

A 3D chiral networked MX compound

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MX-ladder is a new family of metal–organic ladder compound based on mixed-valence halogen-bridged transition-metal complex (MX-chain), which shows unique electronic states, and physical properties.¹ Although we have synthesized a variety of MX-ladder compounds, the so-called two-legged MX-ladder, four-legged MX-tube, and ghost-legged MX-sheet,^{2–5} the development of 3D-extended type MX compound is still challenging. In this work, for the first time, we successfully synthesized a new 3D networked MX-type compound, [Pt(en)(dppe)I]₂(NO₃)₄ (en: ethylenediamine, dppe: 1,2-Di(4-pyridyl)ethane).

The target compound was synthesized from following two steps:

- (a) 2Pt(en)(NO₃)₂ + 2dppe → [Pt(en)(dppe)]₂(NO₃)₄ (**1**)
 (b) [Pt(en)(dppe)]₂(NO₃)₄ + I₂ → [Pt(en)(dppe)I]₂(NO₃)₄ (**2**)

Figure 1 shows the X-ray crystal structure of **2** at 100 K. **2** crystallizes in tetragonal *P*4₁2₁2 or *P*4₃2₁2 space group due to spontaneous resolution. Macrocyclic Pt units are helically aligned with a 4-fold periodicity along the *c*-axis and bridged by I[−] with each other to form a 3D networked structure. Focusing on the MX-chain part, the bridging I[−] sites are disordered with a half occupancy around the midpoint between adjacent Pt ions, indicating that electronic state within one MX-chain is in the mixed-valence charge-density-wave state (CDW: ...Pt²⁺...I[−]–Pt⁴⁺–I[−]...Pt²⁺...I[−]–Pt⁴⁺–I[−]...), as also confirmed by optical measurements. Details are presented.

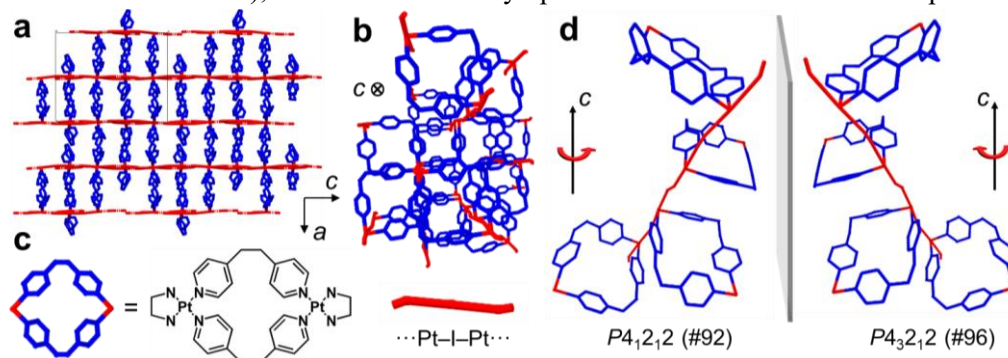


Figure 1. Crystal structure of compound **2** (*P*4₁2₁2 form). (a) View along *b*-axis. (b) View along *c*-axis. (c) Building block. (d) Two enantiomers. The en unit, H₂O and NO₃[−] have been omitted for clarity.

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