Supplementary Information file

Mechanochromic Luminescence of *N,N'*-dioxyde-*4,4'*-bipyridine Bismuth Coordination Polymers

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1] Experimental part.

The two first materials, **1** and **2**, were obtained by the slow liquid-gaz diffusion method, from a mixture of 1 eq. of $BiBr_3$ and 1 eq. of (*bp4do*)·$2H_2O$ (see the following table for details). For each synthesis, the solvent was the *dmso* while the anti-solvent was *EtOH* for [Bi_2Br_6(*bp4do*)(*dmso*)$_4$] (1), and ethyl acetate for [$BiBr_3$(*bp4do*)(*dmso*)] (2). After two weeks, big orange block–like crystals of 1, orange/red crystals of 2 were filtered off and washed with ethanol or ethyl acetate.

Compound	Reagents		solvent	Anti-solvent	product	weight
(**1**) [Bi_2Br_6(*bp4do*)(*dmso*)$_4$]	$BiBr_3$, $9{,}0\times10^{-5}$ mol, 40,4 mg	(*bp4do*)·$2H_2O$, $8{,}9\times10^{-5}$ mol, 20,0 mg	dmso	ethanol	Big orange block-like crystals	44.5 mg
(**2**) [$BiBr_3$(bp4do)(dmso)]	BiBr3, $9{,}0\times10^{-5}$ mol, 40,4 mg	(*bp4do*)·$2H_2O$, $8{,}9\times10^{-5}$ mol, 20,0 mg	dmso	ethyl acetate	Big orange-red crystals	50.3 mg

Compound **3** was synthesized by solvothermal method, reacting on 2 eq. of $BiBr_3$ with 1 eq. of (*bp4do*)·$2H_2O$ in the mixture of solvents, *dmso* (1 mL) and *ACN* (2 mL). The reaction mixture was heated for 6 h from 25 to 90°C, then kept for 48 h at 90°C, followed by a cooling down to 25°C during 8 h. The big plate-like crystals with orange-red colour of the phase 3, were then filtered off and washed with acetonitrile.

Compound	Reagents		solvent	product	weight
(**3**) [Bi_2Br_6(*bp4do*)$_3$]	$BiBr_3$, $1{,}8\times10^{-4}$ mol, 80,8 mg	(*bp4do*)·$2H_2O$, $8{,}9\times10^{-5}$ mol, 20,0 mg	*dmso* + *ACN*	Big orange plate-like crystals	79,2 mg

2] Single Crystal X-ray diffraction.

Summary of crystal data and structure refinement for **1-3**

2.1] (1): [Bi_2Br_6(*bp4do*)(dmso)$_4$]

Empirical formula	C18 H32 Bi2 Br6 N2 O6 S4
Formula weight	1398.12
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 9.3733(12) A alpha = 90 deg.
	b = 16.7116(10) A beta = 96.009(15) deg.
	c = 12.128(2) A gamma = 90 deg.
Volume	1889.3(4) A^3
Z, Calculated density	2, 2.458 Mg/m^3
Absorption coefficient	15.899 mm^-1
F(000)	1284
Crystal size	0.29 x 0.16 x 0.15 mm
Theta range for data collection	3.58 to 32.06 deg.
Limiting indices	-13<=h<=13, -24<=k<=24, -15<=l<=18
Reflections collected / unique	25488 / 6515 [R(int) = 0.0802]
Completeness to theta = 32.06	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.092 and 0.044
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6515 / 0 / 184
Goodness-of-fit on F^2	1.010
Final R indices [I>2sigma(I)]	R1 = 0.0445, wR2 = 0.0921
R indices (all data)	R1 = 0.1481, wR2 = 0.1307
Largest diff. peak and hole	1.687 and -3.720 e.A^-3

2.2] (2): [$BiBr_3$(*bp4do*)(dmso)]

Empirical formula	C12 H14 Bi Br3 N2 O3 S
Formula weight	715.02
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 9.3688(9) A alpha = 90 deg.
	b = 15.8997(18) A beta = 96.310(9) deg.
	c = 12.740(2) A gamma = 90 deg.
Volume	1886.3(4) A^3
Z, Calculated density	4, 2.518 Mg/m^3
Absorption coefficient	15.823 mm^-1
F(000)	1312
Crystal size	0.22 x 0.16 x 0.14 mm
Theta range for data collection	3.84 to 29.07 deg.

Limiting indices	-12<=h<=12, -21<=k<=21, -17<=l<=15
Reflections collected / unique	17145 / 4930 [R(int) = 0.0533]
Completeness to theta = 29.07	97.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.109 and 0.060
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4930 / 0 / 203
Goodness-of-fit on F^2	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0692
R indices (all data)	R1 = 0.0830, wR2 = 0.0820
Largest diff. peak and hole	1.145 and -1.398 e.A^-3

2.3] (3): $[Bi_2Br_6(bp4do)_3]$

Empirical formula	C30 H24 Bi2 Br6 N6 O6
Formula weight	1461.98
Temperature	214.96(10) K
Wavelength	1.54184 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.8861(3) A alpha = 101.526(3) deg.
	b = 9.0729(3) A beta = 97.031(3) deg.
	c = 12.2059(5) A gamma = 98.281(3) deg.
Volume	942.50(6) A^3
Z, Calculated density	1, 2.576 Mg/m^3
Absorption coefficient	25.992 mm^-1
F(000)	670
Crystal size	0.47 x 0.09 x 0.08 mm
Theta range for data collection	3.74 to 76.39 deg.
Limiting indices	-8<=h<=11, -11<=k<=9, -15<=l<=15
Reflections collected / unique	8439 / 3887 [R(int) = 0.0480]
Completeness to theta = 76.39	98.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.2302 and 0.0288
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3887 / 0 / 226
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0987
R indices (all data)	R1 = 0.0465, wR2 = 0.1047
Largest diff. peak and hole	1.428 and -2.442 e.A^-3

3] Powder X-ray diffraction.

3-1 : compound **1**

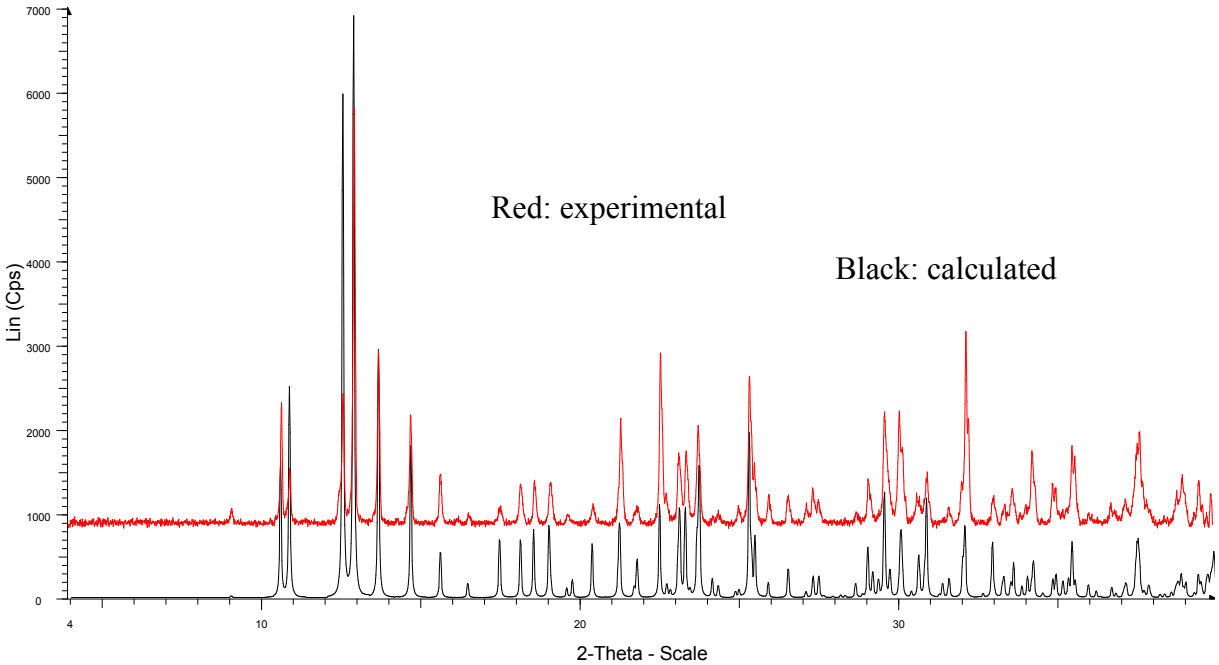


Figure S1- Calculated and experimental X-ray powder diffraction pattern of **1**.

3-2 : compound **2**

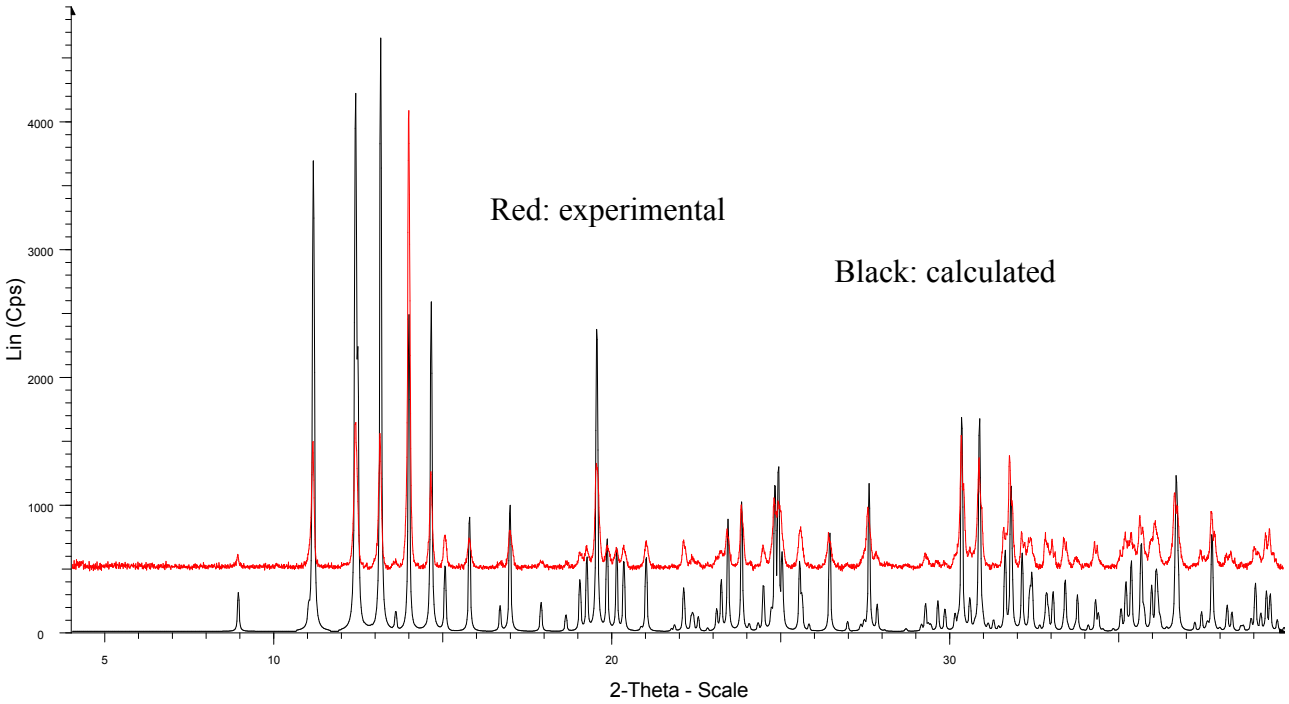


Figure S2- Calculated and experimental X-ray powder diffraction pattern of **2**

3-3 : compound **3**

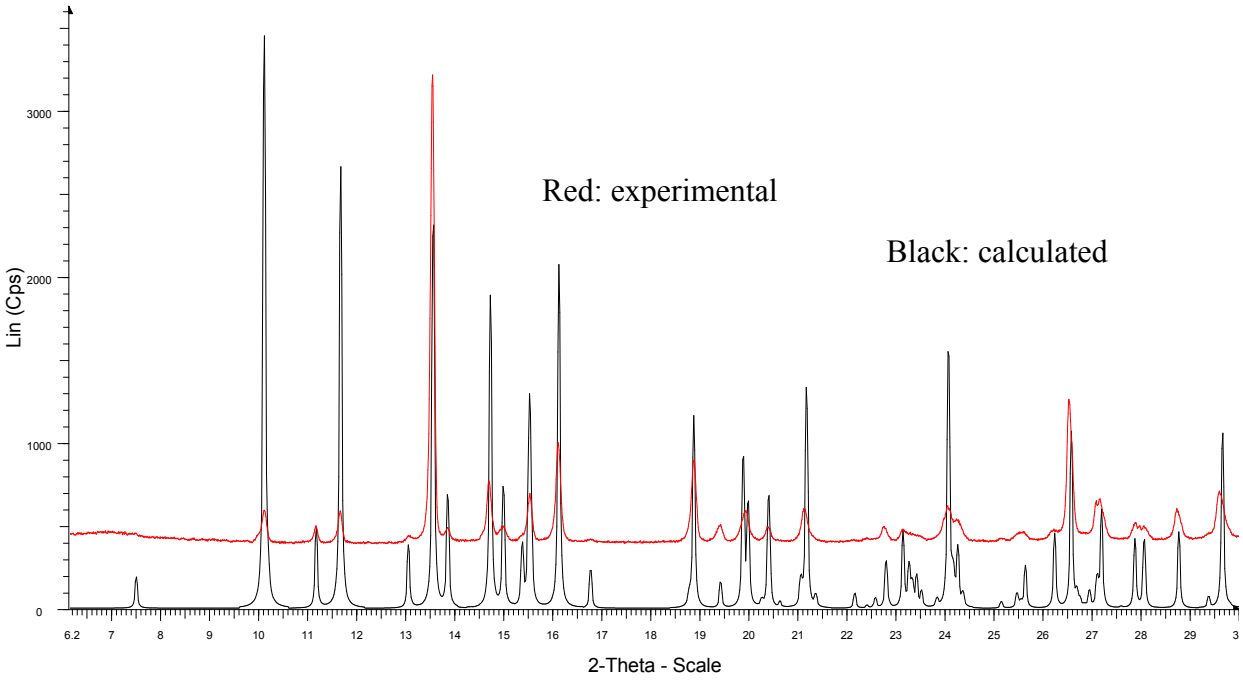


Figure S3- Calculated and experimental X-ray powder diffraction pattern of **3**

4] TGA analysis

4.1] TGA of (2): [$BiBr_3$(*bp4do*)(dmso)].

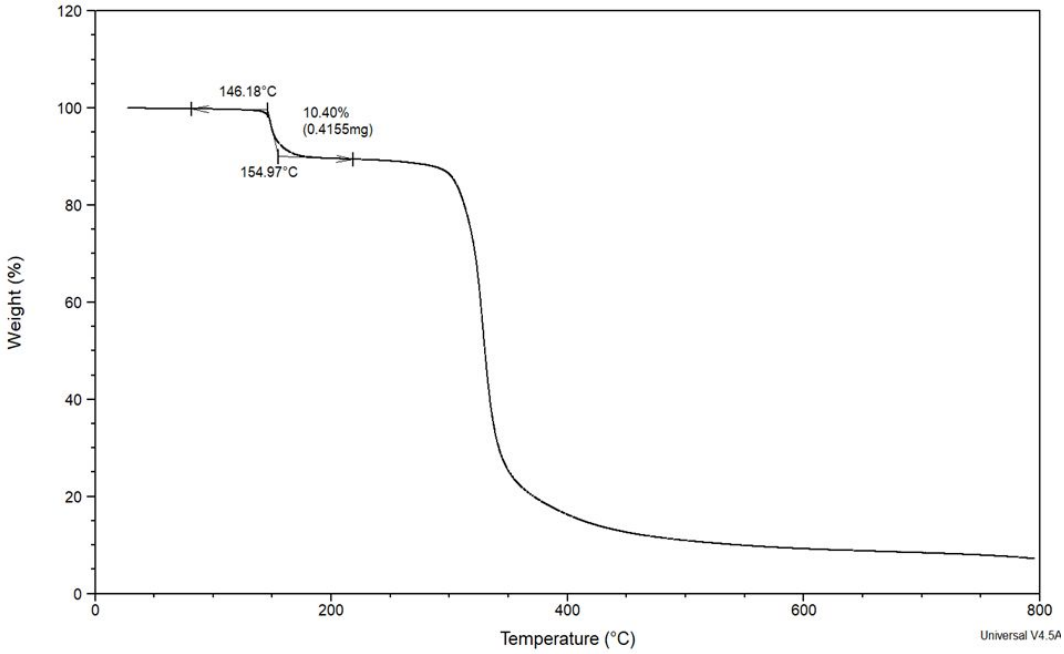
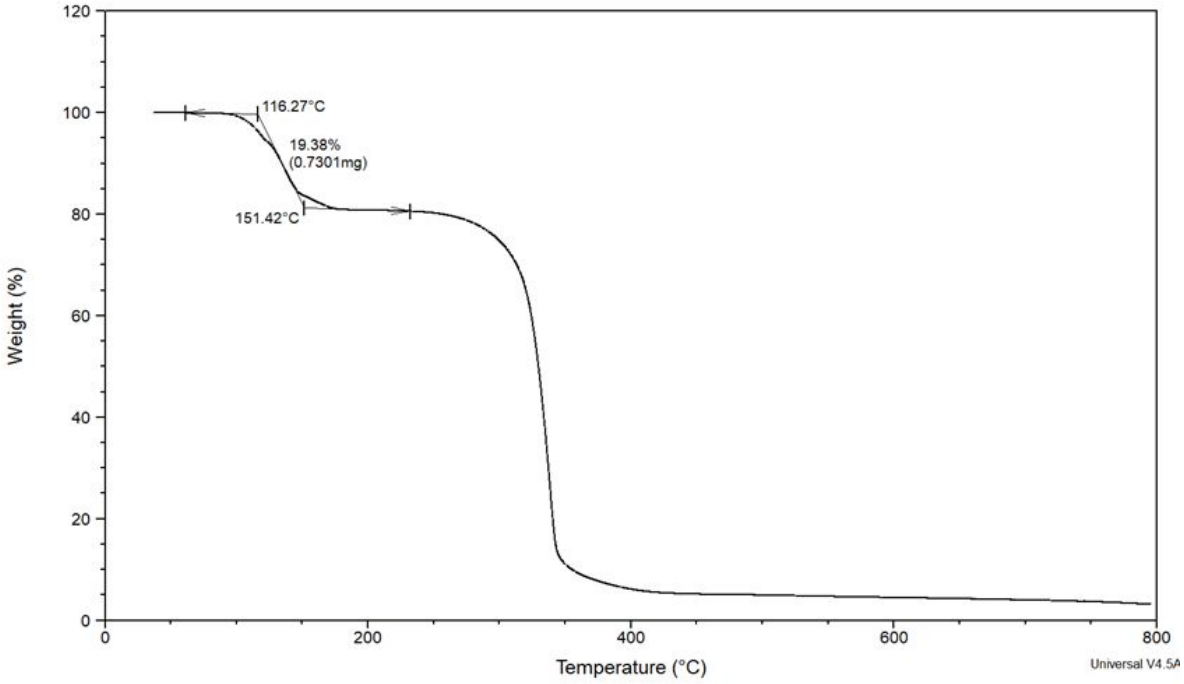


Figure S4- TGA of **2.** Weight loss (removal of *dmso* molecules) : calculated 10.90 % compared to experimental 10.40 %

4.2] TGA of (1): $[Bi_2Br_6(bp4do)(dmso)_4]$ and **PXRD**

a-



b-

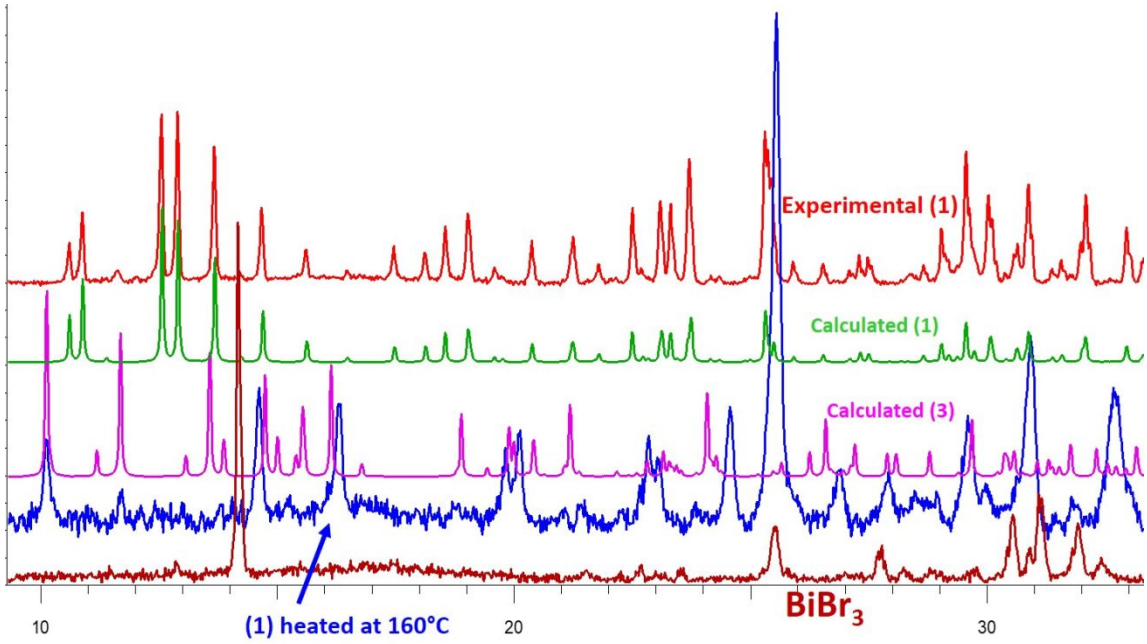


Figure S5- a- TGA of **1 :** Weight loss (removal of all *dmso* molecules) : calculated 22.3% compared to experimental 19.4% ; **b-** PXRD showing that the desolvation of **1** at 160 °C probably leads to the formation of $BiBr_3$ and compound **3** as highlighted by the presence of lines at 10°, 11.8°, 14.7° and 16.2° 2θ (compound **3**), and the lines at 25.6°, 27.8 and 31° ($BiBr_3$).

5] PL properties

5-1) Solution :

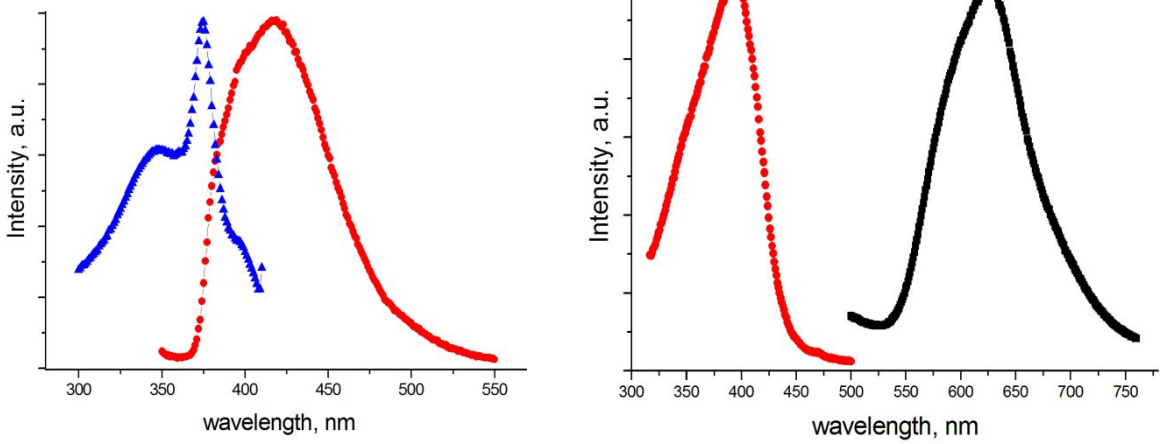


Figure S6- PL and PLE of bp4do (left) and a mixture of *bp4do* and $BiBr_3$ (right) in a dmso solution

5-2) Solid state :

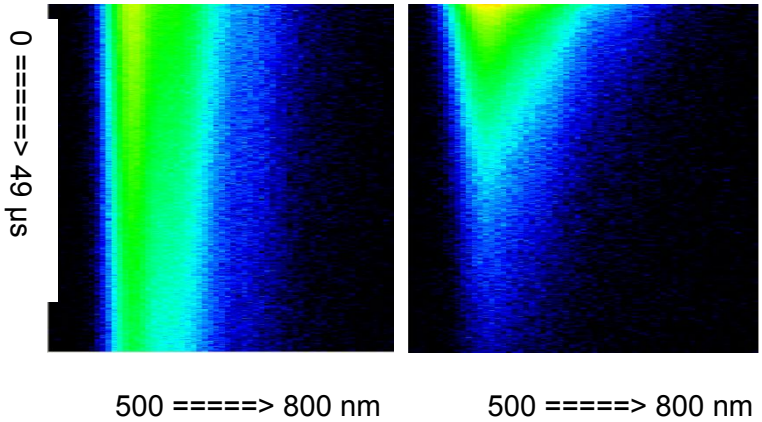


Figure S7- time evolution of the PL of powders of compound **1** (left) and **2** (right) as a function of the emission wavelength. The color scale is logarithmic, and the time span is 50 µ.

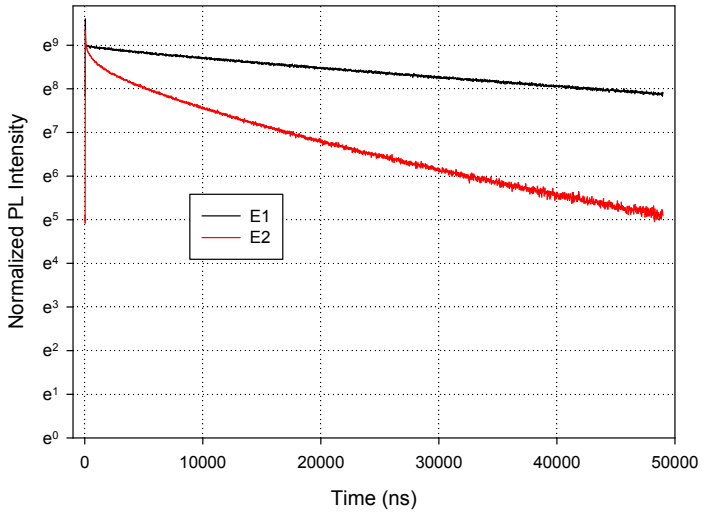


Figure S8- time decay of the PL of powders of compound **1** (black) and **2** (red).

6] MCL properties

6-1 : compound **3** : reversibility of the process

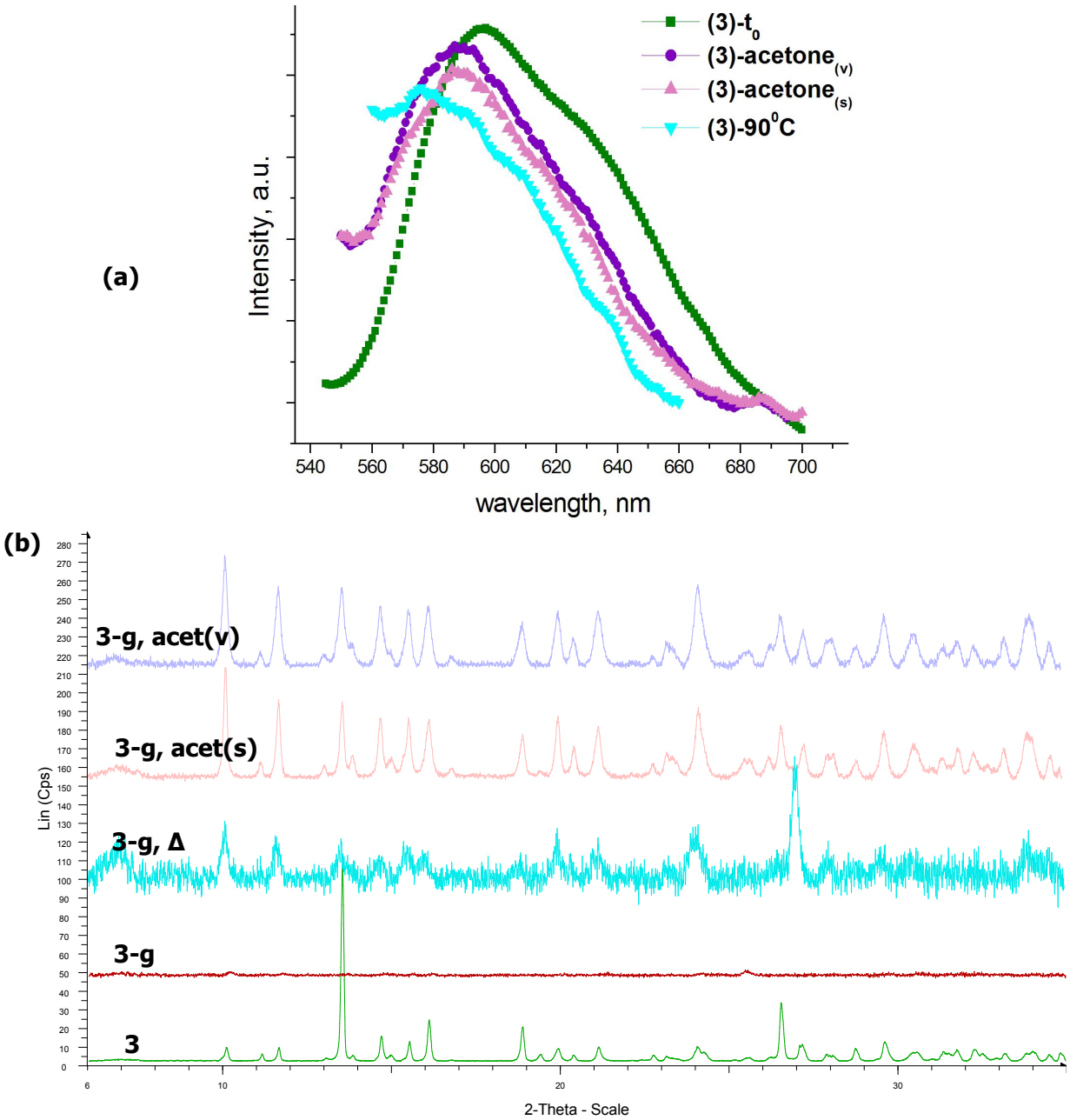
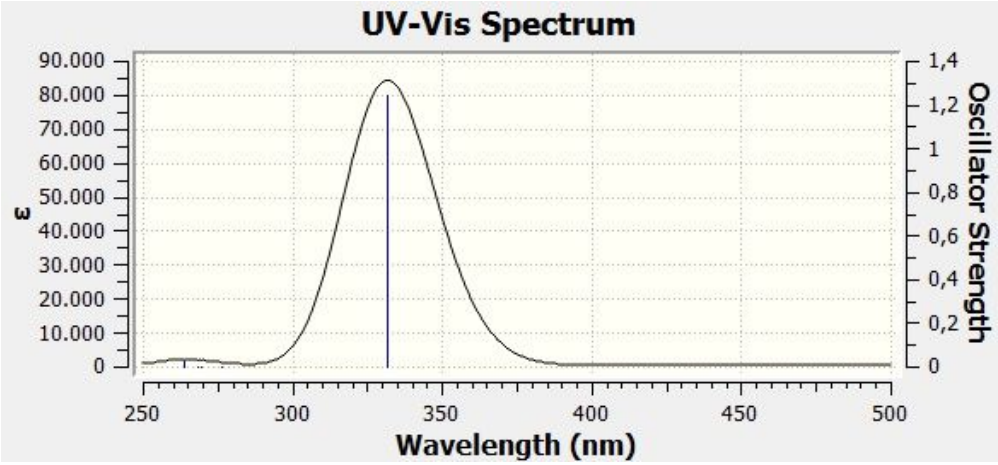
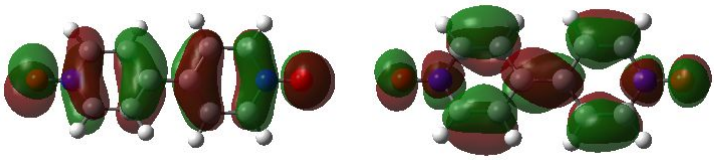


Figure S9- (a) PL spectra of sample **3** before grinding (t_0), and after a rinding/recrystallization process (recrystallization by heating, vapor fuming or by adding a few drops of solution on the ground powder); (b) XRPD patterns of sample **3**, after grinding (**3**-g) and after a grinding-recrystallization process (**3-g**,acet(v), **3-g**,acet(s), **3-g**,Δ

7] Quantum chemical calculations

In Figure S10 we report the IEFPCM-TD-M062X/6-311++G(d,p) absorption spectrum of *bp4do* in *dmso* and a plot of the MOs mainly involved in the lowest energy transition. In Figure S11 we report the IEFPCM-TD-M062X/def2-SVP absorption spectrum of compound **1** in *dmso*. A plot of the MOs mainly involved in the lowest energy transition is reported in Figure 7.





HOMO **LUMO**

Figure S10. *Top:* IEFPCM-TD-M062X/6-311++G(d,p) absorption spectrum of *bp4do* in *dmso*, resulting from convolution of the excitation energies with 0.2 eV of half-bandwidth; *Bottom*: plots of the IEFPCM-M062X/6-311++G(d,p) MOs mainly involved in the lowest energy transition of *bp4do* (isosurfaces value 0.02).

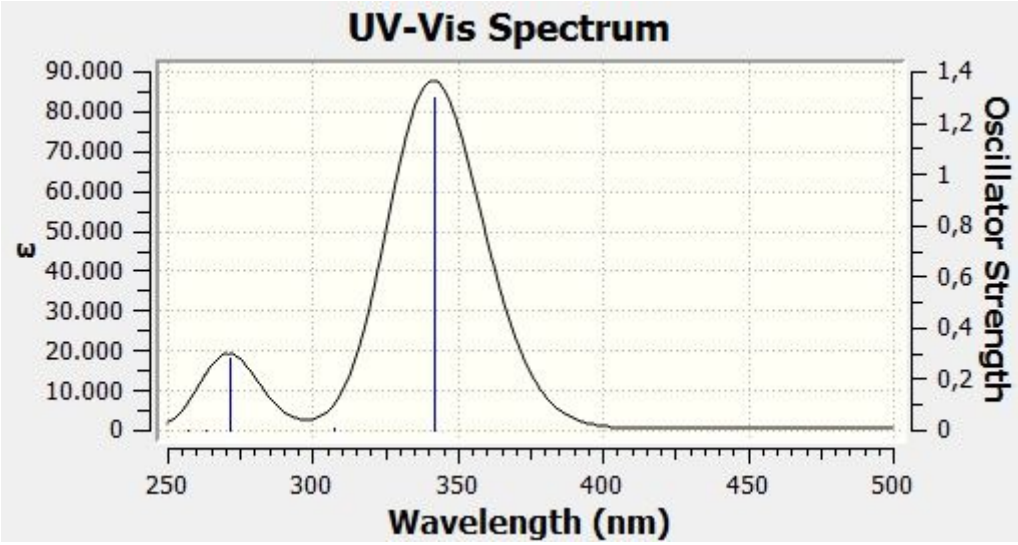


Figure S11. IEFPCM-TD-M062X/def2-SVP absorption spectrum of **1** in *dmso*, resulting from convolution of the excitation energies with 0.2 eV of half-bandwidth