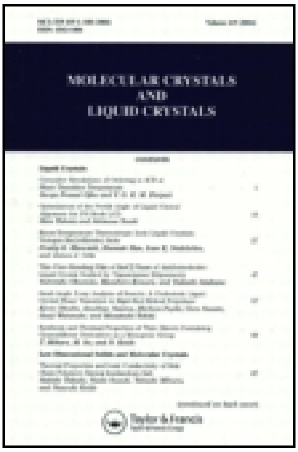

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Stepwise Synthesis of a Mixed Valent Fe(II)-Fe(III) Complex in Cast Multibilayer Films[1]

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STEPWISE SYNTHESIS OF A MIXED VALENT Fe(II)-Fe(III) COMPLEX IN CAST MULTIBILAYER FILMS[1]

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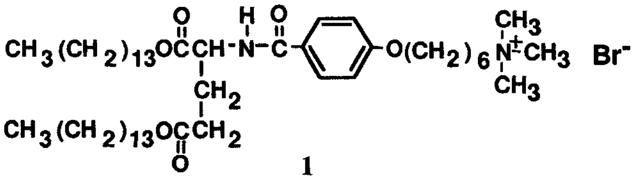
Abstract A mixed valent complex of μ-cyanide Fe(II)-Fe(III) was prepared by stepwise synthesis at the interlayer of multibilayer cast films. The Fe(II)-Fe(III) complex showed altered absorption characteristics in the interbilayer from those of bulk Prussian Blue, probably due to its geometrically confined structure.

INTRODUCTION

The ability to synthesize mesoscopic inorganic materials is of crucial importance not only in the development of novel materials but also for understanding their structure-dependent properties. The use of organized organic assemblies to direct mesoscopic inorganic structures under mild conditions is attracting current interests.[2] We have reported that cast films of synthetic bilayer membranes provide ordered molecular architectures at the molecular as well as macroscopic level.[3,4] The interbilayr space of cast films has been successfully used as two-dimensional matrices for the preparation of quantum-sized CdS particles[5] and a novel $Cd_4Br_{12}S$ cluster.[6] In addition, dimension-control of lead halide clusters was achieved by taking advantage of geometrical matching between regularly positioned cationic head groups and anionic clusters.[7,8] More recently, a two-dimensional cyanide-coordinated complex of $Ni(CN)_4$-Cu(II) was prepared by stepwise synthesis at the interbilayer space of cast films, and it displayed a distinct single-crystal-like anisotropy.[9] In the latter system, the chemical structure of the metal cyanide and its pre-organization at the ordered interbilayer space are crucial to the structural control of the μ-cyanide polymer. It is of importance to extend this stepwise technique to synthesis of mixed valent cyanometalates, since they provide technologically important characteristics such as molecular magnetism[10], optoeletronic properties[11] and catalysis.[12] In addition, there has been no report that mixed valent complexes are immobilized at the interbilayer space. It is of interest if the optical properties of the complex formed is affected by the bilayer matrix. In the present paper, we describe the synthesis of mixed-valent $Fe(CN)_6$-Fe(III) complex at the interbilayer space of cationic amphiphile **1**.



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EXPERIMENTAL METHOD

Preparation of amphiphile **1** was described elsewhere.[13] Templated synthesis of mixed valent $Fe(CN)_6$-Fe(III) complex in cast films was conducted according to the reported procedure.[9] Self-supporting, multibilayer films were prepared by casting aqueous bilayer dispersions of **1** onto quartz plates or fluorocarbon membrane filters as described previously.[4-9] Anionic hexacyano-ferrate(II) $[Fe(CN)_6^{4-}]$ was chosen as μ-cyanide precursor. Cast films of **1** were first dipped in aqueous potassium hexacyanoferrate (II) (100 mM, for 5 days at room temperature), to effect anion exchange with bromide ion. After rinsing with deionized water, the film (abbreviated as **1-Fe(CN)$_6$**) was dipped in aqueous ferrous nitrate (100 mM, for 5 days at 5 °C), and then in pure water for 10 min to remove unreacted Fe^{3+} ion (film **1-Fe(CN)$_6$-Fe**). Atomic absorption analysis (instrument : Seiko SAS-760) was conducted for cast films dispersed by ultrasonication in 0.1 N hydrochloric acid which contains 0.25 % sodium hypochlorite. The X-ray diffraction (reflection method) was carried out on a Rigaku Denki Rotaflex RAD-R-32 at room temperature.

RESULTS AND DISCUSSION

Incorporation of anionic hexacyanoferrate(II) in the first step was confirmed by IR spectra (KBr) of the film **1-Fe(CN)$_6$** (ν_{CN} at 2045 cm^{-1}). Atomic absorption analysis gave an Fe content that corresponds to the Fe : **1** ratio of 1 : 3.9 for **1-Fe(CN)$_6$**. The observed ratio clearly indicates the quantitative exchange of bromide ion with hexacyanoferrate(II) ion, that is electrostatically bound to the cationic interbilayer space of **1**. Similar stoichiometric exchange has been reported for lead halide clusters,[7] anionic porphyrins,[14] and myoglobin.[15]

After the second dipping, the resulting film turned deep blue and showed a CN stretching band at 2080 cm^{-1}, which is shifted to a higher wavenumber from that observed for the **1-Fe(CN)$_6$** film. This shift indicates that hexacyanoferrate(II) ion preorganized in the interbilayer reacted with subsequently introduced Fe^{3+} ion to form a mixed valent μ-cyanide complex.[16] A similar IR spectral shift has been observed for composite cast film of **1-Ni(CN)$_4$-Cu(II)**.[9] When the stepwise dipping was conducted in the reversed order (dipping first in aqueous Fe^{3+} and then in aqueous hexacyanoferrate) or when a co-cast film of 1-Fe(NO)$_3$ (ratio of **1** : Fe^{3+} = 2 : 1) is dipped in the second solution, Fe^{3+} ion leaked substantially from the cast films during the final dipping step. Therefore, the preorganization of anionic hexacyano-ferrate at the interlayer is prerequisite for the template synthesis.

A cast film of **1-Fe(CN)$_6$-Fe(III)** gave series of Xray diffraction patterns that correspond to a long spacing of 42.2 Å with up to 9 th order (Fig.1). It is clear that the ordered multibilayer structures remain intact during the complex formation. In addition, a fairly strong diffraction peak observed at $2\theta = 17.5°$ (5.1 Å) is ascribed to Fe(II)-CN-Fe(III) framework formed in the cast film.[17]

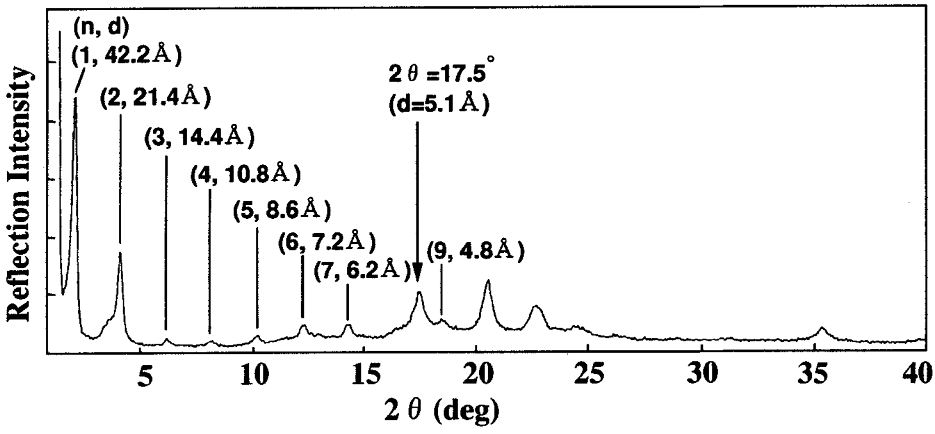

FIGURE 1. Reflection Xray diffraction pattern of **1-Fe(CN)$_6$-Fe(III)** cast film.

Absorption spectrum of **1-Fe(CN)$_6$-Fe(III)** dissolved in chloroform is shown in Fig. 2(a). A broad absorption peak centered at 750 nm is related to intermetal charge transfer from Fe(II) to Fe(III).[18] Interestingly, this absorption λ_{max} is red-shifted by ca. 50 nm from those of the following Prussian Blue's : electrochemically prepared on electrodes,[19] synthesized in aqueous poly(vinylammonium),[20] and co-cast with hexadecyltrimethylammonium from chloroform.[21] When an aqueous solution of **1** (1 mM) was co-cast with an equimolar amount of pre-mixed aqueous $K_2Fe(CN)_6$-$Fe(NO_3)_3$, the resulting film gave λ_{max} at 700 nm (Fig. 2b), which is typical of bulk Prussian Blue .[19-21]

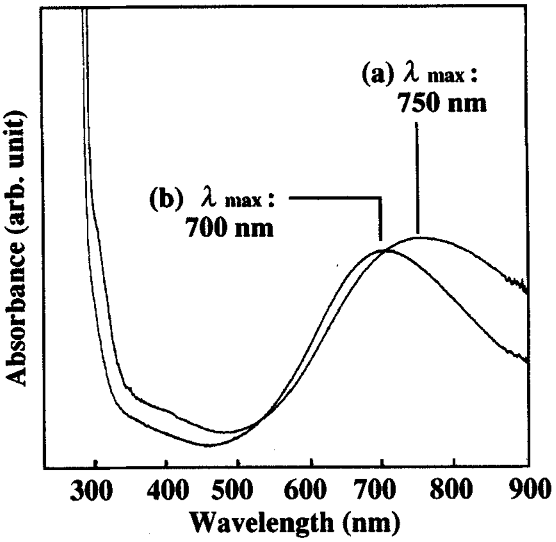

FIGURE 2. Absorption spectra of **1-Fe(CN)$_6$-Fe(III)** in chloroform prepared by (a) stepwise synthesis and (b) co-casting method.

The energy of the charge transfer band in Prussian Blue is written as the sum of three terms[18]

$$h\nu\ (\mathrm{cm^{-1}}) = 13400 - E_{one} + E_{crystal} \qquad (1)$$

where the change in intra-atomic electrostatic energies is 13400 cm^{-1}, E_{one} is the difference in the one electron energies of a t_{2g} electron in an iron in a nitrogen-coordinated Fe(III) and in a carbon-coordinated Fe(II). $E_{crystal}$ is the coulombic energy expended in transferring the electron from the carbon-coordinated Fe(II) to the nitrogen-coordinated

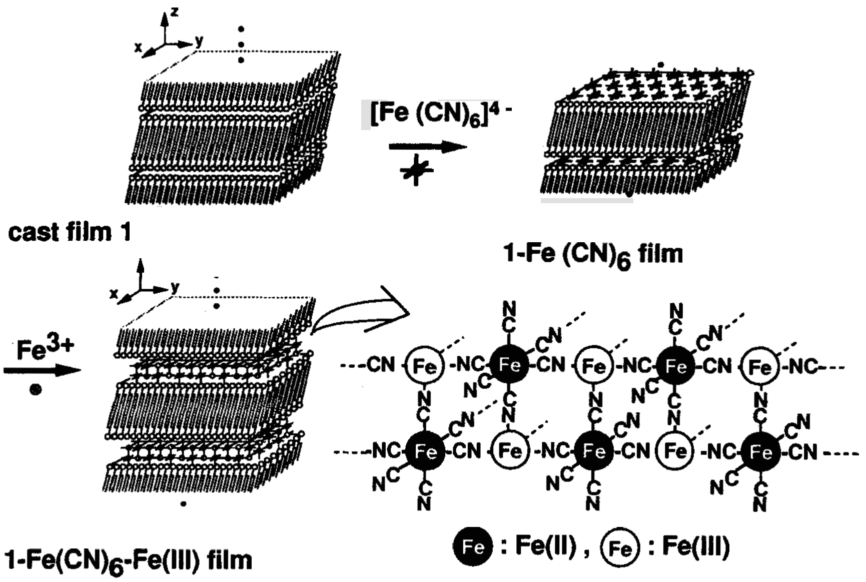

FIGURE 3. Schematic illustration of stepwise synthesis of mixed-valent $Fe(CN)_6$-Fe(III) complex by the use of multibilayer film.

Fe(III) in the electrostatic field of all the ions in the complex. Fe(III) ion positioned at the complex surface is less coordinated by anionic hexacyanoferrate(II) ion compared to that in the hexa-coordinated Fe(III) in the bulk complex. In addition, the surface of the μ-cyanide complex is in contact with the cationic bilayer surface. The existing electrostatic field will lower the coulombic energy to transfer an electron from hexacyano-ferrate(II) ion to the surface Fe(III) species, thus resulting in the decreased $E_{crystal}$ value. This effect would become more significant as the mixed valent complex adopt lower-dimensional structures in which contribution of the charge transfer absorption at surface $Fe^{II}(CN)_6$-Fe(III) species dominates. It is thus possible that the interbilayer $Fe^{II}(CN)_6$-Fe(III) complex display red-shifted absorption spectra if the templated synthesis afforded geometrically confined thin coordination network structures.

Although additional studies are required before the complex structure is determined unequivocally, we conclude from the above results that the template synthesis leads to altered mixed valent structures different from the complex prepared in the bulk. This feature is in contrast with the macroscopically controlled formation of Prussian Blue in Nafion membrane matrix.[22] Two-dimensional interbilayer surface that consists of regularly positioned cationic head groups, must affect the complex formation process and prevents from the formation of a bulk three-dimensional complex.

The stepwise template synthesis of a μ-cyanide mixed valent complex is schematically depicted in Fig.3. It is apparent that organized multibilayer films do not remain a passive host. Structural anisotropy as well as electrostatic interactions influence electronic properties of the interlayer complex. Combination of bilayer assembly and mixed valent material is unprecedented, and the present technique offer a new perspective on the structural control of mixed valent materials.

REFERENCES

1. Contribution No. 1022 from Department of Chemical Science and Technology.
2. S. Mann, D. D. Archibald, J. M. Didymus, T. Douglas, B. R. Heywood, F. C. Meldrum, and N. J. Reeves, Science, 261, 1286 (1993).
3. T. Kunitake, Mol. Cryst. Liq. Cryst., 255, 7 (1994). and references therein.
4. Y. Wakayama, T. Kunitake, Chem. Lett., 1283 (1993).
5. N.Kimizuka, T. Miyoshi, I. Ichinose, and T. Kunitake, Chem. Lett., 2039 (1991).
6. I. Ichinose, N. Kimizuka, and T. Kunitake, J. Phys. Chem., 99, 3736 (1995).
7. N. Kimizuka, T. Maeda, I. Ichinose, and T. Kunitake, Chem. Lett., 941 (1993).
8. N. Kimizuka, T. Maeda, I. Ichinose, and T. Kunitake, Trans. Mat. Res. Soc. Jpn., 15A, 595 (1994).
9. N. Kimizuka, T. Handa, I. Ichinose, and T. Kunitake, Angew. Chem. Int. Ed. Engl., 33, 2483 (1994) .
10. T. Mallah, S. Thiebaut, M. Verdaguer, and P. Veillet, Science. 262, 1554 (1993).
11. W. M. Laidlaw, R. G. Denning, T. Verbiest, E. Chauchard, A. Persoons, Nature, 363, 58 (1993).
12. K. Itaya, N. Shoji, and I. Uchida, J. Am. Chem. Soc., 106, 3423 (1984).
13. Y. Ishikawa and T. Kunitake, J. Am. Chem. Soc., 113, 621 (1991).
14. H. Wakayama and T. Kunitake, unpublished results.
15. I. Hamachi, T. Honda, S. Noda, and T. Kunitake, Chem. Lett., 1121 (1991).
16. K. Nakamoto, Infrared spectra of inorganic and coordination compounds, 2nd ed. (Wiley-Interscience, New York,1970).
17. J. F. Keggin, F. D. Miles, Nature, 137, 577 (1936).
18. M. B. Robin, Inorg. Chem., 1, 337 (1962).
19. K. Itaya, T. Ataka, S. Toshima, J. Am. Chem. Soc., 104, 4767 (1982).
20. T. Koyama, R. Hayashi, T. Yamane, E. Masuda, A. Kurose, K. Hanabusa, H. Shirai, T. Hayakawa, and N. Hojo, Colloid & Polymer Sci., 265, 786 (1987).
21. N. Toshima, R. -J. Lin, and M. Kaneko, Chem. Lett., 485 (1990).
22. K. Honda, H. Hayashi, and K. Chiba, Chem. Lett., 191 (1988).