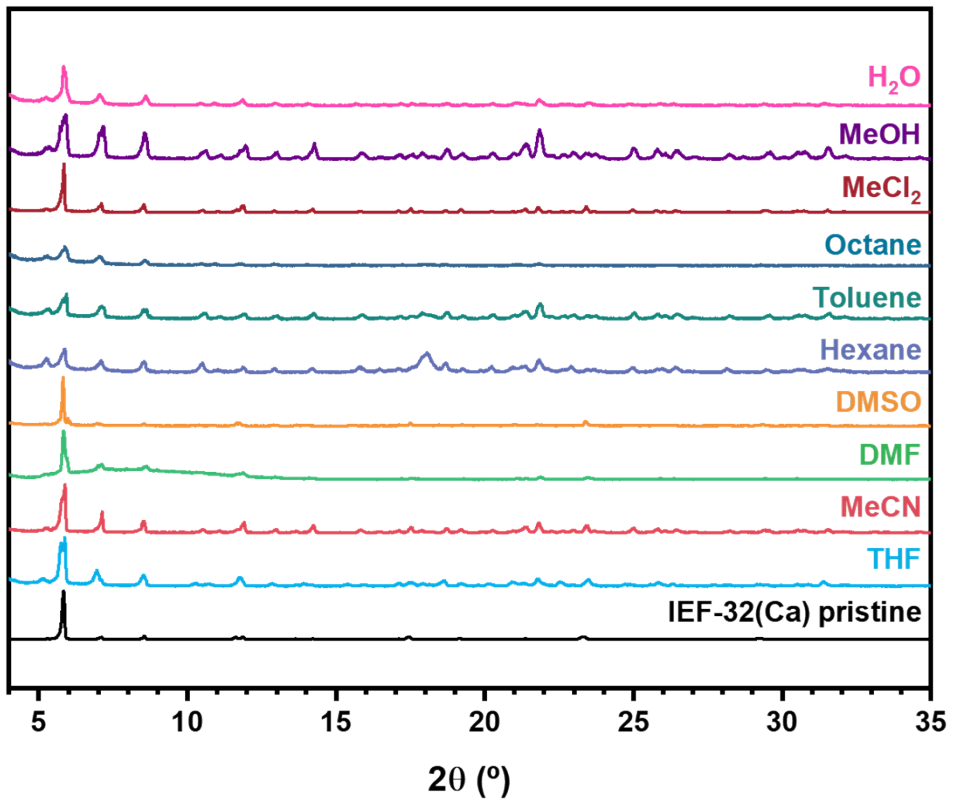


Figure S13 PXRD patterns of IEF-32 before and after chemical stability test.

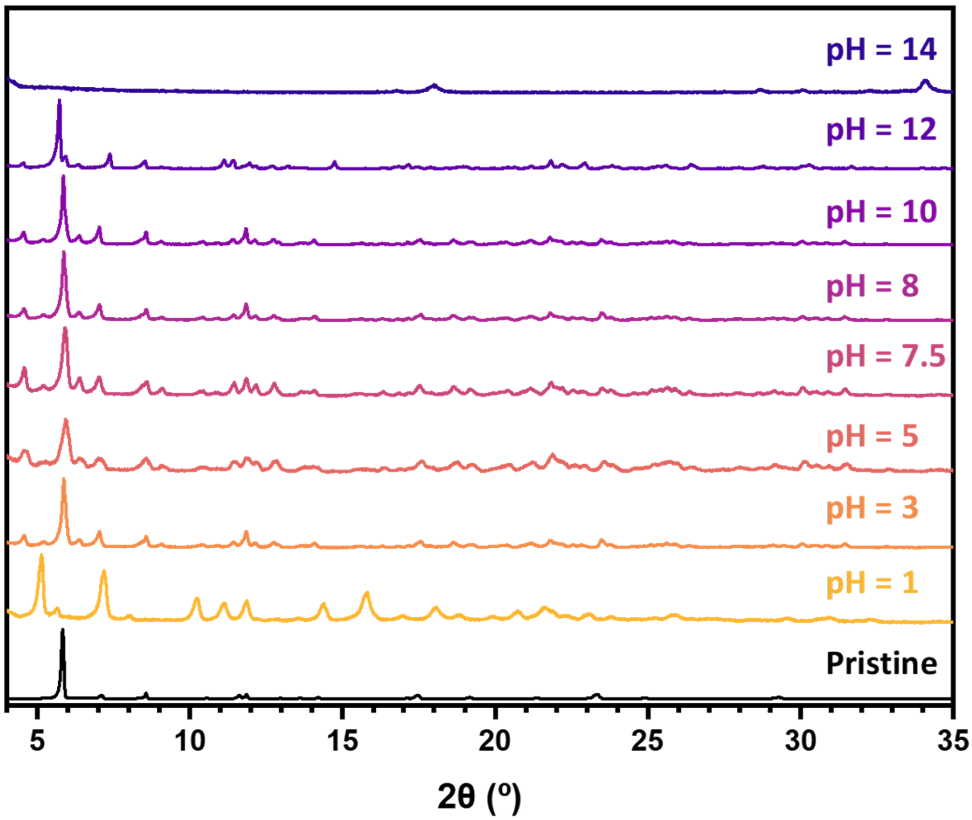


Figure S14. PXRD patterns of IEF-32 before and after chemical stability test at different pHs.

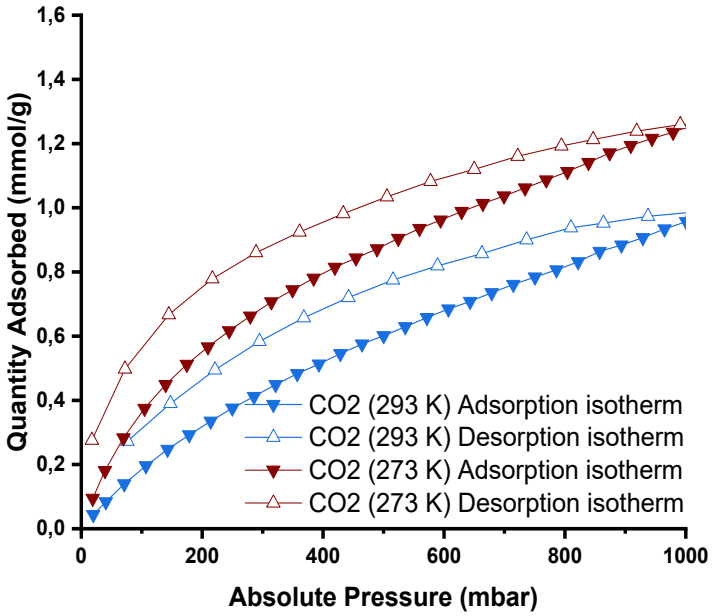


Figure S15. CO_2 adsorption isotherms for IEF-32 at 1 bar and 273 K (red) and 293 K (blue) after being exposed at pH=1.

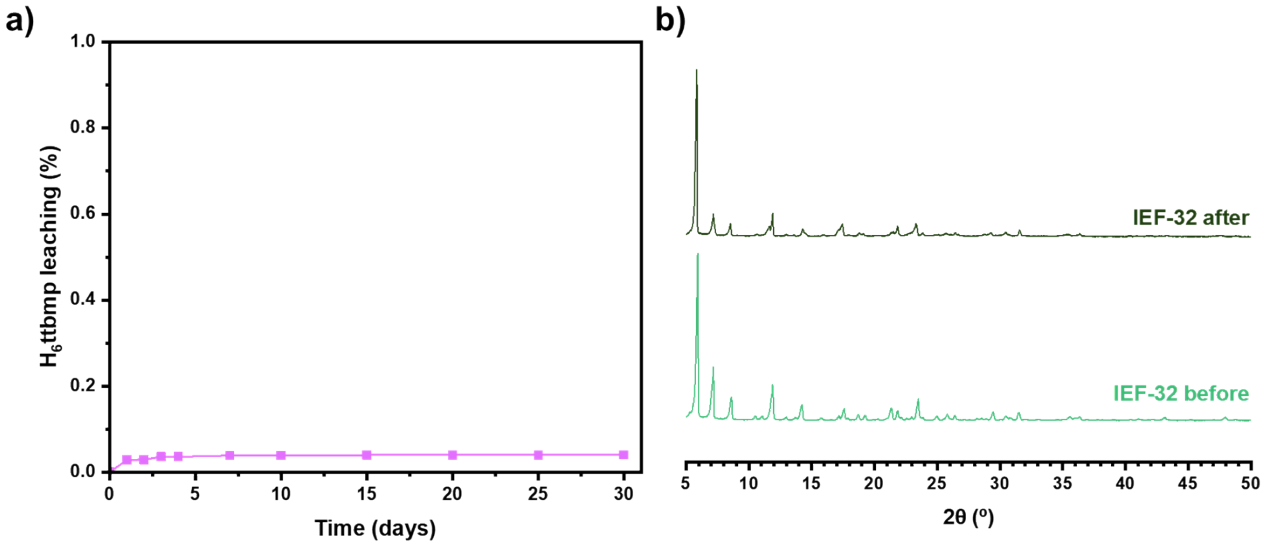


Figure S16. (a) IEF-32 degradation by ligand releasing over time in Milli-Q water and (b) PXRD patterns of IEF-32 before and after the preservation experiment. [MOF] = 5 mM, t = 30 days, under suspension.

Figure S17. Image tracking the preservation effects in grapes treated with (green) IEF-32, its (purple) constituent ligand, and (orange) metal precursor, including (grey) control for 0, 14, and 30 days.

REFERENCES

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