Electronic Supporting Information (ESI):

Moisture-Responsive Structural Transformation in Manganochlorine for Water-Soluble Luminescent Switching Ink

Yang-Peng Lin[1], Lin-Cong Rao[2], Ming-Jun Zhao[1], Xiao-Ying Huang[2], Ke-Zhao Du*[,1]

[1] College of Chemistry and Materials Science, Fujian Provincial Key Laboratory of Polymer Materials, Fujian Normal University, Fuzhou 350007, China.

[2] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, 350002, China.

* Corresponding author:

duke@fjnu.edu.cn (K.-Z. D.)

1. DFT calculation

The density functional theory (DFT) calculations were performed by the Materials Studio software. We used the Dmol[3] package to analyze the bandgap and density of states of two title compounds.[1, 2]

The exchange-correlation interactions were described using the Perdew-Burke-Ernzerhof (PBE) general gradient approximation (GGA). We took up with the double numeric quality basis set with polarization functions (DNP). The quality was selected as “fine”. The SCF tolerance was set as 10^{-6} eV/atom. The fermi smearing of 0.005 Hartree was adopted to accelerate convergence. We used a 4×5×3 Monkhorst-Pack grid for the Brillouin-zone integrations. The CASTEP package was carried out to calculate LUMO and HOMO orbitals as well.[3] PBE-GGA and Norm conserving were used for all calculations. The energy cutoff was set to 830 eV and the SCF tolerance was set as 5×10^{-6} eV/atom. The other parameters were set as default.

2. Experimental Section

Chemical. CsCl (99.99%, Adamas), MnO_2 (92%, Adamas), $MnCl_2{\cdot}4H_2O$ (≥99.0%, Greagent), MnO (99.0%, Macklin) and HCl (36 ~ 37%, Sinopharm Chemical Reagent Co., Ltd) were used without any further purification.

Synthesis of $CsMnCl_3(H_2O)_2$ (CMCH) with different Mn sources. For CMCH-1, 117 mg CsCl and 690 mg MnO2 were dissolved in 3 mL HCl (36 ~ 37%). Then the mixture was added into a PTFE-line stainless tank and kept at 150 °C for 65 h. Finally, when the tank was cooled down to room temperature, the colorless and transparent crystals could be collected. For CMCH-2 and CMCH-3, instead of MnO2, 42 mg MnO and 118 mg MnCl2·4H2O were used to produce light yellow and light red crystals under a similar condition, respectively. Their yields were 85%, 76% and 73%, respectively.

Characterization. Powder X-ray diffraction (PXRD) patterns were collected on a Miniflex Ⅱ diffractometer (Rigaku) with Cu Kα radiation (λ = 1.54178 Å). Thermogravimetric analysis (TGA) was obtained using a NETZSCH STA 449F3 at a heating rate of 10 K/min under nitrogen atmosphere. Energy-dispersive spectroscopy (EDS) was performed on a JEOL JSM-6700F scanning electron microscope. The UV-vis spectrum measurement was implemented on a UV-2600 from Shimadzu in Japan. The photoluminescence (PL) and photoluminescence excitation (PLE) of title compounds were obtained from an Edinburgh FS5 spectrofluorometer.

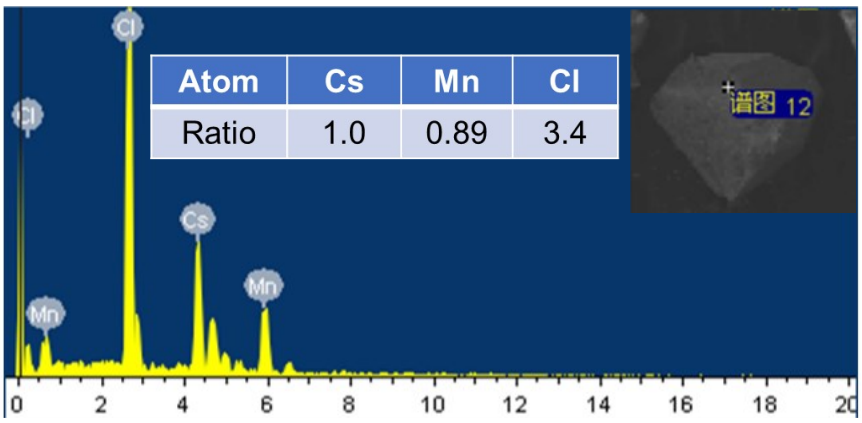

Figure S1. EDS data of CMCH-1 compound.

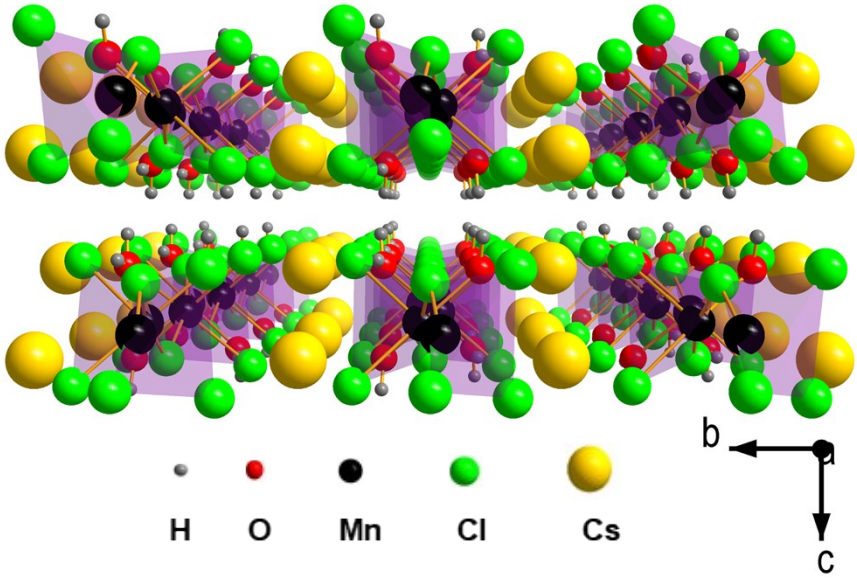

Figure S2. The structure of CMCH along with the *a*-direction. The structural data is obtained from ref.4 .[4]

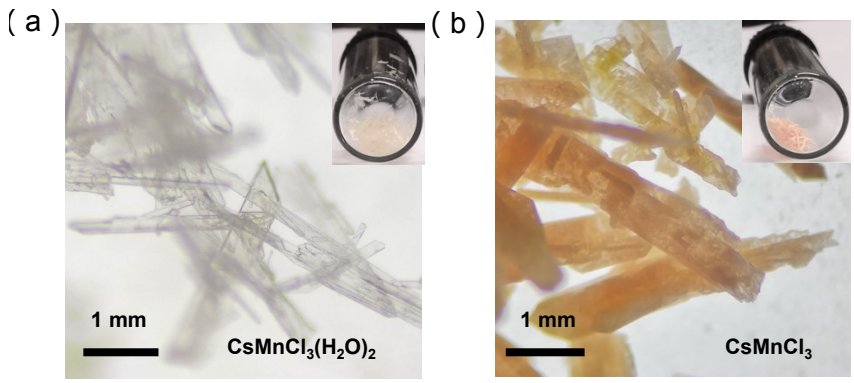

Figure S3. (a) and (b) display optical photographs of CMCH-1 and CMC crystal, respectively.

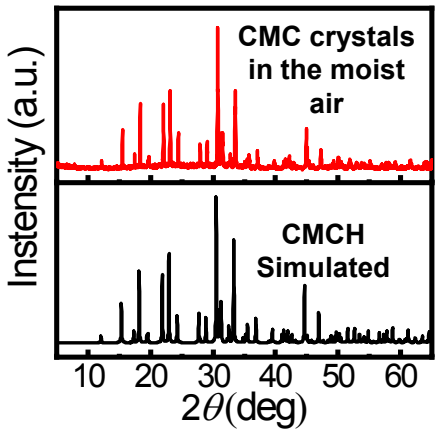

Figure S4. Experimental PXRD shows the product of CMC crystals in the moist air for 24 h. Obviously, CMC can convert into CMCH under moisture treatment.

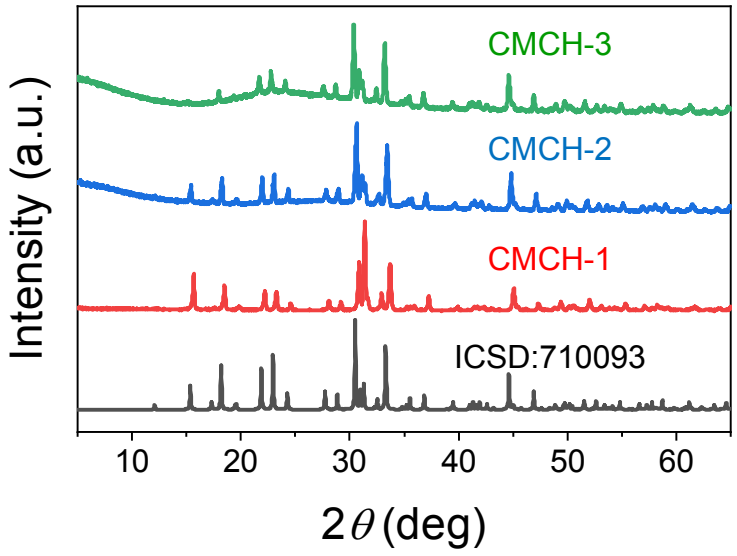

Figure S5. PXRD patterns of CMCH-1, CMCH-2 and CMCH-3 compounds.

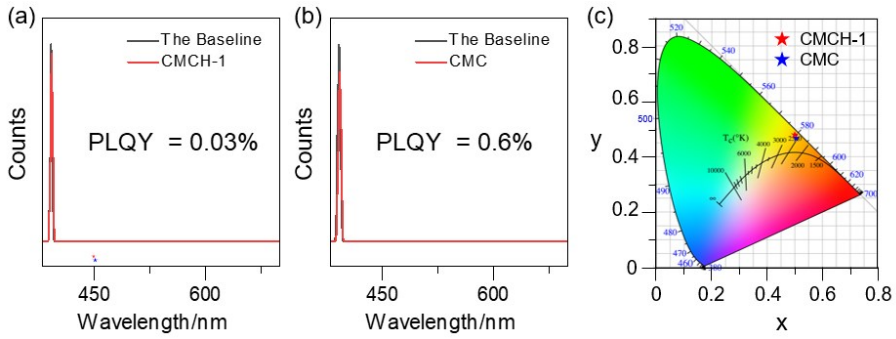

Figure S6. Photoluminescence quantum yield (PLQY) of CMCH-1 (a) and CMC (b). The coordinate of CMCH-1 and CMC in CIE map (c).

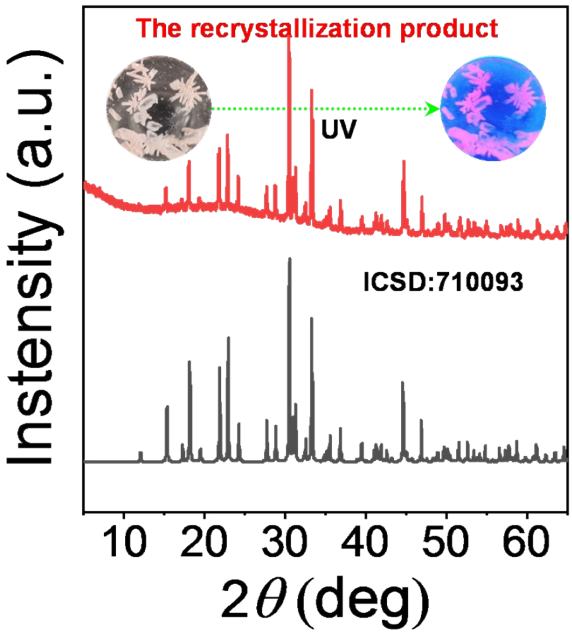

Figure S7. PXRD pattern of CMCH-1 compound recrystallized from aqueous solution (the inserts show compound under natural light and UV light, respectively).

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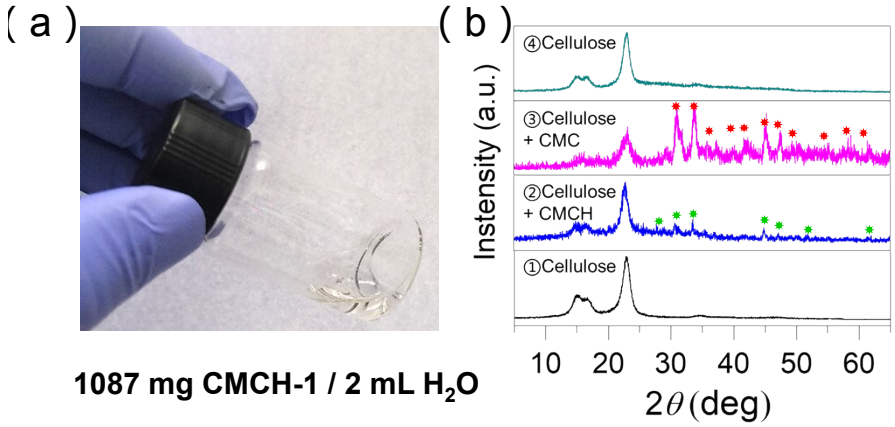

Figure S8. CMCH-1 aqueous solution (a). The PXRD of the products during the CMCH-1 and CMC structural transformation in the filter paper (b): ① the PXRD of blank filter paper; ② the PXRD of filter paper printed by CMCH-1aqueous solution; ③ the PXRD of ② after heat treatment at 125 °C for 30 min;④ the PXRD of ③ after water vapour treatment.

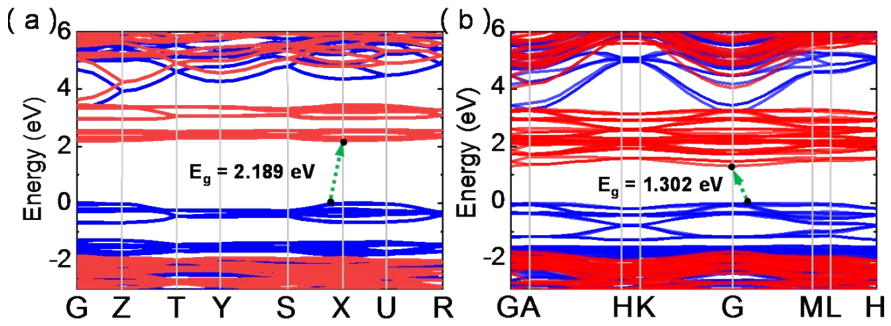

Figure S9. Band structure of CMCH (a) and CMC (b). Blue and red represent the spin-up and spin-down, respectively.

Reference

1. B. Delley, *J. Chem. Phys.,* 1990, **92**, 508-517.
2. B. Delley, *J. Chem. Phys.,* 2000, **113**, 7756-7764.
3. J. C. Stewart, D. S. Matthew, J. P. Chris, J. H. Phil, I. J. P. Matt, R. Keith and C. P. Mike, *Z. Kristallogr. Cryst. Mater,* 2005, **220**, 567-570.
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