

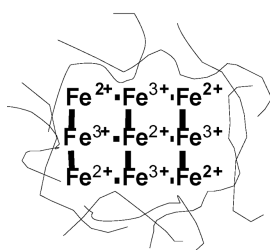
Communication

## Prussian Blue Nanoparticles Protected by Poly(vinylpyrrolidone)

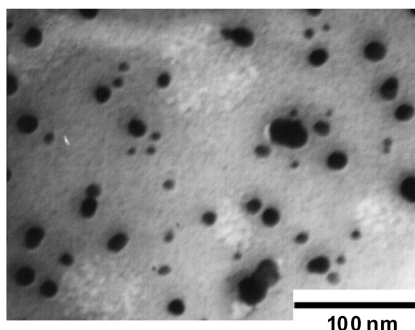
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PVP-protected  
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## Prussian Blue Nanoparticles Protected by Poly(vinylpyrrolidone)

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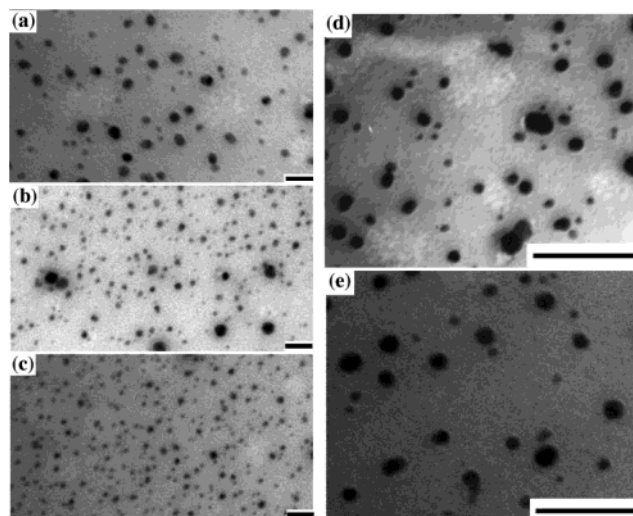
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Nanoscale particles based on metals, metal oxides, and metal sulfides have been developed extensively during the past decade.<sup>1</sup> A burst of research activity is seen in the area of synthesis and functionalization of the nanoparticles because of their interesting size- and shape-dependent properties.<sup>1</sup>

Self-assembled coordination polymers from transition metal ions and bridging ligands show many prominent features, for example, redox property, magnetism, conductivity, gas adsorption, anion exchange, etc.; however, most of the research has focused on properties of bulk crystalline solids.<sup>2</sup> Recently, controlling the growth of the coordination polymers under spatial confinement has emerged as a promising subject of future nanomaterial science.<sup>3</sup> It is now eagerly desired to investigate the unexpected chemical and physical properties of the coordination polymers in the nanometer-size regime. Nevertheless, few studies on the nanoparticle synthesis of the coordination polymers have been reported so far,<sup>4</sup> and size effects of the coordination polymers are still unexplored.

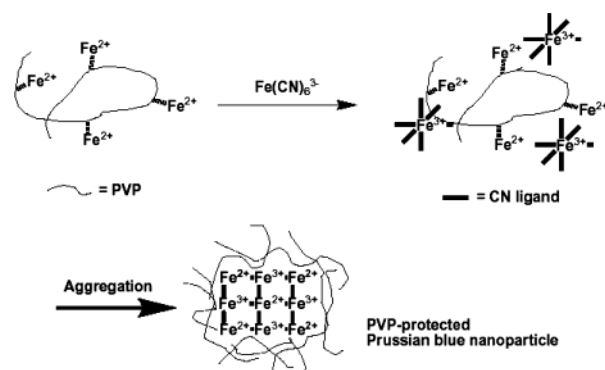
Prussian blue (PB) analogues  $M_1^{m+}[M'(CN)_6]^{n-}$  are representatives of the coordination polymers and have played important roles in the field of molecular magnets.<sup>5</sup> They exhibit unique magnetic behaviors depending on their constituents and ratios of transition metal ions.<sup>5</sup> In this paper, we report on a formation of highly dispersed PB nanoparticles controlled by poly(vinylpyrrolidone) (PVP) as a protecting polymer. We also demonstrate a new and important size-dependent effect of PB on the magnetic property.

Equimolar amounts of aqueous  $FeCl_2$  and  $K_3Fe(CN)_6$  solutions were mixed in the presence of PVP (K-30; average  $M_w = 40\,000$ ) with final concentrations of  $[Fe^{2+}]$ ,  $[Fe^{3+}] = 10\text{ mM}$ ,  $[PVP] = 200\text{ mM}$ , readily producing a blue color solution. The UV-vis spectrum of the resulting solution showed a broad band with  $\lambda_{max}$  at 689 nm, which is consistent with an intermetal charge-transfer band from  $Fe^{2+}$  to  $Fe^{3+}$  in PB.<sup>6</sup> Transmission electron microscopy (TEM) images of the sample after being air-dried onto the grid revealed well-dispersed nanoparticles with the average diameter of 27 nm (Figure 1a). A powdery sample was obtained as a precipitate after adding acetone to the aqueous PVP-PB solution. X-ray powder diffraction (XRPD) analysis of the powder showed broad peaks at  $17.6^\circ$  (200),  $24.8^\circ$  (220),  $35.2^\circ$  (400),  $39.6^\circ$  (420), and  $43.5^\circ$  (422), which can be indexed as the PB cubic space group  $Fm\bar{3}m$ .<sup>7</sup> The IR spectrum of the sample exhibited a peak at  $2086\text{ cm}^{-1}$  attributed to the CN stretching in the  $Fe^{2+}-CN-Fe^{3+}$  of PB. The spectrum also showed a peak for C=O stretching of the PVP amide unit at  $1656\text{ cm}^{-1}$  along with a shoulder peak around  $1600\text{ cm}^{-1}$ . Appearance of the latter shoulder peak suggested a part of the amide unit in PVP binds to the outer shell Fe ion of the PB nanoparticles. As a control experiment, synthesis of PB at the same Fe ion concentrations without PVP produced large particles ( $>300\text{ nm}$ ) with a broad size distribution. These results indicate that, during nucleation and growth processes of PB, the amide moiety of PVP is weakly coordinated to an Fe ion; consequently, PVP provided



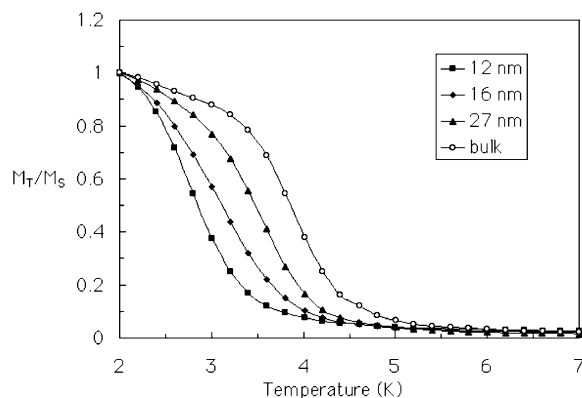
**Figure 1.** TEM images of PVP-protected PB nanoparticles prepared at  $[Fe^{2+}] = [Fe^{3+}] = 10\text{ mM}$ . The feed ratios of  $PVP/Fe^{2+} =$  (a) 20, (b) 50, and (c) 100, respectively. PB nanoparticles (d) prepared at  $[Fe^{2+}] = [Fe^{3+}] = 1\text{ mM}$ ,  $PVP/Fe^{2+} = 100$ , and (e) obtained from the redispersed sample in  $CHCl_3$  (average size of the original particles was 16 nm). Scale bars = 100 nm.

### Scheme 1



steric stabilization. Formation of the PVP-protected PB nanoparticles is schematized (Scheme 1).

The averaged diameter size of the nanoparticles can be controlled by the  $PVP/Fe^{2+}$  feed ratio and the initial Fe ion concentrations. At the same Fe concentration conditions (10 mM) as above, the diameters of the nanoparticles became smaller with an increase of the PVP content. The mean diameters of the particles were found to be 20 and 16 nm for reactions at  $PVP/Fe^{2+} = 50$  and 100, respectively (Figure 1b and c). Lowering the Fe ion concentration to  $[Fe^{2+}] = [Fe^{3+}] = 1\text{ mM}$  gave, to some extent, smaller particles as compared to those given at 10 mM Fe concentrations (25 and 12 nm in the case of  $PVP/Fe^{2+} = 20$  and 100, respectively) (Figure 1d). Reaction at  $[Fe^{2+}] = [Fe^{3+}] = 30\text{ mM}$  seems ineffective in



**Figure 2.** Field-cooled magnetization versus temperature curves for PB nanoparticles (average diameters = 12, 16, and 27 nm, respectively) and bulk at an external magnetic field of 50 G.

producing the nanoparticles with narrow size distributions, where large cubic particles (>100 nm) of PB were partially obtained at any PVP/Fe<sup>2+</sup> ratios.

Bulk PB is insoluble in organic medias, which limits applications of the molecular magnets as functional materials. It is noteworthy that the PB nanoparticles obtained at PVP/Fe<sup>2+</sup> = 100 could be completely dissolved in various organic solvents, for example, MeOH, EtOH, CH<sub>3</sub>CN, DMF, DMSO, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>, due to the dispersed nanoparticle formation.<sup>8</sup> When the nanoparticles with the average diameter of 16 nm were dissolved in CHCl<sub>3</sub>, the solution showed a typical broad charge-transfer band for PB at 672 nm. The absorption intensity is proportional to the concentration and shows no change over 1 month. TEM images of the sample after evaporation of CHCl<sub>3</sub> showed well-dispersed nanoparticles with size dimensions (Figure 1e, average diameter = 15 nm) similar to the original ones. In addition, the particle sizes were independent of the sample concentration in CHCl<sub>3</sub>. These results suggest that PVP prevented the nanoparticles from further aggregation and dissociation in CHCl<sub>3</sub> at any concentration. It is unusual that such a supramolecular compound as PB preserves the nanocluster forms, keeping the original degrees of assembling in a pseudosolution system.

Figure 2 shows field-cooled magnetization curves for the PB nanoparticles and bulk at an external magnetic field of 50 G. The critical temperature ( $T_c$ ) where PB turns to a ferromagnetic compound decreases with the smaller diameter of PB: 5.5 K (bulk), 4.6 K (27 nm), 4.3 K (16 nm), and 4.0 K (12 nm).<sup>9</sup> The  $T_c$  of PB analogues is expressed as the following equation.<sup>5d</sup>

$$T_c = \frac{2\sqrt{Z_{ij}Z_{ji}|J_{ij}|}}{3k_B} \sqrt{S_i(S_i + 1)S_j(S_j + 1)}$$

In the case of PB,  $i = j = \text{Fe}^{3+}$ ,  $S_i = S_j = 5/2$ ,  $k_B$  is the Boltzmann constant,  $J$  is the magnetic interaction constant, and  $Z_{ij}$  is the number of the nearest-neighbor  $i$ -site ions surrounding a  $j$ -site ion. The  $T_c$  value drops of the PB nanoparticles can be explained by decreases of the  $Z$  value due to diminution of the average number of the nearest magnetic interaction neighbors.  $T_c$  values of the nanoparticles with diameters of 12, 16, and 27 nm might be estimated to be 4.3, 4.6, and 4.9 K, respectively, by use of the equation, on the assumption that the nanoparticles are spherical shapes with mean

diameters observed by TEM images and the  $Z$  value of the surface unit of the particles is one-half of the interior. The calculated  $T_c$  values roughly agreed with the experimental ones. To our knowledge, this is the first size-dependent control of the magnetic property of the coordination polymers.

In conclusion, we have succeeded in the facile preparations of the PVP-protected PB nanoparticles by mixing Fe<sup>2+</sup>, Fe(CN)<sub>6</sub><sup>3-</sup>, and PVP in water. The dispersed nanoparticle formations in the polymer matrix offered PB not only the enhanced solubilities in organic solvents but also a film-forming property when the colloidal dispersions of the composites were evaporated. Retaining the nanoparticle formations without size change in CHCl<sub>3</sub> is particularly worthy of mention. The controllable magnetic properties by their particle sizes would give valuable information for future applications of the PB analogues to nanomagnetic materials that attract growing interest because of their potential in ultrahigh-density magnetic recording systems.<sup>10</sup>

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**Supporting Information Available:** Synthetic procedures, ICP-MS data, size histograms, XRPD pattern, IR spectra, UV-vis absorption spectra, and  $T_c$  calculation process (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) A preliminary experimental result that PB nanoparticles protected by poly-(diallyldimethylammonium chloride) as a cationic polymer have shown a similar  $T_c$  decrease behavior indicates the  $T_c$  decreases of the PB nanoparticles are not caused by polymer-nanoparticle interactions.
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