

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, 2H₂O):



According to the literature [1,2], 3,4 g 4,4-bipyridine ($2,1 \cdot 10^{-2}$ mol) are dissolved in 25 ml of acid acetic glacial under heating at 70°C. After, 2,18 g of hydrogen peroxide ($2,1 \cdot 10^{-2}$ mol) is added drop by drop. Solution is left for agitation under heating at 70°C during 24 hours and after that, cooled down to the ambient temperature. Then, 37 g of NaHCO₃ (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 (SiO₂, 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, 2H₂O is obtained.

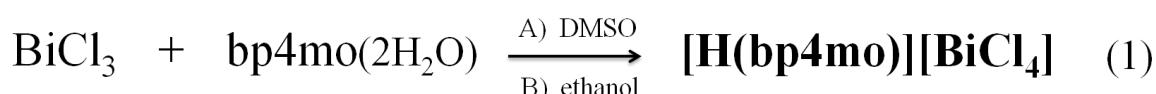
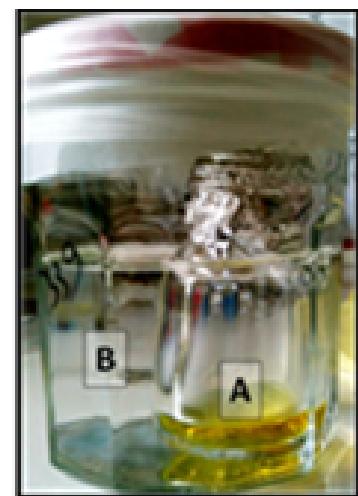
RMN ¹H (300 MHz, D₂O): δ=8,48 (d, 2H, J=6,3 Hz, ortho-N), 8,27 (d, 2H, J=7,5 Hz, ortho-N⁺-O⁻), 7,76 (d, 2H, J=7,5 Hz, meta-N), 7,56 (d, 2H, J=6,3 Hz, meta-N⁺-O⁻).

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

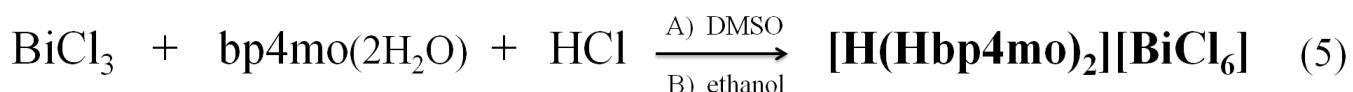
A2 - Procedure for the preparation of compounds:

- Compounds **1** and **5** were obtained, with a slow liquid – gaz diffusion method from bp4mo(H₂O), BiCl₃ and hydrochloric acid (**5**), the starting bp4mo(H₂O) being first synthesized as described above. The starting materials are dissolved in the minimum of DMSO in a pillbox (A) (**1** : bp4mo(H₂O) (31.4 mg, 0.151 mmol), BiCl₃ (47.5 mg, 0.150 mmol); **2** : bp4mo(H₂O) (26.5 mg, 0.127 mmol), BiCl₃ (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).



47,5 mg 31,4 mg colorless plate – like crystals

$1,5 \times 10^{-4}$ mol $1,51 \times 10^{-4}$ mol (38,9 mg, 82%)

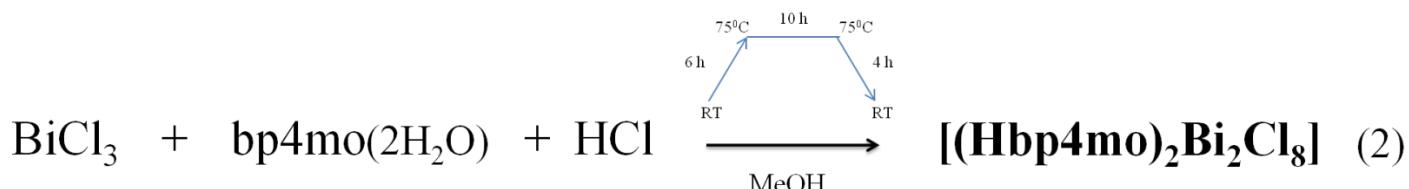


40,4 mg 26,5 mg 20 drops big, colorless plate – like crystals

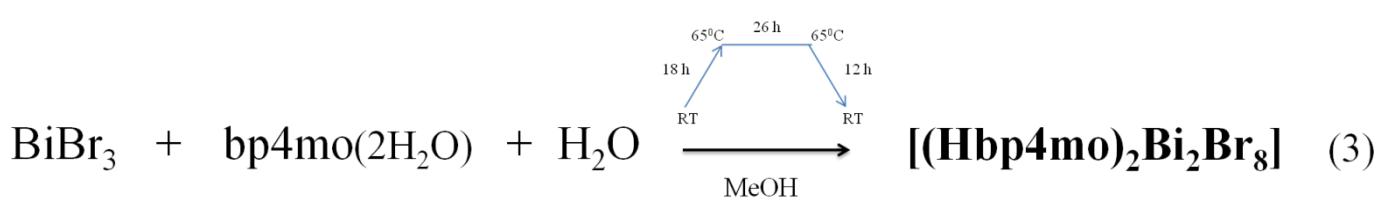
$1,28 \times 10^{-4}$ mol $1,27 \times 10^{-4}$ mol $8,18 \times 10^{-3}$ mol (36,7 mg, 91%)

- 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 BiCl₃ (40.2 mg), 0.127 mmol of bp4mo(H₂O) (26.5 mg) and 0.327 mmol of HCl (1 drop); **3** : To 0.127 mmol of BiBr₃ (57.0 mg), 0.127 mmol of bp4mo(H₂O) (26.5 mg) and H₂O (10 drops); **4** : To 0.127 mmol of BiBr₃ (57.0 mg), 0.127 mmol of bp4mo(H₂O) (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 BiCl₃); **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 BiBr₃); **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.

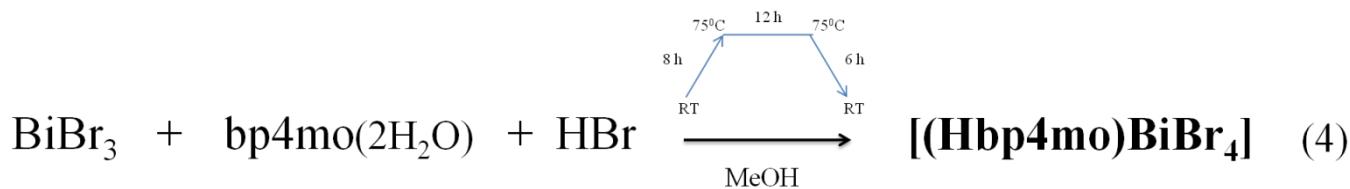
Yellow crystals were collected by filtration and washed with methanol (yield 80% on the basis of BiBr_3).



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



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



57 mg	26,5 mg	1 drop	10 ml	yellow crystals
$1,27 \times 10^{-4}$ mol	$1,27 \times 10^{-4}$ mol	$1,98 \times 10^{-4}$ 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).

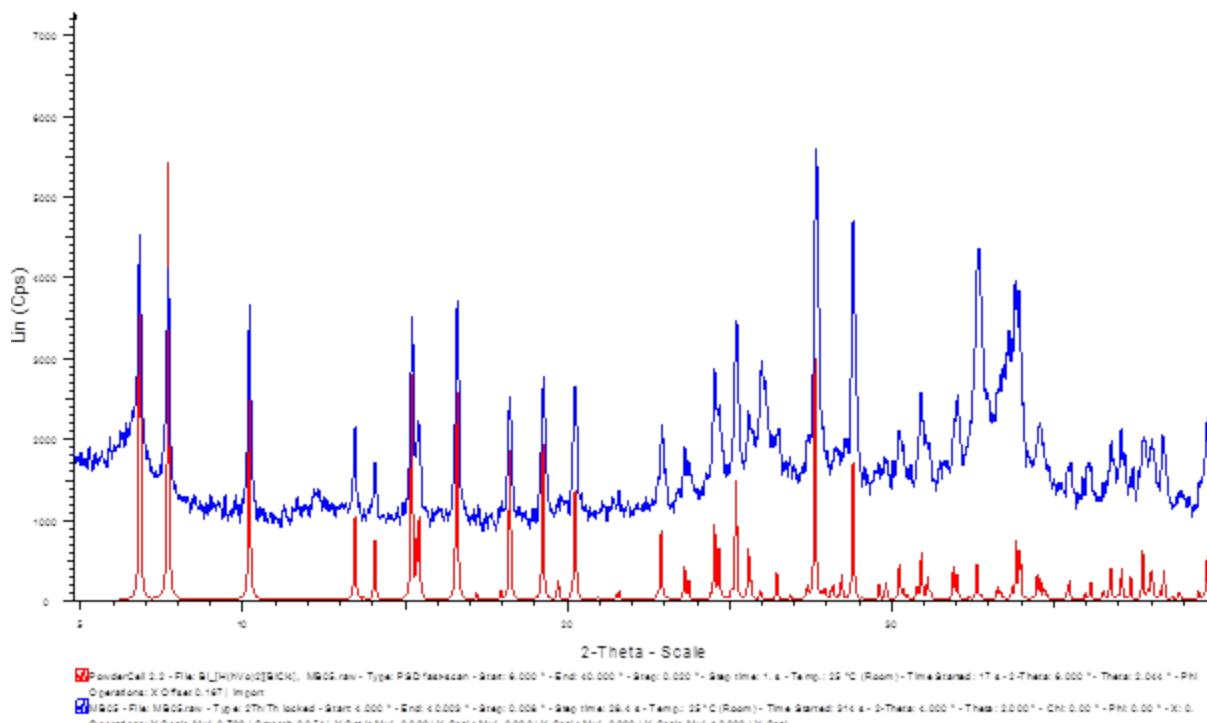
B- Single crystal and powder X-ray diffraction analysis

B-I- [H(bp4mo)][BiCl₄] (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 Å
Crystal system, space group monoclinic, C2/c
Unit cell dimensions a = 23.6950(10) Å alpha = 90 deg.
b = 26.6618(10) Å beta = 95.950(10) deg.
c = 7.2913(5) Å gamma = 90 deg.
Volume 4581.5(4) Å³
Z, Calculated density 8, 2.019 Mg/m³
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 F²
Data / restraints / parameters 7990 / 0 / 285
Goodness-of-fit on F² 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.Å⁻³

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



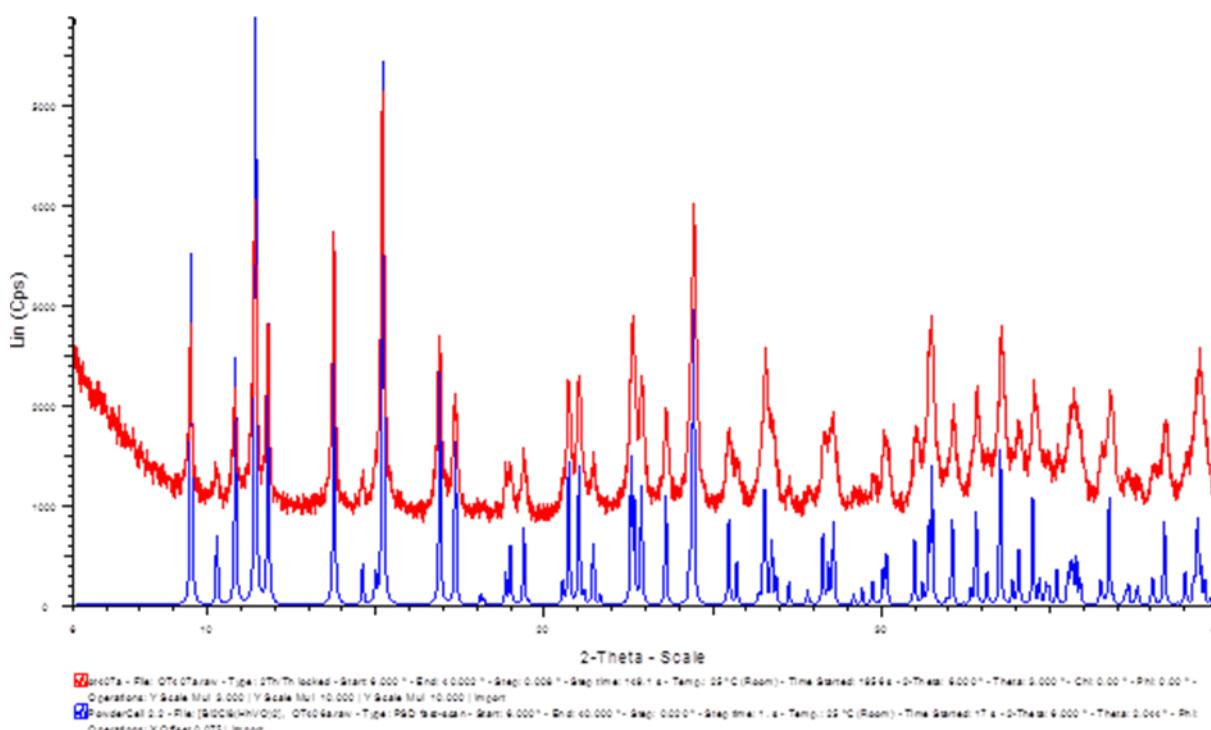
PowderCell 2.2 - File: R-[H]p[4m][BiCl4].M00.raw - Type: P&D fastscan - Start: 4.000 ° - End: 40.000 ° - Step: 0.000 ° - Step time: 1.0 s - Temp: 29.10 °C (Room) - Time Started: 17 s - 2-Theta: 4.000 ° - Theta: 2.000 ° - Phi: 0.000 ° - Psi: 0.000 ° - Zeta: 0.000 ° - Omega: 0.000 ° - Phi: 0.000 ° - X: 0.000 ° - Y: 0.000 ° - Z: 0.000 ° - X2: 0.000 ° - Y2: 0.000 ° - Z2: 0.000 ° - X3: 0.000 ° - Y3: 0.000 ° - Z3: 0.000 ° - X4: 0.000 ° - Y4: 0.000 ° - Z4: 0.000 ° - X5: 0.000 ° - Y5: 0.000 ° - Z5: 0.000 ° - X6: 0.000 ° - Y6: 0.000 ° - Z6: 0.000 ° - X7: 0.000 ° - Y7: 0.000 ° - Z7: 0.000 ° - X8: 0.000 ° - Y8: 0.000 ° - Z8: 0.000 ° - X9: 0.000 ° - Y9: 0.000 ° - Z9: 0.000 ° - X10: 0.000 ° - Y10: 0.000 ° - Z10: 0.000 ° - X11: 0.000 ° - Y11: 0.000 ° - Z11: 0.000 ° - X12: 0.000 ° - Y12: 0.000 ° - Z12: 0.000 ° - X13: 0.000 ° - Y13: 0.000 ° - Z13: 0.000 ° - X14: 0.000 ° - Y14: 0.000 ° - Z14: 0.000 ° - X15: 0.000 ° - Y15: 0.000 ° - Z15: 0.000 ° - X16: 0.000 ° - Y16: 0.000 ° - Z16: 0.000 ° - X17: 0.000 ° - 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Y211: 0.000 ° - Z211: 0.000 ° - X212: 0.000 ° - Y212: 0.000 ° - Z212: 0.000 ° - X213: 0.000 ° - Y213: 0.000 ° - Z213: 0.000 ° - X214: 0.000 ° - Y214: 0.000 ° - Z214: 0.000 ° - X215: 0.000 ° - Y215: 0.000 ° - Z215: 0.000 ° - X216: 0.000 ° - Y216: 0.000 ° - Z216: 0.000 ° - X217: 0.000 ° - Y217: 0.000 ° - Z217: 0.000 ° - X218: 0.000 ° - Y218: 0.000 ° - Z218: 0.000 ° - X219: 0.000 ° - Y219: 0.000 ° - Z219: 0.000 ° - X220: 0.000 ° - Y220: 0.000 ° - Z220: 0.000 ° - X221: 0.000 ° - Y221: 0.000 ° - Z221: 0.000 ° - X222: 0.000 ° - Y222: 0.000 ° - Z222: 0.000 ° - X223: 0.000 ° - Y223: 0.000 ° - Z223: 0.000 ° - X224: 0.000 ° - Y224: 0.000 ° - Z224: 0.000 ° - X225: 0.000 ° - Y225: 0.000 ° - Z225: 0.000 ° - X226: 0.000 ° - Y226: 0.000 ° - Z226: 0.000 ° - X227: 0.000 ° - Y227: 0.000 ° - Z227: 0.000 ° - X228: 0.000 ° - Y228: 0.000 ° - Z228: 0.000 ° - X229: 0.000 ° - Y229: 0.000 ° - Z229: 0.000 ° - X230: 0.000 ° - Y230: 0.000 ° - Z230: 0.000 ° - X231: 0.000 ° - Y231: 0.000 ° - Z231: 0.000 ° - X232: 0.000 ° - 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Y253: 0.000 ° - Z253: 0.000 ° - X254: 0.000 ° - Y254: 0.000 ° - Z254: 0.000 ° - X255: 0.000 ° - Y255: 0.000 ° - Z255: 0.000 ° - X256: 0.000 ° - Y256: 0.000 ° - Z256: 0.000 ° - X257: 0.000 ° - Y257: 0.000 ° - Z257: 0.000 ° - X258: 0.000 ° - Y258: 0.000 ° - Z258: 0.000 ° - X259: 0.000 ° - Y259: 0.000 ° - Z259: 0.000 ° - X260: 0.000 ° - Y260: 0.000 ° - Z260: 0.000 ° - X261: 0.000 ° - Y261: 0.000 ° - Z261: 0.000 ° - X262: 0.000 ° - Y262: 0.000 ° - Z262: 0.000 ° - X263: 0.000 ° - Y263: 0.000 ° - Z263: 0.000 ° - X264: 0.000 ° - Y264: 0.000 ° - Z264: 0.000 ° - X265: 0.000 ° - Y265: 0.000 ° - Z265: 0.000 ° - X266: 0.000 ° -

B-II- ap - $[Hbp4mo]_2Bi_2Cl_8J$ (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 Å
Crystal system, space group	Monoclinic, C 1 2/c 1
Unit cell dimensions	$a = 18.8244(8)$ Å $\alpha = 90$ deg. $b = 9.7773(2)$ Å $\beta = 94.968(5)$ deg. $c = 16.5190(7)$ Å $\gamma = 90$ deg.
Volume	3028.93(19) Å 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.Å ⁻³

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

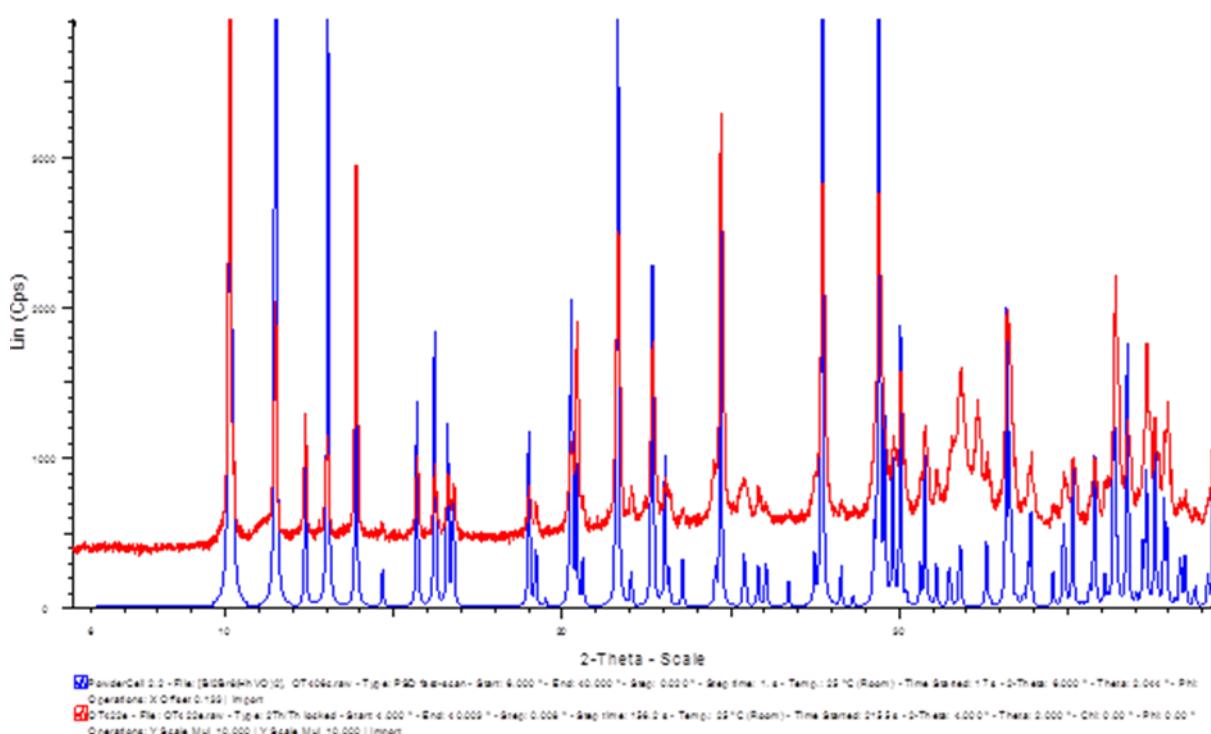


B-III-eq - $[(Hbp4mo)_2Bi_2Br_8] (3)$

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 Å
Crystal system, space group	Monoclinic, P 1 21/n 1
Unit cell dimensions	a = 10.1031(6) Å alpha = 90 deg. b = 12.8928(5) Å beta = 104.077(6) deg. c = 12.5741(10) Å gamma = 90 deg.
Volume	1588.68(17) Å 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.Å ⁻³

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

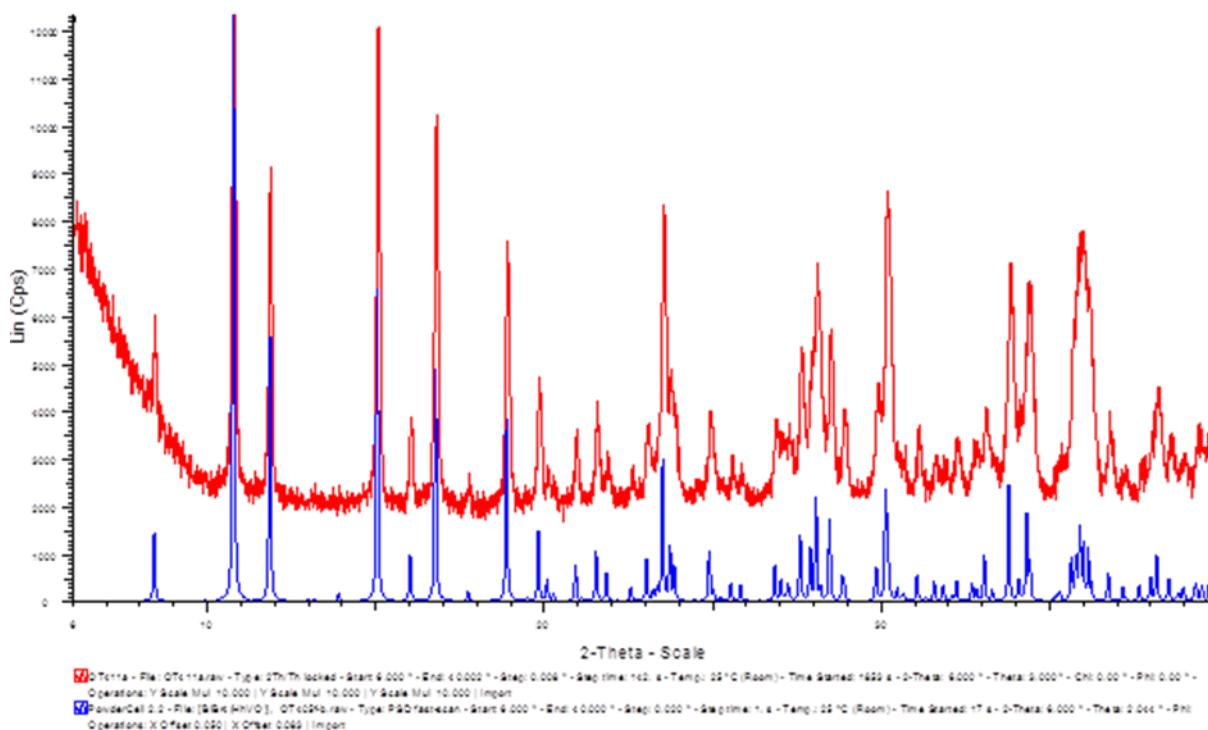


B-IV- J(Hbp4mo)BiBr₄] (4)

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 Å
Crystal system, space group	Monoclinic, P 21/a
Unit cell dimensions	a = 8.4049(8) Å alpha = 90 deg. b = 21.2014(18) Å beta = 107.241(5) deg. c = 9.3965(6) Å gamma = 90 deg.
Volume	1599.2(2) Å 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.Å ⁻³

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

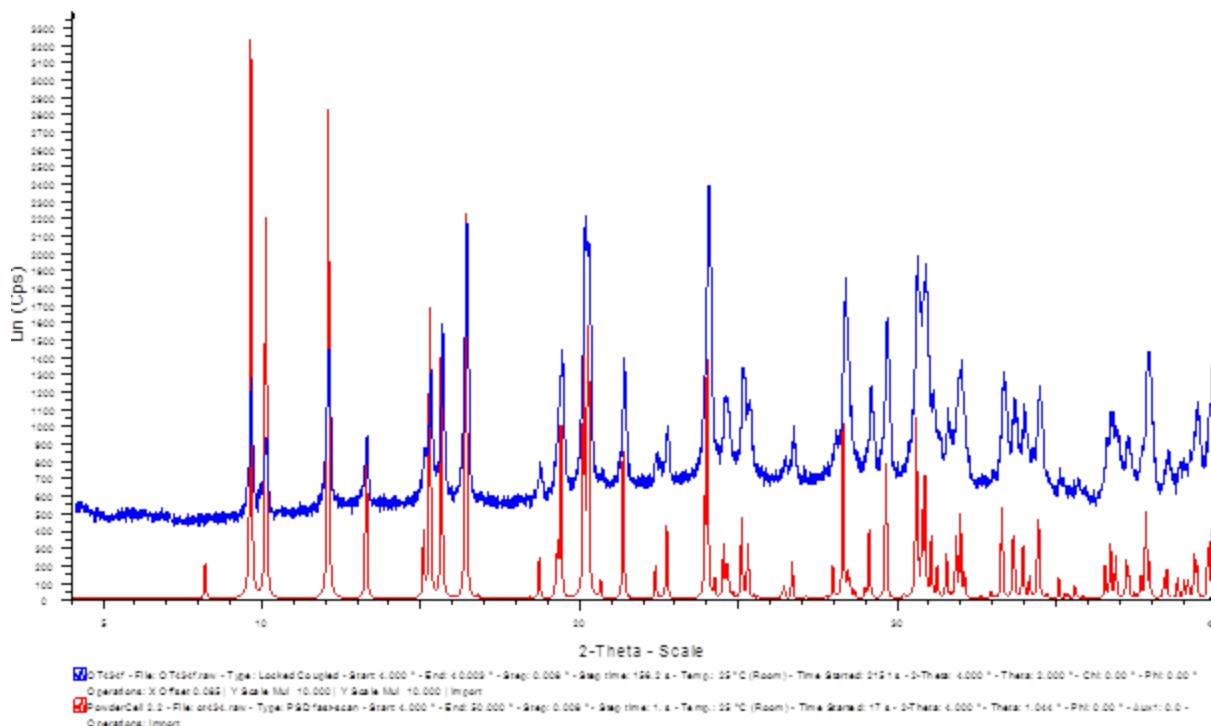


B-V- [H(Hbp4mo)₂][BiCl₆]dmso (5)

B-V-A- Summary of crystallographic data

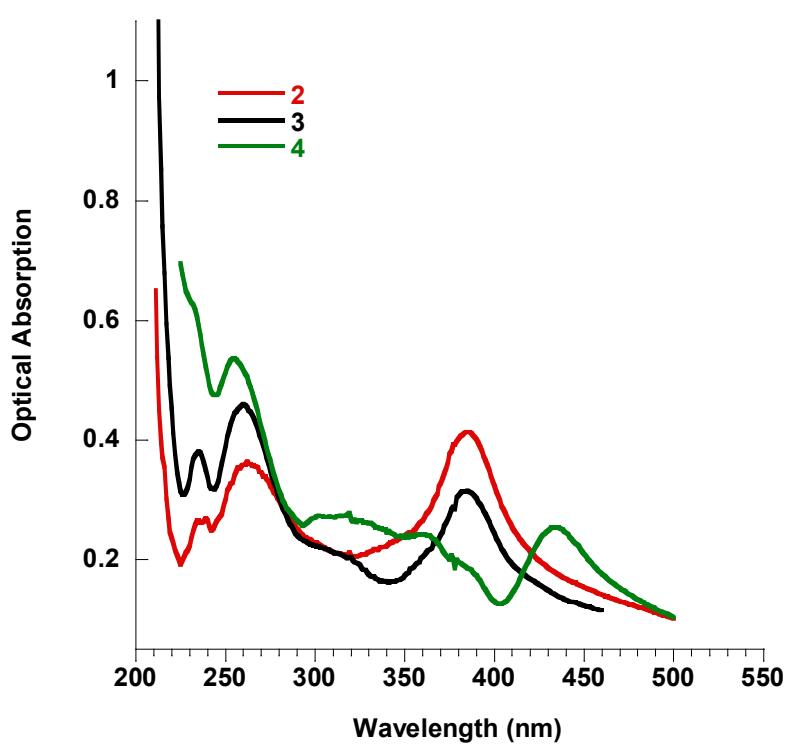
-	Empirical formula	C22 H25 Bi Cl6 N4 O3 S
Formula weight	847.23	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, C 1 2/c 1	
Unit cell dimensions	a = 19.2567(8) Å alpha = 90 deg. b = 13.3429(5) Å beta = 107.434(3) deg. c = 12.3084(7) Å gamma = 90 deg.	
Volume	3017.2(2) Å 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.Å ⁻³	

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



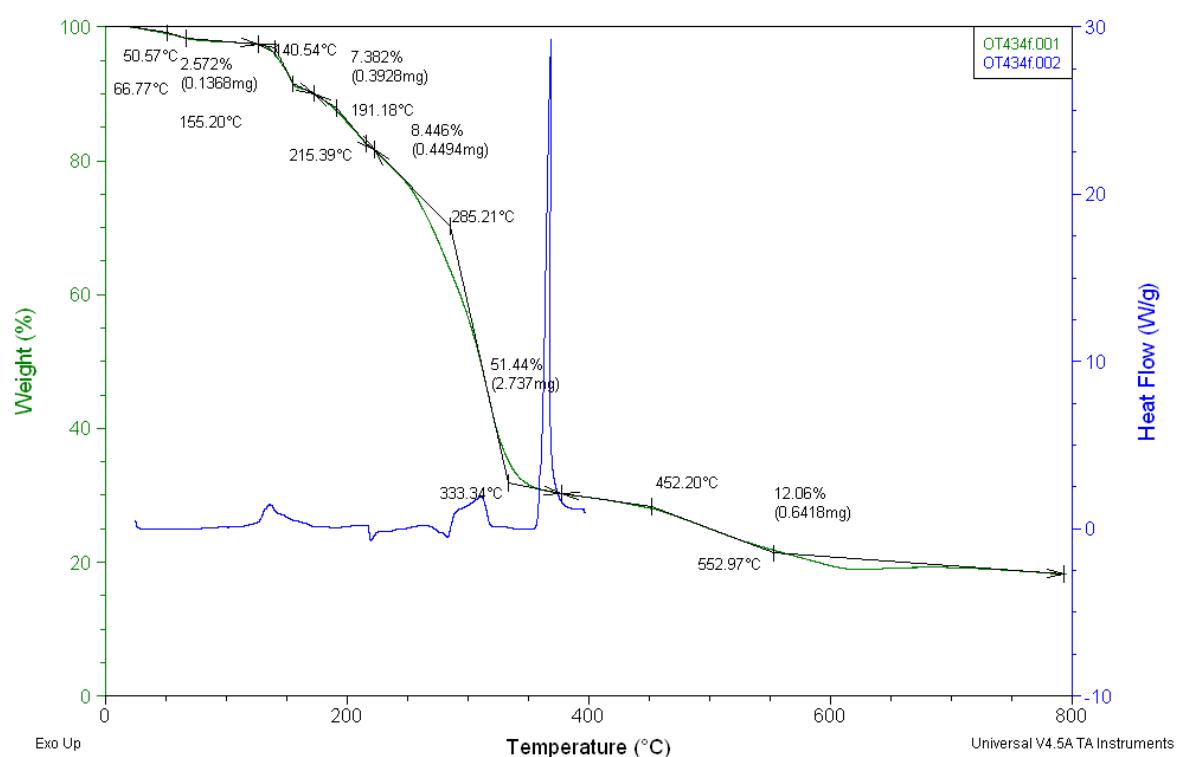
C- Characterizations of compounds: UV-Vis, TGA-DSC

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



Optical absorption of the powders of **2** (*ap*-[(Hbp₄mo)₂Bi₂Cl₈]), **3** (*eq*-[(Hbp₄mo)₂Bi₂Br₈]), **4** [((Hbp₄mo)BiBr₄)] 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 ($M(dmso)/M(\text{formula unit}) = 78.13/847.23 = 9.22\%$).