

## Effect of Non-covalent Interactions for Stabilizing Single Pt-Br Chains with Aromatic Ligand

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Organic–inorganic composite materials have shown significant interest in both pure and applied sciences. Owing to their outstanding diversity, organic–inorganic hybrid materials focusing on the compound having a one dimensional (1D) electron system has expanded the research. 1D electron system combining both organic and inorganic materials "Quasi-1D halogen-bridged metal complexes" (so-called MX chains) have been reported to exhibit excellent properties.<sup>1</sup> So far, all of the single MX chains have been synthesized using aliphatic ligands. However, modification of aliphatic ligands to design robust framework has limitations because of their flexibility. Due to the inherent rigidity and  $\pi$ - $\pi$  stacking, aromatic ligand can be the promising candidate to design new multi-functional materials based on MX chains.

In this work, we have focused to synthesize bromide-bridged Pt chains using only aromatic ligand, 2-aminomethyl pyridine (amp). We synthesized new Pt-based hybrid chains  $[\text{Pt}(\text{amp})_2\text{Br}]\text{Br}\cdot\text{TsO}\cdot 5\text{H}_2\text{O}$  and  $[\text{Pt}(\text{amp})_2\text{Br}]_2\cdot[\text{Pt}(\text{amp})_2\text{Br}_2]\cdot(\text{HSO}_4)_2\cdot(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$  whose strategy is defined by  $\pi$ - $\pi$  interactions as well as H-bonding interactions. In the case of  $[\text{Pt}(\text{amp})_2\text{Br}]\text{Br}\cdot\text{TsO}\cdot 5\text{H}_2\text{O}$ , H-bonding between ligand and two types of counteranions and  $\pi$ - $\pi$  stacking simultaneously exist to stabilize the chain structure. The co-existence of 1D chains with Pt(IV) complexes like crystalline hybrid materials were achieved for the first time in the case of  $[\text{Pt}(\text{amp})_2\text{Br}]_2\cdot[\text{Pt}(\text{amp})_2\text{Br}_2]\cdot(\text{HSO}_4)_2\cdot(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$ , Pt(IV) complexes have important role of stabilizing chain structures via  $\pi$ - $\pi$  stacking. The distortion parameter values for all complexes indicate that they exist in  $-\text{X}\cdots\text{PtII}\cdots\text{X}-\text{PtIV}-\text{X}\cdots$  state, so-called mixed valence state.<sup>2</sup>

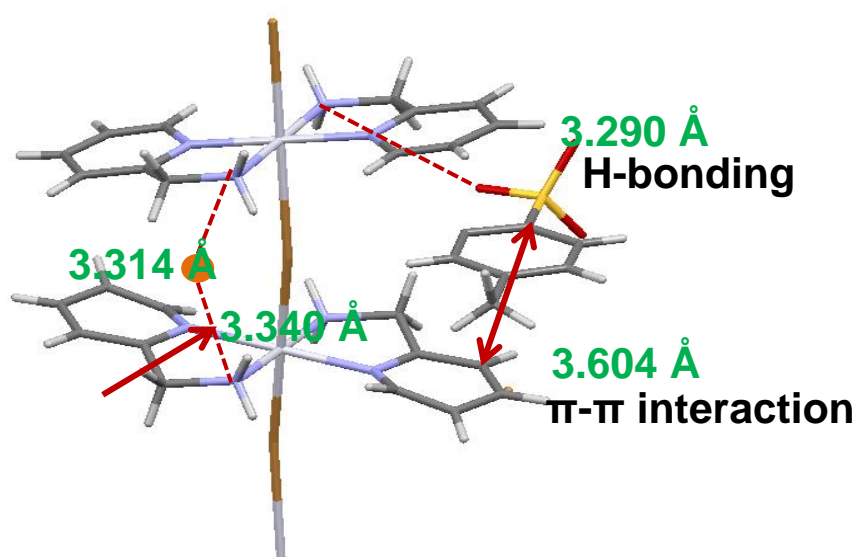


Figure 1. Crystal Structure of  $[\text{Pt}(\text{amp})_2\text{Br}]\text{Br}\cdot\text{TsO}\cdot 5\text{H}_2\text{O}$

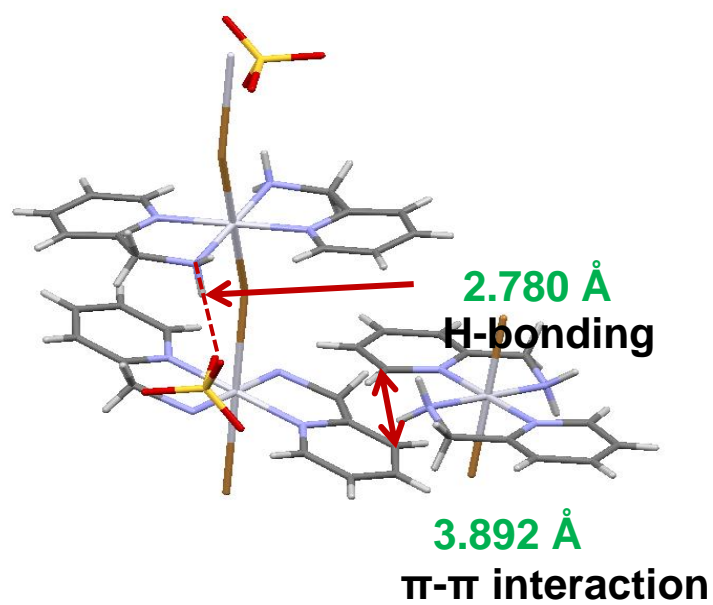


Figure 2.  $[\text{Pt}(\text{amp})_2\text{Br}]_2 \cdot [\text{Pt}(\text{amp})_2\text{Br}_2] \cdot (\text{HSO}_4)_2 \cdot (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

### [References]

- [1] Kishida et al. *Nature* **2000**, *405*, 929.
- [2] Okamoto et al., *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2023.