<Electronic Supplementary Information>

In-Situ Formed $[M(CN)_9]$ (M = W, Mo) as Building Block for the Construction of Two Nona-Cyanometalate-Bridged Heterometallic Coordination Polymers

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Supplementary Index

1. Topological analysis

The topological structures of compounds **1** and **2** were both analyzed by programs OLEX[S1] and TOPOS[S2] with the CIF files. The topological cell of OLEX shows that the short (Schläfli) symbol of the net for **mot** is $\{6^6\}\{6^4\cdot 8^2\}_2$, which is consistent with the result of TOPOS.

References:

S1. O. V. Dolomanov, A. J. Blake, N. R. Champness, M. Schröder, *J. Appl. Cryst.* 2003, **36**, 1283–1284.

S2. C. Bonneau, O. Delgado-Friederichs, M. O'Keeffe, O. M. Yaghi, *Acta Cryst. A* 2004, **60**, 517–520.

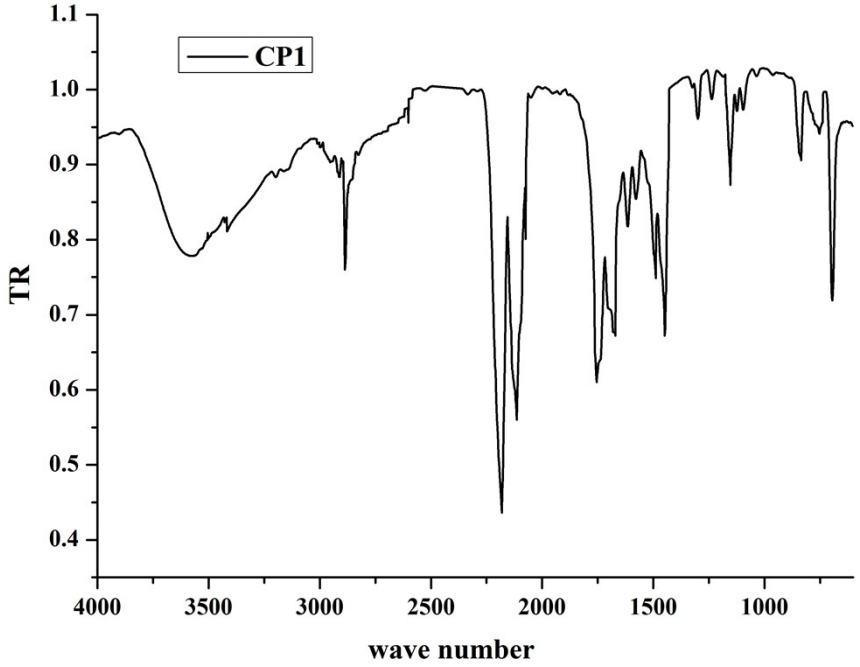


Fig. S1 IR spectrum of CP-**1**.

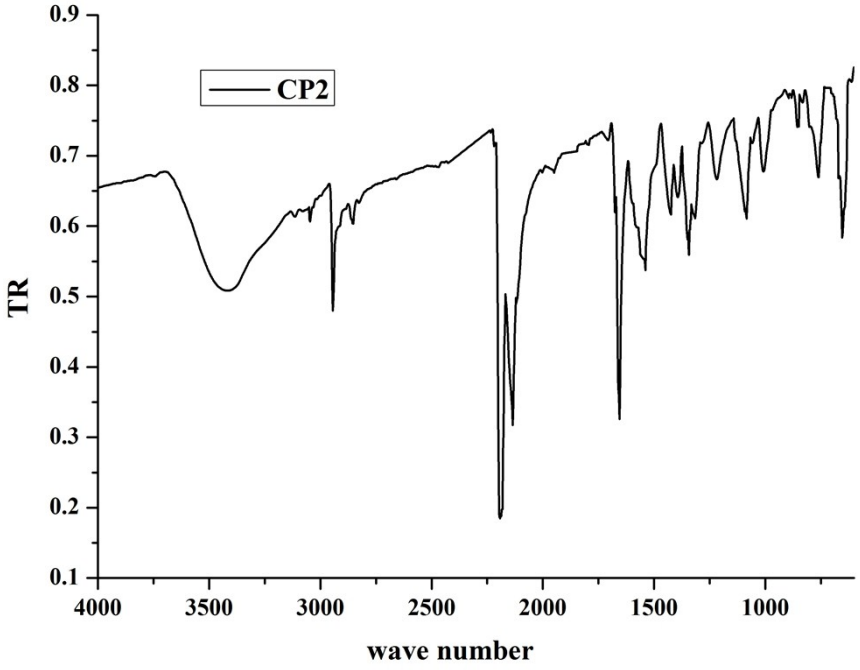


Fig. S2 IR spectrum of CP-**2**.

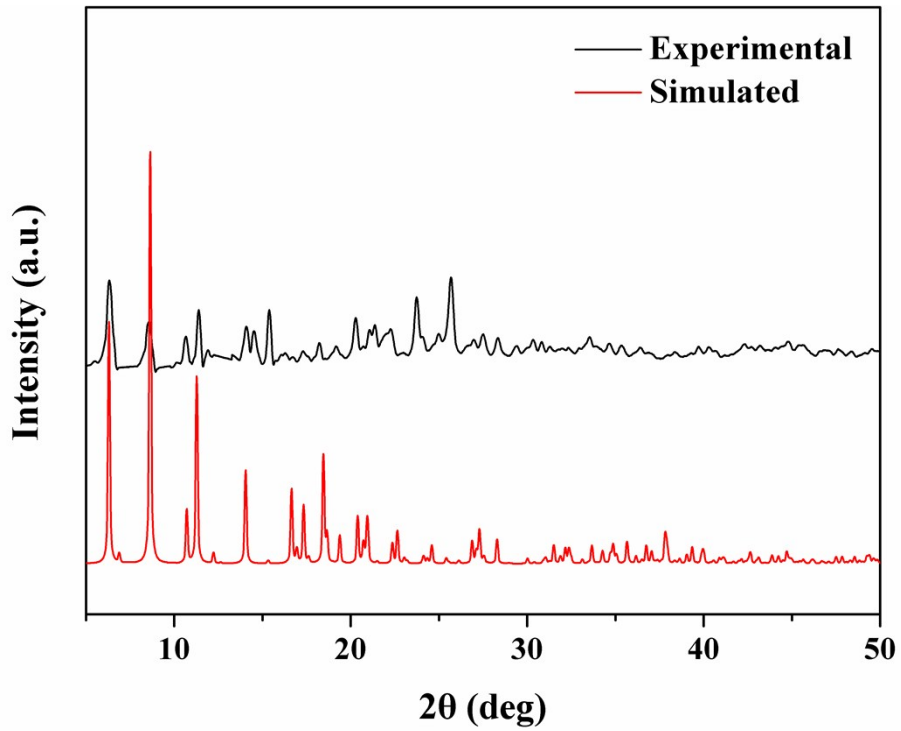


Fig. S3 The experimental powder X-ray diffraction pattern (wavelength λ = 1.5406 Å) of CP-**1**. The simulated diffraction pattern generated from the single-crystal X-ray diffraction data is given for comparison.

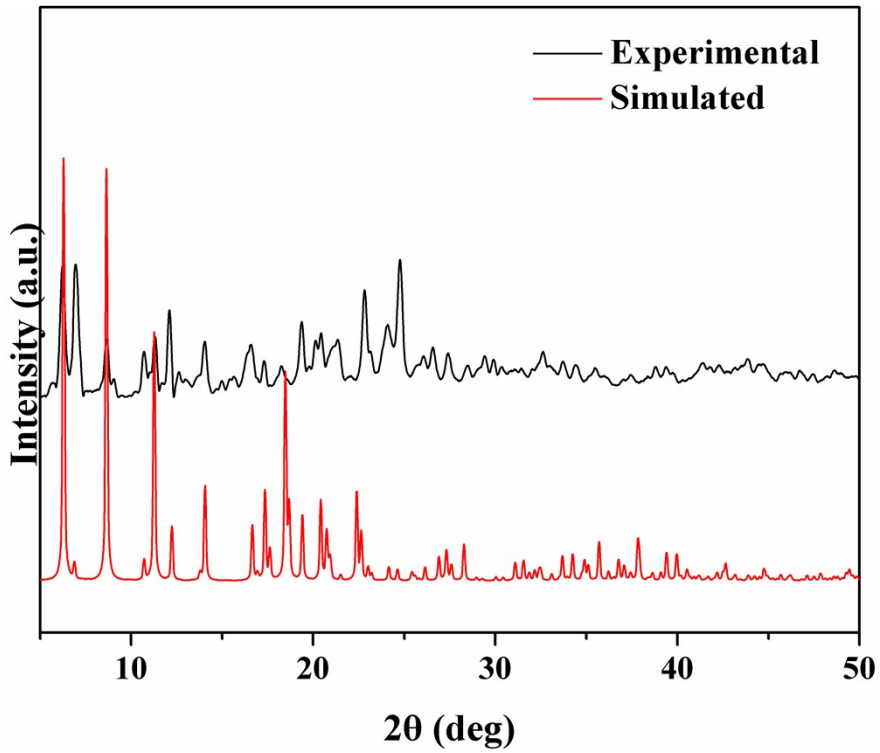


Fig. S4 The experimental powder X-ray diffraction pattern (wavelength λ = 1.5406 Å) of CP-**2**. The simulated diffraction pattern generated from the single-crystal X-ray diffraction data is given for comparison.

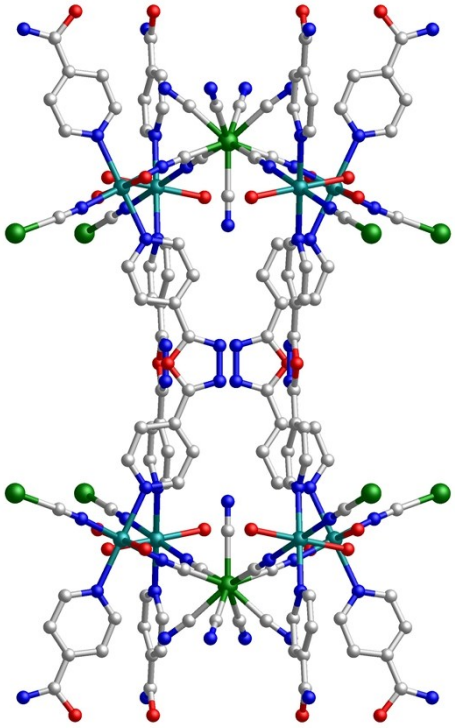


Fig. S5 The connection mode of building blocks $[M(CN)_9]^{4-}$ (M = W, Mo) (W, Mo, green; Mn, cyan; C, gray; N, blue; O, red). All the hydrogen atoms are omitted for clarity.

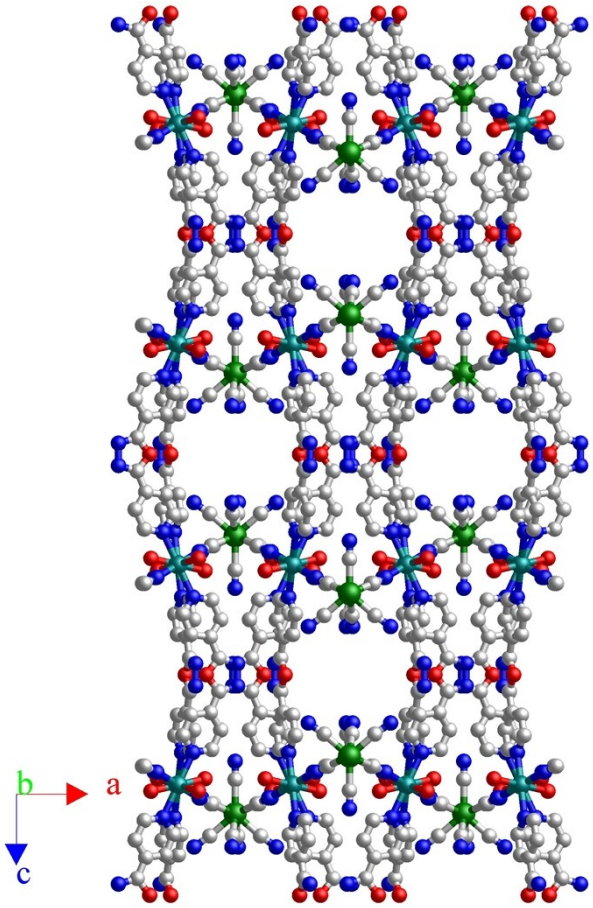
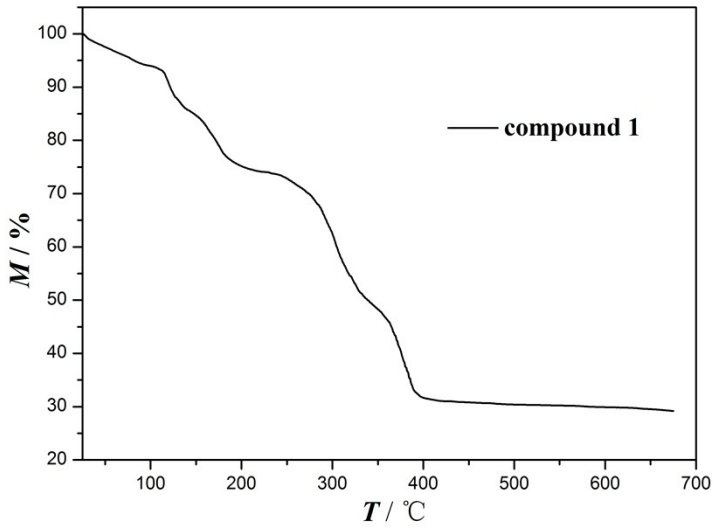


Fig. S6 Packing structure of CPs **1** and **2** viewed along the *b* axis (W, Mo, green; Mn, cyan; C, gray; N, blue; O, red). Carbon and nitrogen atoms in DMF molecules as well as all the hydrogen atoms are omitted for clarity.



Figu. S7 TG curve of CP **1**. The TG curve shows that CP **1** releases a solvent DMF molecule and four coordinated DMF molecules per formula unit below 250 °C.

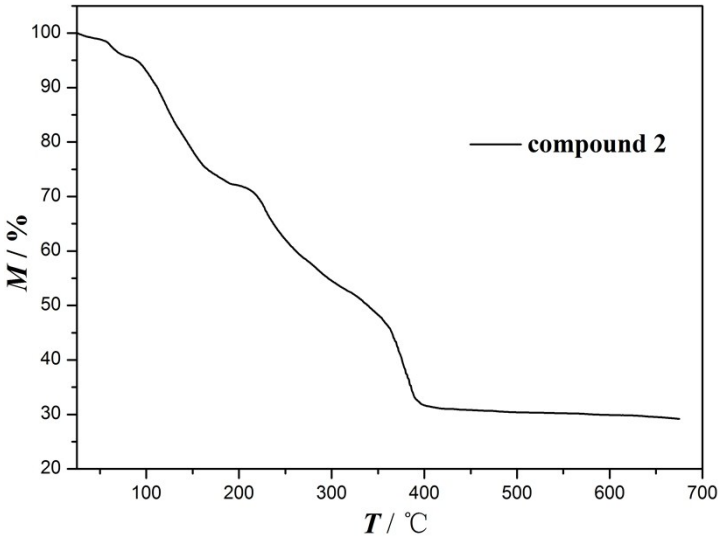


Fig. S8 TG curve of CP **2**. The TG curve shows that CP **2** releases a solvent DMF molecule and four coordinated DMF molecules per formula unit below 250 °C.