

## Structural and Electronic Properties of a Metal-Organic Mixed-Valence Nanotube

Nanotubes are generally prepared from constituent elements at high temperatures and thus it is difficult to control their size, shape and electronic states. One useful synthetic approach for well-defined nanostructures is using building blocks such as metal ions and organic molecules. We report the successful fabrication of a porous metal-organic nanotube obtained from simple polymerization using a square-shaped metal-organic frame. This nanotube exhibits selective gas sorption of water and alcohol. Synchrotron X-ray and theoretical studies revealed that it shows a unique electronic structure of charge-density wave (CDW) quartets based on a four-legged ladder system.

The synthesis of nanotubes with a well-defined structure is very challenging, as is investigating their structural and electronic properties. Since the discovery of carbon nanotubes, many tubular nanomaterials have been reported [1]. However, sometimes it is difficult to control the structural and electronic tuning of such nanotubes because extreme conditions are needed for their synthesis. Here, we report the bottom-up fabrication of a porous metal-organic nanotube,  $[\text{Pt}(\text{en})(\text{bpy})\text{I}_2(\text{NO}_3)_2 \cdot 16\text{H}_2\text{O}]_n$  (**1**, en: ethylenediamine, bpy: 4,4'-bipyridine), which shows selective sorption of water and alcohol. In addition, this nanotube consists of a one-dimensional (1D) halogen-bridged transition-metal covalent chain (MX-chain) that shows a variety of physical properties due to the high degree of electronic freedom [2]. X-ray, optical and theoretical studies were used to reveal its unique electronic structure based on the four-legged ladder system.

Single crystals of **1** were successfully obtained from the reaction of the square-shaped complex  $[\text{Pt}(\text{en})(\text{bpy})_2(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}]$  and  $\text{I}_2$  in a mixture of water and methanol at room temperature. The crystal structure of **1** was determined using single-crystal X-ray crystallography at 100 K. Each square-shaped platinum complex is bridged by  $\text{I}^-$  to form a quadrangular prism-shaped tubular structure (Fig. 1). Viewed differently, this nanotube **1** is composed of four iodide-bridged MX-chains, which form the four-legged ladder lattice (MX-tube).

We firstly examined the sorption property of the dehydrated form (**1a**) obtained by drying as-synthesized **1** under vacuum. High uptakes of water, methanol, and ethanol were observed at 298 K, whereas no  $\text{N}_2$  adsorption was observed at 77 K. To elucidate the origin of this selective sorption behavior, synchrotron X-ray powder diffraction (XRPD) measurements were carried out at BL-8B [3]. The results revealed that dehydration of **1** caused broadening of the XRPD pattern, indicating that the long-range order disappeared. However, its crystallinity was smoothly recovered when **1a** was exposed to water, methanol, or ethanol vapor. The hydrogen bond network between host framework and guest molecules might play a key role in the recovery of the long-range order and selective sorption behavior.

The optical conductivity spectrum and Raman spectrum of **1** indicated that the electronic state within one MX-chain is the charge-density wave (CDW:  $\dots\text{Pt}^{2+}\dots\text{I}^-\text{Pt}^{4+}\dots\text{I}^-$ ) state. In **1**, sheet-shaped diffuse X-ray scattering was observed at  $l = n + 0.5$  ( $n$  being an integer) positions originating from the two-fold periodic charge ordering of the CDW state, indicating that there can be a short-range ordering such as intra- or inter-tube correlations of the MX-chain (Fig. 2(a)). If the three-dimensionally ordered CDW state is realized in this compound, X-ray scattering derived from the CDW state would be observed not as diffuse scattering but as superlattice reflection. Because **1** has a ladder lattice [4], where each MX-chain constitutes its legs, we expected **1** to exhibit a distinctive electronic structure compared with similar MX-typed analogues. Four types of four-legged ladder-shaped valence arrangements like “quartets” of CDWs (Fig. 2(b)) composed of adjacent MX-chains are predicted to appear according to a theoretical study [5]. The metal-halogen distance is dominated by the valence of the adjacent metal ions, and therefore X-ray scattering reveals the CDW state through displacements of the halide ions [6]; this was studied using diffuse X-ray scattering analysis at BL-4C.

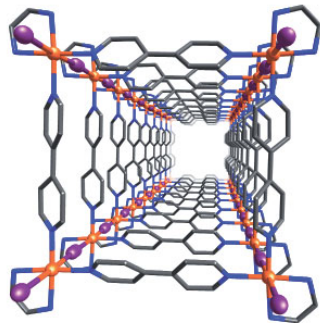


Figure 1  
The tubular structure of MX-tube **1**. Platinum, iodine, carbon, and nitrogen atoms are shown in orange, purple, gray, and blue, respectively.

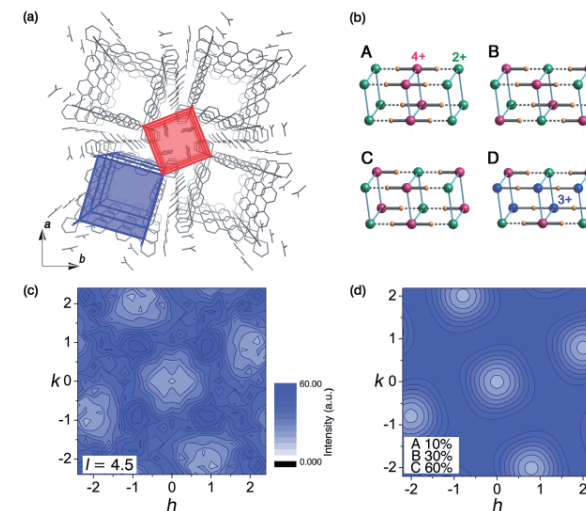


Figure 2

(a) Perspective views of two types of quartets of MX-chains composed of the intra- (blue) and inter-tube (red) correlations in the crystal structure. These intra- or inter-tube quartets can be considered as candidates to form CDW quartets, respectively. (b) Four types of “CDW quartets” composed of adjacent MX-chains based on a theoretical study (for details, see refs. [3] and [5]). (c) Contour map of the diffuse X-ray scattering intensity distribution measured at the  $(h k 4.5)$  plane. (d) Contour map of calculated intensity distribution.

Figure 2(c) shows the diffuse X-ray scattering intensity distribution measured at the  $(h k 4.5)$  reciprocal lattice plane. If there is no inter-chain electronic interaction, a flat diffuse X-ray scattering intensity distribution can be observed. However, X-ray diffuse scattering intensity is not constant. As shown in Fig. 2(c), clear intensity minima were observed. The  $d$ -value corresponding to  $1.99\mathbf{a}^* + 0.82\mathbf{b}^*$  is 8.75 Å. Surprisingly, this value is close to the inter-tube distance (Fig. 2(a)). In order to determine this inter-tube phase correlation, we made a model calculation of the diffuse scattering intensity distribution. We obtained successful results on the assumption that B and C type CDW states coexist as major phases (Fig. 2(d)), whereas the model calculation of every single electronic state and that of the intra-tube correlation could not reproduce the experimental result. Considering these findings, the valence arrangement in our four-legged MX-tube system might be selected to keep the charge neutrality in the same layer, because the average valence state of Pt ions in the same layer of both B and C type CDW states is +3, whereas that of A type is +2 or +4. The results of theoretical calculations using Hartree-Fock and configuration-interaction meth-

ods were also consistent with experimental observations [3].

## REFERENCES

- [1] (a) S. Iijima, *Nature* **354** (1991) 56; (b) N.G. Chopra, R.J. Luyken, K. Cherrey, Vincent H. Crespi, Marvin L. Cohen, Steven G. Louie and A. Zettl, *Science* **269** (1995) 966; (c) R. Tenne, L. Margulis, M. Genut and G. Hodes, *Nature* **360** (1992) 444.
- [2] H.J. Keller, D.S. Martin, Jr., in *Extended Linear Chain Compounds*, J.S. Miller, Ed. 1 (Plenum, New York, 1982) 357.
- [3] K. Otsubo, Y. Wakabayashi, J. Ohara, S. Yamamoto, H. Matsuzaki, H. Okamoto, K. Nitta, T. Uruga and H. Kitagawa, *Nat. Mater.* **10** (2011) 291.
- [4] M. Azuma, Z. Hiroi, M. Takano, K. Ishida and Y. Kitaoka, *Phys. Rev. Lett.* **73** (1994) 3463.
- [5] J. Ohara and S. Yamamoto, *Europhys. Lett.* **87** (2009) 17006.
- [6] (a) Y. Wakabayashi, A. Kobayashi, H. Sawa, H. Ohsumi, N. Ikeda, H. Kitagawa, *J. Am. Chem. Soc.* **128** (2006) 6676. (b) A. Kobayashi and H. Kitagawa, *J. Am. Chem. Soc.* **128** (2006) 12066.

## BEAMLINES

4C and 8B

K. Otsubo<sup>1</sup> and H. Kitagawa<sup>2</sup> (<sup>1</sup>Kyoto Univ., <sup>2</sup>CREST)