

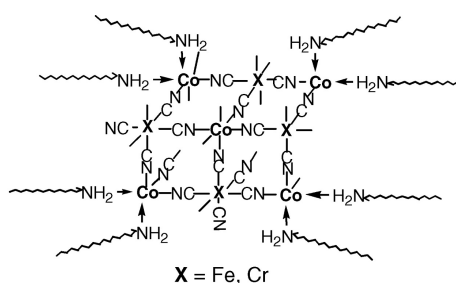
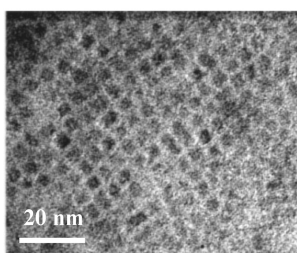
Communication

**Synthesis and Isolation of Cobalt Hexacyanoferrate/Chromate
 Metal Coordination Nanopolymers Stabilized by
 Alkylamino Ligand with Metal Elemental Control**

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Synthesis and Isolation of Cobalt Hexacyanoferrate/Chromate Metal Coordination Nanopolymers Stabilized by Alkylamino Ligand with Metal Elemental Control

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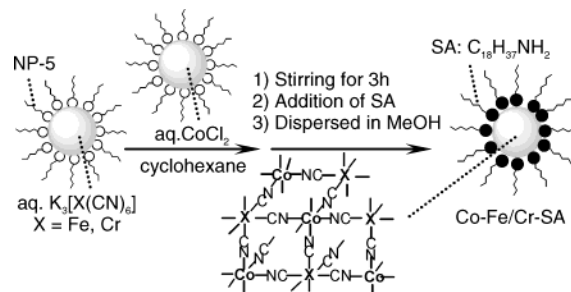
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Inorganic and organic hybrid nanomaterials (e.g., nanoparticles,¹ nanowires,² and nanorods³) are a fascinating research area, due to the highly promising potential for versatile properties provoked by combining the merits of both sources and by the nanometer size effect, which is entirely different from that in a bulk material.⁴ From this point of view, we have reported several synthesis methods, the unique electronic properties of noble metal nanoparticles stabilized by alkyl ligands, and their highly ordered assembly on a substrate.⁵ Recently, we have focused on another hybrid material, metal coordination polymers,⁶ in which the various metal ions are connected by an organic linker. These polymers are usually obtained in a bulk form. Reports about preparing a metal coordination polymer on a nanometer scale have been very few to date, and none of them includes a precise purification process.⁷ The metal coordination “nanopolymer” (MCNP) is a very attractive subject, not only for its specific properties due to its large rate of surface atoms compared to a bulk polymer, but also for its high potential as a new nanomaterial precursor. We intend to transform the obtained MCNP into another style of nanomaterial, such as a nanoceramic or an alloy metal nanoparticle, after applying an oxidation or a reduction process accompanied by removal of the bridging ligands between metal ions in MCNPs.

This Communication describes the first step of our strategy, the novel isolation with metal elemental control of cobalt hexacyanoferrate/chromate MCNPs, stabilized by stearylamine (Co–Fe/Cr–SA) as a protecting coordination ligand in a reverse micelle technique (Scheme 1). We have demonstrated that each Co–Fe/Cr–SA can be isolated with high uniformity of particle size and elemental composition, and the ratio of the metal component depends on the fundamental characteristics of Co–Fe/Cr–SA, including magnetic properties.

Co–Fe/Cr–SA with different metal ratios were synthesized in a sample tube by mixing two transparent reverse micelle solutions, each of which was prepared from 2 mL of 0.4 M poly-(ethylene glycol) mono 4-nonylphenyl ether (NP-5: HO(CH₂-CH₂O)_nC₆H₄C₉H₁₉, *n* = 5)/cyclohexane with addition of 70 μL of 0.1 M aqueous cobalt chloride (Co^{II}Cl₂) or 0.1 M aqueous potassium hexacyanometalate (K₃[X^{III}(CN)₆], X = Fe and/or Cr; Fe: Cr = 1:0 (**1**), 3:1 (**2**), 2:2 (**3**), 1:3 (**4**), 0:1 (**5**)). After 3 h of stirring, stearylamine (SA, 5 equiv relative to all of the included metal constituents) was added to the reaction mixture, which was vigorously stirred for another 1 h, followed by the addition of methanol (ca. 50 mL) sufficient to deposit a slurry product on the bottom of the sample tube by a centrifuge. The crude specimen was redissolved in a small amount of hexane (ca. 0.5 mL) and again dispersed in excess methanol. The finally filtered precipitate was

Scheme 1



dried overnight in a vacuum at room temperature to give a quantitative powdery compound.

The elemental analysis of **1–5** is summarized in Table 1. From the resulting formulas, the ratio of the metal components in Co–Fe/Cr–SA is controllable by changing the molar ratio of the starting metal complexes in the reaction mixture. The molar ratio of SA is ca. 0.4–0.6 relative to the Co sites, a value which agrees with the calculated value of 0.5, assuming that SA is attached to the Co sites located on a Co–Fe/Cr surface with almost 1:1 complexation, and the sphere particle size of Co–Fe/Cr–SA is 6 nm in diameter with a lattice constant of ca. 10 Å (see below). The stable and strongly coordinated protection by an alkyl ligand around the particle surface enables MCNPs to be isolated with removal of excess contamination by a stabilizer. TEM images of the compounds confirmed the formation of Co–Fe/Cr–SA, displaying small particles with a diameter of ca. 5–7 nm (Supporting Information, Figure S1). In particular, compound **1**, comprised of only Co and Fe complexes, exhibited the typical cubic shape, stacked by self-assembly in a ca. 80 × 80 nm² range (Figure 1a). The powder X-ray diffraction (XRD) patterns of the samples showed a typical face-centered cubic (fcc) structure with broadened peaks, due to the size effect (Figure S2).⁸ The lattice constant, *a*, is in good accordance with that of a bulk form (e.g., *a* = 10.06 and 10.54 Å for **1** and **5**, respectively, while *a* = 9.98 Å for Na_{0.91}Co^{III}_{1.15}[Fe^{II}(CN)₆]·3.0H₂O (low spin state)¹⁰ and 10.67 Å for Co^{II}_{1.5}[Cr^{III}(CN)₆]^{11a} in a bulk form). The value of *a* shifted almost linearly from **1** to **5** with an increase of the Cr component, suggesting that the metal units were uniformly dispersed in the nanopolymer crystal.

All of the obtained compounds could redissolve with high stability in generally less polar solvents, such as CH₂Cl₂, CHCl₃, THF, and pyridine, and in nonpolar solvents containing a small amount of a surface-active agent (e.g., NP-5, tetraammonium bromide/hexane, cyclohexane), while their bulk form⁹ was insoluble in any solvent. Figure 1b displays the THF solution of **1–5**, the color is altered from dark red to pale pink by controlling a metal elemental ratio in Co–Fe/Cr–SA. This color variation is explained by the UV–vis spectra of the compounds shown in Figure 2a; the absorption maximum (*λ*_{max}) for **1** at 375 nm, assigned to the ligand-

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Table 1. Formula of the Prepared Co–Fe/Cr–SA

compound	formula ^a
1	K _{1.04} Co _{1.10} [Fe(CN) ₆](SA) _{0.41} ·2.1H ₂ O
2	K _{0.81} Co _{1.10} [Fe(CN) ₆] _{0.72} [Cr(CN) ₆] _{0.28} (SA) _{0.53} ·3.0H ₂ O
3	K _{0.80} Co _{1.01} [Fe(CN) ₆] _{0.62} [Cr(CN) ₆] _{0.38} (SA) _{0.60} ·2.4H ₂ O
4	K _{0.82} Co _{1.30} [Fe(CN) ₆] _{0.32} [Cr(CN) ₆] _{0.68} (SA) _{0.46} ·3.1H ₂ O
5	K _{0.30} Co _{1.35} [Cr(CN) ₆](SA) _{0.69} ·4.3H ₂ O

^a Determined by thermogravimetric analysis (TGA), inductively coupled plasma (ICP) analysis, and the common CHN analysis method. The ratio of the hexacyano complexes is normalized as 1.

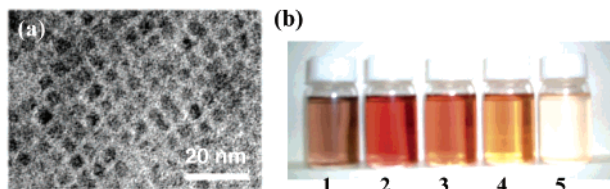


Figure 1. (a) TEM image of Co–Fe/Cr–SA (1). (b) THF solution of Co–Fe/Cr–SA (1–5). The number at the bottom of (b) refers to that of the compound.

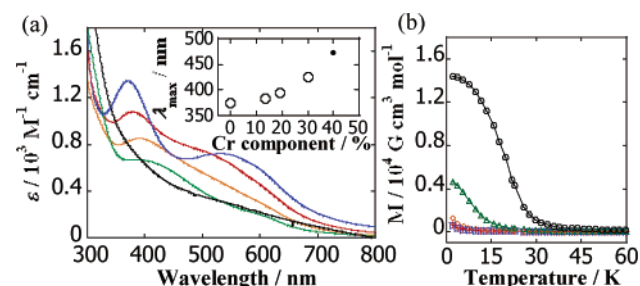


Figure 2. (a) UV–vis spectra of Co–Fe/Cr–SA in THF. (b) Field-cooled magnetization curves of Co–Fe/Cr–SA in an external magnetic field of 0.1 T: blue, 1; red, 2; orange, 3; green, 4; and black, 5. (Inset in panel a) λ_{\max} vs ratio of the Cr component for all of the metal constituents in the compounds (circles). Dot represents λ_{\max} of Co^{II}_{1.5}[Cr^{III}(CN)₆] in a bulk form.

to-metal charge-transfer (LMCT) band of the Fe^{II}–CN–Co^{II} unit,^{6c} which was produced by the reduction of some Fe^{II}–CN–Co^{III} (low spin state, $\lambda_{\max} = 545 \text{ nm}^{10}$) units with an amino group of SA during the protection process, is red-shifted toward 480 nm, attributable to Cr^{III}–CN–Co^{II} moieties^{11,12} almost proportionally to the rate of the Cr component in Co–Fe/Cr–SA (Figure 2a, inset). This observation supports the XRD results showing that the arrangement of the metal constituents is regularly formed inside a nanopolymer crystal: this linear change of the λ_{\max} value cannot be observed when some nonuniformity of metal elements in Co–Fe/Cr–SA exists. As for the FT-IR spectra of 1–5, $\nu(\text{NH})$ at 1475 cm^{-1} and $\nu(\text{CH})$ at 2930 and 2854 cm^{-1} of the attached SA were observed independent of the metal elemental ratio (Figure S3). The broad peaks in the regions from 2050 to 2090 cm^{-1} , from 2120 to 2130 cm^{-1} , and from 2140 to 2242 cm^{-1} can be assigned to $\nu(\text{CN})$ of Fe^{II}–CN–Co^{II} (reduced form), Fe^{II}–CN–Co^{III} (low spin state), and Cr^{III}–CN–Co^{II}, respectively.^{6c} The variation in the intensity rate between the CN stretching caused by the Fe–CN–Co and the Cr–CN–Co units is reasonably related to the metal elemental ratio in the compound, supporting the UV–vis and XRD results.

It has been also demonstrated that the magnetic properties of the prepared Co–Fe/Cr–SA depend on the metal elemental composition. Field-cooled magnetization versus temperature curves of 1–5 indicate that compounds 4 and 5, containing a high ratio of Cr units, exhibit ferromagnetism with spontaneous magnetization at the Curie temperature (T_c),¹³ shown in Figure 2b. The magnitude of magnetization for 5 is enhanced more than that of 4 with increasing T_c value (16 K for 4, and 30 K for 5) because of the higher ratio of the Cr component.¹¹ These findings indicate that

the isolated Co–Fe/Cr–SA would be a valuable substance for the field of coordination chemistry in a nanoscale range; the comparison between the obtained Co–Fe/Cr–SA and its bulk form is under investigation in our laboratory.

In conclusion, we have described the novel preparation and isolation of cobalt hexacyanoferrate/chromate metal coordination nanopolymers protected by an alkyl ligand of stearylamine (Co–Fe/Cr–SA) using a reverse micelle technique. The prepared Co–Fe/Cr–SA particles were uniform in size and elemental composition, obtained as a powdery form to redissolve in a less polar solvent with surrounding hydrophobic SA ligands. The metal elemental ratio of Co–Fe/Cr–SA was controlled by changing the molar ratio of the adopted starting complex between Co^{II}Cl₂ and K₃[X^{III}(CN)₆] (X = Fe, Cr) in the reaction mixture, affecting the physical and chemical characteristics of Co–Fe/Cr–SA such as particle shape, color, and magnetism. The second step of our strategy, to transform the isolated Co–Fe/Cr–SA into another nanomaterial, has already started, simultaneously exploring the attractive character of Co–Fe/Cr–SA as a metal complex by controlling other important parameters, e.g., size with high monodispersity, and ligand species on a Co–Fe/Cr surface. We believe that the combination of “nanoparticle science” and “coordination chemistry” will cultivate a new research field for nanotechnology.

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Note Added after ASAP Posting. After this paper was posted ASAP on July 14, 2004, an author’s name was changed. The corrected version was posted July 21, 2004.

Supporting Information Available: TEM image, XRD patterns with the calculated lattice constant, and FT-IR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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