Synthesis of One-Dimensional Metal-Containing Insulated Molecular Wire with Versatile Properties Directed toward Molecular Electronics Materials

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S *Supporting Information*

ABSTRACT: We report, herein, the design, synthesis, and properties of new materials directed toward molecular electronics. A transition metal-containing insulated molecular wire was synthesized through the coordination polymerization of a Ru(II) porphyrin with an insulated bridging ligand of well-defined structure. The wire displayed not only high linearity and rigidity, but also high intramolecular charge mobility. Owing to the unique properties of the coordination bond, the interconversion between the monomer and polymer states was realized under a carbon monoxide atmosphere or UV irradiation. The results demonstrated a high potential of the metal-containing insulated molecular wire for applications in molecular electronics.

Insulated molecular wires (IMWs),[1] composed of π-conjugated polymer chains covered with protective sheaths that limit π−π interactions between the conjugated backbones, have received particular attention due to their potential applications as wiring materials in molecular electronics. For use as wiring materials, π-conjugated polymers must satisfy two requirements: (1) compatible processability resulting from high solubility and defined molecular structure, and (2) appropriate material properties such as high linearity, rigidity, and, in particular, high conductivity. We previously succeeded in the synthesis of IMWs which adequately satisfied properties (1) and (2); in these wires, the conjugated moieties were isolated through insulation using α-cyclodextrin (α-CD) derivatives.[2] We also clarified the utility of IMWs for molecular electronics by achieving highly efficient wiring to nanoelectrodes as compared with the corresponding uninsulated molecular wires.[3,4] However, it is not necessary for IMWs to strictly mimic their conventional inorganic wiring materials. In other words, molecular wires that contain stimuli-responsive units in their polymer chains are expected to perform as higher-order nanodevices owing to their functionalities; i.e., electrodes connected to functionalized molecular wires could exhibit not only conductivity but also physical property change by external stimuli.[5]
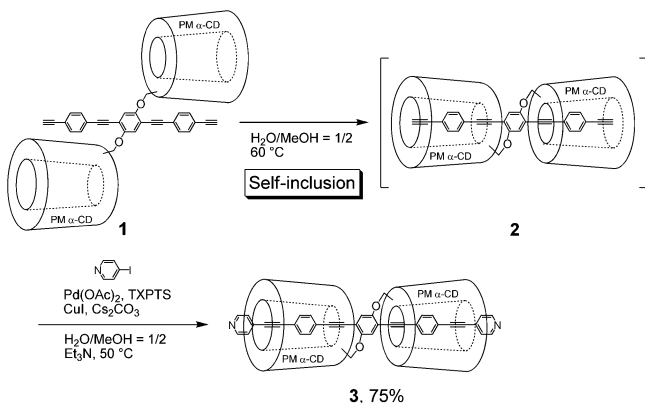
Therefore, we have focused on one-dimensional coordination polymers containing transition metals,[6] which combine the advantages of organic IMWs mentioned above, with those of transition metal complexes. In the field of molecular electronics, they are expected to form wiring materials with novel properties including: (3) various characteristics derived from the transition metal complexes such as redox behavior,[7] triplet state properties,[8] and the Kondo effect;[9] and (4) enhanced processability such as recyclability and self-healing through reversible monomer−polymer interconversion brought on by the reversible nature of the noncovalent bonds as opposed to covalently bonded molecular wires.[10] In spite of their potential utility, however, there are no suitable examples of organic−inorganic wiring materials that display rigidity, linearity, and especially, conductivity, probably owing to their weak connections and/or localized molecular orbitals at the organic−inorganic bonding interfaces. Herein, we present the successful synthesis of a transition metal-containing IMW with desirable properties for wiring materials including high rigidity, linearity, and high charge mobility as compared to conventional π-conjugated polymers. We accomplished this through the coordination polymerization of Ru(II) porphyrin complexes with insulated bridging ligands having well-defined structures,[11] and this IMW displayed novel processability as a result of its noncovalent bonding motif.

We first prepared an insulated bridging ligand **3** with high coverage, structural regularity, and conductivity, and demonstrated its applicability as a component of molecular wires. Scheme 1 shows the synthetic route to obtain **3**. Using ^{1}H NMR, we confirmed the quantitative self-inclusion of precursor **1**,[2a] oligo(phenylene ethynylene) (OPE) containing two permethylated (PM) α-CDs in CH_3OH/H_2O (2:1),[2e] resulting

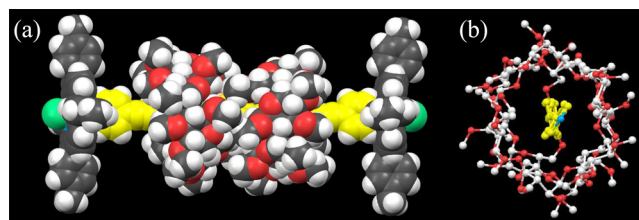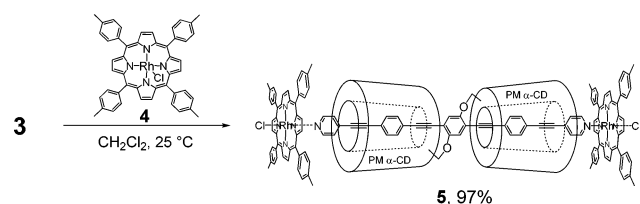Scheme 1. Synthesis of the Insulated Bridging Ligand 3

Figure 1. Single crystal structure of 5: (a) lateral (space-filling model) view; (b) top (ball and stick model) view. Hydrogen atoms and porphyrin 4 are omitted.

in the inclusion complex 2. Using the same solvent combination, we reacted the intermediate pseudorotaxane structure of 2 with *p*-iodopyridine via Sonogashira coupling to form 3 bearing coordinating groups at both ends, in good yield. The fixed [3]rotaxane structure of 3 could be constructed by elongation of the π-conjugated unit of 2 without the introduction of bulky stopper groups at both ends due to its linkages between the axis and rings. The structure of 3 was confirmed using ROESY NMR spectroscopy (Figure S2). 3 displayed high solubility in various organic solvents because of the insulating PM α-CDs. The thermal stability of the rotaxane structure was validated using ¹H NMR, as the insulation was retained in toluene under reflux (Figure S3).

We then investigated the electron transport properties of the monomeric insulated bridging ligand 3 using the scanning tunneling microscopy breakjunction (STM BJ) method.[12] We anticipated that the pyridyl groups of 3 would be suitable for STM BJ because they could act as anchoring units on gold electrodes via Au-N coordination. The insulation of monomer 3 revealed a fixed conductance value (Figure S5) due to the restricted intramolecular motion in the conjugated system. Clear steps in the conductance traces could be observed because of the limited intermolecular π−π interactions due to shielding from the PM α-CDs.[4] The resulting conductance of 3 was 7×10^{-6} G_0, which was high enough to be considered as a potential component of conducting molecular wires.[13]

To examine the detailed structure of 3 using X-ray crystal structure analysis, the heavy atom-bearing coordination complex 5 was synthesized by the reaction of 3 with Rh(TTP)Cl (TTP: tetratolylporphyrin) 4 in high yield (Scheme 2).

Single crystals suitable for X-ray crystallography were grown through vapor diffusion of MeOH into a solution of 5 in THF. In the solid state, 5 clearly exhibited a fixed [3]rotaxane structure due to the linkages between the PM α-CDs and OPE,

which prevented their shuttling and rotation, inhibited the disordering of the components of 5 (Figure 1).[14] The two PM α-CDs clearly insulated the OPE skeleton in the absence of solvent molecules at their interface. The similar diameters of the PM α-CDs and TTPs resulted in a pillar-like structure. It was apparent that the three insulated benzene rings of the π-conjugated guest were almost planar as the torsion angles between adjacent benzene rings were 11.1° and 12.8°. The dihedral angle between the TTP planes at both ends of 5 was nearly parallel (178°), resulting in the high linearity of the π-conjugated guest unit of 5. As shown above, 3 revealed considerable potential as a bridging ligand for a one-dimensional coordination polymer because of its high solubility, structural stability, conductivity, and linearity.

To synthesize a one-dimensional metal-containing insulated molecular wire with strong coordinate bonds, we carried out a complexation of 3 with Ru(II) porphyrin, which was generated in situ from Ru(II) carbonyl porphyrin 6 by UV irradiation with a mercury lamp to release the coordinated carbon monoxide (Scheme 3).[15,16] Since the Ru-pyridyl coordinate bonds were

Scheme 3. Synthesis of Molecular Wire 7
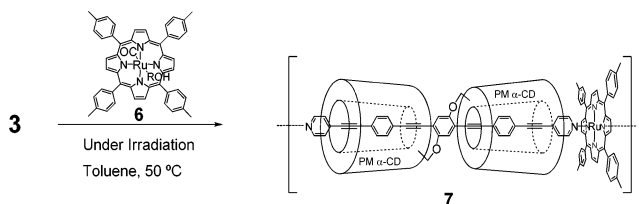
fixed in the *trans*-configuration at the six-coordinate Ru center, we expected that a stable linear coordination polymer would be formed without isomerization. The formation of coordination polymer 7 ($M_w = 7.1 \times 10^4$, $M_n = 2.7 \times 10^4$)[17] was confirmed using size-exclusion chromatography (SEC) and IR spectroscopy.[18] The coordination polymer exhibited high solubility in organic solvents such as toluene and CHCl₃ as well as high stability. Decomplexation was not observed in coordinating solvents such as THF and pyridine at room temperature (Figure S8).

Next, we evaluated the rigidity and linearity of molecular wire 7. Figure 2a displays a polarized optical micrograph of 7 in a concentrated CHCl₃ solution. Notably, 7 formed a cholesteric liquid crystal phase as confirmed by its clear fingerprint texture. We confirmed that this observed phase arose from the rigidity of the insulating bridging ligand and chirality of the cyclodextrins because the corresponding uninsulated coordination reference wires, 7′ and 7″ (Figure 2c), did not form cholesteric phases, but rather formed isotropic liquids (Figure S9). In addition, according to the unperturbed wormlike
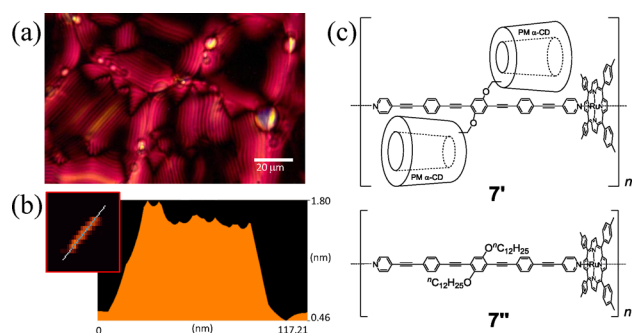
Scheme 2. Synthetic Route To Obtain Coordination Complex 5

Figure 2. (a) Polarized optical micrograph of **7** in CHCl₃. (b) Section analysis of white line in tapping-mode AFM image of **7**. (c) Structures of uninsulated wires **7′** and **7″**.

cylinder model,[19] the persistence length (L) of **7** was estimated to be 43.4 nm, while the uninsulated wire **7′** exhibited a lower persistence length (8.10 nm) confirming that the rigidity of the backbone in **7** was significantly enhanced by the insulation. The linearity of molecular wire **7** was investigated by atomic force microscopy (AFM) experiments on cleaved graphite substrates. The morphology of the singly dispersed molecular wires **7** was highly linear, whereas **7′** exhibited aggregated structures (Figures 2b and S11−S14). This suggested that the high independency and linearity of **7** were reinforced by the insulation, which inhibited π−π interactions and prevented the backbone of the polymer from bending, and by the *trans*-configuration of Ru−porphyrin complex. These results suggested that through appropriate coordination polymer design, rigid and linear transition-metal-containing IMWs comparable to organic IMWs could be obtained.

We then examined the intramolecular charge mobility characteristics of molecular wire **7** in the solid state by combining the electrode-free transient conductivity measurements throughtime-resolved microwave conductivity (TRMC), with transient absorption spectroscopy (TAS).[20] Upon excitation, clear conductivity transients were observed as shown in Figure 3a, with a delayed evolution of 10 μs and
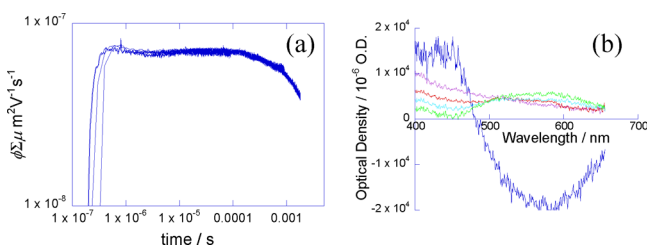

Figure 3. (a) Conductivity transient observed for **7** upon excitation at 355 nm with 2.3 × 10¹⁵ photons cm⁻². (b) Transient absorption spectra of **7** at 0.2 (blue), 1 (violet), 3 (red), 10 (green), and 25 μs (turquoise) after pulse irradiation at 355 nm with 2.4 × 10¹⁶ photons cm⁻².

ultralong lifetime over 1 ms. The delayed evolution is due to triplet−triplet annihilation processes on the conjugated backbones, which is addressed clearly and quantitatively by the conversion of the triplet state of **7** with Ru−porphyrin (400 nm) into the radical cations (620 nm) with an isosbestic point as shown in Figure 3b. The effects of oxygen on the triplet states were also observed for the transients, in addition to the second-order kinetic analysis of the triplet states under a variety of excitation conditions. (Figure S16). The complementary

transient absorption of triplet states and radical cations strongly suggest that the major charge carriers are positive holes on the backbone of **7** as indicated by the identical kinetic traces of the latter in the conductivity transients. On the basis of the molar absorption coefficient of the radical cations (7 × 10⁴ mol⁻¹ dm³ cm⁻¹), the estimates of charge carrier generation yield (ϕ) as 1.0 × 10⁻² lead the intramolecular charge mobility (μ^+ = 0.22 cm² V⁻¹ s⁻¹) along the conjugated backbone of **7**. This intramolecular charge mobility is comparable to that of the insulated all-organic poly(phenylene ethynylene) wire (insulated PPE: structure, see Figure S15b), which we reported previously (0.52 cm² V⁻¹ s⁻¹).[2b] Notably, **7** exhibited the same order (10⁻¹ cm² V⁻¹ s⁻¹) of intramolecular hole mobility as insulated π-conjugated polymers measured by TRMC.[2d,21] **7** was probably better at "relaying" charges, which led to enhanced charge transport and mobility.[22] This was because the Ru-pyridyl coordinate bonds were efficiently hybridized due to compatible energy levels and strong π-back-donation between the metal and ligand in the organic−inorganic hybrid orbitals. The observed conductivity of **7′** and **7″**, however, dropped over 2 orders of magnitude despite their identical backbone structures (Figure S17−S19). The jump of L in **7** (43.4 nm) from **7′** (8.10 nm) suggests a 5-fold higher locking (elongation) energy (ε) of the backbone of **7** based on the wormlike chain model ($L = \varepsilon/kT$),[19] and hence higher tensile stress (dξ) in the conjugated backbone of **7**. The electronic transmission and β value over the elongated conjugated backbone has been interpreted in terms of dξ,[23] and this gives the higher mobility of holes along the backbone of **7**. In addition, the lifetime of the charge carriers was 10-fold longer than that of insulated PPE (Figure S15a). The extremely long lifetime might come from the confinement of charges along the conjugated backbone by not only α-CD units[2b] but also the ring-peripherals of porphyrin units[16a] leading to the shielded conjugated backbones from an access of counter superoxide anions and/or hole scavengers such as amines.

A remarkable property of coordination polymer **7** is its interconversion between monomer and polymer states under certain conditions due to the reversibility of its coordinate bonds. Carbon monoxide (CO) underwent ligand exchange with the pyridyl groups on Ru(II) porphyrin complexes[24] of **7**, because of its stronger coordination ability, thereby yielding monomers **3** and **8**. The resulting monomeric porphyrin complex was expected to subsequently release CO upon UV irradiation to reform molecular wire **7**. Although molecular wire **7** was stable in toluene/EtOH at 55 °C,[25] decomplexation into monomers **3** and **8** occurred with 1 atm of CO, as confirmed by SEC. Recomplexation of the air stable monomers could subsequently be induced by UV irradiation of the resulting solution (Figure 4). The degree of polymerization after recomplexation (M_n = 2.7 × 10⁴) was perfectly consistent with that before decomplexation (M_n = 2.7 × 10⁴). Thus, in spite of the stability of molecular wire **7** and its monomeric components under normal conditions, monomer-to-polymer interconversion could be induced under specific conditions, i.e., either 1 atm of CO or UV irradiation. This property is unique to metal-containing molecular wires bearing coordinate bonds, and may be applied in molecular wiring applications such as recycling and self-healing of wiring materials, in addition to as sensory materials for CO.

In conclusion, we successfully synthesized a well-defined insulated bridging ligand **3**, which was a suitable building block for the metal-containing molecular wire **7**. Molecular wires
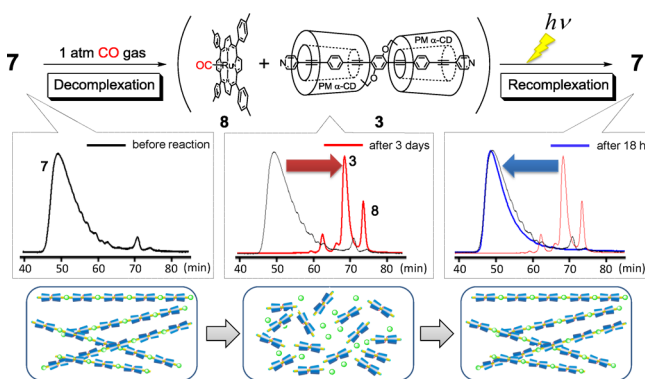
Figure 4. Schematic and SEC monitoring of polymer–monomer interconversion (eluent: THF).

prepared by complexation of the bridging ligand with Ru(II) porphyrins showed high intramolecular charge mobility in addition to high rigidity and linearity. To our knowledge, this is the first example of a one-dimensional coordination polymer that displays this level of charge mobility. Finally, we demonstrated the monomer-to-polymer interconversion of **7**. Such a transition is not feasible for conventional organic molecular wires based on covalent bonds, and this feature could be applied in efficient molecular wiring processes. These results indicated that metal-containing insulated molecular wires have potential for other applications beyond wiring materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed synthetic procedures, chromatogram and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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