

# One-Dimensional Organometallic Molecular Wires via Assembly of Rh(CO)<sub>2</sub>Cl(amine): Chemical Control of Interchain Distances and Optical Properties

Kwonho Jang, Il Gu Jung, Hye Jin Nam, Duk-Young Jung,\* and Seung Uk Son\*

Department of Chemistry and Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea

Received May 26, 2009; E-mail: sson@skku.edu

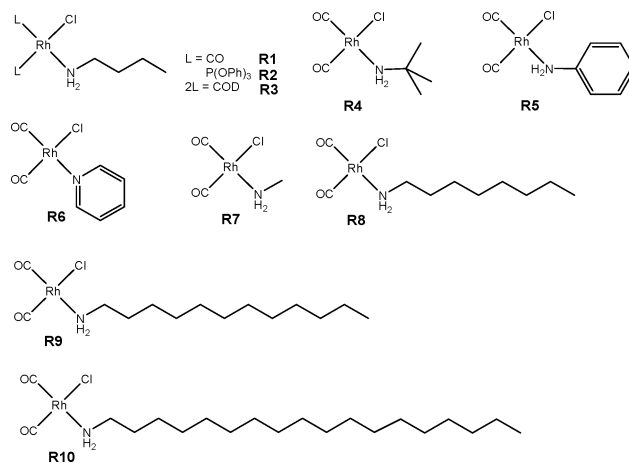
One-dimensional solid materials are one of the most attractive subjects in materials science because of their suitability for processing in practical applications and the relatively facile access to theoretical models.<sup>1</sup> For example, carbon-based materials such as carbon nanotubes and organic conducting polymers have had a great impact on materials science.<sup>2</sup> One-dimensional materials can be formed via electrical interactions between the molecular building blocks.<sup>3</sup> For example, it has been reported that the self-assembly of transition-metal complexes via metal–metal interactions can generate unprecedented one-dimensional chains via assembly of [Pt(CN)<sub>4</sub>]<sup>2-</sup>.<sup>4b</sup> These building blocks, which have square-planar geometry, showed weak but clear metal–metal interactions along the *z* axis (arbitrary notation). The origin of these peculiar interactions has been suggested to be a molecular orbital symmetry interaction.<sup>5</sup> Furthermore, the interesting optical and electrical properties of these one-dimensional materials, such as reflection of polarized light parallel to the chain, generating a metallic luster, have been intensively studied.<sup>4,6</sup> Currently, the assembled platinum compounds have been applied as new vapochromic sensor materials.<sup>7</sup>

Although assembly via molecular orbital symmetry interactions and the resultant properties have triggered academic curiosities in physics and materials science, the number of well-defined systems is still quite limited.<sup>8</sup> Usually, the known building blocks have a negative or positive charge, which is an obstacle in assembly because of electrostatic repulsion between the assembled building blocks.<sup>8,9</sup> In addition, the range of applicable ligands is quite limited.<sup>8</sup> In this work, we report a new series of molecular wires based on the assembly of *neutral* Rh(CO)<sub>2</sub>Cl(amine) building blocks (Chart 1) via Rh(I)–Rh(I) interactions along with control of the interchain distances. It is noteworthy that the structures of the building blocks with variable amine ligands determine the formation of self-assembly as well as the optical properties.

The building block Rh(CO)<sub>2</sub>Cl(*n*-butylamine) (**R1**) was prepared via reaction of [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> with *n*-butylamine in methylene chloride at room temperature as a representative among the selected building blocks. The following observations clearly indicated the assembly of building blocks through Rh(I)–Rh(I) interactions (see below). First, the solution of **R1** showed a concentration-dependent dramatic color change (Figure 1e), similar to those reported in the literature.<sup>10</sup> A 1.0 mM solution of **R1** in methylene chloride was yellow with maximum absorption peaks at 264 and 338 nm (Figure 1a,e). As the concentration was increased above 20 mM, the solution darkened, and a new broad absorption peak appeared at 500–700 nm. When the solvent was evaporated completely, there was a dramatic change in color, as shown in Figure 1a–c. Eventually, green-colored solids were obtained (Figure 1c), and the color change was reversible (Figure 1d).

Second, the solid of **R1** exhibited a metallic luster, a unique observation for chains assembled via metal–metal interactions.<sup>4</sup> As shown in Figure 1f, under bright light, the resultant materials reflected

Chart 1. Rhodium Building Blocks **R1**–**R10** Used in This Study



the light to show a golden metallic luster. In contrast, when the intensity of the light was reduced, the solid materials showed the original green-blue color (Figure 1c).

Third, the assembled structures were further investigated using X-ray powder diffraction (XRPD). The XRPD pattern of the assembled **R1**

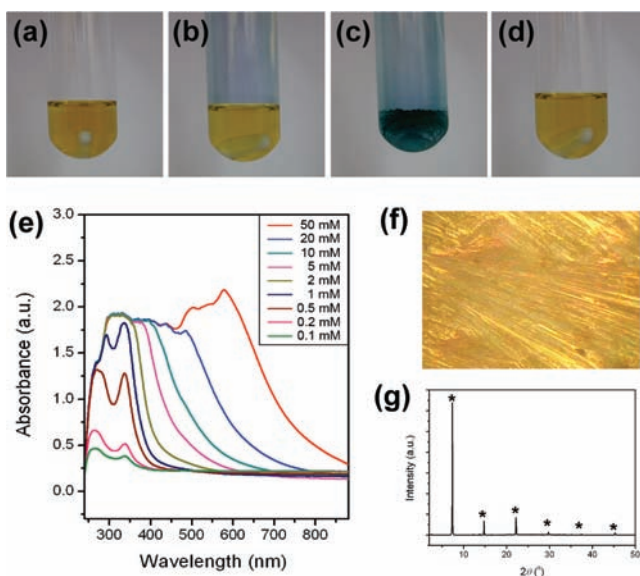
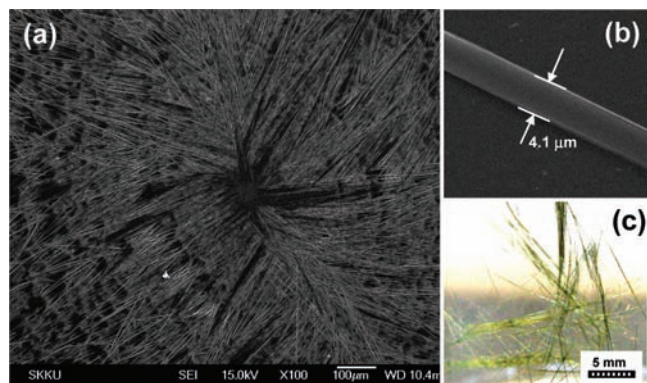


Figure 1. Photographs of (a) a 1.0 mM methylene chloride solution of **R1**, (b) the solution under vacuum evaporation, (c) after the removal of solvent, and (d) after redissolution of **R1** in methylene chloride. (e) Concentration-dependent UV–vis absorption spectra of **R1**. (f) Photograph showing the golden luster of the assembled **R1** materials under light from a 100 W halogen (HOYA-SCHOTT) lamp. (g) XRPD pattern of assembled **R1**.



**Figure 2.** SEM images of the self-assembled architecture of **R1** at (a) low and (b) high magnification. (c) Photograph of single-crystalline materials with golden luster that were grown by slow diffusion of *n*-hexane into a methylene chloride solution of **R1**.

structures showed very sharp and regular peaks corresponding to the interchain distance and clearly supports the facile assembly of **R1** [Figure 1g; see the Supporting Information (SI) for details].

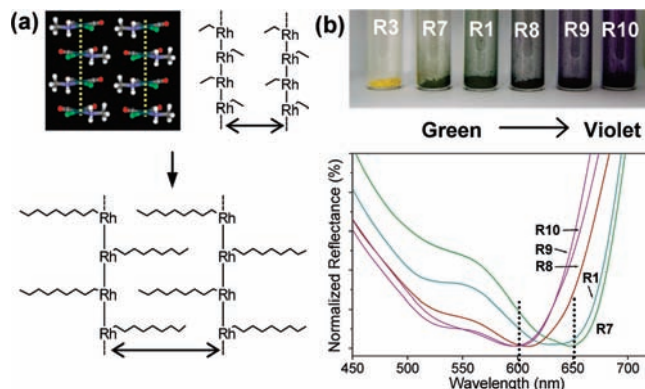
Fourth, the self-assembled materials were directly investigated by scanning electron microscopy (SEM). The solution of **R1** (50 mM) was prepared in methylene chloride. The self-assembled materials were obtained on bare glass via simple drop-casting of the solution. As expected, the SEM images showed the assembled one-dimensional wires with a thickness of  $\sim 4 \mu\text{m}$  and lengths of a several millimeters (Figure 2a,b). Also, the single-crystalline rods could be grown by slow diffusion of *n*-hexane into a methylene chloride solution of **R1** (Figure 2c).

With a synthetic procedure similar to that for **R1**, building blocks **R2** and **R3** were prepared from  $\{\text{Rh}[\text{P}(\text{O}i\text{Pr})_2\text{Cl}]_2\}$  and  $[\text{Rh}(\text{COD})\text{Cl}]_2$ , respectively. In addition, the selected seven building blocks (**R4**–**R10**) were prepared to investigate the amine-group dependence of the self-assembly behavior and optical properties (see Chart 1 and the SI). Interestingly, building blocks **R2**, **R3**, and **R4** (*tert*-butylamine) showed no assembly behavior, possibly because of steric effects due to the ligands. In sharp contrast with **R6** (pyridine), which showed no crystallinity in the XRPD analysis, building block **R5** (aniline) showed excellent self-assembly behavior, as evidenced by the concentration-dependent color change and XRPD analysis, indicating that the electronic effect of the ligands is also critical for achieving the assembled structure.

Building blocks **R7** (methylamine), **R8** (octylamine), **R9** (dodecylamine), and **R10** (octadecylamine) showed good assembly behavior. Figure 3a shows the crystal structure of the assembled **R7**, in which the Rh–Rh distances were 3.41 and 3.39 Å at room temperature. It is noteworthy that the Pt–Pt distances in the packed  $[\text{Pt}(\text{CN})_4]^{2-}$  are in the range of 3.09 and 3.75 Å.<sup>4</sup>

On the basis of the packing structure of the assembled **R7** (interchain distance 8.10 Å), we expected that the interchain distances would gradually increase with the alkyl chain length of the amine ligands (Figure 3a). According to XRPD pattern analysis, the interchain distances in assembled **R1**, **R8**, **R9**, and **R10** were 11.97, 15.88, 20.16, and 26.27 Å, respectively (see Figure S4 in the SI).

Dilute (1.0 mM) solutions of **R7**–**R10** showed the yellow color with nearly the same maximum UV–vis absorption peaks at  $264 \pm 2$  and  $338 \pm 1$  nm. In contrast, the solids of **R7**–**R10** displayed colors ranging from green to violet, with a gradual shift in the maximum UV–vis reflectance peaks from 650 to 600 nm (Figure 3b). It has been well-documented that the band gap of molecular wires increases as the metal–metal bond length increases.<sup>11</sup> Thus, it can be speculated



**Figure 3.** (a) Single-crystal X-ray structure of the assembled **R7** and cartoons showing alkyl amine ligand-dependent interchain distances. (b) Photographs showing the colors of the assembled **R7**, **R1**, and **R8**–**R10** and the corresponding reflectance spectra.

that the van der Waals interaction between the alkyl groups induces the elongation of the metal–metal bonds, resulting in the blue shift of the band gap. As far as we are aware, this is the first observation of a systematic change of the optical properties of molecular wires by direct introduction of designed ligands.

In conclusion, this study has introduced new and rare examples of *chemically controllable*, *neutral* molecular wires that can be applied to the fabrication of molecular devices.

**Acknowledgment.** This research was supported by the World Class University (WCU) Program (R31-2008-000-10029-0) and a Korea Research Foundation Grant (KRF-2005-005-J11901) funded by the Korean Government (MOEHRD).

**Supporting Information Available:** Experimental details, additional SEM images, XRPD patterns, characterization of new compounds, and crystallographic data for assembled **R7** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Palmer, L. C.; Stupp, S. I. *Acc. Chem. Res.* **2008**, *41*, 1674. (b) Zang, L.; Che, Y.; Moore, J. S. *Acc. Chem. Res.* **2008**, *41*, 1596. (c) Day, P. *Chem. Br.* **1983**, 306. (d) Little, W. A. *Phys. Rev. A* **1964**, *134*, 1416.
- (2) (a) Iijima, S. *Nature* **1991**, *354*, 56. (b) Heeger, A. J.; Kivelson, S.; Schrieffer, J. R.; Su, W. P. *Rev. Mod. Phys.* **1988**, *60*, 781.
- (3) (a) Tanaka, H.; Okano, Y.; Kobayashi, H.; Suzuki, W.; Kabayashi, A. *Science* **2001**, *291*, 285. (b) Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355. (c) Bryce, M. R.; Murphy, L. C. *Nature* **1984**, *309*, 119.
- (4) Underhill, A. E.; Watkins, D. M. *Chem. Soc. Rev.* **1980**, *9*, 429. (b) Krogmann, K. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 35.
- (5) (a) Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3553. (b) Miller, J. S. *Extended Linear Chain Compounds*; Plenum: New York, 1982; Vols. 1–3.
- (6) Underhill, A. E. *Philos. Trans. R. Soc. London, Ser. A* **1985**, *314*, 125.
- (7) (a) Buss, C. E.; Mann, K. R. *J. Am. Chem. Soc.* **2002**, *124*, 1031. (b) Grate, J. W.; Moore, L. K.; Janzen, D. E.; Veltkamp, D. J.; Kaganove, S.; Drew, S. M.; Mann, K. R. *Chem. Mater.* **2002**, *14*, 1058.
- (8) (a) Bera, J. K.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 4453, and references therein. (b) Tejel, C.; Ciriano, M. A.; Villarroya, B. E.; Gelpi, R.; López, J. A.; Lahoz, F. J.; Oro, L. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4084. (c) Prater, M. E.; Pence, L. E.; Clérac, R.; Finniss, G. M.; Campana, C.; Auban-Senzier, P.; Jérôme, D.; Candell, E.; Dunbar, K. R. *J. Am. Chem. Soc.* **1999**, *121*, 8005.
- (9) For rare examples of neutral molecular chains, see: (a) Mitsumi, M.; Goto, H.; Umebayashi, S.; Ozawa, Y.; Kobayashi, M.; Yokoyama, T.; Tanaka, H.; Kuroda, S.; Toriumi, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 4164. (b) Sun, Y.; Ye, K.; Zhang, H.; Zhang, J.; Zhao, L.; Li, B.; Yang, G.; Yang, B.; Wang, Y.; Lai, S.-W.; Che, C.-M. *Angew. Chem., Int. Ed.* **2006**, *45*, 5610.
- (10) Mann, K. R.; Lewis, N. S.; Williams, R. M.; Gray, H. B.; Gordon, J. G., II. *Inorg. Chem.* **1978**, *17*, 828.
- (11) Gliemann, G.; Yersin, H. *Structure & Bonding*, Vol. 62; Springer: Berlin, 1985.

JA904247E