Protonated \(N\)-oxide-4,4’-bipyridine: from luminescent \(\text{Bi}^{(III)}\)
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,
\(2\text{H}_2\text{O}\)):

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\hline \\
\text{O} \\
\hline \\
\text{H}_2\text{O} \\
\end{array}
\]

\(M = 208,22 \text{ g/mol}\)

According to the literature [1,2], 3,4 g 4,4-bipyridine (2,1\(\times10^{-2}\) mol) are dissolved in 25 ml of acid acetic glacial under heating at 70\(^{\circ}\)C. After, 2,18 g of hydrogen peroxide (2,1\(\times10^{-2}\) mol) is added drop by drop. Solution is left for agitation under heating at 70\(^{\circ}\)C 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\(\times\)200 ml). Afterwards, the resulting pink solution which was obtained, is concentrated and is put into the chromatographic column (SiO\(_2\), 20\(\times\)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, 2\(\text{H}_2\text{O}\) is obtained.

RMN \(^1\text{H}\) (300 MHz, D\(_2\)O): \(\delta=8,48\) (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’).


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).

\[
\text{BiCl}_3 + \text{bp4mo}(2\text{H}_2\text{O}) \xrightarrow{\text{A) DMSO, B) ethanol}} [\text{H(bp4mo)}][\text{BiCl}_4] \quad (1)
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38.9 mg</td>
<td>82%</td>
</tr>
<tr>
<td>2</td>
<td>36.7 mg</td>
<td>91%</td>
</tr>
</tbody>
</table>

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 6 h of cooling down to 25°C.
Yellow crystals were collected by filtration and washed with methanol (yield 80% on the basis of BiBr₃). 

\[
\text{BiCl}_3 + \text{bp4mo}(2\text{H}_2\text{O}) + \text{HCl} \xrightarrow{\text{MeOH}} [(\text{Hbp4mo})_2\text{Bi}_2\text{Cl}_8] \quad (2)
\]

- 40,2 mg
- 26,5 mg
- 1 drop
- 10 ml
- pale yellow crystals

- 1,27×10⁻⁴ mol
- 1,27×10⁻⁴ mol
- 3,27×10⁻⁴ mol
- (38,19 mg, 95%)

\[
\text{BiBr}_3 + \text{bp4mo}(2\text{H}_2\text{O}) + \text{H}_2\text{O} \xrightarrow{\text{MeOH}} [(\text{Hbp4mo})_2\text{Bi}_2\text{Br}_8] \quad (3)
\]

- 57 mg
- 26,5 mg
- 10 drops
- 10 ml
- big yellow block-like crystals

- 1,27×10⁻⁴ mol
- 1,27×10⁻⁴ mol
- (50,1 mg, 88%)

\[
\text{BiBr}_3 + \text{bp4mo}(2\text{H}_2\text{O}) + \text{HBr} \xrightarrow{\text{MeOH}} [(\text{Hbp4mo})\text{BiBr}_4] \quad (4)
\]

- 57 mg
- 26,5 mg
- 1 drop
- 10 ml
- yellow crystals

- 1,27×10⁻⁴ mol
- 1,27×10⁻⁴ mol
- 1,98×10⁻⁴ 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- \[\text{[H(bp4mo)]\text{[BiCl}_4\text{]} (I)}\]

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) Å^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 eÅ^-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                   C\(_{20}\) H\(_{18}\) Bi\(_2\) Cl\(_8\) N\(_4\) O\(_2\)
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)**

![XRPD Graph](image-url)
**B-III- eq - [(Hbp4mo)\textsubscript{2}Bi\textsubscript{2}Br\textsubscript{8}] (3)**

**B-III-A- Summary of crystallographic data**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C\textsubscript{20} H\textsubscript{18} Bi\textsubscript{2} Br\textsubscript{8} N\textsubscript{4} O\textsubscript{2}</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>1403.62</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>293(2) K</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>0.71073 Å</td>
</tr>
<tr>
<td><strong>Crystal system, space group</strong></td>
<td>Monoclinic, P 1 21/n 1</td>
</tr>
<tr>
<td><strong>Unit cell dimensions</strong></td>
<td>a = 10.1031(6) Å, alpha = 90 deg.</td>
</tr>
<tr>
<td></td>
<td>b = 12.8928(5) Å, beta = 104.077(6) deg.</td>
</tr>
<tr>
<td></td>
<td>c = 12.5741(10) Å, gamma = 90 deg.</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>1588.68(17) Å\textsuperscript{3}</td>
</tr>
<tr>
<td><strong>Z, Calculated density</strong></td>
<td>2, 2.934 Mg/m\textsuperscript{3}</td>
</tr>
<tr>
<td><strong>Absorption coefficient</strong></td>
<td>21.148 mm\textsuperscript{-1}</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>1256</td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
<td>0.251 x 0.176 x 0.167 mm</td>
</tr>
<tr>
<td><strong>Theta range for data collection</strong></td>
<td>3.36 to 30.00 deg.</td>
</tr>
<tr>
<td><strong>Limiting indices</strong></td>
<td>-14\leq h \leq 14, -18\leq k \leq 18, -17\leq l \leq 17</td>
</tr>
<tr>
<td><strong>Reflections collected / unique</strong></td>
<td>22302 / 4610 [R(int) = 0.0650]</td>
</tr>
<tr>
<td><strong>Completeness to theta = 30.00</strong></td>
<td>99.6%</td>
</tr>
<tr>
<td><strong>Absorption correction</strong></td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td><strong>Max. and min. transmission</strong></td>
<td>0.1329 and 0.0766</td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
<td>Full-matrix least-squares on F\textsuperscript{2}</td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>4610 / 0 / 167</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F\textsuperscript{2}</strong></td>
<td>1.038</td>
</tr>
<tr>
<td><strong>Final R indices [I&gt;2sigma(I)]</strong></td>
<td>R\textsubscript{1} = 0.0375, wR\textsubscript{2} = 0.0505</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R\textsubscript{1} = 0.0764, wR\textsubscript{2} = 0.0579</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole</strong></td>
<td>1.050 and -1.097 e.Å\textsuperscript{3}</td>
</tr>
</tbody>
</table>

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

![XRPD graph](image-url)
B-IV- [(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.
c = 9.3965(6) Å gamma = 90 deg.
Volume 1599.2(2) Å³
Z, Calculated density 4, 2.915 Mg/m³
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 F²
Data / restraints / parameters 5525 / 0 / 167
Goodness-of-fit on F² 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 eÅ⁻³

B-IV-B- XRPD of (4) : theoretical (blue) and experimental (red)
B-V- \[\text{H(Hbp4mo)}_2\]\[\text{BiCl}_6\]dms (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) Å³
- **Z, Calculated density**: 4, 1.865 Mg/m³
- **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 F²
- **Data / restraints / parameters**: 4384 / 0 / 175
- **Goodness-of-fit on F²**: 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)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 ($M(\text{dmso})/M(\text{formula unit}) = 78.13/847.23 = 9.22\%$).