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Development and mechanism of fluorescent probe for Mn(II) ionic complex capable of recognizing chloroform vapor molecules

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Experimental details:

Materials and instruments. All chemical reagents used in the synthesis are commercially purchased and can be used without further purification. All experiments were performed at room temperature unless otherwise noted. Single-crystal structure determinations were performed on a Bruker Smart APEX II single-crystal diffractometer with graphite-monochromatized Mo-K α radiation at 296(2) K ($\lambda = 0.71073$ Å, 1 Å = 0.1 nm, Germany). PXRD were identified by the X-ray diffraction (SHIMADZU, LabX XRD-6100, Cu K α radiation) at 40 kV and 30 mA, and the spectra were measured 2θ range from 10° to 50°. A Bruker FT-IR spectrometer with KBr as the diluent was employed to measure IR spectra, which was recorded in the range of 4000~400 cm⁻¹. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of the two crystals were performed with a German NETZSCH STA 449F5 synchronous thermal analyzer at a heating rate of 10 °C·min⁻¹ in nitrogen atmosphere. Fluorescence spectra were measured on a fluorescence spectrophotometer (Fluoromax-4, HORIBA, USA). All photos are taken with an industrial camera (a2A2448-23gcPRO, BASLER, Germany).

Synthesis

[PPh₃(Me)]₂[MnBr₄] (Crystal 1). A mixture of methyltriphenylphosphonium bromide (1.25 g, 3.5mmol) and MnBr₂·4H₂O (0.5 g, 1.75 mmol) in acetone (100 mL) was refluxed under N₂ for 6 h. The insoluble substances in the solution were filtered off while hot, and finally the obtained filtrate was placed at room temperature for more than 48 hours. After the acetone was slowly volatilized, green transparent crystals suitable for X-ray analyses were precipitated. Crystal 1 was obtained after washing with a small portion of cold acetone and drying (1.072g, Yield = 68%).

[PPh₃(Me)]₂[MnBr₄]·CHCl₃ (Crystal 2). A small amount of bright green crystal 1 were dissolved in chloroform solvent. The insoluble substances in the solution were then filtered out and the resulting filtrate was placed at room temperature for a period of time. With the volatilization of chloroform solvent, yellow transparent crystals suitable for X-ray analysis were gradually precipitated. Crystal 2 were obtained after washing with a small portion of cold chloroform and drying.

X-ray Crystallographic Data Collection and Refinement.

Data collection: Bruker SMART APEX II; cell refinement: SAINT v7.68A (Bruker, 2009); data reduction: SAINT v7.68A (Bruker, 2009); structure solution: SHELXT 2018/2 (Sheldrick, 2018); structure refinement: XL (Sheldrick, 2008); software used to prepare material for publication: Olex2 1.3 (Dolomanov et al., 2009); molecular graphics: ORTEP-3 for Windows (Farrugia et al., 2012); visualization and analysis of crystal structures: Mercury (Macrae et al., 2020).

Single crystal samples 1 and 2 suitable for X-ray analyses were supported on a glass fiber. Single crystal structure determinations were performed on single crystal diffractometer. SADABS-2008/1 (Bruker, 2008) was used for absorption correction. Reflections were merged by SHELXL according to the crystal class for the calculation of statistics and refinement. Table S1 presents the relevant crystal data and structure

refinement results for crystal 1 and 2. The crystal structure is drawn and analyzed with Mercury software, as shown in the Fig S6 and Fig S7.

Chloroform Vapor Response Tests. First, poured some chloroform solvent into a glass bottle and kept the solution about one-fifth the depth of the bottle. Then, several crystalline particles (crystal 1) were placed over the chloroform solvent to avoid direct contact of the solvent. Seal the bottle mouth to allow the chloroform solvent evaporate into gas in contact with crystal 1. After 5 h, 24 h, 48 h and 96 h, a small number of samples were taken out to test their performance. The schematic diagram of the test device is shown in Fig. S1.

Heat Treatment Tests. A small amount of the complex samples placed in chloroform steam for 96 h were heat treated in an oven at 100°C for an hour. In addition, a small amount of crystal 2 was also heat treated in the oven at 100 °C for half an hour. Finally, took out the two kinds of samples to be used for testing other properties.

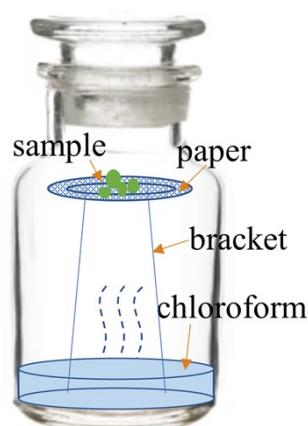


Fig. S1 Schematic diagram of the chloroform steam response tests.

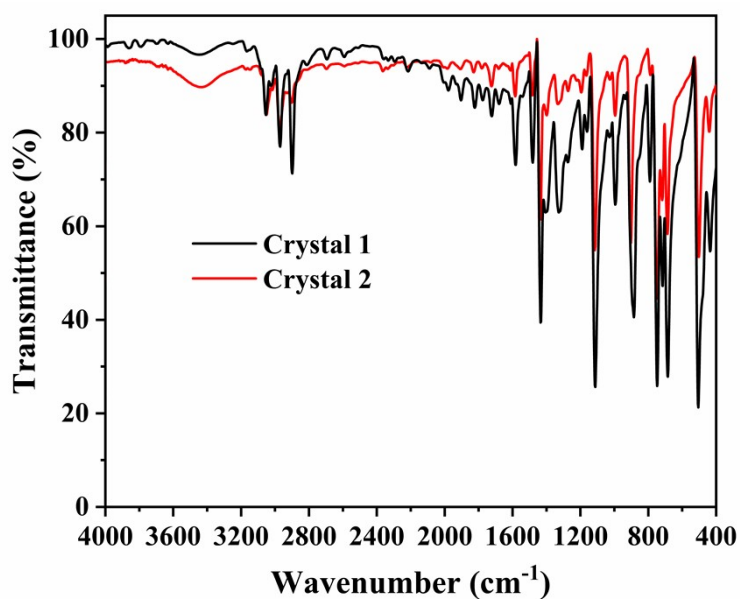


Fig. S2 IR spectrum of crystal 1 (black) and 2 (red).

Table. S1 Crystallographic data and refinement parameter for crystal 1 and 2.

| Sample | 1 | 2 |
|---|--|--|
| Formula | [PPh ₃ (Me)] ₂ [MnBr ₄] | [PPh ₃ (Me)] ₂ [MnBr ₄]·CHCl ₃ |
| Chemical Formula | C ₃₈ H ₃₆ Br ₄ MnP ₂ | C ₃₉ H ₃₇ Br ₄ MnP ₂ Cl ₃ |
| Formula Weight (g·mol ⁻¹) | 929.19 | 1048.55 |
| <i>D</i> _{calc.} /g·cm ⁻³ | 1.572 | 1.633 |
| μ/mm ⁻¹ | 4.514 | 4.346 |
| Colour | colorless | colorless |
| Shape | block-shaped | block-shaped |
| Size/mm ³ | 0.30×0.20×0.20 | 0.30×0.20×0.20 |
| T/K | 296(2) | 296(2) |
| Crystal system | monoclinic | trigonal |
| Flack parameter | 0.033(11) | 0.19(2) |
| Space group | <i>P</i> 2 ₁ | <i>P</i> 31c |
| <i>a</i> /Å | 9.7773(12) | 10.852(4) |
| <i>b</i> /Å | 12.5160(14) | 10.852(4) |
| <i>c</i> /Å | 16.6131(19) | 41.832(14) |
| α/° | 90 | 90 |
| β/° | 105.096(2) | 90 |
| γ/° | 90 | 120 |
| <i>V</i> /Å ³ | 1962.8(4) | 4266(3) |
| <i>Z</i> | 2 | 4 |
| <i>Z</i> ' | 1 | 2/3 |
| Wavelength/Å | 0.71073 | 0.71073 |
| Radiation type | Mo Kα | Mo Kα |
| <i>θ</i> _{min} /° | 1.27 | 1.947 |
| <i>θ</i> _{max} /° | 25.025 | 25.022 |
| Measured Refl's | 10035 | 20862 |
| Indep't Refl's | 6317 | 5040 |
| Refl's I≥2σ(I) | 4800 | 3127 |
| <i>R</i> _{int} | 3.52 | 5.56 |
| Parameters | 336 | 252 |
| Restraints | 13 | 13 |
| Largest Peak | 0.369 | 0.413 |
| Deepest Hole | -0.507 | -0.471 |
| GooF | 0.998 | 1.016 |
| <i>wR</i> ₂ (all data) | 9.08 | 9.11 |
| <i>wR</i> ₂ | 9.94 | 10.60 |
| <i>R</i> ₁ (all data) | 6.90 | 8.87 |
| <i>R</i> ₁ | 4.54 | 4.44 |
| CCDC | 2183912 | 2183915 |

$$R_1 = (\sum ||F_0| - |F_c||) / (\sum F_0), wR_2 = [(\sum w (F_0^2 - F_c^2)^2) / (\sum w (F_0^2))]^{1/2}.$$

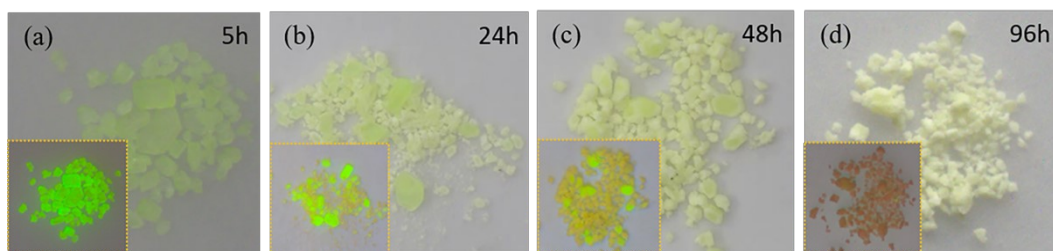


Fig. S3 Photographs of crystal 1 before and after exposure to chloroform vapor for different times (5 h, 24 h, 48 h, 96 h) under ambient light and under UV light at room temperature.

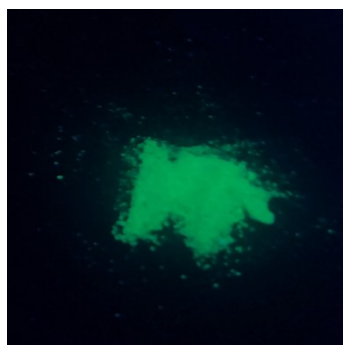


Fig. S4 Photographs of crystal 1 exposed to Chloroform vapor for 96 h after being heated at 100 °C for an hour under UV light.

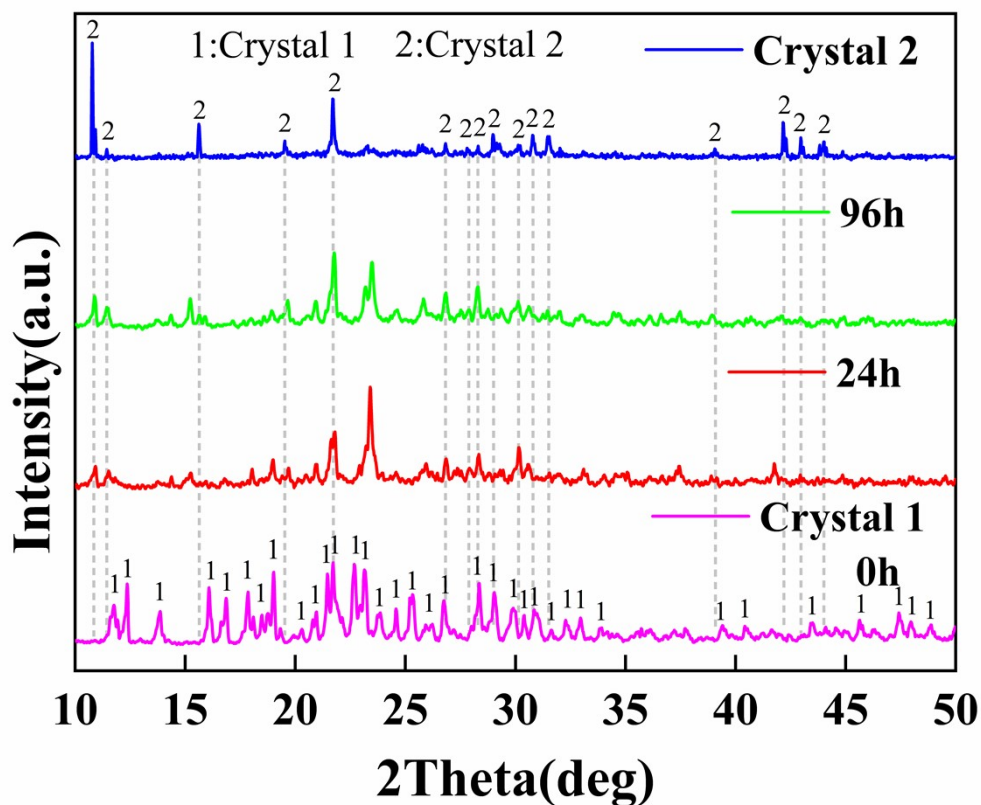


Fig. S5 PXRD patterns of crystal 1 upon exposure to vapors of chloroform at different time intervals (0–96 h) and crystal 2. Notice the significant changes in the peak position and the intensity.

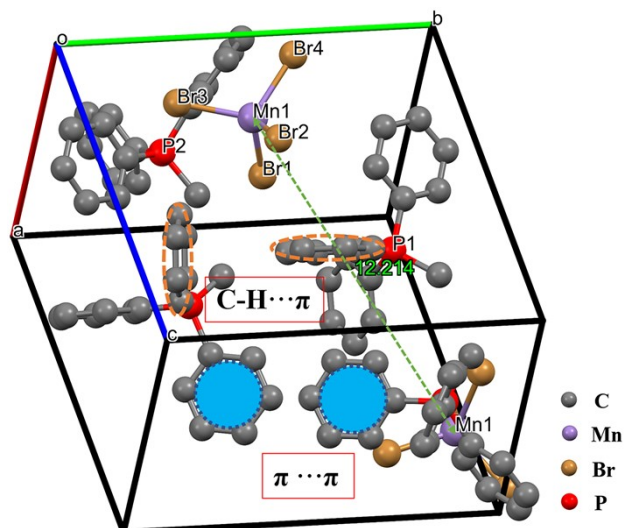


Fig. S6 The unit cell of complex 1. Atom colors: Mn (purple), Br(brown), P(red), C(grey), and H (no show). (Macrae et al, 2020)

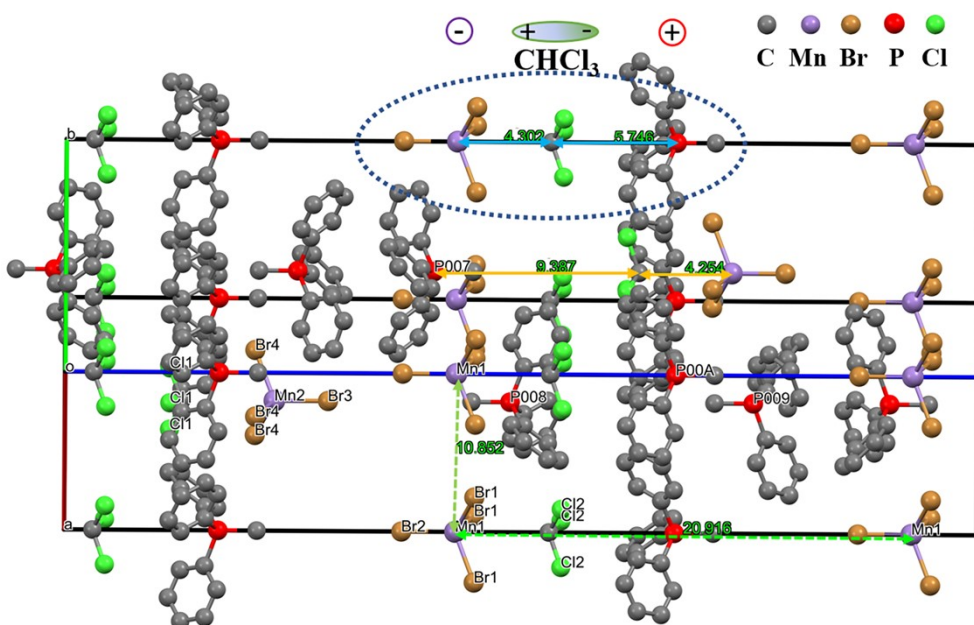


Fig. S7 The unit cell of complex 2. Atom colors: Mn (purple), Br(brown), Cl(green), P(red), C(grey), and H (no show). (Macrae et al, 2020)

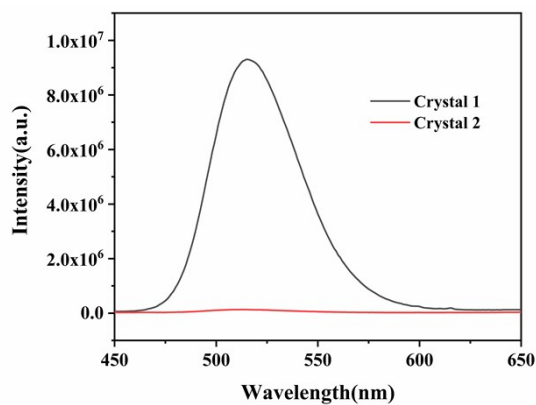


Fig. S8 Emission spectra of crystal 1 and 2 ($\lambda_{ex} = 365\text{nm}$).

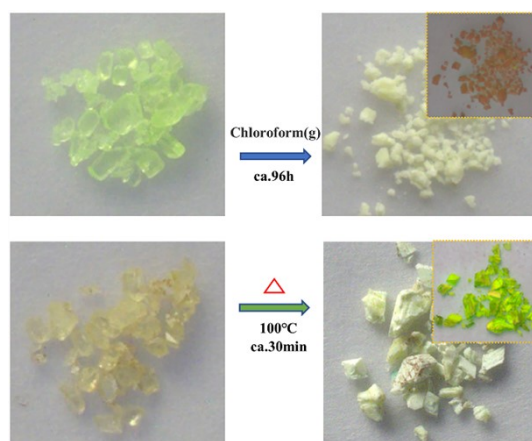


Fig. S9 Photographs of the crystal 1 (top) under ambient light and UV light before and after exposure (ca. 96 h) to the chloroform vapor. Photographs of the crystal 2 (bottom) under ambient light and UV light before and after heating treatment (ca. 30 min).

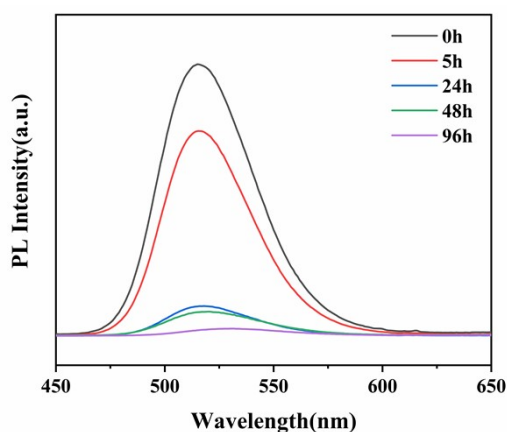


Fig. S10 Emission spectra of crystal 1 in chloroform vapor for different times (0h, 5h, 24h, 48h ,96h) at 298K($\lambda_{\text{ex}}=365\text{nm}$).

References

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