Supplementary Information for

Synthesis of Uniform Prussian Blue Nanoparticles by a Polyol Process Using a Polyethylene Glycol Aqueous Solution

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Change of size distribution of particles by the progress of reaction

Fig. S1 shows size distributions of PB nanoparticles at different reaction time. The width of distribution seems to be similar within measuring error for all the reaction time excepting for at 5 min in the PEG #20000 system. The somewhat narrower size distribution at 5 min in Fig. S1(a) suggests nucleation was incomplete at 5 min.

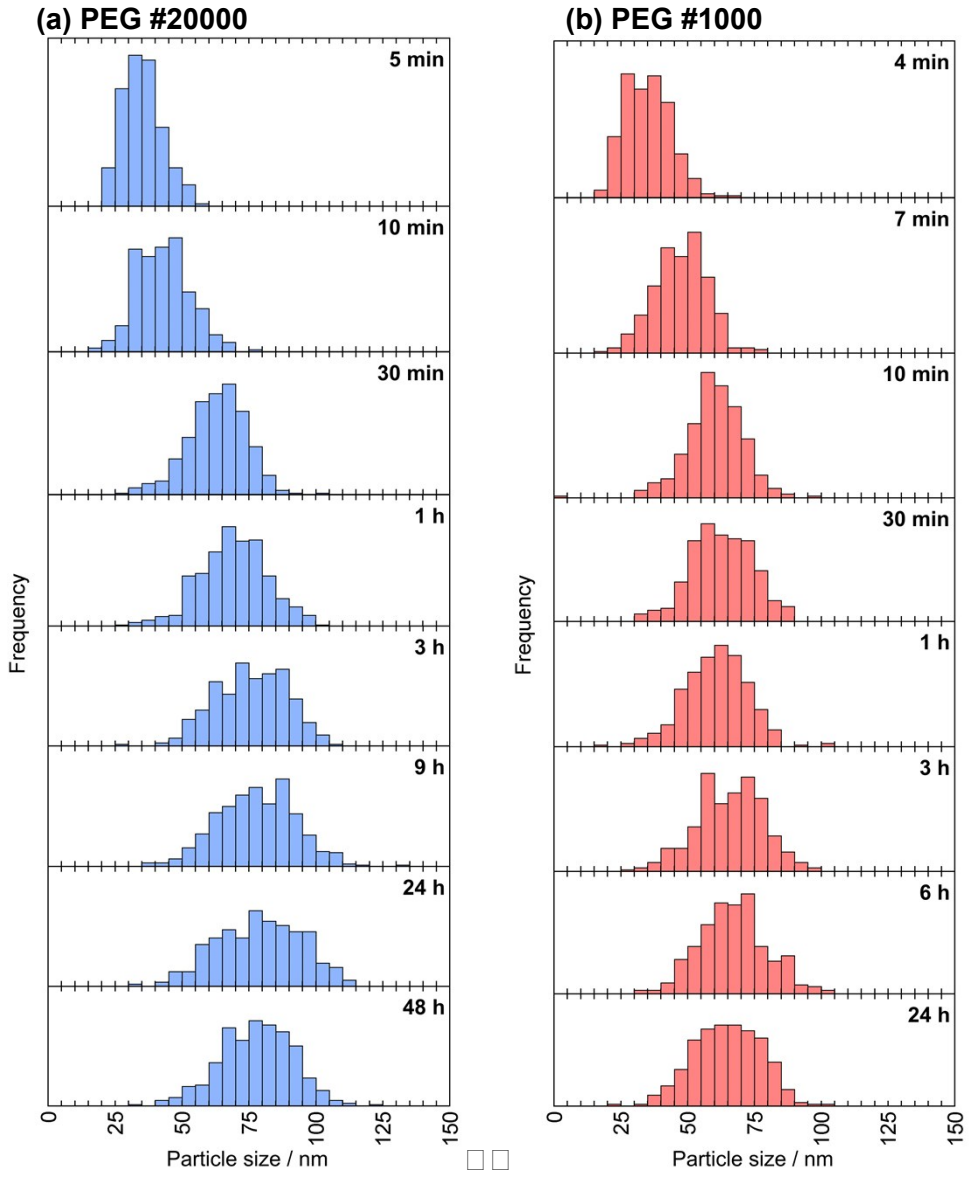

Fig. S1 Change in size distribution of PB nanoparticles during the formation reaction using (a) PEG #20000 and (b) PEG #1000 at 50 °C.

Growth behavior of Prussian blue nanoparticles prepared with PEG #1000

Fig. S2 shows time changes of particle size and Fe concentration (relative to the initial one) in liquid phase during the formation process using PEG #1000. The increase in the mean size and the consumption of precursor seem to complete in 30 min. On the other hand, as indicated in Fig. 8, the IVCT absorption continued to increase until 6 h. Such the behaviors are similar to, but faster than, those for the PEG #20000 system in Fig. 6. The final particle size, 67 nm, is somewhat smaller than of PEG #20000. Note that the time range of upper figure (up to 24 h) in Fig S2 is different from Fig. 6 for PEG #20000 (up to 48 h).

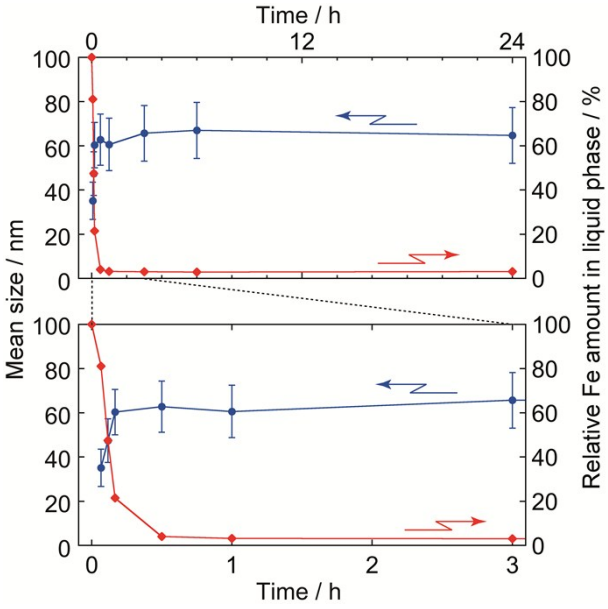

Fig. S2 Time evolutions of particle size (●) and Fe amount remaining in the liquid phase (◆) in the PEG #1000 system. Error bars for the mean size indicate ± one standard deviation of the size distribution, where the top and bottom figures indicate the whole and early stages of formation, respectively. The Fe amount, relative to initial one, was evaluated by atomic absorption spectrometry.

Estimation of reduction rate constants from the absorbance data

Since increase in the IVCT absorption at 730 nm reflects increase of the Fe^{3+}–$[Fe^{II}(CN)_6]^{4-}$ unit, and thus the decrease of the precursor (probably soluble Fe^{3+}–$[Fe^{III}(CN)_6]^{3-}$ complex), the absorbance data could be applied to a kinetic analysis. Assuming a first-order reaction of Fe^{3+}–$[Fe^{III}(CN)_6]^{3-}$ concentration, C, regardless in the form of the soluble complex or of the PG component, the rate equation is expressed as

$$\ln C = \ln C_o - kt \,, \qquad \text{(S1)}$$

where k is the rate constant and C_o is the initial concentration.

By using Lambert-Beer relationship, the value of C can be denoted with absorbance at 730 nm, A, as

$$C = \Delta A/\alpha\varepsilon l \,, \qquad \text{(S2)}$$

where α, ε and l are the dilution ratio at sampling (= 1/100), the extinction coefficient, and the optical path length, respectively, and ΔA is

$$\Delta A = A_{100} - A \qquad \text{(S3)}$$

where A_{100} is the absorbance when all the precursors are reduced to Fe^{3+}–$[Fe^{II}(CN)_6]^{4-}$. Thus one obtains

$$\ln\Delta A = \ln\Delta A_o - kt \qquad \text{(S4)}$$

from eqs. S1 and S2, where ΔA_o is ΔA at $t = 0$.

In Fig. S3, the value of $\ln\Delta A$, calculated from the absorbance data in Fig. 8, is plotted to reaction time, t, where the values of A_{100} are assumed to be equal to the values of A at 48 h and 6 h for PEG #20000 and PEG #1000 systems, respectively. In both systems, the plots can be fitted with two straight lines of different slopes that correspond to the rete constants for reduction of the soluble precursor, k_1, and of the component of PG nanoparticles, k_2. The estimated values of the rate constants are listed in Table S1.

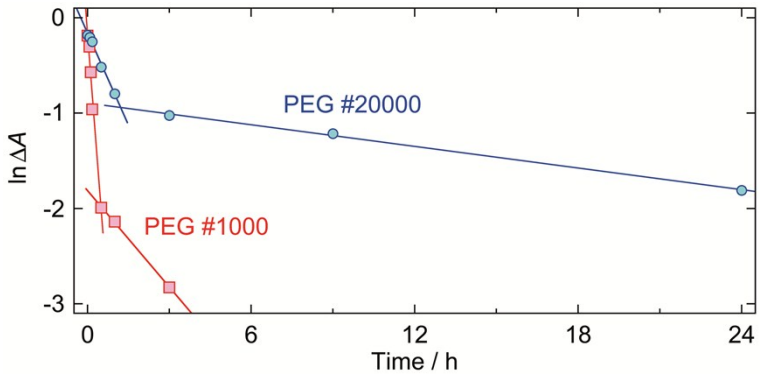

Fig. S3 Relationships between $\ln\Delta A$ and reaction time.

Table S1 Reduction rate constants ratio estimated from the slopes in Fig. S3.

	Rate constant / s^{-1}		k_2/k_1 ratio
	Precursor to PG (k_1)	PG to PB (k_2)	
PEG #20000	1.8×10^{-4}	1.1×10^{-5}	0.061
PEG #1000	1.0×10^{-3}	9.4×10^{-5}	0.094