

## Systematic Bathochromic Shift of Charge-transfer Bands of Mixed-metal Prussian-blue Nanoparticles Depending on Their Composition Ratios of Fe and Ni

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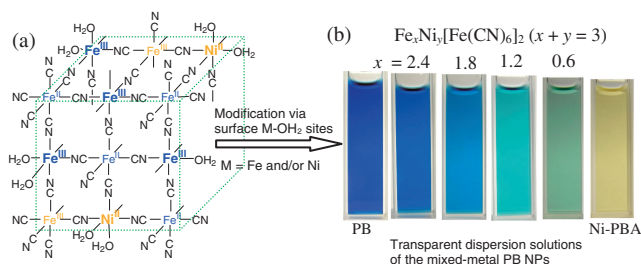
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Mixed-metal Prussian-blue nanoparticles,  $\text{Fe}_x\text{Ni}_y[\text{Fe}(\text{CN})_6]_2 \cdot z\text{H}_2\text{O}$  ( $x + y = 3$ ,  $z = 8-12$ ), were dispersed into *n*-butanol by hybrid surface modification with hexacyanoferrate(II) ions,  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ , and *n*-hexylamines. In their transparent dispersion solutions, a systematic bathochromic shift of charge-transfer bands due to the  $\text{Fe}^{\text{II}}\text{-CN-Fe}^{\text{III}}$  components was observed depending on the metal composition ratios of Fe and Ni.

Over three centuries,<sup>1</sup> the multifunctionalities of Prussian blue (PB) and its analogs (PBAs) have resulted in recently renewed scientific and industrial applications.<sup>2-5</sup> Systematic control of the metal composition ratios of PBAs has been an essential factor to create a variety of electronic and magnetic interactions via the cyano-bridged  $d-\sigma$  and  $d-\pi$  bonding network.<sup>6,7</sup> To fabricate thin films and fine patterns of such functional materials, the importance of printed electronics has globally increased<sup>8-10</sup> because wet techniques, represented by ink-jet printing, will provide simpler, greener, and more versatile processes. Nanoparticles (NPs) are a promising printable material, and syntheses of their dispersion solutions will be a key technology for printed electronics.<sup>9,10</sup> Moreover, transparent dispersion solutions of colored NPs will be an indispensable new target of spectroscopic studies for intrinsically insoluble solids. We have found that the historically insoluble PB pigment is made of aggregated NPs with a dimension of ca. 10 nm.<sup>9</sup> The 3-D cyano-bridged network is discontinuous, and an ideal 10-nm nanocube of PB inevitably bears 15% active surface reaction sites,  $\text{Fe}^{\text{III}}\text{-OH}_2$ , on the basis of the total number of Fe.<sup>9,11,12</sup> We have demonstrated that the insoluble PB can be transformed into dispersion solutions by surface modifications with hexacyanoferrate(II) ions<sup>9,11</sup> and alkylamines<sup>9,12</sup> via the  $\text{Fe}^{\text{III}}\text{-OH}_2$  sites (Figure 1a). The hexacyanoferrate(II) ion-modified PB NPs were well dispersed in water.<sup>9</sup> The dispersibility of the alkylamine-modified PB NPs into various organic solvents was controlled by its alkyl-chain lengths.<sup>9,12</sup>

In this study, the metal composition ratios of Fe and Ni have been systematically controlled in mixed-metal PB NPs,  $\text{Fe}_x\text{Ni}_y\text{-}[\text{Fe}(\text{CN})_6]_2$  ( $x + y = 3$ ) (Figure 1a). Hybrid surface modification with both hexacyanoferrate(II) ions and *n*-hexylamines has been performed to improve the dispersibility of the mixed-metal PB NPs into *n*-butanol, which is a greener solvent suitable for printed electronics. In transparent dispersion solutions of surface-modified NPs (Figure 1b), a systematic bathochromic shift of charge-transfer (CT) bands due to the  $\text{Fe}^{\text{II}}\text{-CN-Fe}^{\text{III}}$  components was revealed as the Fe contents numerically decreased.

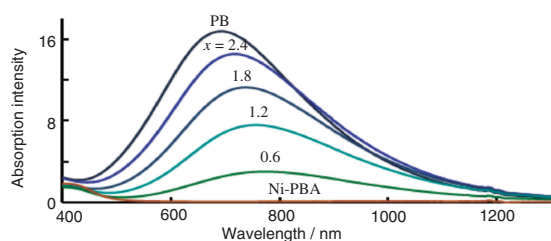


**Figure 1.** (a) Mixed-metal PB showing a  $3 \times 3$  metal arrangement and (b) photographs of highly transparent dispersion solutions of their surface-modified nanoparticles.

An aqueous solution (12 mL) of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (3.34–0 g, 12.0–0 mmol) and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0–3.49 g, 0–12.0 mmol) was added to an aqueous solution (24 mL) of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (2.63 g, 8.00 mmol), where four types of the mixed-metal PB,  $\text{Fe}_x\text{Ni}_y\text{-}[\text{Fe}(\text{CN})_6]_2$ , along with  $\text{Ni}^{\text{II}}_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2$  (Ni–PBA)<sup>9,11</sup> and  $\text{Fe}^{\text{II}}_3\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$  (PB) were prepared in  $x:y$  (Fe contents to total metals,  $\text{Fe}/(\text{Fe} + \text{Ni})$  (mol/mol)) = 2.4:0.6 (0.88), 1.8:1.2 (0.76), 1.2:1.8 (0.64), and 0.6:2.4 (0.52). The reaction mixtures were vigorously stirred for 30 min. The resulting water-insoluble solids were centrifuged at 4000 rpm (2600 G), washed with water five times and with methanol three times, and dried under reduced pressure.

In the as-prepared mixed-metal PB solids, the Fe contents were estimated to be 0.87, 0.74, 0.63, and 0.51 by wavelength-dispersive X-ray spectroscopy (WDX), and they were less than the adjusted values in a preparation within 3% deviation.<sup>13</sup> From line broadening of the powder X-ray diffraction signals, Scherrer's crystalline sizes were maintained between 8 and 10 nm independent of the metal compositions (Figure S1).<sup>14</sup> The mixed-metal PB NPs visually changed from blue to green as their Fe contents decreased, and the color change arising from the yellow component,  $\text{Fe}^{\text{III}}\text{-CN-Ni}^{\text{II}}$ , increased against the blue,  $\text{Fe}^{\text{II}}\text{-CN-Fe}^{\text{III}}$ , as seen in FT-IR spectroscopy (Figure S2).<sup>14</sup>

The above solid-state analyses are still less informative of the mixed-metal PB NPs, in which Ni and Fe are randomly distributed, unlike a mechanical mixture of NPs of PB (hexacyanoferrate(II) salt) and Ni–PBA (hexacyanoferrate(III) salt). In the electrochromism of the electrochemically deposited PB film, a bathochromic shift of the CT band was reported in the incomplete oxidation forms of PB,<sup>15</sup> known as “Berlin green” as a random hexacyanoferrate(II) and -ferrate(III) mixture. If the mixed-metal PB NPs are grouped into hexacyanoferrate(II) and -ferrate(III) mixtures of their controlled composition ratios, a



**Figure 2.** UV-vis-near IR absorption spectra of the surface-modified nanoparticles of  $\text{Fe}_x\text{Ni}_y[\text{Fe}(\text{CN})_6]_2$  dispersed in *n*-butanol. The absorption intensity is defined by [absorbance]/([concentration/mg mL<sup>-1</sup>] × [light pass length/cm]).

similar bathochromic shift will be found from their transparent dispersion solutions. According to the previous literature,<sup>9,11,12</sup> we attempted to prepare dispersion solutions exhibiting high transparency suitable for UV-vis-near IR spectroscopy, comparable to the usual transparent solutions of small molecules and ions.

The mixed-metal PB solids (0.60 g) were stirred with an aqueous solution (1.5 mL) of  $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$  (87.9–100 mg, 33% of the total number of surface M–OH<sub>2</sub> sites (M = Fe and/or Ni)<sup>16</sup>) for 1 day. The resulting slurry of the hexacyanoferrate(II) ion-modified NPs combined with *n*-butanol (20 mL) and an excess amount of *n*-hexylamine (73.5–83.4 mg, 133% of the total number of surface M–OH<sub>2</sub> sites<sup>16</sup>) was stirred for 3 days. Thus, surface-modified NPs with both hexacyanoferrate(II) ions and *n*-hexylamines<sup>16</sup> were centrifuged at 6000 rpm (3540 G), washed with diethyl ether (15 mL) three times to remove unreacted *n*-hexylamines, and dried under air for 30 min. To obtain highly transparent dispersion solutions, the dried surface-modified NPs were stirred with *n*-butanol (30 mL) for 3 days. If the transparency of the dispersion solutions was determined to be insufficient, the visually suspended particles were removed by centrifugation at 4000 rpm (2600 G) to improve the transparency.<sup>17</sup>

The number-averaged dynamic light-scattering (DLS) particle sizes in diluted dispersion solutions of the mixed-metal PB NPs (0.125 mg mL<sup>-1</sup>) were less than 20 nm (Figure S3).<sup>14</sup> The much smaller DLS sizes than the wavelengths of UV-visible regions evidence the high transparency of the dispersion solutions (Figure 1b). In the UV-vis-near IR absorption spectra of the dispersion solutions, a systematic bathochromic shift of the CT bands due to the  $\text{Fe}^{\text{II}}\text{CN-Fe}^{\text{III}}$  components was observed depending on the metal composition ratios (Figure 2), while the CT excitation energy of PB NPs was never influenced by the Ni–PBA NPs coexisting in mechanical mixtures of their dispersion solutions (Figure S4).<sup>14</sup> When the colloidal NPs of  $\text{M}_3[\text{Fe}(\text{CN})_6]_2$  are immediately generated from a stoichiometric aqueous mixture of  $3\text{M}^{2+}$  (M = Fe<sup>2+</sup> and Ni<sup>2+</sup>) and  $2[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$  through random coordination reactions of Fe<sup>2+</sup> and Ni<sup>2+</sup> and thus formed hexacyanoferrate(III)  $\text{Fe}^{\text{III}}\text{CN-Fe}^{\text{III}}$  components are transformed into hexacyanoferrate(II)  $\text{Fe}^{\text{II}}\text{CN-Fe}^{\text{III}}$  components via electron transfer, the formulae of the mixed-metal PB solids are  $(a, b, c, d, e) = (0.4, 2.0, 0.6, 2.0, 0)$  ( $x = a + b = 2.4$ ),  $(0, 1.8, 1.2, 1.8, 0.2)$  ( $x = 1.8$ ),  $(0, 1.2, 1.8, 1.2, 0.8)$  ( $x = 1.2$ ), and  $(0, 0.6, 2.4, 0.6, 1.4)$  ( $x = 0.6$ ) as  $\text{Fe}^{\text{II}}_a\text{Fe}^{\text{III}}_b\text{Ni}^{\text{II}}_c[\text{Fe}^{\text{II}}(\text{CN})_6]_d[\text{Fe}^{\text{III}}(\text{CN})_6]_e$  ( $a + b + c = 3$ ,  $d + e = 2$ ,  $b = d$ ). In fact, the absorption intensities of the CT bands due to the  $\text{Fe}^{\text{II}}\text{CN-Fe}^{\text{III}}$  components show a linear correlation with  $d$

(Figure S5a).<sup>14</sup> Increased Ni contents resulted in the distribution of the hexacyanoferrate(III) components,  $\text{Fe}^{\text{III}}\text{CN-Ni}^{\text{II}}$  and/or  $\text{Fe}^{\text{III}}\text{CN-Fe}^{\text{III}}$ , on the basis of  $e$ . The FT-IR absorption due to the hexacyanoferrate(III) ions appeared along with their UV-vis absorption at 404 nm (Figures 2 and S2).<sup>14</sup> The CT excitation energies are affected by the coexisting hexacyanoferrate(III) ions, according to their correlation with  $e$  (Figure S5b).<sup>14</sup> The spectroscopic behavior suggests that the mixed-metal PB NPs are random hexacyanoferrate(II) and -ferrate(III) mixtures.

In summary, we have achieved a high-yield preparation of highly dispersible mixed-metal PB NPs in a hydrophobic and hydrophilic boundary alcohol via hybrid surface modification with a hydrophilic  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  and a hydrophobic *n*-hexylamine. We have demonstrated that transparent dispersion solutions of NPs will be a good target for spectroscopic investigation, especially, that of insoluble colored solids. The CT bands are under further investigation on the basis of the electrochromic behavior of the spin-coated films of the mixed-metal PB NPs.

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- 13 The hydration numbers of the mixed-metal PB ranged from 8 to 12 on the basis of thermogravimetric analyses.
- 14 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
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- 16 The surface M–OH<sub>2</sub> sites were partially modified by hexacyanoferrate(II) ions, and the remaining M–OH<sub>2</sub> sites were then modified by excess *n*-hexylamines. From the WDX analyses of the surface-modified NPs, sodium ions were detected, derived from surface-attached  $\text{Na}_4[\text{Fe}(\text{CN})_6]$ . CH stretching bands due to surface-attached *n*-hexylamines were observed in the FT-IR spectra.
- 17 The starting mixed-metal PB solids were transformed into butanol-dispersible NPs with yields between 89 and 99%.