# Norfloxacin-derivative Functionalized Octamolybdate: Unusual Carbonyl Coordination and Acidity Sensitive Luminescence

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## 1. Materials and methods

All the reagents were purchased commercially and used without further purification. The precursor $[(C_4H_9)_4N]_2[Mo_6O_{19}]$ was synthesized according to the literature method.[1] Elemental analyses were performed for C, H and N on a Perkin/Elmer 2400 CHN elemental analyzer. FTIR spectra were recorded in the 4000-400 $cm^{-1}$ region on an VERTEX 70 spectrophotometer (KBr pellets). Emission spectra were recorded with a 970CRT luminescence spectrophotometer. UV-vis absorption spectra were collected on a Hitachi-4100 UV-vis spectrophotometer (Japan). $^{13}C$ NMR experiments were carried out on a Bruker 400M Hz spectrometer.

## 2. General procedure for synthesis of $(dNF)_2[\gamma\text{-}Mo_8O_{26}(dNF)_2]\cdot 10H_2O$ (1).

A mixture of $[(C_4H_9)_4N]_2[Mo_6O_{19}]$ (0.13 g, 0.1 mmol), NF (0.13 g, 0.4 mmol) and $ErCl_3\cdot 3H_2O$ (0.06 g, 0.02 mmol) were added to 8 mL $H_2O$, magnetically stirring for 1 h at room temperature. The pH was then adjusted to 4.2 with 1 mol $L^{-1}$ HCl and then sealed in a 25 mL Teflon-lined reactor and kept at 150 °C for 4 days. the reactor was slowly cooled to room temperature over a period of 12 h. Yellow block crystals of **1** were filtered, washed with water, and dried at room temperature (30% yield based on Mo). Anal. calcd. for $C_{60}H_{96}F_4Mo_8N_{12}O_{40}$: C, 29.19; N, 6,81; H, 3.92%. Found: C, 30.03; N, 6.85; H, 4.02%. IR (KBr, $cm^{-1}$): 3439(w), 3048(w), 1718(w), 1630(s), 1615(s), 1558(s), 1524(m), 1493(s), 1471(s), 1451(s), 1394(m), 1364(m), 1269(s), 1196(w), 1132(w), 1090(w), 1033(w), 1014(w), 941(s), 899(s), 831(s), 690(s), 640(m), 602(m).

## 3. Crystallographic data collection and refinement

X-ray single crystal diffraction data for complex **1** was collected on a Bruker Apex II CCD detector using graphite monochromatized Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) at room temperature. All data were corrected for Lorentz polarization and absorption effects. The program package SHELX-97 (SHELXTL) was used for structure solution and least-squares refinement on $F^2$.[2, 3] H atoms (N–H and C–H) were placed at calculated positions and were allowed to ride on the carrier-C/N atoms with $U_{iso}$ = $1.2U_{eq}$. The O atoms from water molecules are located from difference Fourier maps, but the H atoms of water molecules could not be located from difference Fourier maps and thus were not included in the final refinement. The detailed crystallographic data and structure refinement parameters are summarized in Table S1. Selected bond distances for complex **1** were listed in Tables S2. CCDC 948997 (**1**) contains the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

## 4. Antimicrobial tests.

4.1 *Kirby–Bauer disc diffusion method. Bacillus subtilis* and *Escherichia coli* were freshly isolated from clinical material and dissolved in 15 mL of sterilized agar culture media at 40 °C and inoculated on a sterilized culture dish. The bacterial suspensions were incubated at 37 °C for 24 h. Then, nutrient agar was sterilized at 121 °C for about 20 min and poured into the Petri dishes with a thickness of 3 mm. Then, 0.1 mL diluted bacterial suspension of *Escherichia coli* or *Bacillus subtilis* was spread uniformly on the surface of the nutrient agar. Thirty minutes later, the as-prepared filter paper slices were placed on the bacteria. The Petri dishes were incubated at 37 °C for 12 h. The diameters of the inhibition zone were measured by caliper and the results were recorded by camera. The inhibition zone diameter are 18.56 mm (complex **1**) and 23.59 mm (NF) against *Bacillus subtilis*, while, for *Escherichia coli,* the inhibition zone diameter are 11.12 mm (complex **1**) and 24.41 mm (NF), respectively.

4.2. *Minimum inhibitory concentration.* The MIC was defined as the lowest concentration of antimicrobial agent showing complete inhibition of growth. MIC was determined using twofold serial dilutions in liquid media containing 160-0.02 $\mu$g $mL^{-1}$ of the complex **1** being tested. The MIC values against *Escherichia coli* and *Bacillus subtilis* for **1** are 4.20 $\mu$g $mL^{-1}$ and 1.00 $\mu$g $mL^{-1}$.

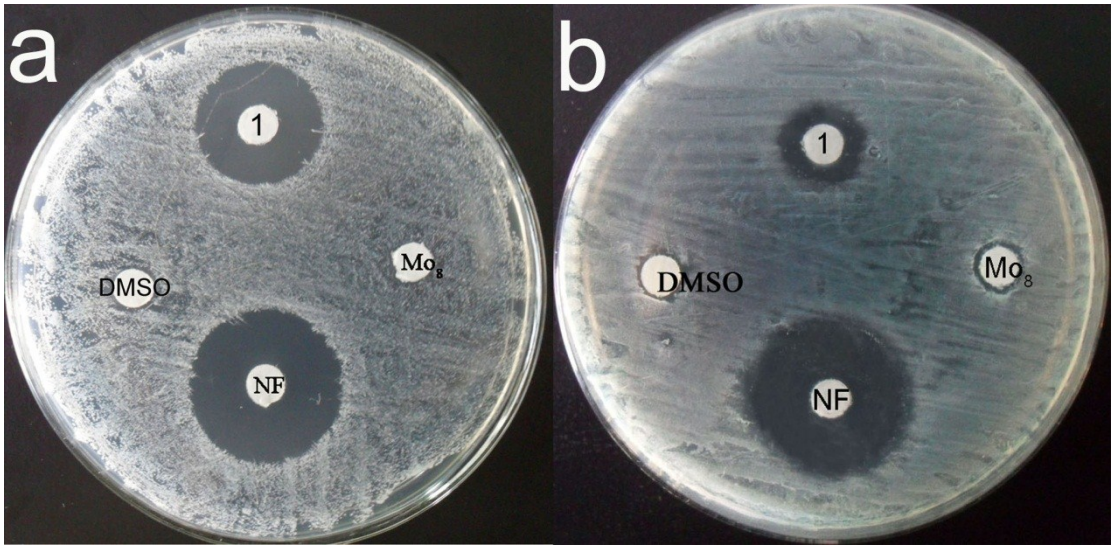


**Fig. S1** The inhibition zone diameter of 20 $\mu$g/disc complex **1**, NF, DMSO and octamolybdate polyoanion ($Mo_8$) against *Bacillus subtilis* (a) and *Escherichia coli* (b), respectively.

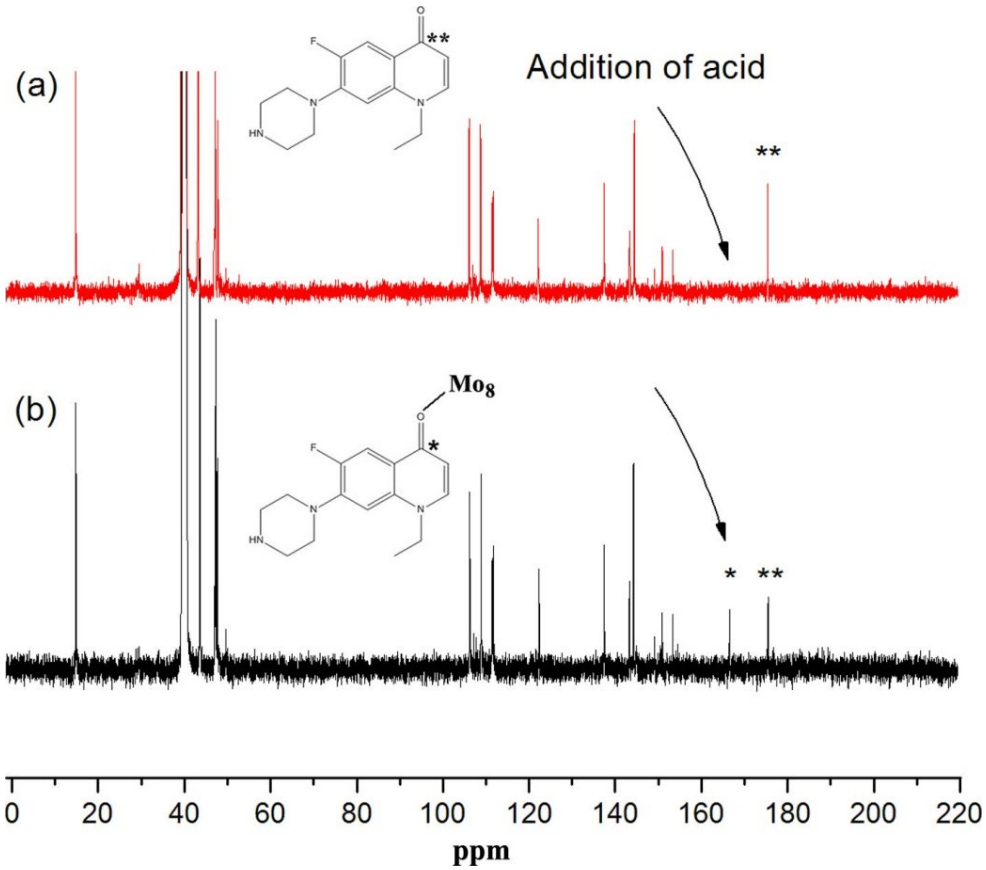


**Fig. S2** $^{13}C$ NMR spectra of complex **1** in DMSO-$d_6$ solution (2 mmol $L^{-1}$) without (a) and with (b) addition of HCl acid (HCl concentration is controlled as 60 mmol $L^{-1}$).

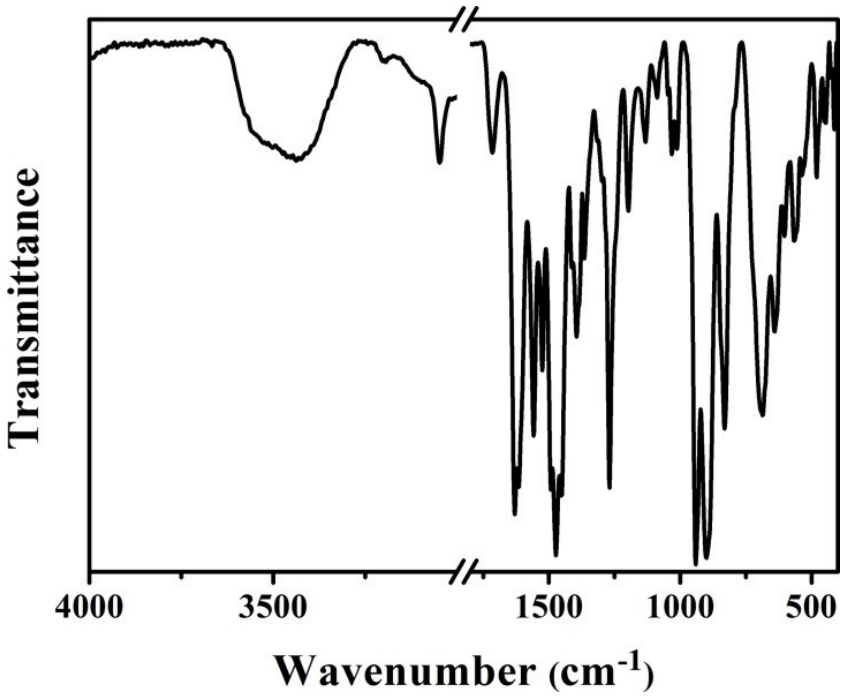


**Fig. S3** FTIR spectrum of complex **1**.

**Table S1** Crystal data and structure refinement for complex **1**.

| Parameters | **1** |
|---|---|
| Empirical formula | $C_{60}H_{96}F_4Mo_8N_{12}O_{40}$ |
| Formula weight | 2468.97 |
| Temperature | 293(2)K |
| Wavelength | 0.71073Å |
| Crystal system, space group | Triclinic, *P*-1 |
| Unit cell dimensions | $a$ = 11.5529(6)Å $\alpha$ = 80.182(4)° |
| | $b$ = 14.2950(7)Å $\beta$ = 71.327(5)° |
| | $c$ = 14.7162(7)Å $\gamma$ = 69.012(5)° |
| Volume | 2145.39(18)Å$^3$ |
| $Z$, Calculated density | 1, 1.910 Mg/m$^3$ |
| Absorption coefficient | 1.234 mm$^{-1}$ |
| $F$(000) | 1212 |
| Limiting indices | $-13 \le h \le 13$, $-17 \le k \le 17$, $-17 \le l \le 16$ |
| Measured reflections | 16259 |
| Independent reflections | 7712 |
| $R_{(int)}$ | 0.0376 |
| Data / restraints / parameters | 7712 / 0 / 519 |
| Goodness-of-fit on $F^2$ | 1.010 |
| $R_1{}^a$, w$R_2{}^b$ [$I > 2\sigma(I)$] | $R_1$ = 0.0492, $wR_2$ = 0.1268 |
| $R_1{}^a$, $wR_2{}^b$ (*all data*) | $R_1$ = 0.0742, $wR_2$ = 0.1406 |

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$ ; [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$

**Table S2.** Selected bond lengths (Å) and angles (°) for complex **1**.

| **1** | | | | | |
|---|---|---|---|---|---|
| Mo(1)-O(2) | 1.695(4) | Mo(4)-O(13) | 1.707(5) | C(4)-N(1) | 1.387(9) |
| Mo(1)-O(5)#1 | 2.456(4) | Mo(4)-O(14) | 2.109(4) | C(19)-N(4) | 1.388(17) |
| Mo(2)-O(4) | 1.930(4) | O(1)-Mo(2)#1 | 2.386(4) | C(22)-C(23) | 1.405(14) |
| Mo(2)-O(1)#1 | 2.386(4) | O(14)-C(1) | 1.248(19) | C(26)-N(6) | 1.488(12) |
| Mo(3)-O(10) | 1.712(5) | O(15)-C(16) | 1.878(12) | C(28)-N(5) | 1.472(11) |
| Mo(3)-O(3)#1 | 2.356(4) | C(3)-N(1) | 1.343(9) | C(29)-N(4) | 1.388(18) |
| O(2)-Mo(1)-O(1) | 102.6(2) | Mo(1)-O(1)-Mo(2)#1 | 115.3(2) | | |
| O(1)-Mo(1)-O(3) | 99.6(2) | Mo(4)#1-O(4)-Mo(1) | 103.60(19) | | |
| O(3)-Mo(1)-O(5) | 142.27(19) | C(1)-O(14)-Mo(4) | 133.4(4) | | |
| O(4)-Mo(1)-O(5)#1 | 81.59(15) | C(26)-N(6)-C(27) | 110.7(7) | | |

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

## Reference


1. W. G. Klemperer, in *Inorg. Synth.*, John Wiley & Sons, Inc., 2007, pp. 74-85.
2. G. M. Sheldrick, *SHELX-97, Program for Crystal Structure Refinement, University of Göttingen, Germany*, 1997.
3. G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany*, 1997.