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Syntheses and Electronic Behaviors of Osmium-Organic Moiety Hybrid Materials

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Several alternating osmium-organic moiety hybrid materials were prepared by reacting osmium chloride with organic diols and dithiols. Osmium-organic moiety units over 60% were thought to be involved in the materials. ESR and XPS spectral analyses indicated that an electron transfer from an organic phenylene moiety to the osmium atom with a partial reduction of the osmium atom took place.

Keywords osmium, hybrid material, synthesis, electron transfer

Introduction

Hybridization of organic and inorganic materials has attracted much attention in expectation of new types of functional materials with unique properties, and many investigations on coordinated hybrid materials have been reported (1–7). However, an electronic interaction in such coordinated materials is considered to be limited to a metal-ligand part. We have thought that the construction of covalent-bonded hybridization will be necessary for extending an electronic interaction over a networked framework.

In previous works on syntheses of networked alternating metal-organic moieties materials with covalent bonding, we reported that an electron transfer from organic moieties to metal took place (8–11). In the present work, as one of a series of metal-organic moiety hybrid materials, we described the syntheses and electronic behaviors of osmium-organic moiety hybrid materials (Scheme 1). Osmium atom is known to change valence number, and the hybridization between osmium atom and organic moieties may provide novel materials with an unique electronic nature.

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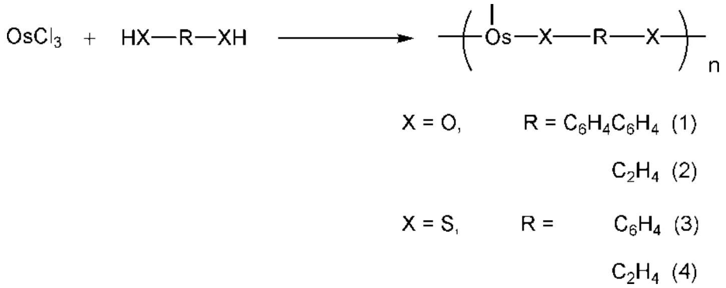


Scheme 1. Syntheses of materials.

Experimental

Reagents

Commercially available osmium chloride, 4,4′-dihydroxydiphenyl, ethyleneglycol, 1,4-benzenedithiol, ethylenedithiol, and anhydrous ethanol were used.

Syntheses

A solution of 4,4′-dihydroxydiphenyl (279 mg, 1.5 mmol) in anhydrous ethanol (20 ml) was added into a solution of osmium chloride (297 mg, 1 mmol) in anhydrous ethanol (20 ml), and the mixture was refluxed using activated aluminum oxide (15 g, 6.8 mol) in a cylindrical filter for 12 hours. The precipitate formed was collected, washed with anhydrous ethanol using a Soxhlet's extractor, and dried at 80°C under vacuum to obtain sample 1. Similar treatments of osmium chloride with ethylene glycol, 1,4-benzenedithiol, and ethylene dithiol gave samples 2, 3, and 4, respectively.

Apparatus

Elemental analyses were performed for C and H using Yanaco MT-6, for S and Cl using Yanaco YS-10, and for Os by inductively coupled plasma atomic emission spectrometry (ICP-AES) using Shimadzu ICPS-7500. TEM-EDX spectra were measured using Hitachi S-300. FT-IR spectra were taken using JASCO FT/IR-470 Plus. UV-VIS spectra were measured using Hitachi U-4000 spectrometer. Electron spin resonance (ESR) spectra

Table 1
Elemental analyses of the materials

Anal. found/Anal. calcd.				
Os (%)	C (%)	H (%)	S (%)	Cl (%)
25.7/40.8	12.0/46.3	2.86/2.53	—	10.7/—
16.7/67.9	1.40/12.9	1.34/2.16	—	14.3/—
41.3/47.5	15.3/27.0	1.55/1.51	13.6/24.0	10.7/—
18.2/57.9	6.07/11.0	1.54/1.84	11.9/29.3	11.9/—

Table 2
IR spectra of materials

Sample	Wave number (cm^{-1})
1	742, 1540 ($-C_6H_4-$)
2	2923 ($-C_2H_4-$)
3	843, 1629 ($-C_6H_4-$) 2922 ($-C-S-$)
4	2921 ($-C_2H_4-$)

were taken using Jeol JES-TE200 spectrometer. X-ray photoelectron spectra (XPS) measurements were done using Shimadzu ESCA-850 spectrometer.

Results and Discussion

The reactions of osmium chloride with diols and dithiols smoothly proceeded to give precipitates. There were several difficulties in analyzing the composition of the obtained materials, and the Os, C, and S contents observed by ICP and elemental analyses seemed too low (Table 1). At the ICP measurements, none of the sample could be dissolved completely in any acidic solutions to yield insoluble residues, which resulted in the lower Os content than the reality. As for C and S, incomplete combustion of the samples in an elemental analyzer seemed responsible, and it was confirmed by TEM-EDX measurement that the combustion residues after an elemental analysis treatment showed the presence of both C and S atoms. Moreover, chlorine was detected in every sample, indicating that the starting material, osmium chloride, had not completely reacted with diols and dithiols. Thus, the composition of the materials were estimated as follows. The degrees of progress in polymerization reaction (Scheme 1) were calculated from the observed chlorine contents to give the proportion of incorporated phenylene or alkyl moiety as 70, 60, 70, and 69% for the samples 1 to 4, respectively. Then the

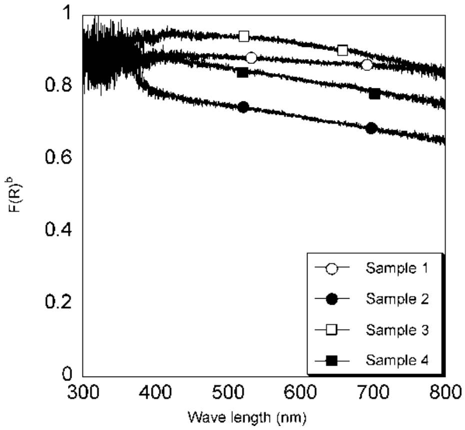


Figure 1. UV-VIS spectra of hybrid materials. a) Spectra were taken by using the diffusion reflecting method. b) F(R) is a coefficient of diffusion reflecting which is calculated by the following equation: $F(R) = \{1 - R(\lambda)\}^2/2R(\lambda)$, $R(\lambda)$: reflection rate of sample.

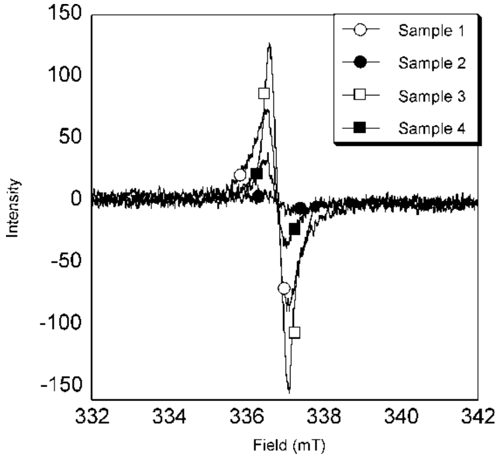


Figure 2. ESR spectra of hybrid materials.

content of each element was calculated (Table 1). The IR spectra of the samples showed the absorption frequencies due to the organic moieties (Table 2). These results together suggest that the osmium-organic moiety units over 60% were involved in the obtained materials.

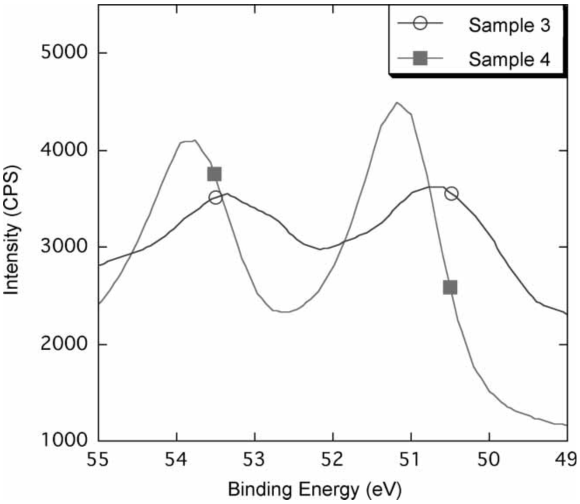
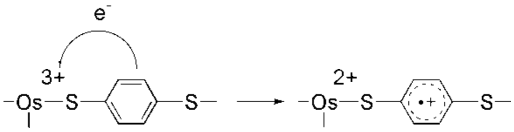


Figure 3. X-ray photoelectron spectra of hybrid materials.



Scheme 2. Plausible electron transfer process.

Every material was dark-colored, and the UV-VIS spectra were thus taken (Figure 1). Absorption bands over the entire range of wavelength were observed and rather higher intensities were shown in the phenylene-containing samples 1 and 3, suggesting that an effective electron excitation took place in the phenylene systems.

Figure 2 showed the ESR spectra of the samples, in which a peak at 337 mT ($g = 2.0032$) due to a free electron was detected and the peak intensities were larger in the order of $3 > 1 > 4 > 2$. Our understanding is that the electron transfer from the organic moieties to the osmium atom took place and the phenylene group caused the more effective electron transfer than alkyl group, resulting in the enhancements of the peak intensities of UV-VIS and ESR spectra. In order to examine electronic states on the metal atom of the materials, the XPS measurements of samples 3 and 4 were performed (Figure 3). A peak due to a 4f 7/2 orbital of the osmium atom in sample 3 appeared at 50.7 eV which was rather lower than that in sample 4 (51.2 eV), indicating that the electron density at the osmium atom in 3 was higher than that in 4. In other words, a partial reduction of Os is presumed to take place in sample 3, as shown in Scheme 2.

Spectra were taken by using 5 mg of sample. Measurement conditions: C. Field 337.00 mT, Power 1.00 mW, Sweep width 5 mT, Modulation width 0.5 mT, Time constant 0.1 s, Temp. room temp.

Non-monochromatic Mg-Ka(1253.6 eV) radiation was sourced from an X-ray gun operated at 8 kV and 30 mA.

Conclusions

We reported that, in alternating osmium-organic moiety hybrid materials, the electron transfer from organic moiety to osmium took place. Further characterizations of the obtained materials are planned as future works. We suggest that hybrid materials will be useful in many fields, for example, as electronic, magnetic, and optical devices.

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