

Synthesis and electronic behaviors of alternating indium–organic moiety binary hybrid copolymer

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Several binary indium–organic moiety hybrid copolymers were synthesized and their electronic behaviors were examined. The results of UV-VIS and ESR spectra analyses and *ab-initio* calculation showed that an electron transfer takes place from the organic moiety to the indium atom. When the copolymer of bis(4-hydroxyphenyl)sulfone system was cross-linked at the indium center by reacting with bipyridyl, the cross-linked copolymer showed a higher degree of the electron transfer.

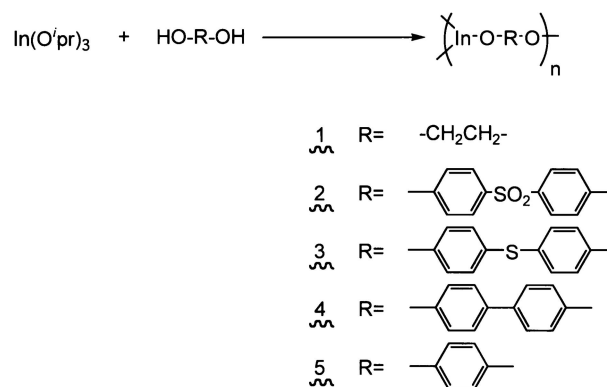
Organic and inorganic hybrid materials have been attracting much attention as materials having novel properties [1, 2], and many studies focusing on metal–organic coordination polymerization have been reported for building up two- and/or three-dimensional networks [3–9].

We have considered that copolymers with covalent metal–organic structure will provide novel composite materials with new electrical, magnetic, and/or optical properties, because an electron interaction between an inorganic element and an organic moiety is expected to be extended beyond the metal–organic bond, and also, to be controlled by changing the organic moiety in a framework. In previous papers on networked hybrid copolymers having covalent metal–organic units, an electron transfer was shown to take place from organic moieties to such metal atoms as Ti, Zr, Y, Ta, and Yb [10–15].

In the present study, we wish to report the syntheses and the electronic behaviors of alternating indium–organic moiety binary hybrid copolymers (Scheme 1). Indium is an important key atom in the field of electronic and photochemical industries, and thus, an indium–organic moiety hybrid material is expected to show unique properties.

A typical example of the synthesis of copolymer is as follows. A mixture of indium isopropoxide (0.3 mmol) and ethylene glycol (0.9 mmol) in anhydrous

1,4-dioxane (20 mmol) was refluxed for 3 h to yield a precipitate, which was washed with anhydrous 1,4-dioxane and dried under vacuum to obtain copolymer **1**.



Scheme 1

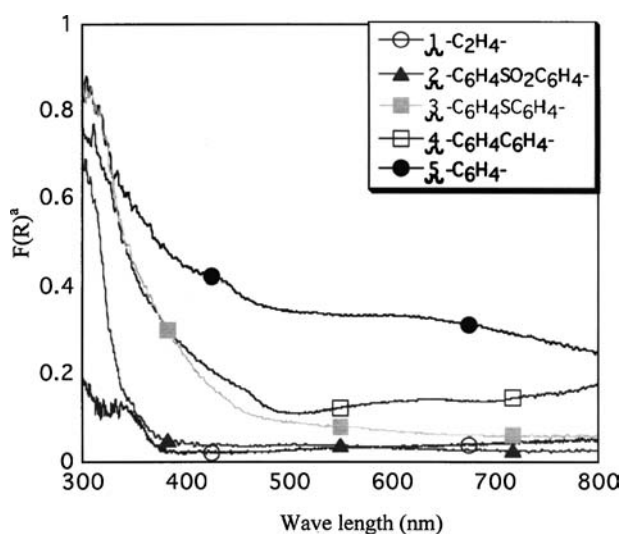


Figure 1 The UV-VIS spectra of the hybrid copolymers. The spectra were taken by using the diffusion reflecting method. $F(R)$ is a coefficient of diffusion reflecting which is calculated by the following equation: $F(R) = \{1 - R(\lambda)\}^2 / 2R(\lambda)$, $R(\lambda)$: reflection rate of sample.

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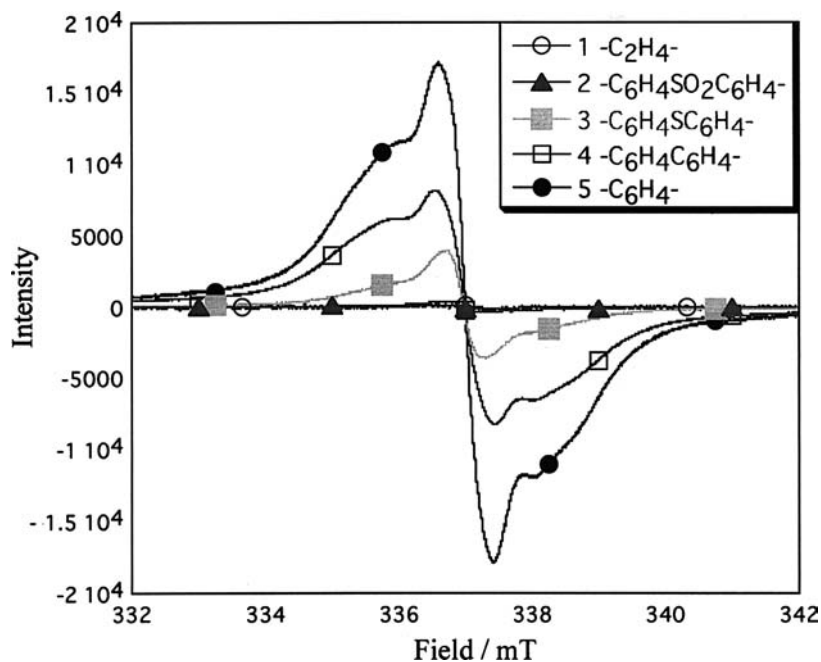


Figure 2 The ESR spectra of the hybrid copolymers. The spectra were taken by using 10 mg of sample. The measurement conditions: C. Field 337.00 mT; power 1.00 mW; sweep width 10 mT; modulation width 0.5 mT; time constant, 0.3 s; temperature, room temperature.

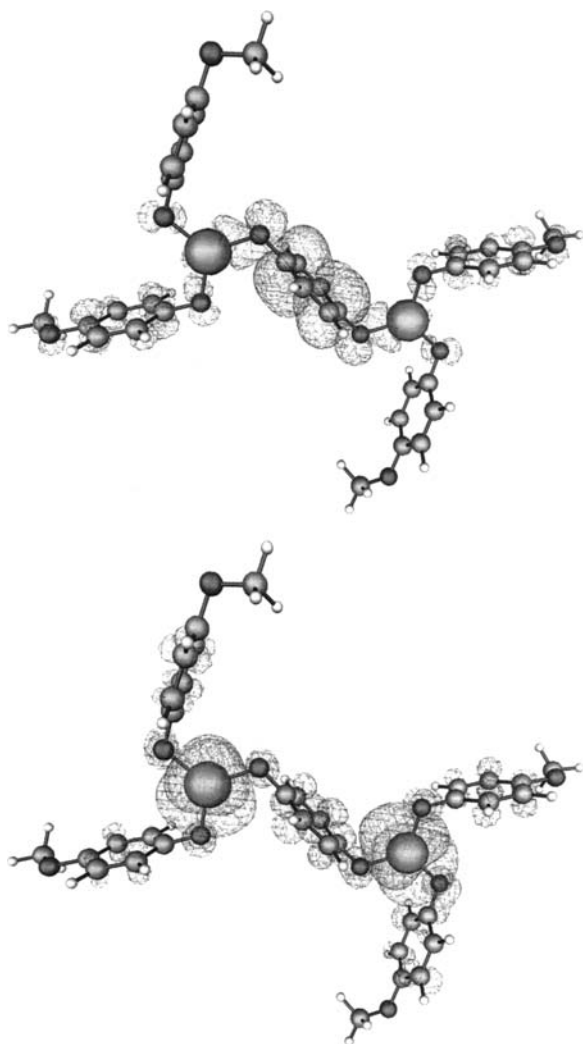


Figure 3 HOMO/LUMO distribution of the phenyl system models: (a) HOMO and (b) LUMO.

The ICP and elemental analyses of the copolymers were performed,¹ however, disagreement between observed and calculated values was obtained, perhaps due to an incomplete substitution reaction. It is noted that the percentages of the introduction of organic moieties for **2** and **3**, were calculated from the observed sulfur contents to be 57 and 56%, respectively. FT-IR spectral analyses showed the absorption bands of aryl groups at 1500–1600 cm^{-1} for **2–5**, the sulfide group at 687 cm^{-1} for **3**, and the methylene group at 2800–3000 cm^{-1} for **1**. On the basis of these findings, the binary indium–organic units can be believed to be formed in the copolymers.¹

The colors of the copolymers varied by changing organic moieties, and the UV-Vis spectra of the copolymers were thus taken (Fig. 1). Copolymer **5** showed the absorption bands over the whole wavelength range, and the order of intensities was $5 > 4 > 3 > 2 > 1$. Our explanation is that an electron transfer may take place between the phenylene group and the indium atom. Thus, in order to verify this cause, the ESR spectra of the copolymers were obtained (Fig. 2), and a peak at 337 mT due to an organic free electron was observed, and further, the peak intensities were found to be in the order of $5 > 4 > 3 > 2 > 1$.

In order to evaluate the electron transfer process theoretically, *ab-initio* calculations by using a model corresponding to copolymer **5** was performed (Fig. 3). HOMO uses the phenylene moiety and LUMO mainly uses the indium atom, therefore, the HOMO/LUMO orbital combination is considered to cause the effective electron transfer

¹ Found/Calcd. (%): I: In 41.8/56.0; C 12.8/17.6. II: In 26.6/22.9; C 26.4/44.4; S 5.5/9.5. III: In 28.5/25.3; C 26.0/50.2; S 5.9/10.6. IV: In 28.0/29.4; C 20.5/55.3. V: In 31.5/41.5; C 32.4/39.0.

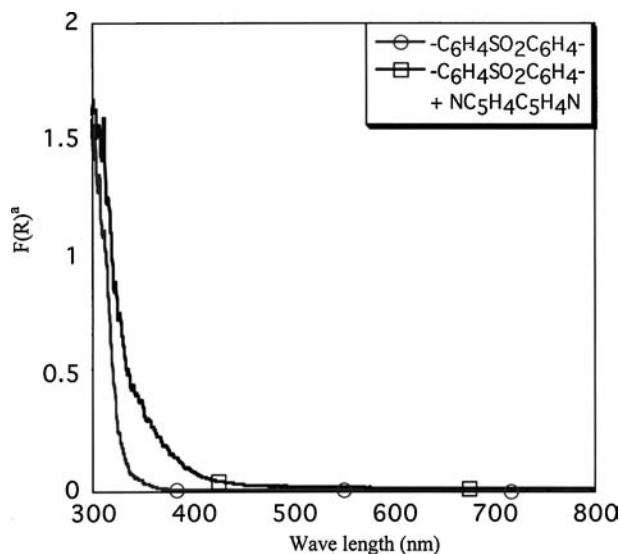


Figure 4 The UV-Vis spectra of the hybrid copolymers. ^aThe spectra were taken by using the diffusion reflecting method. ^b $F(R)$ is a coefficient of diffusion reflecting which is calculated by the following equation: $F(R) = \{1 - R(\lambda)\}^2 / 2R(\lambda)$, $R(\lambda)$: reflection rate of sample.

from the phenylene moiety to the indium atom, resulting in the formation of a stable radical cation on the phenylene moiety.

It is known that an indium compound has an sp^2 -type plane configuration. When such a planar indium atom in a copolymer is linked by a cross-linker forming a multi-dimensional network, an effective electron movement may appear through the networked framework. Thus, the cross-linking reaction of **2** with bipyridyl was performed. Into a reaction mixture of indium isopropoxide (0.3 mmol) and bis(4-hydroxyphenyl) sulfone (0.9 mmol) in anhydrous 1,4-dioxane (20 ml) under refluxing for 3 h was added bipyridyl (0.9 mmol), and the mixture was refluxed for 3 h to yield a light yellow-colored precipitate, which was washed with anhydrous 1,4-dioxane by using a Soxhlet extractor and dried under a vacuum. Introduction of the cross-linker into **2** was confirmed with the presence of nitrogen by elemental analysis,² and also of $-CH_2-$ absorption bands at $2800\text{--}3000\text{ cm}^{-1}$ by IR spectral measurement. Absorption bands of UV-Vis spectra of the cross-linked product were found to shift to longer wavelengths (Fig. 4). ESR spectra measurement showed that, in the cross-linked product, a significant increase of the peak intensity due to the organic free electron at 337 mT was detected in comparison with **2** (Fig. 5). These findings indicate that the ability of the electron transfer is significantly increased by cross-linking with an aromatic cross linker.²

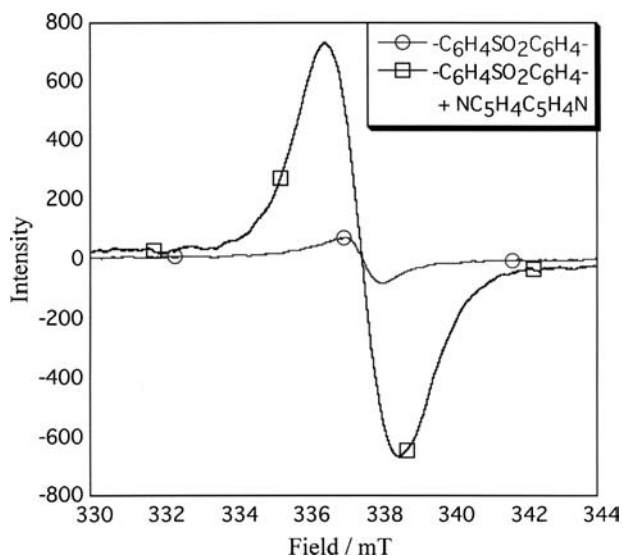


Figure 5 The ESR spectra of the hybrid copolymers. The spectra were taken by using 10 mg of sample. The measurement conditions: C. Field 337.00 mT; power 1.00 mW; sweep width 10 mT; modulation width 0.5 mT; time constant 0.3 s; temperature room temperature.

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² Found (%). In 23.77, C 32.62, N 1.03.