Synthesis of Yttrium−Organic Hybrid Networks

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Organic and inorganic hybrid materials have been attracting much attention as materials with novel properties,[1,2] and many investigations of metal−organic coordination polymerization have been reported for building up 2- and 3-dimensional networks.[3−8]

In 1990, Burch reported the synthesis of an amorphous precipitate by reacting $Ti(NMe_2)_4$ with hydroquinone aimed at constructing a porous high-surface-area material,[9] and Wolczanski et al. made clear that the hybrid material produced upon alcoholysis of $Ti(O^iPr)_4$ with hydroquinone has a covalent three-dimensional titanium(IV)−quinone network.[10] Alternative organic−inorganic hybrid materials are new types of multiaggregated composite materials with unusual properties because the solid-state structure of the hybrid materials can be controlled by changing both inorganic element and organic moiety as well as the solvent.

In this work, we report the syntheses of networked organic−inorganic hybrid materials from the reaction of yttrium isopropoxide with organic diols and also the formation of nanosized half-transparent particles. Yttrium compounds are widely used as optical, electric, and magnetic devices, e.g., a laser element and a fluorescent substance for oxide, and a permanent magnet for alloy. If the electronic interaction between yttrium atoms can be controlled by the organic moieties in the alternative network, we can provide novel hybrid materials with unique electronic properties.

A toluene solution of commercially available yttrium isopropoxide was used. Other reagents and solvents were purified by standard procedures.

Into a solution of 1 mmol of yttrium isopropoxide in 10 mL of anhydrous THF was added dropwise a solution of 1.5 mmol of organic diol in 10 mL of anhydrous THF, and the mixture was stirred at room temperature for 3 h. The precipitate was collected, washed with anhydrous THF by Soxhlet extraction, and dried with heating under vacuum. UV−vis spectra of the products were taken by using a Hitachi U-4000. ESR spectra were taken by using a JEOL TE-200. TEM images were taken by using a JEOL JEM-3010. The reactions of yttrium isopropoxide with organic diols proceeded smoothly to give the powders.

To determine the ratio of organic moiety against yttrium content in the powders, elemental analysis of product 5 revealed a ratio of 1.43,[11,12] which is slightly small in comparison with the values of the ideal ratio, 1.5. The IR spectra of product 5 showed peaks due to the phenyl and sulfonyl groups of bis(4-hydroxyphenyl) sulfone at 1584 and 1142 cm^{-1}, respectively. These results show the successful formation of the nearly alternating hybrid structure.

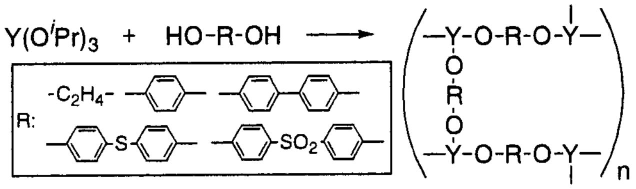

Figure 1.

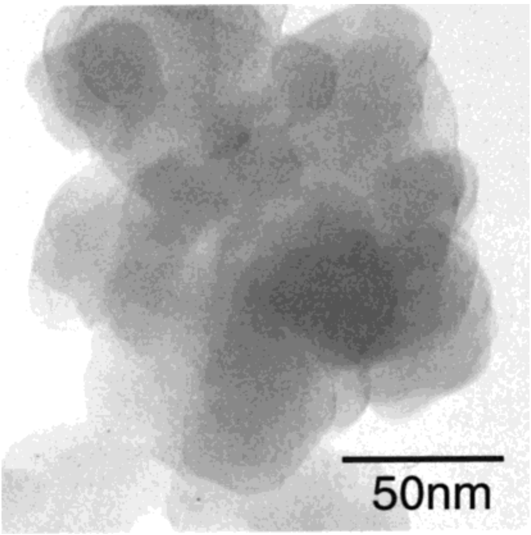

Figure 2. TEM image of product 4. Measurement conditions: AcV, 300 kV; magn, 300 K.

To see the size and form of the powders, their TEM images were taken, and every image was found to be essentially the same. A typical example is shown in Figure 2, indicating that the diameter of the particle was 10−50 nm. Another interesting finding in Figure 2 is that an electron beam from an electron microscope penetrates through the particles, and the overlapped parts of the particles become dim, suggesting that the particles are half-transparent. This seems to indicate the presence of hollow regions in the particles.

The colors of the powders were interestingly found to vary with the organic moieties, and thus their UV−vis spectra were taken. As shown in Figure 3, the absorption bands of the powders obtained by the reactions with aromatic diols, especially hydroquinone and 4,4′-biphenol, shift to longer wavelengths. One possible assumption is the occurrence of an electron transfer from the aromatic moieties to yttrium atom. Therefore, the ESR spectra of the powders were taken, and the results are shown in Figure 4, indicating that a peak at $g = 2.0024$ due to free electrons was detected, and the intensities increased in the order of $C_6H_4SC_6H_4 > C_6H_4C_6H_4 > C_6H_4 > C_6H_4SO_2C_6H_4 > CH_2CH_2$.

To evaluate the electron transfer theoretically, ab initio calculations were done by using the $Y(OROMe)_3$ models, and the results of RHF/STO-3G calculations are as follows.[13] Energy differences of HOMO/LUMO for the

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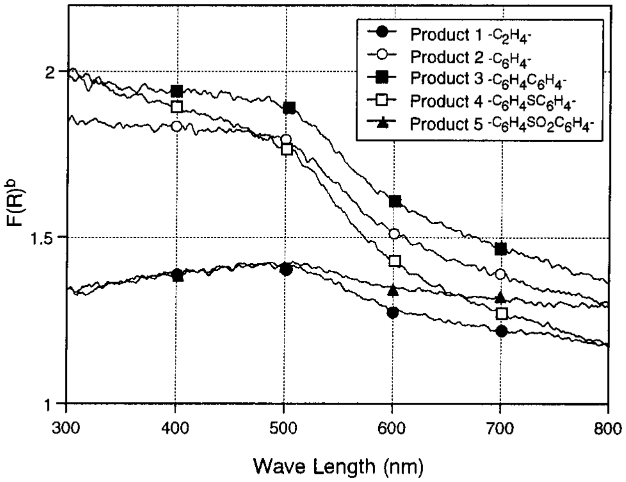

Figure 3. UV–vis spectra of the hybrid copolymers. The spectra were taken by using the diffusion reflecting method. $F(R)$ is a coefficient of diffusion reflecting which is calculated by the following equation: $F(R) = \{1 - R(\lambda)\}^2/2R(\lambda)$, where $R(\lambda)$ is the reflection rate of the sample.

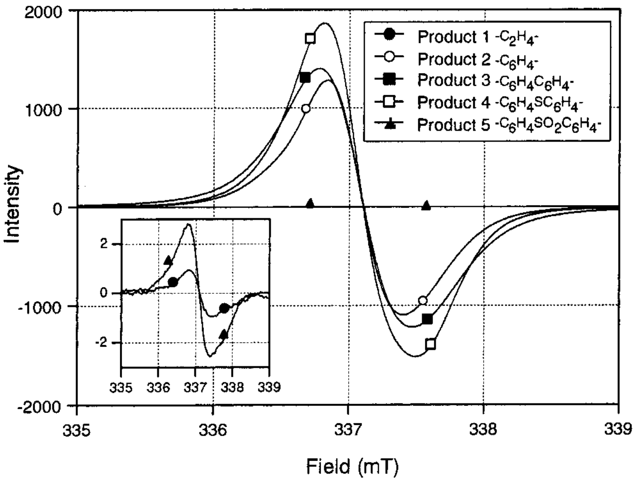

Figure 4. ESR spectra of the hybrid copolymers. The spectra were taken by using 1 mg of sample. Measurement conditions: C.field, 337.00 mT; power, 1.00 mW; sweep width, 5 mT; modulation width, 0.5 mT; time constant, 0.1 s; temp, room temperature.

aromatic series are lower than those for the nonaromatic series, namely C_6H_4 (0.322) < $C_6H_4C_6H_4$ (0.332) < $C_6H_4SC_6H_4$ (0.341) < $C_6H_4SO_2C_6H_4$ (0.359) < CH_2CH_2 (0.439).[14] This order comparatively corresponds to that of ESR spectra, suggesting that the free electron observed in the ESR spectra is caused by HOMO/LUMO excitation. Nevertheless, the order of energy difference for product 2 (C_6H_4 moiety) was not necessarily united to the order of ESR spectra. This may be caused by some degradation of the product with water or oxygen molecules in air because the black color initially observed for the product changed to brown color during standing in contact with water moisture and to blackish blue in contact with oxygen molecule atmosphere.

It is noteworthy that the calculations show the use of the orbital of the organic moiety for HOMO and that of yttrium atom for LUMO, resulting in an electron transfer from the organic moiety to yttrium atom with reduction of the yttrium oxidation state from +3 to +2. It was thus found that the degree of electron transfer can be controlled by changing organic moieties, and therefore electronical properties of the hybrid material will depend on the organic moieties.

In conclusion, we have succeeded in synthesizing novel networked alternating organic–yttrium hybrid materials with semitransparent forms. The hybrid materials show the electron-transfer character, and the ability is controlled by changing the organic moieties. We believe that similar alternating organic–inorganic hybrid materials can be produced from the reactions of various metal alkoxides with diols and/or dithiols and also from the reactions of various metal halides with sodium and/or lithium salts of diols and/or dithiols and that such hybrid materials having novel electronic properties will be widely useful in many fields, for example, as electric, magnetic, and optical devices.

References and Notes

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(11) Anal. Found: Y, 18.57%; S, 9.50%.
(12) The smaller part would be composed of an extraneous substance, perhaps yttrium oxide, which may be formed from the second reaction of either the formed polymer or remaining yttrium isopropoxide with moisture while after-treating the reaction mixture because a slight color change on the surface of the precipitate was noticed in the operation.
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(14) The dimension of energy level is hartree (1 hartree = 4.36 × 10^{-18} J).

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