Photo-, Thermo-chromic and Adsorption Properties of Porous Coordination Polymers based on *Bipyridinium Carboxylate* Ligands.

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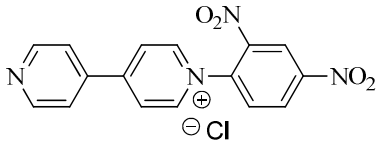
Supporting Information

A- Synthesis of *hpc1* and materials

A1- Synthesis of *hpc1*

Step1: N-(2,4-Dinitrophenyl)-4,4'-bipyridinium chloride



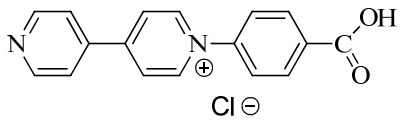
M = 358,50 g/mol

According to the literature[1], a solution of 2,4-dinitrochlorobenzene (3.25 g, 16 mmol) and 4,4'-bipyridyde (2.50 g, 16 mmol) in ethanol (25 mL) is heated under reflux for 23 h. The solution is cooled to room temperature and added to diethyl ether (250 mL), with stirring. The golden – brown precipitate is filtered off and washed with diethyl ether: 4.6 g, (80 %) golden – brown powder of *N*-(2,4-Dinitrophenyl)-4,4'-bipyridinium chloride is obtained.

RMN ^{1}H (300 MHz, D_2O, ppm): δ=9.38 (d, 1H, J = 3.0 Hz, H3), 9.24 (d, 2H, J = 9.0 Hz, C_5H_4N-Ph), 8.92 (dd, 1H, J = 3.0, 3.0 Hz, H5), 8.83 (d, 2H, J = 3.0 Hz, C_5H_4N), 8.67 (d, 2H, J = 6.0Hz, C_5H_4N-Ph), 8.25 (d, 1H, J = 9.0 Hz, H6), 8.03 (d, 2H, J = 6.0 Hz, C_5H_4N).

[1] R. R. Das, J.-M. Lee, C.-H. Noh, S.-J. Jeon, Electrochromic devices provided with nitrogen heterocyclic electron acceptors, U.S. Pat. Appl. Publ. (2012), US 20120176658 A1 20120712.

Step 2: N-(4-Carboxyphenyl)-4,4'-bipyridinium chloride (H*hpc*1)Cl



M = 312.5 g/mol

To the 4.0 g (11.2 mmol) of *N*-(2,4-Dinitrophenyl)-4,4'-bipyridinium Chloride in 80 mL of ethanol (aq. EtOH, 80%), 1.54 g (11.2 mmol) of 4-aminobenzoic acid is added. The stoichiometric amount of Et_3N is used to prevent protonation of the aromatic – amine moiety, 1.57 mL (11.2 mmol, M = 101.19 g/mol, ρ = 0.726 g/mL). The mixture is stirred together at 80°C during 24 h, and then cooled to the room temperature. At the end, beige – brown mixture is filtered, washed with acetone and dried under vacuum. We obtained 2.96 g (85 %) of the final product, which is beige – brown powder.

RMN ^{1}H (300 MHz, D_2O, ppm): δ=9.26 (d, 2H, J = 6.0 Hz, *ortho*-N^+-Ph), 8.82 (d, 2H, J = 6.0 Hz, *meta*-N^+), 8.59 (d, 2H, J = 6.0 Hz, *ortho*-N), 8.14 (d, 2H, J = 6.0 Hz, *meta*-Ph), 8.02 (d, 2H, J = 6.0 Hz, *ortho*-Ph), 7.83 (d, 2H, J = 6.0 Hz, *meta*-N).

ESI – MS : 277.05 (M_w^+) (M_w^{teor} = 312.5 g/mol)

MALDI – TOF Biflex III – 277.0

A2- Synthesis of materials (1-3)

Compounds (**1-3**) were synthesized by solvothermal method, by the reaction of $Zn(NO_3)_2 \cdot 6H_2O$ with terephtalic acid (H_2BDC) and *N*-(4-carboxyphenyl)-4,4′-bipyridinium chloride (H*hpc*1)·Cl in the mixture of solvents (DMF, EtOH, H_2O). The three compounds were obtained from the same stoichiometry of starting reagents, but under different heating programs and with different ratios of solvent mixture (see Table S1).

- **(1)** - $[Zn_5(hpc1)_2(BDC)_4(HCO_2)_2] \bullet 2DMF \cdot EtOH \cdot H_2O$
- **(2)** - $[Zn_3(hpc1)(BDC)_2(HCO_2)(OH)(H_2O)] \bullet DMF \cdot EtOH \cdot H_2O$
- **(3)** - $[Zn_{10}(hpc1)_4(BDC)_7(HCO_2)_2(OH)_4(EtOH)_2] \bullet 3DMF \cdot 3H_2O$

Table S1: Experimental conditions of the synthesis for (1-3) compounds.

Compound	(2)	(1)	(3)
$Zn(NO_3)_2 \times 6H_2O$	38.0 mg, 2 eq.	95.2 mg, 2.5 eq.	
(H*hpc*1)Cl	20.0 mg, 1 eq.	40.0 mg, 1 eq.	
H_2BDC	20.6 mg, 2 eq.	37.2 mg, 1.7 eq.	
H_2CO_2 *	-	6.0 mg, 1 eq.	
DMF	1 ml	1 ml	1 ml
EtOH	0.5 ml	0,5 ml	2 ml
H_2O	0.25 ml	0.25 ml	0.5 ml
Heating program	5h, 50h, 7h (100°C)	6h, 48h, 8h (80°C)	4h, 30h, 5h (100°C)

* As already mentioned, the HCO_2^- anion found in the structures of (1-3) compounds comes from hydrolysis of solvent molecules of DMF. In further syntheses, we added formic acid directly in the reaction mixture as starting material to favor the stabilization of the pure (**1**) and (**3**) phases.

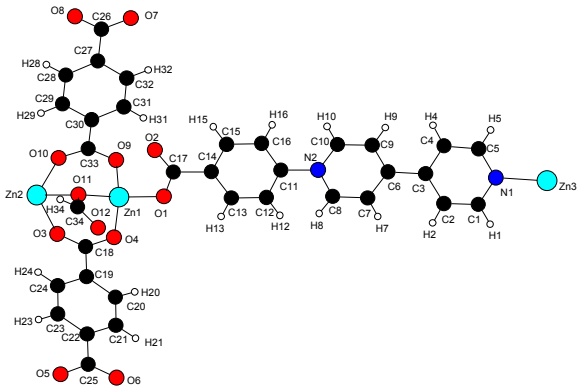
B-Single Crystal data

B1- Summary of crystallographic data of *(1)*

Table 1. Crystal data and structure refinement for (1)

Empirical formula	C76 H64 N6 O28 Zn5
Formula weight	1836.18
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.8071(5) A alpha = 103.75(1) deg. b = 11.615(1) A beta = 104.54(1) deg. c = 16.544(2) A gamma = 95.91(1) deg.
Volume	1745.2(3) A^3
Z, Calculated density	1, 1.747 Mg/m^3
Absorption coefficient	1.790 mm^-1
F(000)	936
Crystal size	0.13 x 0.10 x 0.05 mm
Theta range for data collection	2.78 to 28.03 deg.
Limiting indices	-12<=h<=12, -15<=k<=15, -21<=l<=21

Reflections collected / unique	33319 / 8393 [R(int) = 0.0540]
Completeness to theta = 28.03	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.914 and 0.809
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8393 / 0 / 457
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0514, wR2 = 0.1237 [5355 Fo]
R indices (all data)	R1 = 0.0936, wR2 = 0.1358
Largest diff. peak and hole	0.613 and -0.556 e.A^-3

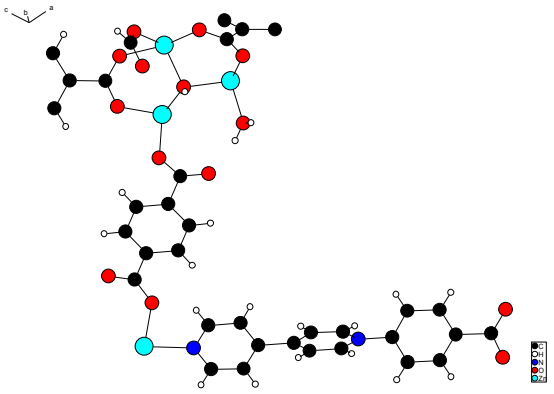


B2- **Summary of crystallographic data of *(2)***

Table 1. Crystal data and structure refinement for 2.

Empirical formula	C39 H39 N3 O17 Zn3
Formula weight	1017.84
Temperature	120(2) K
Wavelength	1.54184 A
Crystal system, space group	Monoclinic, P 1 21/c 1
Unit cell dimensions	a = 11.497(1) A alpha = 90 deg. b = 33.542(3) A beta = 116.84(1) deg. c = 12.106(1) A gamma = 90 deg.
Volume	4165.6(7) A^3
Z, Calculated density	4, 1.623 Mg/m^3
Absorption coefficient	2.697 mm^-1

F(000)	2080
Crystal size	0.11 x 0.07 x 0.04 mm
Theta range for data collection	4.51 to 76.08 deg.
Limiting indices	-14<=h<=10, -40<=k<=28, -13<=l<=14
Reflections collected / unique	15727 / 8211 [R(int) = 0.0513]
Completeness to theta = 67.00	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.728
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8211 / 0 / 514
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0765, wR2 = 0.1677 [6482 Fo]
R indices (all data)	R1 = 0.0943, wR2 = 0.1774
Largest diff. peak and hole	0.988 and -1.370 e.A^-3

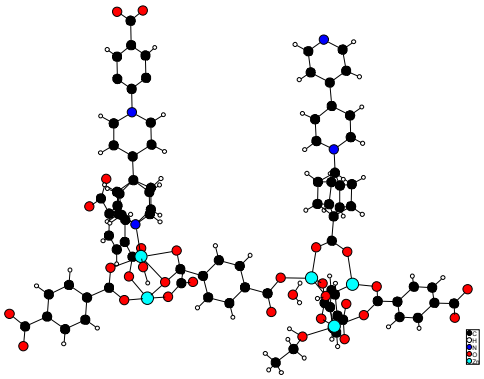


B3- **Summary of crystallographic data of *(3)***

Table 1. Crystal data and structure refinement for 3.

Empirical formula	C139 H121 N11 O52 Zn10
Formula weight	3431.17
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 11.092(1) A alpha = 97.64(1) deg. b = 12.199(2) A beta = 92.01(1) deg.

	c = 28.767(5) A gamma = 115.94(1) deg.
Volume	3450.4(9) A^3
Z, Calculated density	1, 1.651 Mg/m^3
Absorption coefficient	1.802 mm^-1
F(000)	1748
Crystal size	0.38 x 0.3 x 0.06 mm
Theta range for data collection	3.31 to 27.49 deg.
Limiting indices	-14<=h<=14, -15<=k<=15, -37<=l<=37
Reflections collected / unique	70708 / 15266 [R(int) = 0.0363]
Completeness to theta = 25.00	98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.898 and 0.711
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15266 / 0 / 948
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0547, wR2 = 0.1391 [10772 Fo]
R indices (all data)	R1 = 0.0833, wR2 = 0.1506
Largest diff. peak and hole	1.960 and -0.888 e.A^-3



d(N4…C54)= 3.583(6)

d(N4…C38)= 3.699(5)

d(H25..O10)= 2.538(4)

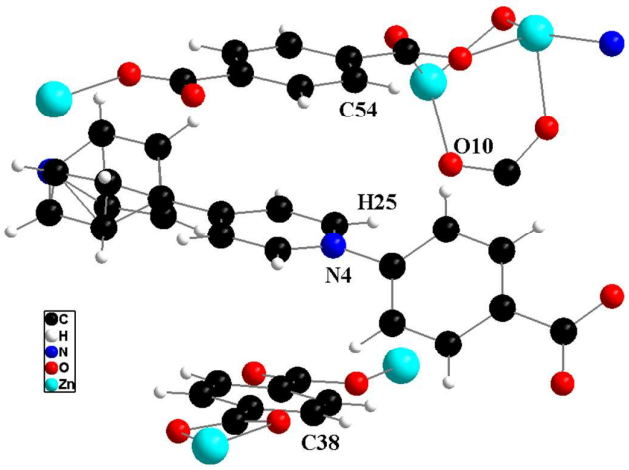


Figure. Details of the structure of 3 showing the envrironnement of one of the two independent hpc1 unit, and selectec intermolecular distances

B4- **Summary of crystallographic data of *(3)'***

Table 1. Crystal data and structure refinement for 3'.

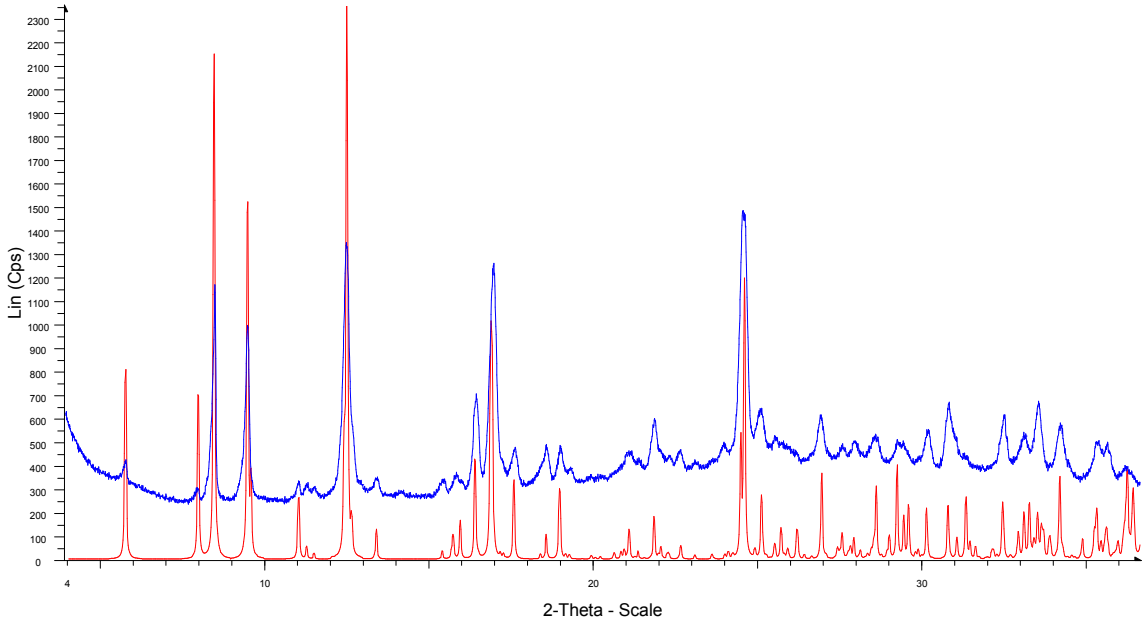
Empirical formula	C124 H106 N8 O54 Zn10
Formula weight	3225.87
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 11.478(1) A alpha = 80.25(1) deg. b = 12.377(1) A beta = 88.09(1) deg. c = 25.794(3) A gamma = 65.25(1) deg.
Volume	3277.0(5) A^3
Z, Calculated density	1, 1.635 Mg/m^3
Absorption coefficient	1.892 mm^-1
F(000)	1638
Crystal size	0.21 x 0.18 x 0.05 mm
Theta range for data collection	2.08 to 27.50 deg.
Limiting indices	-14<=h<=14, -16<=k<=15, -33<=l<=33
Reflections collected / unique	36991 / 13807 [R(int) = 0.0448]
Completeness to theta = 25.00	94.9 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.910 and 0.773
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13807 / 7 / 879
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0609, wR2 = 0.1626 [8523 Fo]
R indices (all data)	R1 = 0.1035, wR2 = 0.1768
Largest diff. peak and hole	1.573 and -0.980 e.A^-3

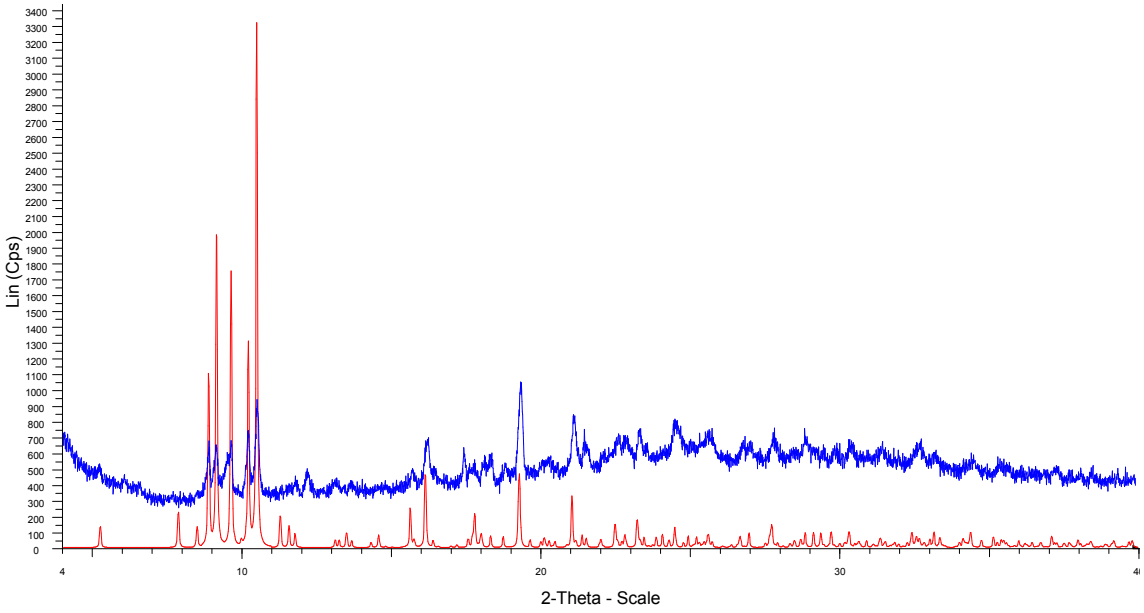
C-XRPD (powder diffraction)

Powder X-Ray patterns of the homogenous samples of **1 – 3** as well as 3' showed that all reflections are indexed in the unit cells obtained from single crystal X-ray diffraction studies: Experimental, BLUE; theoretical, RED.

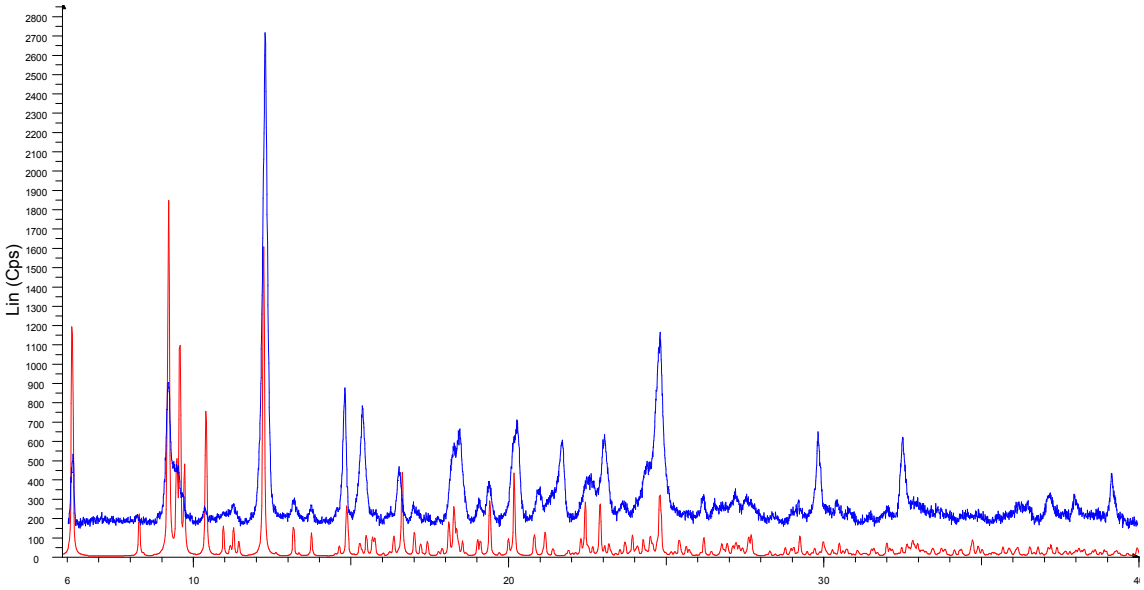
C1- (1)



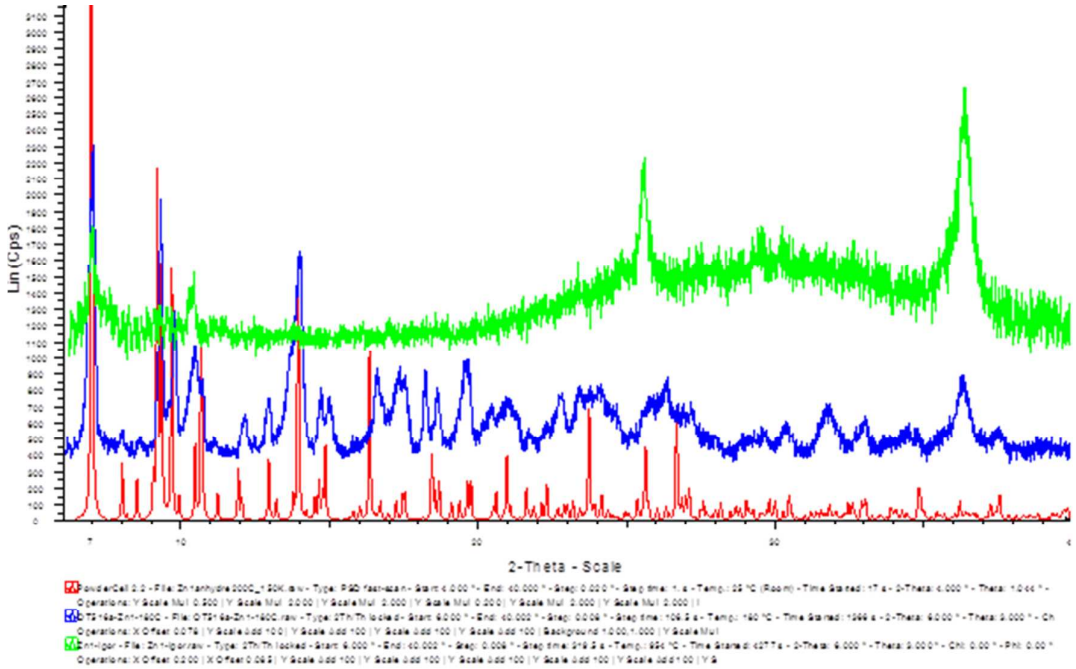
***C2-* (2)**



***C3-* (3)**



***C4-* (3)'**



In green, the XRPD pattern of outgassed sample 3 (180°C under vaccum, one night).

D-Thermodiffractometry : XRPD= f(T)

***D1-* (1)**

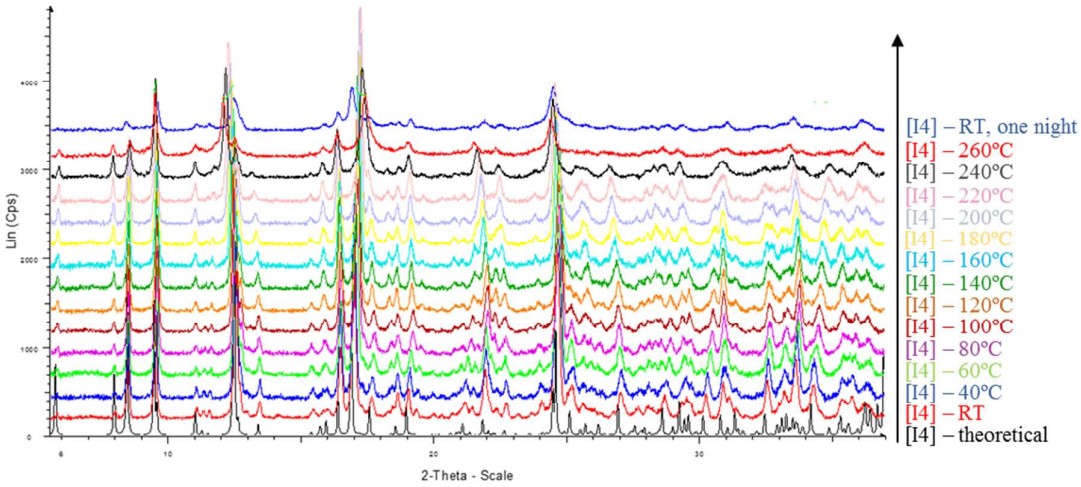


Figure : Thermodiffractometry of the sample **1** in the RT-260°C range.

***D2-* (2)**

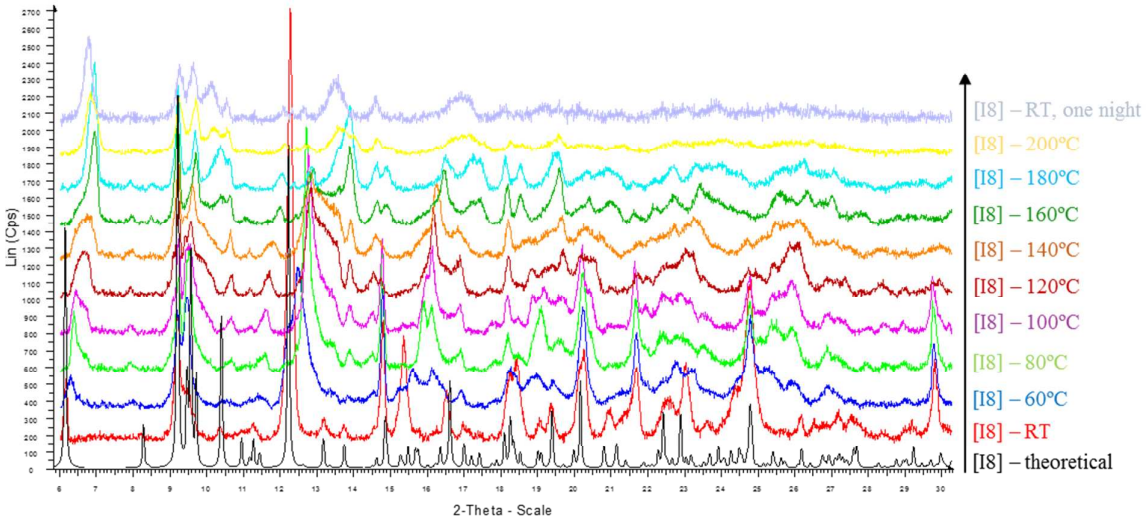


Figure : Thermodiffractometry of the sample **3** in the RT-200°C temperature range.

E-Thermal Analysis

E1-(1)

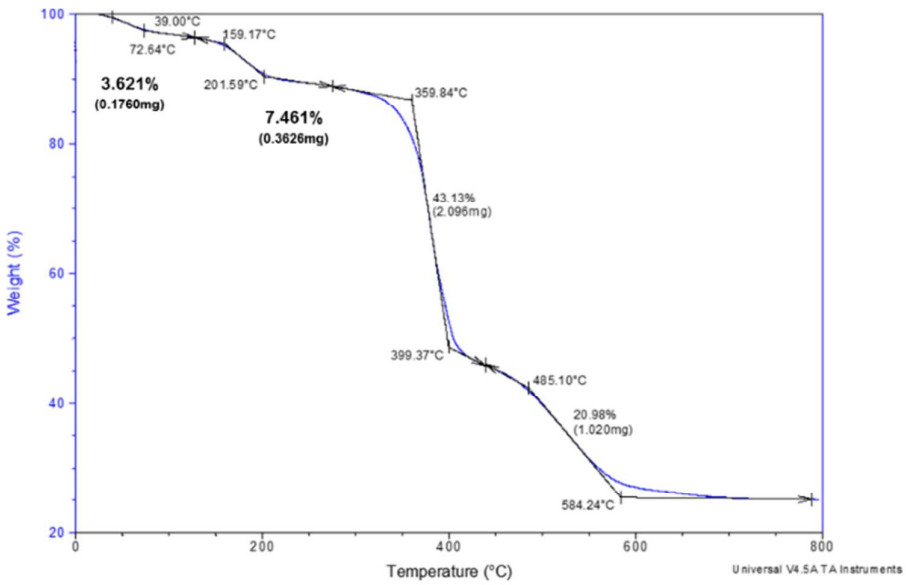


Figure : TGA of sample **1**.

(see comments in the main text)

E2- (2)

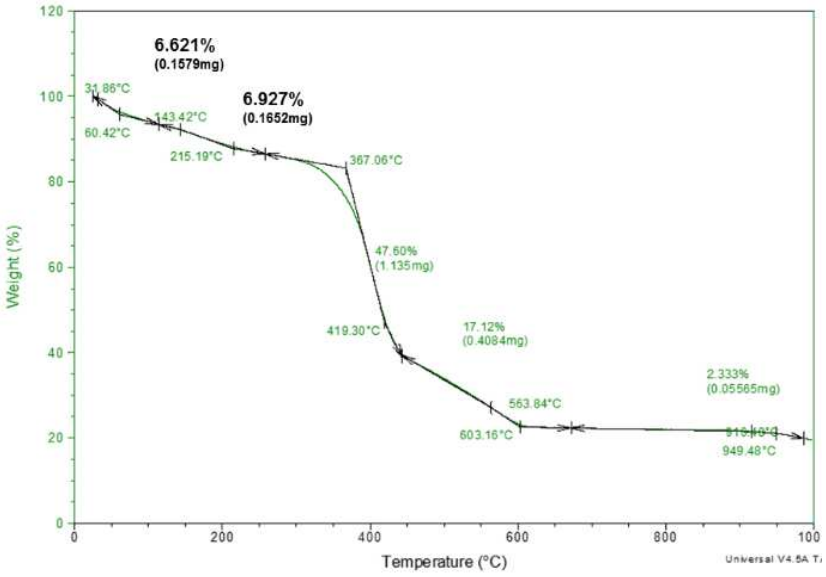


Figure : TGA curve of sample **2**.

(see comments in the main text)

E3- (3)

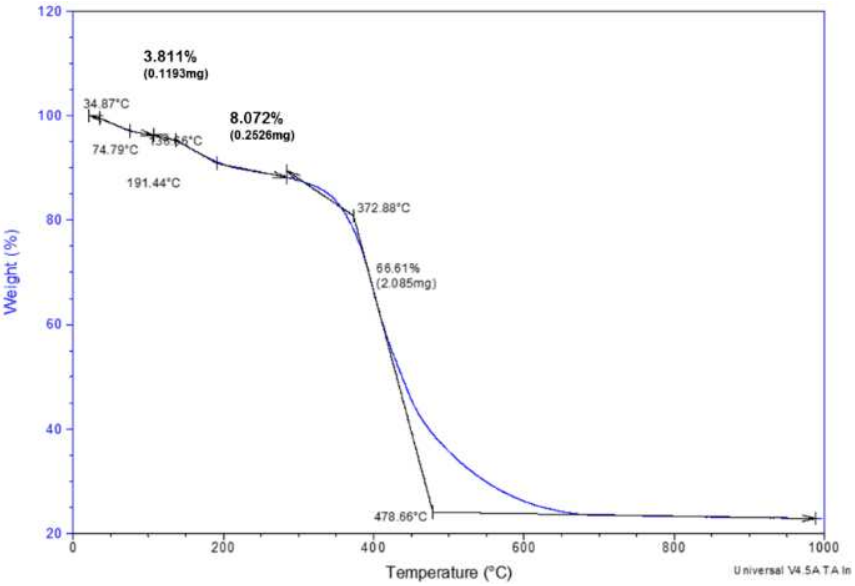


Figure : TGA curve of sample **3**.

(see comments in the main text)

F- EPR measurement

Figure : EPR signal of crystallized sample of **3** under UV irradiation (30 min).