

Synthesis and electronic behavior of a vanadium-phenylene-germanium ternary hybrid copolymer

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Organic and inorganic hybrid materials have been attracting much attention, and many works of metal-organic coordination polymerization have been reported for building up 2- and/or 3-dimensional networks [1–7]. We have considered that an alternative organic-inorganic hybrid copolymer with covalent bonding can provide a new type of composite material having a unique property compared with a coordination polymer, because the covalent bonding electron may be expanded beyond a metal–organic part, while the coordination bonding electron may be localized on a metal–ligand part. In previous works on the electronic natures of metal-organic moiety hybrid copolymers with covalent bonding, we showed that an electron transfer occurs from organic moieties to metal atoms, and the ability can be controlled by changing metals, organic moieties, and their combinations [8, 9]. In the present work, we describe the results of the electronic nature of a ternary, alternating vanadium–phenylene–germanium hybrid copolymer **4** (Fig. 1). Vanadium is known to vary valence number easily, and the oxide is used as a redox catalyst [10]. Germanium compounds are used as a semiconductor and an optical device [11]. Therefore, when an aromatic moiety is sandwiched between the vanadium atom and the germanium atom, novel hybrid material having a unique electronic property is expected to be provided.

Copolymers were synthesized in the following ways. Vanadium trichloride (0.8 mmol) reacted with 1,4-hydroquinone (0.4 mmol) in anhydrous ethanol (20 ml) in the presence of triethylamine (1.8 mmol) with stirring at room temperature for 3 h to give a vanadium–phenylene binary hybrid copolymer **1** (dark green-colored). Similar treatment of vanadium trichloride with 1,4-benzenedithiol gave a binary copolymer **2** (dark red-colored). Germanium tetrabromide (0.6 mmol) did not react with 1,4-hydroquinone but smoothly reacted with 1,4-benzenedithiol (1.2 mmol) in anhydrous ethanol (20 ml) in the presence of triethylamine (2.4 mmol) with stirring at room temperature for 3 h to give a germanium-phenylene binary hybrid copolymer **3** (white yellow-colored). A ternary hybrid

copolymer **4** was thus prepared in the following way. A mixture of germanium tetrabromide (0.6 mmol), 4-hydroxythiophenol (2.4 mmol), and triethylamine (4.8 mmol) in anhydrous ethanol (20 ml) was stirred at room temperature for 24 h, and into the reaction mixture was added a solution of vanadium trichloride (0.8 mmol) in anhydrous ethanol (10 mmol). The resulting mixture was stirred at room temperature for 3 h to give a precipitate, which was washed by anhydrous ethanol using a Soxhlet extractor and dried by heating under vacuum to obtain **4** (dark green-colored).

The elemental analyses and ICP measurements of copolymers were performed.¹ Vanadium contents in copolymers **1**, **2** and **4** were found to be higher than the calculated values, and the observed carbon and sulfur values in **1** and **2** were considerably smaller than the calculated values. The IR spectra of **1–4** showed an absorption band due to the phenylene group, but a band due to $\nu_{\text{V=O}}$ of V_2O_5 was also detected for **1**, **2**, and **4**.² The formation of V_2O_5 is considered to be due to a reaction with a small amount of water contained in ethanol during either a reaction process or an after-treatment, and this may arise the higher observed vanadium contents in **1**, **2**, and **4**, and also the lower observed carbon and sulfur contents in **1** and **2**. The amounts of the metal-phenylene units in copolymers were thus unable to be determined. It is noted that the phenylene units involved in copolymers were calculated using the observed carbon contents to be 12% for **1**, 12% for **2**, 74% **3**, and 81% for **4**, respectively. The XPS measurements of the copolymers showed that a peak of a 2p of vanadium in **1** appeared at 515.9 eV, which corresponds to a $\text{V}^{5+}\text{–O}$ bond energy, indicating the formation of V_2O_5 in **1**. However, a peak of a 2p of vanadium in **4** appeared at 514.1 eV, which corresponds to a $\text{V}^{3+}\text{–O}$ bond energy. On the other

¹ Found/Calcd. (%): **1** V 39.8/23.9, C 6.2/50.7, **2** V 41.8/19.5, C 4.8/41.4, S 3.2/36.81 **3** Ge 14.9/20.6, C 33.4/41.4, S 24.2/36.0; **4** V 18.7/10.7, Ge 7.4/11.4, C 31.8/45.2, S 13.7/20.1.

² IR spectra (cm^{-1}): **1** 1470, 1086, 988, 874; **2** 1469, 988, 867, 674; **3** 1472, 817, 689; **4** 1491, 990, 831, 678.

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Research grant-FAPER.

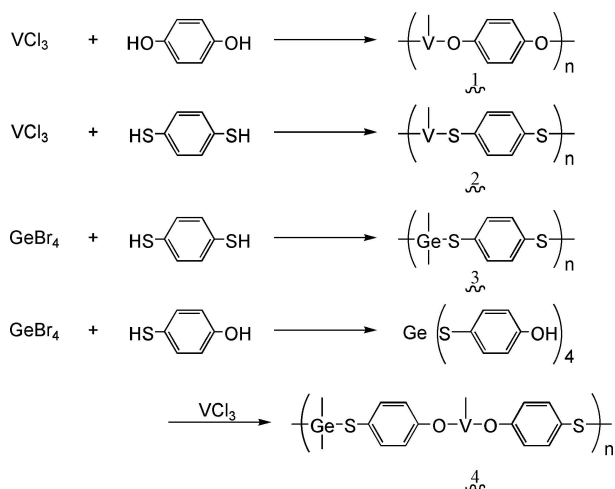


Figure 1. (a) The calculation method was STO3-G. (b) The dimension of energy level is eV.

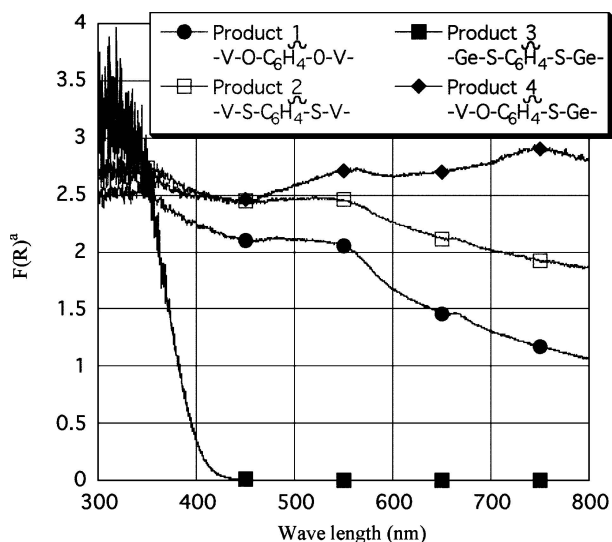


Figure 2. The UV-VIS spectra of the hybrid copolymers (a) The spectra were taken by using the diffusion reflecting method. (b) $F(R)$ is a coefficient of diffusion reflecting which is calculated by the following equation: $F(R) = \{1 - R(\lambda)\}^2 / 2R(\lambda)$, $R(\lambda)$: reflection rate of sample.

hand, a peak of a 3d of germanium in both **3** and **4** appeared at 30.2 eV, which correspond to a $\text{Ge}^{4+}\text{-S}$ bond energy. Therefore, a main part in **4** is a vanadium (III)—phenylene—germanium (IV) unit.

The UV-VIS spectra of copolymers (Fig. 2) showed that **4** had absorption bands over the whole wavelengths with the highest intensity, suggesting that an effective electron excitation takes place in **4**. ESR spectra measurements (Fig. 3) showed that copolymers **1** and **2** had a large broad peak due to V_2O_5 at 220–450 mT ($g = 1.974$). In the case of **4**, however, a V_2O_5 peak was rather small compared with **1** and **2**, and a sharp peak at 337 mT ($g = 2.003$) due to an organic radical was also observed, whose intensity was higher than that in **3**. From the findings, we wish to postulate that an electron transfer between the phenylene group and metal takes place in **3** and **4**, and a combination of metals increases the degree of the electron transfer.

In order to examine the electron transfer process theoretically, *ab-initio* calculations by using copolymer models were carried out (Fig. 4 and Table I). It was found that both the vanadium atom and the

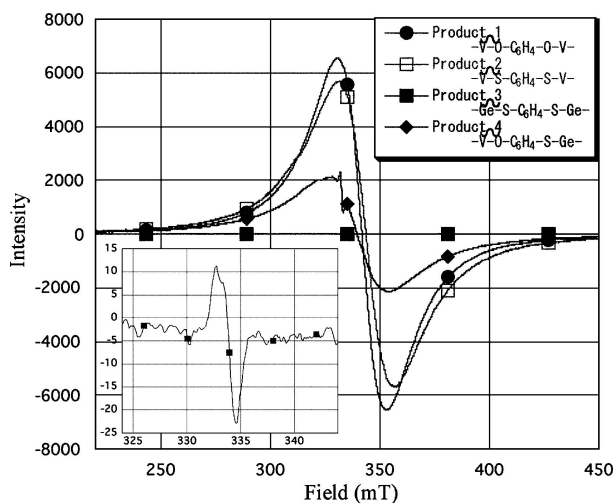


Figure 3. The ESR spectra of the hybrid copolymers. The spectra were taken by using 10 mg of sample. The measurement conditions: C. Field 337.00 mT, Power 1.00 mW, Sweep Width 250 mT, Modulation Width 0.5 mT, Time Constant 0.1 s, Temp. room temp.

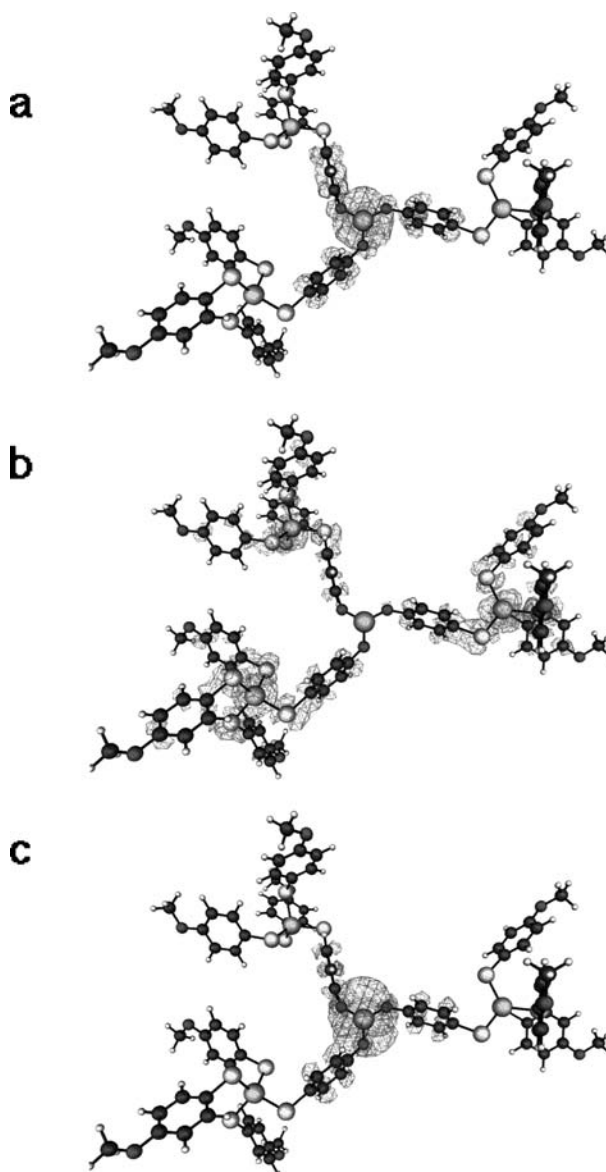


Figure 4. HOMO/LUMO/LUMO + 1 distribution of the copolymer **4** models. (a) HOMO, (b) LUMO, and (c) LUMO + 1.

TABLE I. HOMO/LUMO and LUMO+1 energy levels of the copolymer models (eV)

Copolymer	HOMO	LUMO	ΔE	LUMO + 1	$\Delta E + 1$
1	-5.61	6.23	11.84	-	-
2	-5.09	5.91	11.00	-	-
3	-7.13	4.65	11.78	-	-
4	-5.41	5.63	11.04	6.29	0.66

phenylene group use their HOMO, the vanadium atom uses LUMO + 1, and both the germanium atom and the phenylene group use LUMO. And, further, the value of HOMO / LUMO energy difference ΔE of **4** is smaller than that of **3**, and a small LUMO/LUMO+1 energy difference $\Delta E + 1$ of 0.7 is calculated. Therefore, it is reasonably proposed that the electron transfer in **4** is achieved by a two-step electron excitation from the HOMO of the phenylene group to the LUMO + 1 of the vanadium atom through the LUMO of the germanium atom. This transfer principally corresponds to a PSII-PSI electron transportation of a photosynthesis of plants.

We believe that such multi-stage electron excitation will be achieved by various combinations of organic moieties and metals having different natures, and will provide a source for many useful materials, for ex-

ample, optical, magnetic, and electronic devices, an artificial photosynthesis catalyst, and so on.

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Received 22 July

and accepted 8 November 2004