Protonated *N*-oxide-4,4'-bipyridine: from luminescent $Bi^{(III)}$ complexes to hybrids based on H-bonded dimers or H-bonded open 2D square supramolecular networks.

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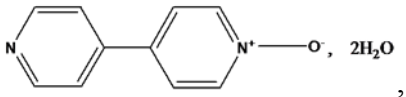
Supporting Information

A- Synthesis

A1- Procedure for the preparation *of the hydrated N-oxide-4,4'-bipyridine (bp4mo, $2H_2O$)* :



, M = 208,22 g/mol

According to the literature [1,2], 3,4 g 4,4-bipyridine ($2{,}1\cdot10^{-2}$ mol) are dissolved in 25 ml of acid acetic glacial under heating at 70^0C. After, 2,18 g of hydrogen peroxide ($2{,}1\cdot10^{-2}$ mol) is added drop by drop. Solution is left for agitation under heating at 70^0C during 24 hours and after that, cooled down to the ambient temperature. Then, 37 g of $NaHCO_3$ (0,44 mol) is added to the solution leading to a white solid. Later, all products, which come from 4,4-bipyridine are extracted in chloroform (4×200 ml). Afterwards, the resulting pink solution which was obtained, is concentrated and is put into the chromatographic column (SiO_2, 20*5 cm). The first eluent is acetone, used to extract the residual 4,4'-bipyridine. The second eluent is mixture acetone/methanol (in proportion 4:1 to 3:1), used to extract the intermediate product, N-oxide-4,4'-bipyridine. After concentration, a crystalline white powder (2,27 g, 63% based on 4,4'-bipyridine) of N-oxide-4,4'-bipyridine, $2H_2O$ is obtained.

RMN ^{1}H (300 MHz, D_2O): δ=8,48 (d, 2H, J=6,3 Hz, ortho-N), 8,27 (d, 2H, J=7,5 Hz, ortho-N^+-O^-), 7,76 (d, 2H, J=7,5 Hz, meta-N), 7,56 (d, 2H, J=6,3 Hz, meta-N^+-O^-).

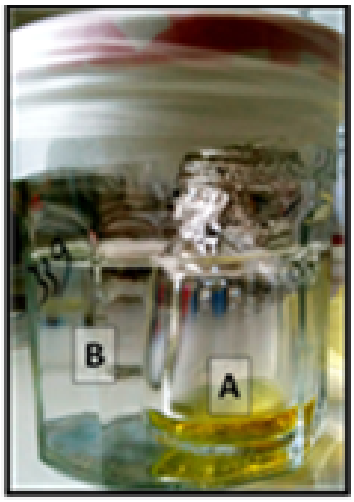
Anal. Elem.: Calc. C, 57,68; H, 5,81; N, 13,45; O, 23,05 – Measured. C, 57,57; H, 5,71; N, 13,50; O, 22,30.

[1] R. Fielden, L. A. Summers, J Heterocyclic Chem, 1974, 11, 299.

[2] H. Brunner, R. Störiko, F. Rominger, Eur J Inorg Chem, 1998, 771

A2 - Procedure for the preparation of compounds:

- Compounds **1** and **5** were obtained, with a slow liquid – gaz diffusion method from bp4mo(H_2O), $BiCl_3$ and hydrochloric acid (**5**), the starting bp4mo(H_2O) being first synthesized as described above. The starting materials are dissolved in the minimum of DMSO in a pillbox (A) (**1** : bp4mo(H_2O) (31.4 mg, 0.151 mmol), $BiCl_3$ (47.5 mg, 0.150 mmol); **2** : bp4mo(H_2O) (26.5 mg, 0.127 mmol), $BiCl_3$ (42.0 mg, 0.128 mmol), HCl (20 drops, 8.18 mol)). The pillbox is then covered with a holed aluminium paper and inserted in a jar of jam filled with ethanol (B). The jar of jam is then covered with a lid and sealed with parafilm (see photo). A few days later, crystals appeared. They are filtered, washed with ethanol and dried in the oven at 50°C (1 : 38.9 mg (82% yield); 2 : 36.7 mg (91% yield).



$$BiCl_3 + bp4mo(2H_2O) \xrightarrow[B)\ ethanol]{A)\ DMSO} \mathbf{[H(bp4mo)][BiCl_4]} \quad (1)$$

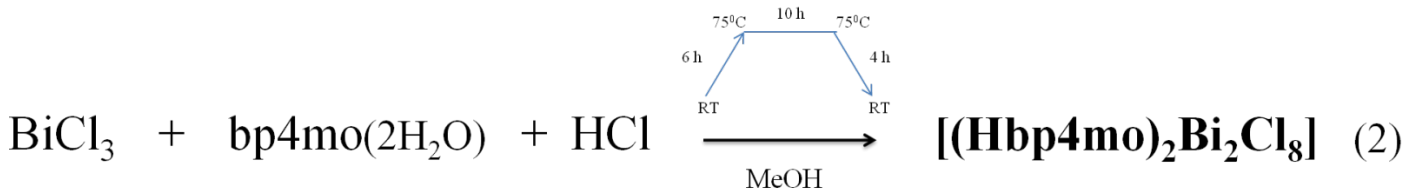
47,5 mg	31,4 mg	colorless plate – like crystals
$1,5\times10^{-4}$ mol	$1,51\times10^{-4}$ mol	(38,9 mg, 82%)

$$BiCl_3 + bp4mo(2H_2O) + HCl \xrightarrow[B)\ ethanol]{A)\ DMSO} \mathbf{[H(Hbp4mo)_2][BiCl_6]} \quad (5)$$

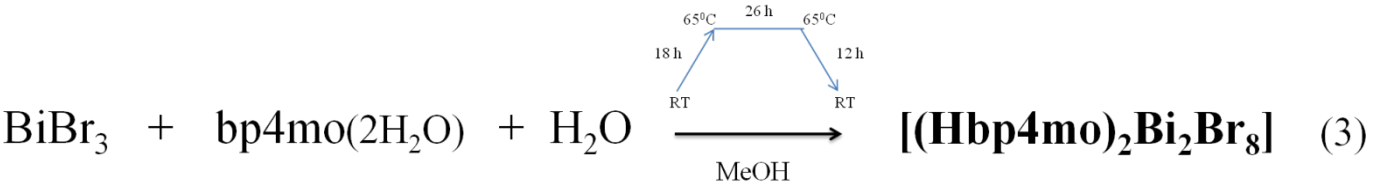
40,4 mg	26,5 mg	20 drops	big, colorless plate – like crystals
$1,28\times10^{-4}$ mol	$1,27\times10^{-4}$ mol	$8,18\times10^{-3}$ mol	(36,7 mg, 91%)

- Compounds 2 – 4 were prepared by a solvothermal method using a Teflon-lined PARR autoclave (internal volume 25 mL). **2** : To 0.127 mmol of $BiCl_3$ (40.2 mg), 0.127 mmol of bp4mo(H_2O) (26.5 mg) and 0.327 mmol of HCl (1 drop); **3** : To 0.127 mmol of $BiBr_3$ (57.0 mg), 0.127 mmol of bp4mo(H_2O) (26.5 mg) and H_2O (10 drops); **4** : To 0.127 mmol of $BiBr_3$ (57.0 mg), 0.127 mmol of bp4mo(H_2O) (26.5 mg) and 0.198 mmol of HBr (1 drop) were added 10 mL of methanol. The autoclave was heated in a programmable oven with the following parameters: **2** : 6 h of heating from 25 to 75°C, 10 h remaining at 75°C, and then 4 h of cooling down to 25°C. Crystals with white – yellow color were collected by filtration and washed with methanol (yield 95% on the basis of $BiCl_3$); **3** : 18 h of heating from 25 to 65°C, 26 h remaining at 65°C, and then 12 h of cooling down to 25°C. Big, nice yellow block like crystals were collected by filtration and washed with methanol (yield 88% on the basis of $BiBr_3$); **4** : 8 h of heating from 25 to 75°C, 12 h remaining at 75°C, and then 6h of cooling down to 25°C.

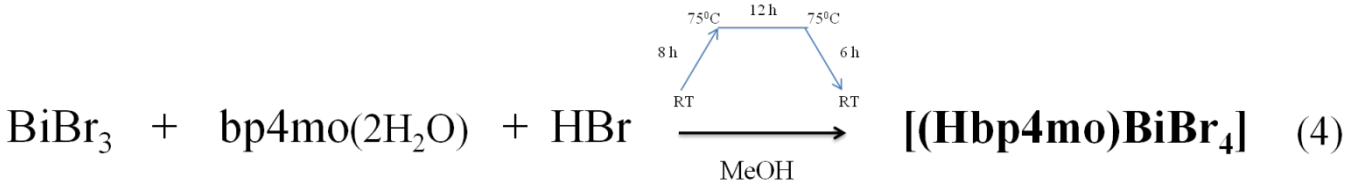
Yellow crystals were collected by filtration and washed with methanol (yield 80% on the basis of $BiBr_3$).



40,2 mg	26,5 mg	1 drop	10 ml	pale yellow crystals
$1,27\times10^{-4}$ mol	$1,27\times10^{-4}$ mol	$3,27\times10^{-4}$ mol		(38,19 mg, 95%)



57 mg	26,5 mg	10 drops	10 ml	big yellow block – like crystals
$1,27\times10^{-4}$ mol	$1,27\times10^{-4}$ mol			(50,1 mg, 88%)



57 mg	26,5 mg	1 drop	10 ml	yellow crystals
$1,27\times10^{-4}$ mol	$1,27\times10^{-4}$ mol	$1,98\times10^{-4}$ mol		(45,6 mg, 80%)

- Powder X-Ray patterns of the homogenous samples of 1 – 5 showed that all reflections are indexed in the unit cells obtained from single crystal X-ray diffraction studies (see below).

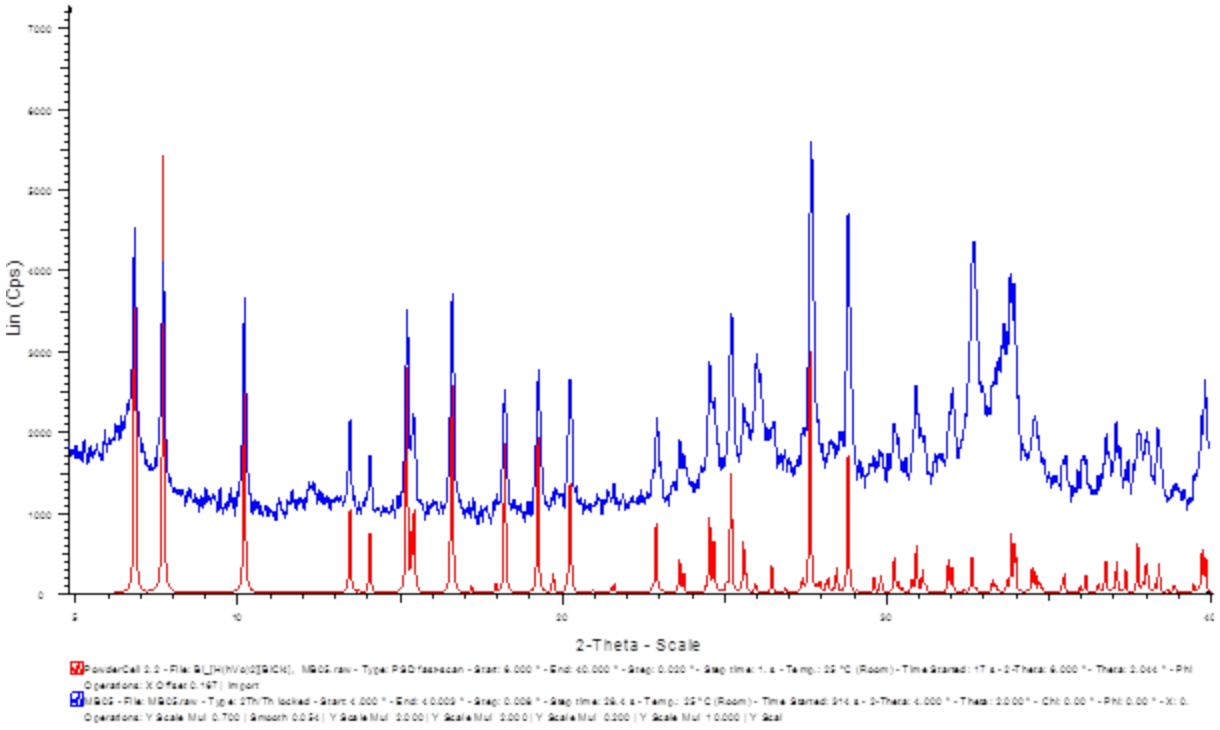
B- Single crystal and powder X-ray diffraction analysis

B-I- [H(bp4mo)][$BiCl_4$] (1)

B-I-A- Summary of crystallographic data

Empirical formula	C20 H17 Bi Cl4 N4 O2
Formula weight	696.16
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, C2/c
Unit cell dimensions	a = 23.6950(10) A alpha = 90 deg.
	b = 26.6618(10) A beta = 95.950(10) deg.
	c = 7.2913(5) A gamma = 90 deg.
Volume	4581.5(4) A^3
Z, Calculated density	8, 2.019 Mg/m^3
Absorption coefficient	8.189 mm^-1
F(000)	2656
Crystal size	0.20 x 0.12 x 0.08 mm
Theta range for data collection	2.70 to 32.08 deg.
Limiting indices	-35<=h<=35, -39<=k<=39, -10<=l<=10
Reflections collected / unique	67247 / 7990 [R(int) = 0.0801]
Completeness to theta = 32.08	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.446 and 0.283
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7990 / 0 / 285
Goodness-of-fit on F^2	1.018
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0441
R indices (all data)	R1 = 0.0999, wR2 = 0.0554
Largest diff. peak and hole	0.877 and -0.951 e.A^-3

B-I-B- XRPD of (1) : theoretical (blue) and experimental (red)

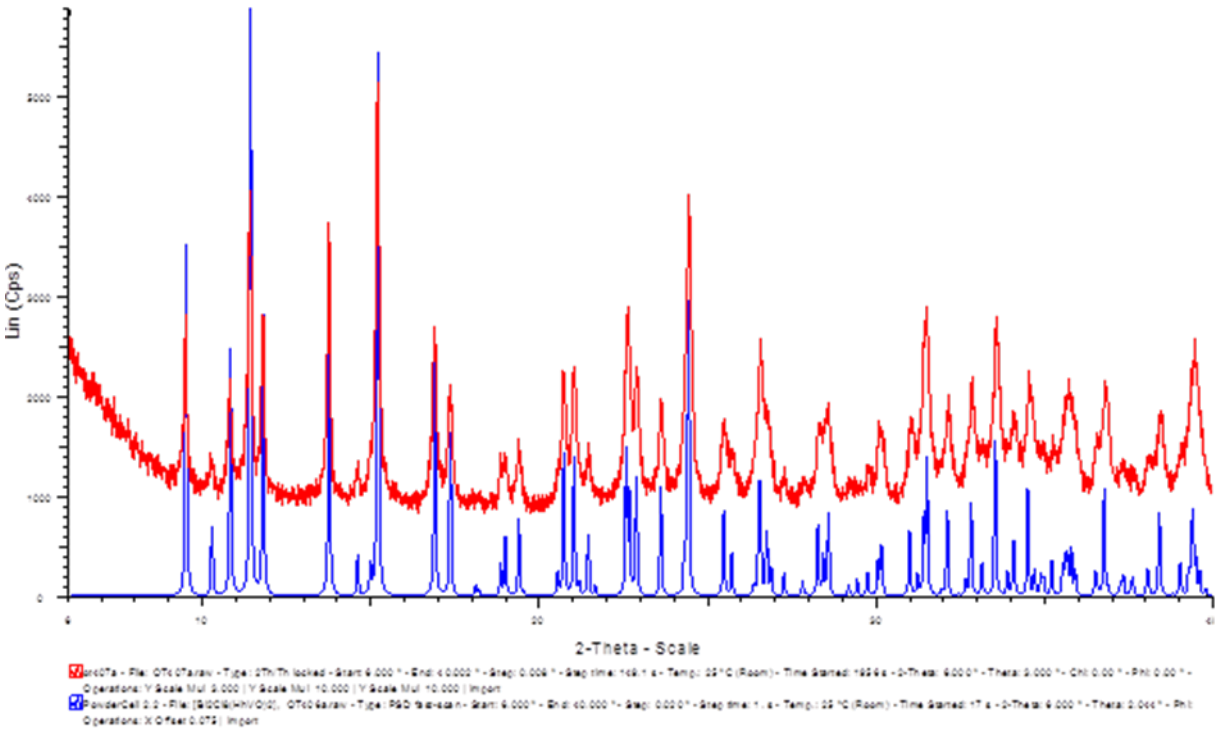


B-II- ap - [(Hbp4mo)$_2$Bi$_2$Cl$_8$] (2)

B-II-A- Summary of crystallographic data

Empirical formula	C20 H18 Bi2 Cl8 N4 O2
Formula weight	1047.94
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 1 2/c 1
Unit cell dimensions	a = 18.8244(8) A alpha = 90 deg. b = 9.7773(2) A beta = 94.968(5) deg. c = 16.5190(7) A gamma = 90 deg.
Volume	3028.93(19) A^3
Z, Calculated density	4, 2.298 Mg/m^3
Absorption coefficient	12.336 mm^-1
F(000)	1936
Crystal size	0.31 x 0.22 x 0.12 mm
Theta range for data collection	3.98 to 32.01 deg.
Limiting indices	-26<=h<=28, -14<=k<=14, -22<=l<=24
Reflections collected / unique	22424 / 5215 [R(int) = 0.0648]
Completeness to theta = 32.01	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3191 and 0.1145
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5215 / 0 / 167
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.0513
R indices (all data)	R1 = 0.1204, wR2 = 0.0626
Largest diff. peak and hole	1.108 and -0.820 e.A^-3

B-II-B- XRPD of (2) : theoretical (blue) and experimental (red)

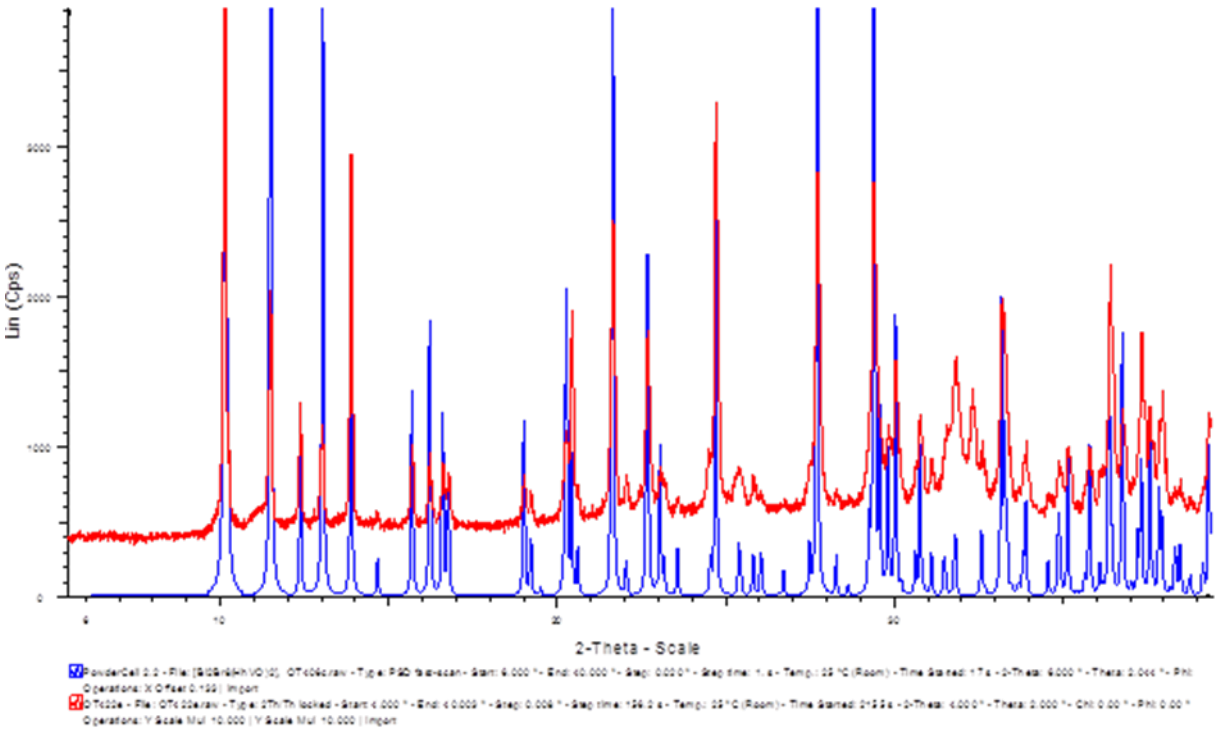


B-III- eq - [(Hbp4mo)$_2$Bi$_2$Br$_8$] (3)

B-III-A- Summary of crystallographic data

Empirical formula	C20 H18 Bi2 Br8 N4 O2
Formula weight	1403.62
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 1 21/n 1
Unit cell dimensions	a = 10.1031(6) A alpha = 90 deg. b = 12.8928(5) A beta = 104.077(6) deg. c = 12.5741(10) A gamma = 90 deg.
Volume	1588.68(17) A^3
Z, Calculated density	2, 2.934 Mg/m^3
Absorption coefficient	21.148 mm^-1
F(000)	1256
Crystal size	0.251 x 0.176 x 0.167 mm
Theta range for data collection	3.36 to 30.00 deg.
Limiting indices	-14<=h<=14, -18<=k<=18, -17<=l<=17
Reflections collected / unique	22302 / 4610 [R(int) = 0.0650]
Completeness to theta = 30.00	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.1329 and 0.0766
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4610 / 0 / 167
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.0505
R indices (all data)	R1 = 0.0764, wR2 = 0.0579
Largest diff. peak and hole	1.050 and -1.097 e.A^-3

B-III-B- XRPD of (3) : theoretical (blue) and experimental (red)

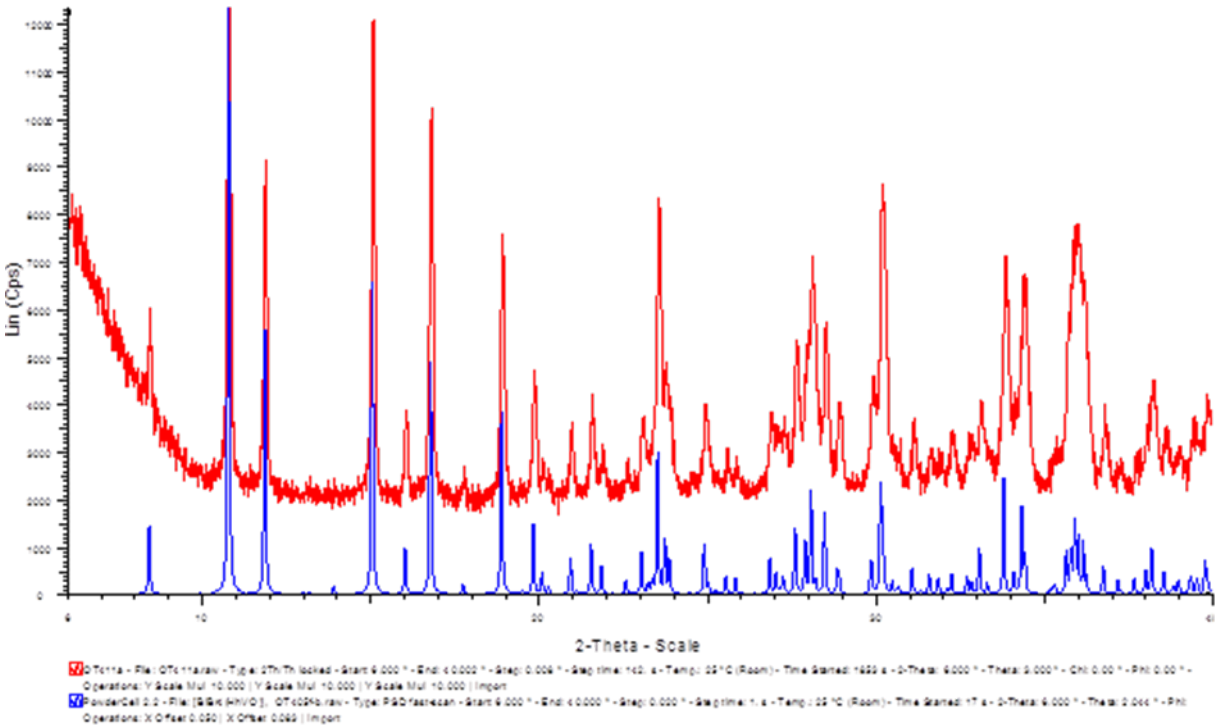


B-IV- [(Hbp4mo)$BiBr_4$] (4)

B-IV-A- Summary of crystallographic data

Empirical formula	C10 H9 Bi Br4 N2 O
Formula weight	701.81
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/a
Unit cell dimensions	a = 8.4049(8) A alpha = 90 deg. b = 21.2014(18) A beta = 107.241(5) deg. c = 9.3965(6) A gamma = 90 deg.
Volume	1599.2(2) A^3
Z, Calculated density	4, 2.915 Mg/m^3
Absorption coefficient	21.009 mm^-1
F(000)	1256
Crystal size	0.30 x 0.08 x 0.06 mm
Theta range for data collection	2.97 to 32.05 deg.
Limiting indices	-12<=h<=12, -30<=k<=31, -14<=l<=13
Reflections collected / unique	30390 / 5525 [R(int) = 0.1097]
Completeness to theta = 32.05	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3654 and 0.0338
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5525 / 0 / 167
Goodness-of-fit on F^2	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0517, wR2 = 0.0973
R indices (all data)	R1 = 0.1326, wR2 = 0.1205
Largest diff. peak and hole	1.291 and -1.732 e.A^-3

B-IV-B- XRPD of (4) : theoretical (blue) and experimental (red)

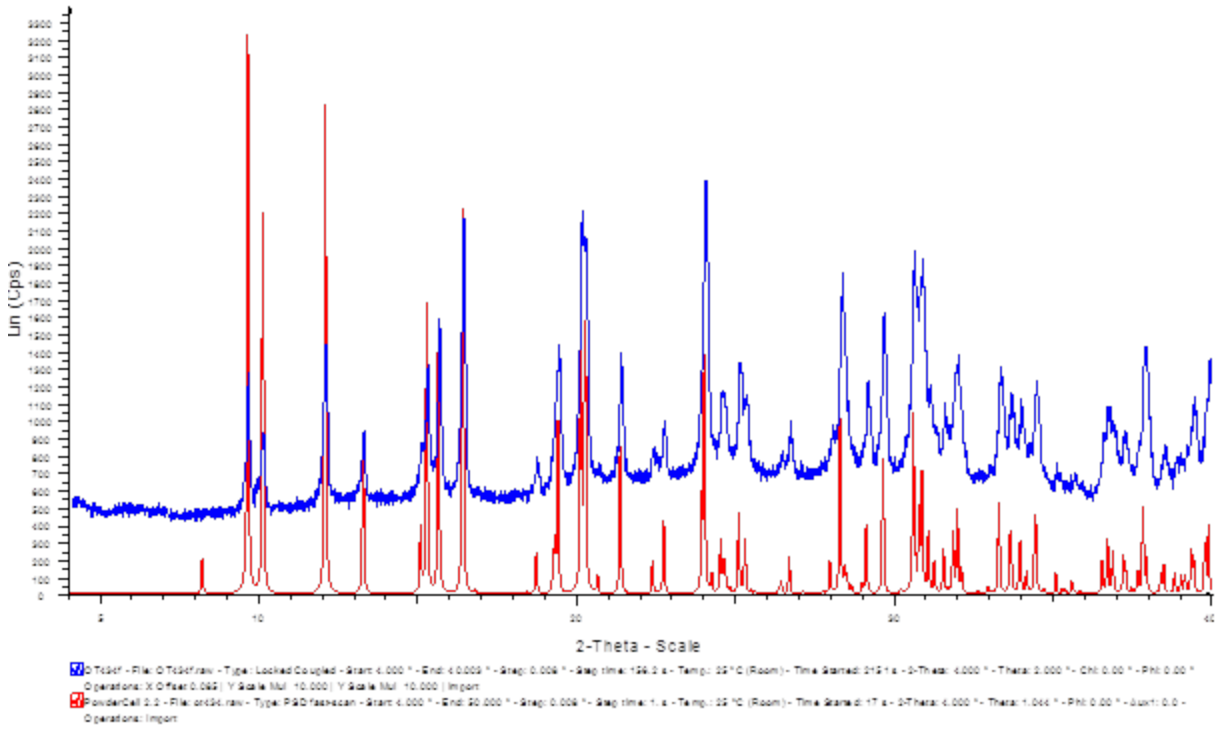


B-V- [H(Hbp4mo)$_2$][BiCl$_6$]dmso (5)

B-V-A- Summary of crystallographic data

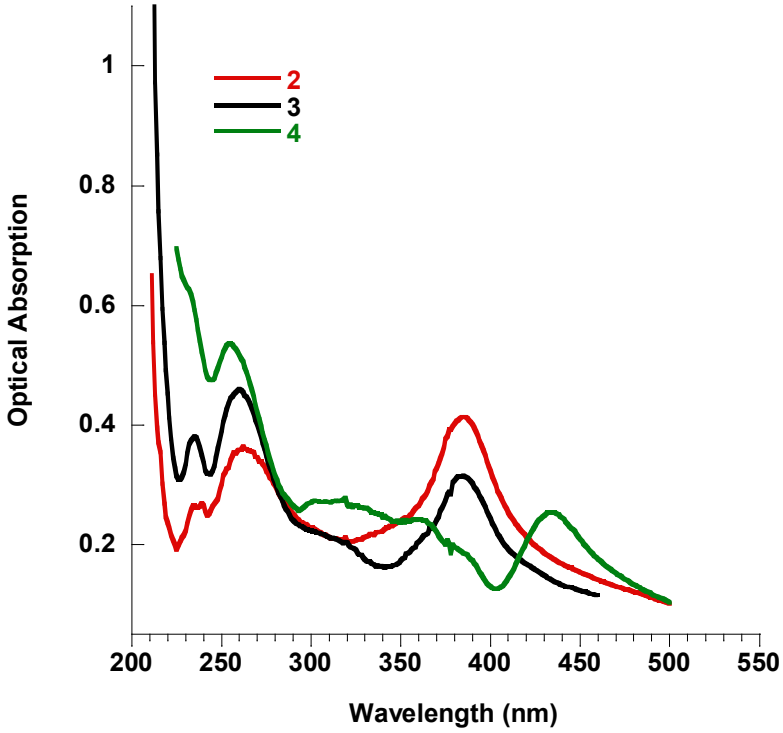
Empirical formula	C22 H25 Bi Cl6 N4 O3 S
Formula weight	847.23
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 1 2/c 1
Unit cell dimensions	a = 19.2567(8) A alpha = 90 deg.
	b = 13.3429(5) A beta = 107.434(3) deg.
	c = 12.3084(7) A gamma = 90 deg.
Volume	3017.2(2) A^3
Z, Calculated density	4, 1.865 Mg/m^3
Absorption coefficient	6.475 mm^-1
F(000)	1640
Crystal size	0.15 x 0.135 x 0.075 mm
Theta range for data collection	3.65 to 30.02 deg.
Limiting indices	-27<=h<=19, -18<=k<=17, -17<=l<=17
Reflections collected / unique	20645 / 4384 [R(int) = 0.0837]
Completeness to theta = 30.02	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.615 and 0.440
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4384 / 0 / 175
Goodness-of-fit on F^2	0.966
Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0500 [2374 Fo]
R indices (all data)	R1 = 0.1143, wR2 = 0.0607
Largest diff. peak and hole	0.582 and -0.596 e.A^-3

B-V-B- XRPD of (5) : theoretical (red) and experimental (blue)



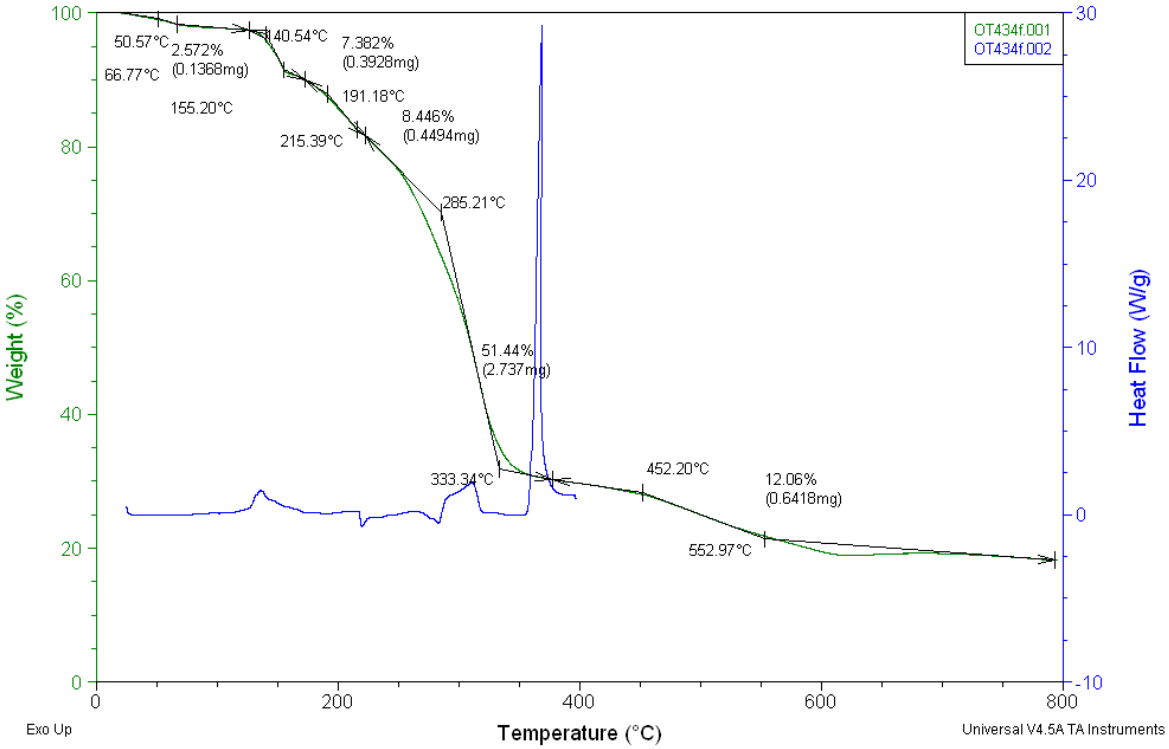
C- Characterizations of compounds: UV-Vis, TGA-DSC

C-I- UV-VIS spectra of (2), (3), (4)



Optical absorption of the powders of **2** (*ap*-[$(Hbp4mo)_2Bi_2Cl_8$]), **3** (*eq*-[$(Hbp4mo)_2Bi_2Br_8$]), **4** ([$(Hbp4mo)BiBr_4$)] dispersed in KBr. The spectra are corrected for the KBr pellet diffusion.

C-II- TGA-DSC analysis of 5 *([H(Hbp4mo)$_2$][BiCl$_6$]dmso)*



The two first weight loss of 2.57% and 7.38% which is 9.95% correctly corresponds to the departure of one dmso molecule per formula unit (M(dmso)/M(formula unit)= 78.13/847.23= 9.22 %).