N-Oxide-4,4'-Bipyridine, a Forgotten Ligand in Coordination Chemistry: Structure-Photoluminescence Property Relationships in 2D and 1D Lead-Coordination Polymer

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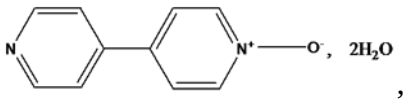
Supporting Information

A- Synthesis

A1- Procedure for the preparation of viologens:

Synthesis 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^-).

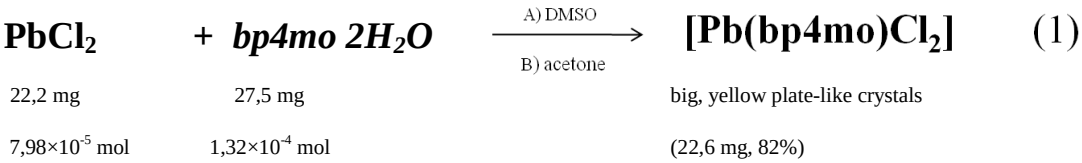
Anal. Elem.: Calc. C, 57,68; H, 5,81; N, 13,45; O, 23,05 – Measured. C, 57,57; H, 5,71; N, 13,50; O, 22,30.

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

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

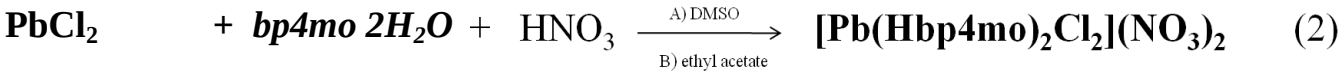
A2 - Procedure for the preparation of compounds:

The compounds **1, 2, A** were obtained, with method of slow liquid – gaz diffusion with special apparatus (see picture). In this method, bp4mo,$2H_2O$ and lead chloride salt are dissolved in the minimum of first solvent, DMSO (for compounds **1, 2**) in a pillbox (A). The pillbox is then covered with a holed aluminium paper and inserted in a jar of jam filled with contra-solvent: acetone (for compounds **1**), or ethyl acetate (for compound **2**) (B). The jar of jam is then covered with a lid and sealed with parafilm. A few days later, crystals appeared. Sample is then washed with contra-solvent and dried in the oven at 50 °C.



22,2 mg — 27,5 mg — big, yellow plate-like crystals

$7{,}98\times10^{-5}$ mol — $1{,}32\times10^{-4}$ mol — (22,6 mg, 82%)



26 mg — 25,7 mg — 20 drops — thin bright-yellow needle-like crystals

$9{,}71\times10^{-5}$ mol — $1{,}23\times10^{-4}$ mol — (23,4 mg, 91%)

B- Single crystal and powder X-ray diffraction analysis for (1), (2)

B-I- [(Pb(bp4mo)Cl_2] (1)

B-I-A- Summary of crystallographic data

Empirical formula	C10 H8 Cl2 N2 O Pb
Formula weight	450.29
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, C2
Unit cell dimensions	a = 16.459(1) A alpha = 90 deg. b = 4.1097(5) A beta = 93.72(1) deg. c = 18.072(1) A gamma = 90 deg.
Volume	1219.84(18) A^3
Z, Calculated density	4, 2.452 Mg/m^3
Absorption coefficient	14.247 mm^-1
F(000)	824
Crystal size	0.24 x 0.08 x 0.06 mm
Theta range for data collection	2.66 to 29.53 deg.
Limiting indices	-22<=h<=22, -5<=k<=5, -25<=l<=24
Reflections collected / unique	6612 / 3161 [R(int) = 0.0467]
Completeness to theta = 29.53	98.7 %
Absorption correction	Multiscan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters 3	161 / 1 / 147
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0381, wR2 = 0.0686
R indices (all data)	R1 = 0.0585, wR2 = 0.0745
Absolute structure parameter	0.052(15)
Largest diff. peak and hole	1.067 and -1.002 e.A^-3

CHECKCIF

```
Bond precision:      C-C = 0.0138 A              Wavelength=0.71073
Cell:         a=16.459(1)     b=4.1097(5)     c=18.072(1)
              alpha=90        beta=93.72(1)   gamma=90
Temperature: 293 K
                    Calculated                      Reported
Volume              1219.84(18)                     1219.84(18)
Space group         C 2                             C 1 2 1
Hall group          C 2y                            ?
Moiety formula      C10 H8 Cl2 N2 O Pb              ?
Sum formula         C10 H8 Cl2 N2 O Pb              C10 H8 Cl2 N2 O Pb
Mr                  450.28                          450.29
Dx,g cm-3           2.452                           2.452
Z                   4                               4
Mu (mm-1)           14.247                          14.247
F000                824.0                           824.0
F000'               812.63
h,k,lmax            22,5,25                         22,5,25
Nref                1932[ 3415]                     3161
Tmin,Tmax           0.265,0.425                     0.305,0.475
Tmin'               0.031
```

```
Correction method= MULTI-SCAN
Data completeness= 1.64/0.93    Theta(max)= 29.530
R(reflections)= 0.0381( 2537)      wR2(reflections)= 0.0745( 3161)
S = 1.054              Npar= 147
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT111_ALERT_2_B ADDSYM Detects (Pseudo) Centre of Symmetry .....
88 PerFi

Alert level C

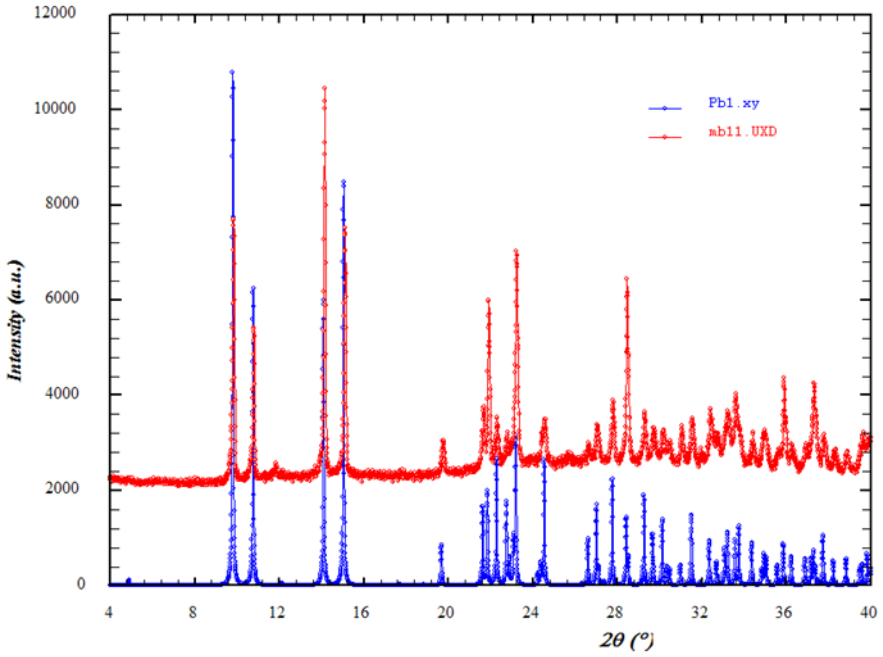
PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for O1
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for Pb1
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for Pb2
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds 0.0138
Ang
PLAT410_ALERT_2_C Short Intra H...H Contact H2 .. H7 .. 1.98 Ang.

Alert level G

REFLT03_ALERT_4_G Please check that the estimate of the number of Friedel
pairs is
correct. If it is not, please give the correct count in the
_publ_section_exptl_refinement section of the submitted CIF.
From the CIF: _diffrn_reflns_theta_max 29.53
From the CIF: _reflns_number_total 3161
Count of symmetry unique reflns 1932
Completeness (_total/calc) 163.61%
TEST3: Check Friedels for noncentro structure
Estimate of Friedel pairs measured 1229
Fraction of Friedel pairs measured 0.636
Are heavy atom types Z>Si present yes
PLAT004_ALERT_5_G Info: Polymeric Structure Found with Dimension . 2
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT113_ALERT_2_G ADDSYM Suggests Possible Pseudo/New Space-group.
C2/c
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum ....
?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum .... ?
PLAT199_ALERT_1_G Check the Reported _cell_measurement_temperature
293 K
PLAT200_ALERT_1_G Check the Reported _diffrn_ambient_temperature
293 K
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Pb2 -- Cl1 .. 6.0 su
PLAT794_ALERT_5_G Note: Tentative Bond Valency for Pb2 (II) 2.20

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
11 **ALERT level G** = General information/check it is not something unexpected

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



B-II- [Pb(Hbp4mo)$_2$Cl$_2$](NO$_3$)$_2$ (2)

B-II-A- Summary of crystallographic data

Empirical formula	C20 H18 Cl2 N6 O8 Pb
Formula weight	748.50
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, C2/c
Unit cell dimensions	a = 16.847(1) A alpha = 90 deg.
	b = 4.0866(5) A beta = 97.55(1) deg.
	c = 35.249(3) A gamma = 90 deg.
Volume	2406.0(4) A^3
Z, Calculated density	4, 2.066 Mg/m^3
Absorption coefficient	7.294 mm^-1
F(000)	1440
Crystal size	0.16 x 0.08 x 0.07 mm
Theta range for data collection	3.99 to 30.06 deg.
Limiting indices	-23<=h<=23, -5<=k<=5, -48<=l<=49
Reflections collected / unique	13502 / 3392 [R(int) = 0.0637]
Completeness to theta = 30.06	95.8 %
Absorption correction	Multiscan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3392 / 0 / 168
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.0617
R indices (all data)	R1 = 0.0856, wR2 = 0.0685
Largest diff. peak and hole	1.283 and -1.883 e.A^-3

CHECKCIF

```
Bond precision:      C-C = 0.0071 A                Wavelength=0.71073
Cell:          a=16.847(1)     b=4.0866(5)     c=35.249(3)
               alpha=90        beta=97.55(1)   gamma=90
Temperature: 293 K
                    Calculated                        Reported
Volume              2405.8(4)                         2406.0(4)
Space group         C 2/c                             C 1 2/c 1
Hall group          -C 2yc                            ?
Moiety formula      C20 H18 Cl2 N4 O2 Pb, 2(N O3)     ?
Sum formula         C20 H18 Cl2 N6 O8 Pb              C20 H18 Cl2 N6 O8 Pb
Mr                  748.50                            748.50
Dx,g cm-3           2.067                             2.066
Z                   4                                 4
Mu (mm-1)           7.295                             7.294
F000                1440.0                            1440.0
F000'               1428.56
h,k,lmax            23,5,49                           23,5,49
Nref                3538                              3392
Tmin,Tmax           0.501,0.600                       0.405,0.528
Tmin'               0.308
Correction method= MULTI-SCAN
Data completeness= 0.959        Theta(max)= 30.060
R(reflections)= 0.0399( 2294)      wR2(reflections)= 0.0685( 3392)
S = 1.039              Npar= 168
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full Low 0.958

Alert level C

PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for O1
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for Pb1
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of N3
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 1
C20 H18 Cl2 N4 O2 Pb

Alert level G

PLAT004_ALERT_5_G Info: Polymeric Structure Found with Dimension . 1
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms 1
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum ....
?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum .... ?
PLAT199_ALERT_1_G Check the Reported _cell_measurement_temperature
293 K
PLAT200_ALERT_1_G Check the Reported _diffrn_ambient_temperature
293 K
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Pb1 -- Cl1 .. 16.6 su

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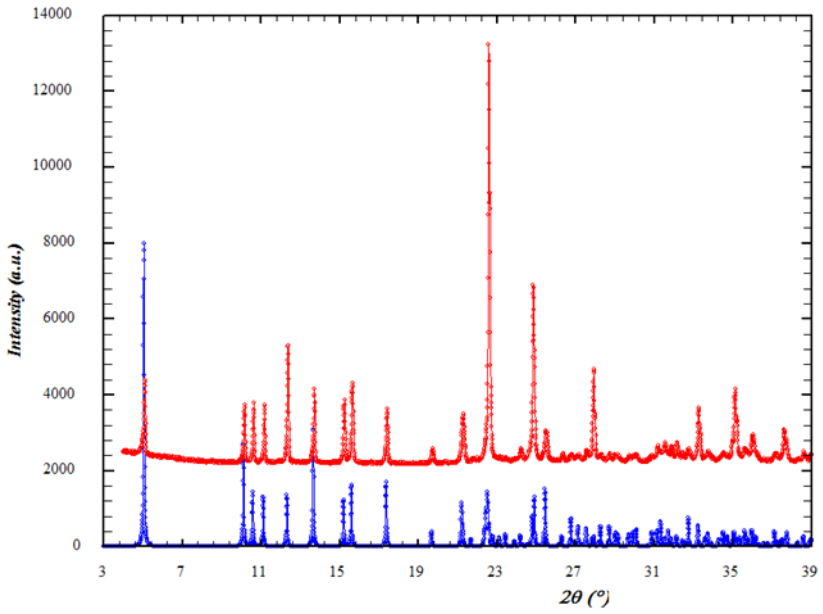
B-II-B- XRPD of (1) : theoretical (blue) and experimental (red)



C- Synthesis and XRPD characterization of (A), (B_β), (B_α)

C-I- [Pb(bp4do)Cl_2] (A)

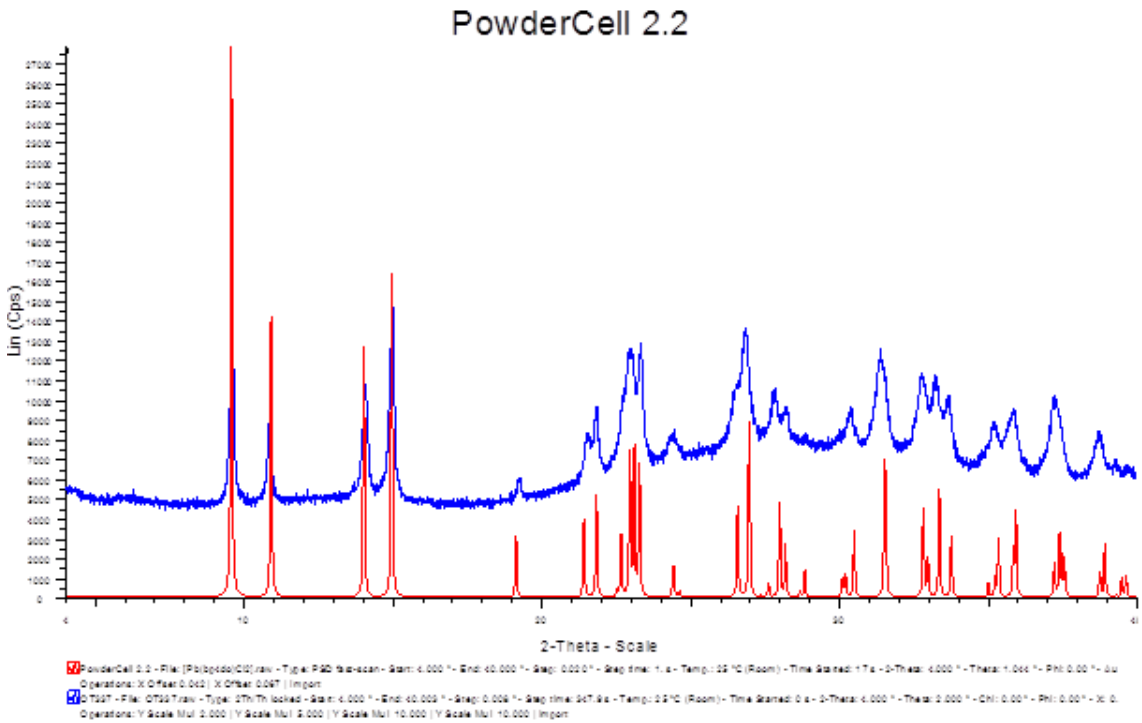
C-I-A- Synthesis

A has been synthesized according to the literature (ref **4** in main text) (*bp4do* $2H_2O$ commercially available):

$$\mathbf{PbCl_2} \quad + \ \textit{bp4do}\ 2H_2O \xrightarrow[\text{B) acetone}]{\text{A) } H_2O} \mathbf{[Pb(bp4do)Cl_2]} \qquad (A)$$

32,9 mg	26,5 mg	big and nice orange needle-like crystals
$1{,}18\times10^{-4}$ mol	$1{,}05\times10^{-4}$ mol	(23 mg, 87%)

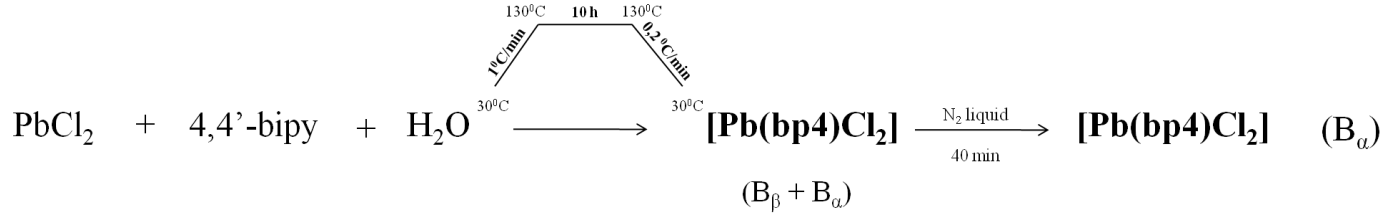
C-I-B- XRPD of (A) : theoretical (red) and experimental (blue)



C-II- [Pb(bp4)Cl$_2$] (B$_\alpha$)

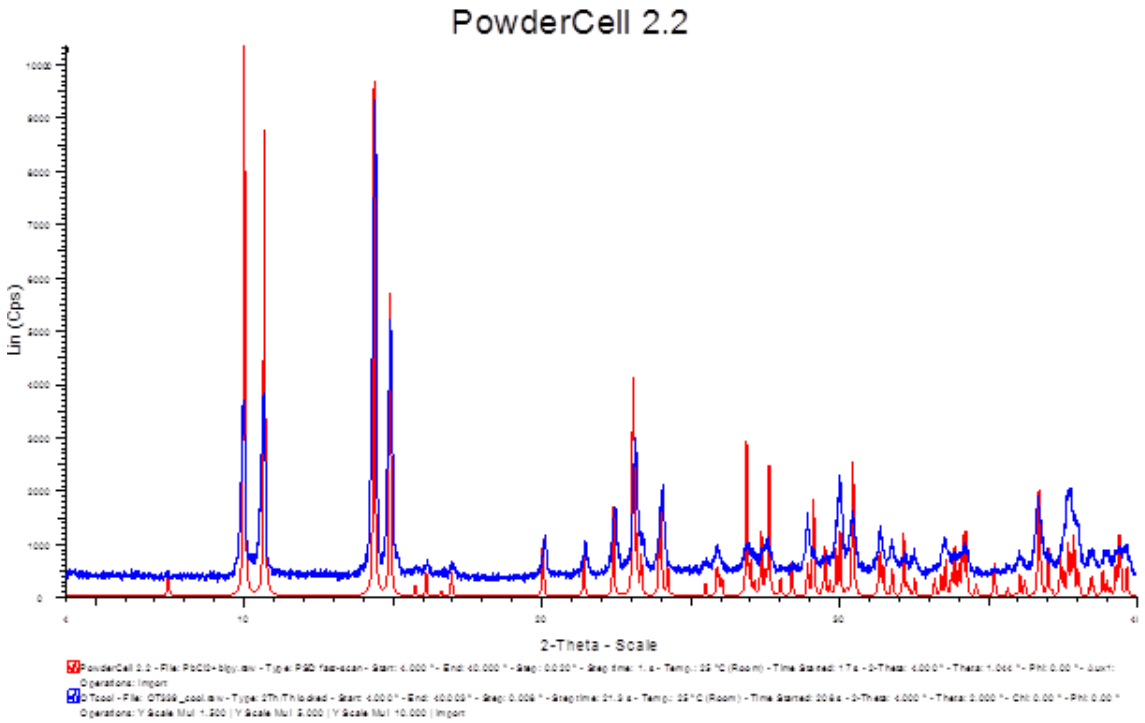
C-II-A- Synthesis

B_α has been synthesized in two steps. The synthesis described in the literature (ref **7** in main text) has here lead to a mixture of phase (Bα and Bβ). B_α has been obtained as a pure phase after cooling down the mixture at low temperature during one hour:



135,5 mg	62,8 mg	4 ml		white powder
4,87×10^{-4} mol	4,02×10^{-4} mol			(49 mg, 78%)

C-II-B- XRPD of (B$_\alpha$) : theoretical (red) and experimental (blue)



C-III- [Pb(bp4)Cl$_2$] (B_β)

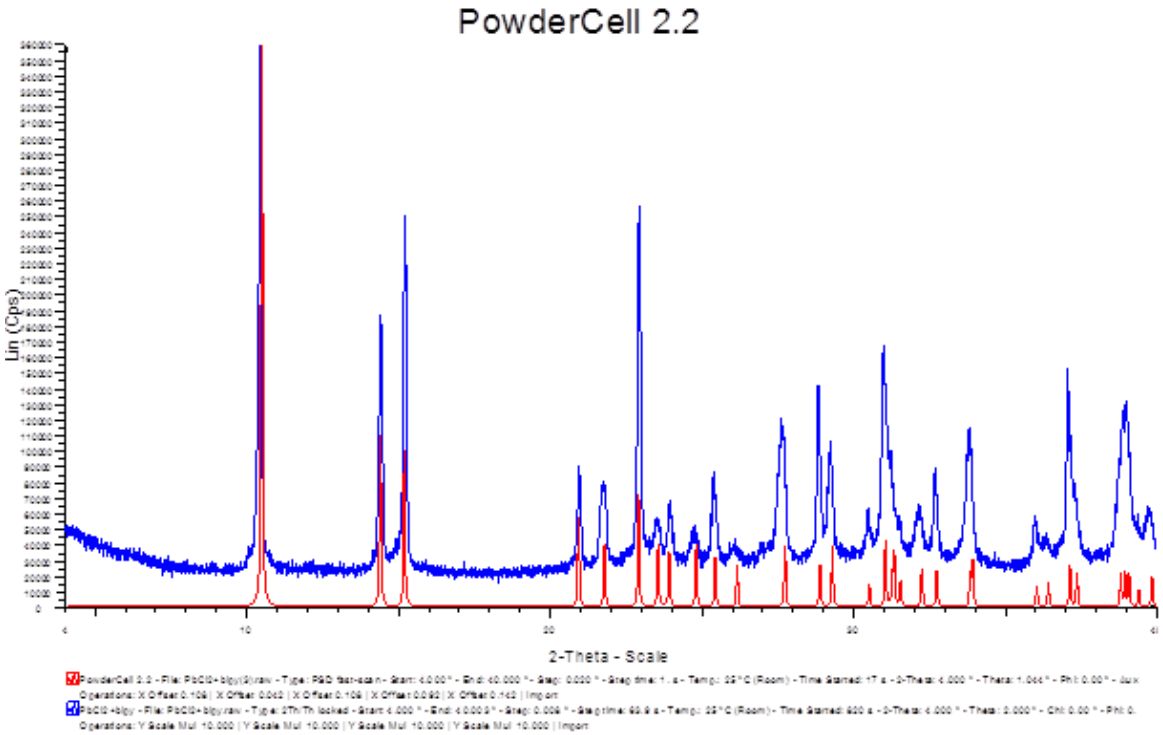
C-III-A- Synthesis

B_β has been synthesized according to the literature (ref **8** in main text):

$$PbCl_2 + 4,4'\text{-bipy} \xrightarrow[\text{acetone}]{H_2O} \mathbf{[Pb(bp4)Cl_2]} \quad (B_\beta)$$

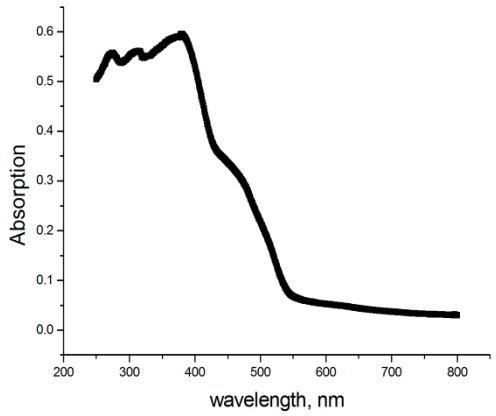
47,2 mg	26,5 mg	white powder
$1{,}70\times10^{-4}$ mol	$1{,}70\times10^{-4}$ mol	(25,4 mg, 96%)

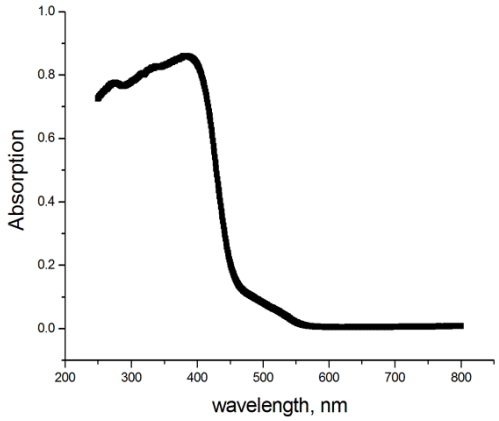
C-III-B- XRPD of (B_β) : theoretical (red) and experimental (blue)



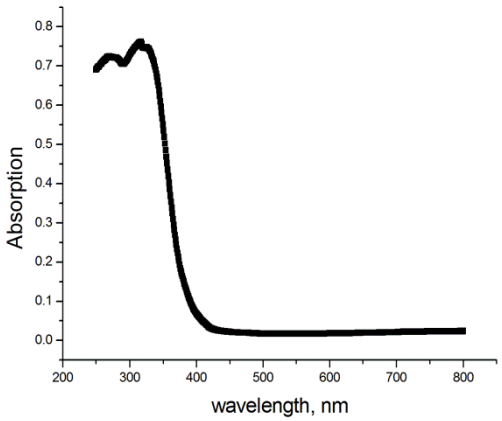
D- Characterizations of (1), (2), (A), (B_α), (B_β): UV-Vis, photoluminescence, TGA-DSC

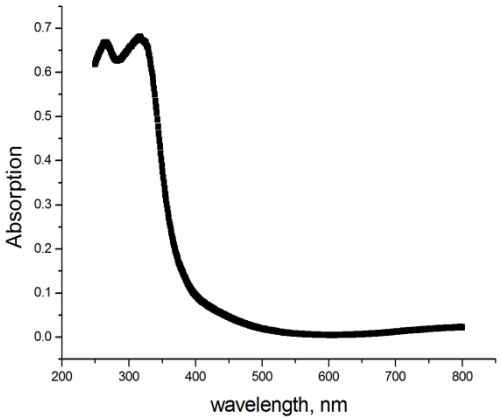
D-I- UV-VIS spectra of (1), (2), (A), (B_α), (B_β) and of starting material (bp4mo, $2H_2O$)



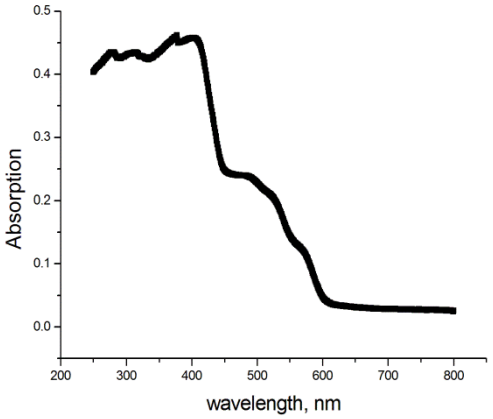


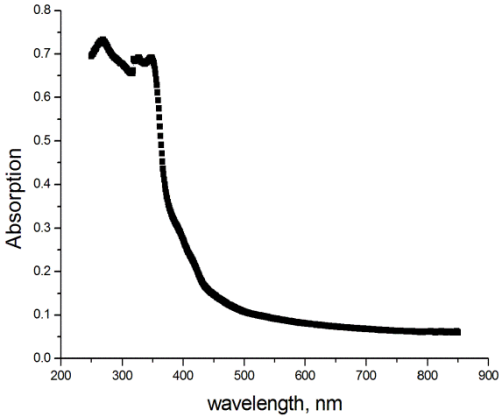
UV-VIS spectra of (**1**) - [(Pb(bp4mo)Cl_2] (left) and (**2**) - [(Pb(Hbp4mo)$_2Cl_2$]$(NO_3)_2$ (right)





UV-VIS spectra of (**B_β**) - [(Pb(bp4)Cl_2] (left) and (**B_α**) - [(Pb(bp4)Cl_2] (right)

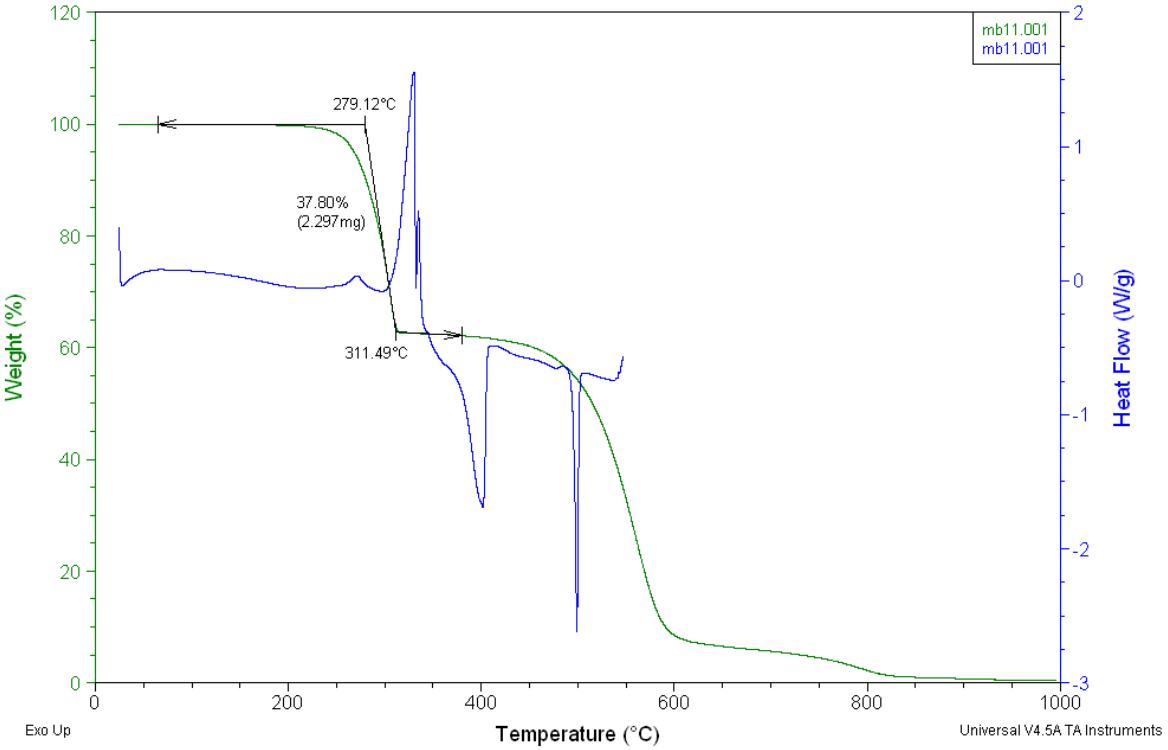




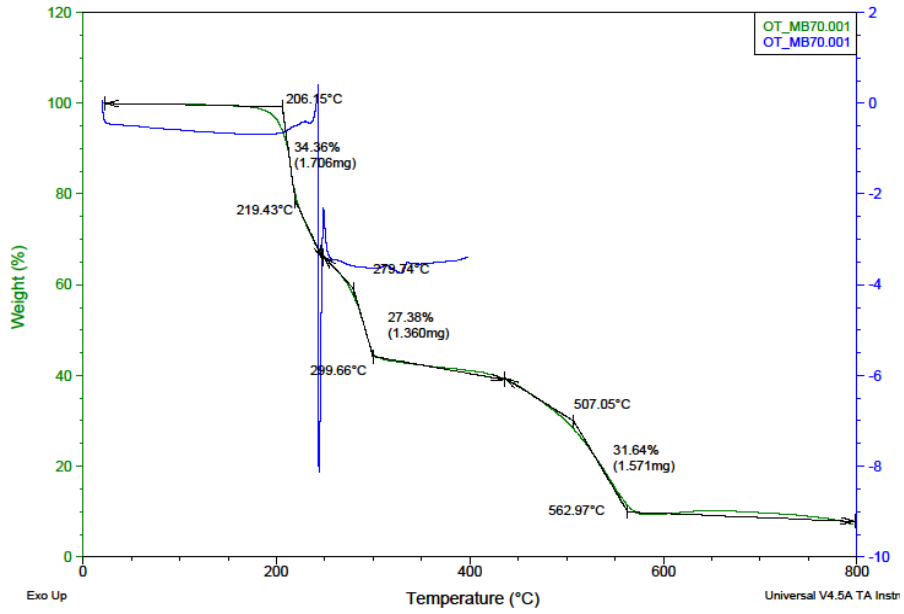
UV-VIS spectra of (**A**) - [(Pb(bp4do)Cl_2] (left) and starting material – bp4mo,$2H_2O$ (right)

D-II- TGA-DSC analysis of (1) and (2)

*D-II-1- TGA-DSC analysis of compound (**2**) – [(Pb(bp4mo)Cl_2]*

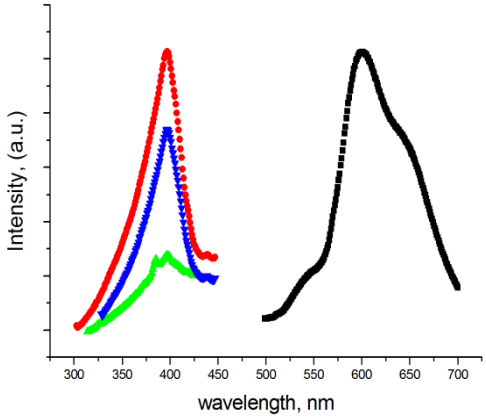


*D-II-2- TGA-DSC analysis of compound (**2**) – - [(Pb(Hbp4mo)$_2Cl_2$](NO$_3$)$_2$*



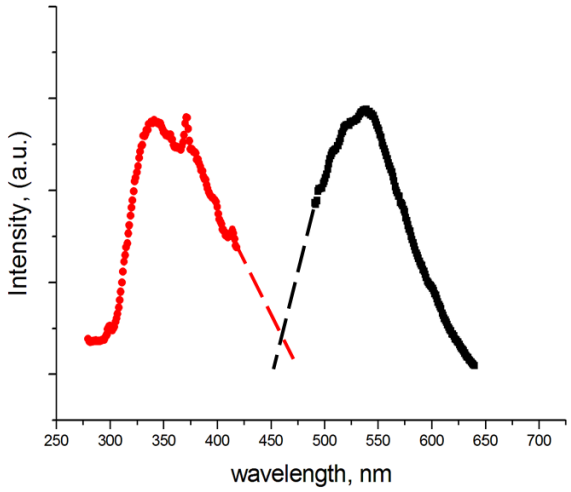
D-III- Photoluminescence

D-III-1- Photoluminescence of (1) - [Pb(bp4mo)Cl_2]



Solid-state emission (λ_{ex}= 400 nm) and excitation (green: λ_{em}= 550 nm; blue: λ_{em}= 640 nm; red: λ_{em}= 600 nm) spectra of (**1**) - [Pb(bp4mo)Cl_2] at room temperature.

D-III-2- Photoluminescence of (B_α) - [Pb(bp4)Cl_2]



Solid-state emission (black line, λ_{ex}= 350 nm) and excitation (red line, λ_{em}= 540 nm) spectra of (B_α) - [Pb(bp4)Cl_2] at room temperature.

D-III-2- Photos of samples of 1, 2, B_α and B_β taken under white light (top) and UV-light (bottom)