Ion-based Organic Nanoparticles: Synthesis, Characterization, and Optical Properties of Pseudoisocyanine Dye Nanoparticles

Hiroshi Yao,* Zhongmin Ou, and Keisaku Kimura
Graduate School of Material Science, University of Hyogo, 3-2-1 Koto, Kamigori-cho, Ako-gun, Hyogo 678-1297

We demonstrate a simple and versatile method for preparing ion-based organic nanoparticles in aqueous solution. Ion association between a cationic pseudoisocyanine dye and a tetraphenylborate anion in water produced the dye nanoparticles from several tens to hundreds of nanometers. Particle size could be controlled by changing the molar ratio of the loaded anions to the dye cations.

Nanometer-sized particles composed of semiconductors, metals, and other inorganic materials have been numerously reported as have a few composed of common organic molecules.[1] In recent years, the number of studies of organic nanoparticles has been increasing with the progress of pharmaceutical researches,[2] but many studies still focus on polymers. Needless to say, there is scientific and technological interest in organic nanoparticles owing to their special characteristics which lie between the properties of molecules and those of bulk crystals.[3]

For nanoparticles of organics that are poorly soluble or insoluble in water, the formation strategy lies mostly on the conversion of the products dissolved in a suitable organic solvent into nanodispersed systems in aqueous media by a precipitation/condensation procedure.[3] On the other hand, nanoparticles of hydrophilic organic compounds have been prepared in slightly different ways; salting-out or reprecipitation method that is based on the adjustment of their inherent solubility by some electrolytes or organic solvents.[4] Further additives such as surfactants or polymers are frequently involved for the role of colloidal stabilizers.[3] In this letter, we report a simple and versatile method for preparing ion-based organic dye nanoparticles in aqueous solution using "ion-association technique". No specific organic solvents or surface-active colloidal stabilizers are needed.

The organic molecule we chose is a cationic pseudoisocyanine (PIC) dye. The procedure to prepare dye nanoparticles is as follows: Rapid addition of 0.5–1.0 mL of aqueous PIC bromide solution (0.1 mM) into the ultrasonicated aqueous solution of 2.0–3.0 mL of sodium tetraphenylborate (NaTPB, 0.1 mM) produced slightly turbid solution of nanoparticles. Ultrasonication was further continued for 10 min. Note that NaTPB includes a hydrophobic TPB anion, and is often used for ion-pair extraction. Hence ion association between PIC cations and TPB anions, $(PIC^+ \cdot TPB^-)_m$, leads to water-insoluble nanoparticle formation.[5] Particle size could be controlled by changing the molar ratio (ρ) of the loaded NaTPB to PICBr. Before the measurements of dynamic light scattering (DLS), UV–vis absorption spectra and transmission electron microscopic (TEM) images, the solutions were filtered by a 200-nm pore size membrane filter.

The size distributions of PIC nanoparticles[5] prepared at different ρ are shown in Figures 1a–1c, in which the average nanoparticle diameters are 125, 84, and 64 nm, respectively. Note that the size distribution widths are in the range between 11–17%. The histograms were obtained by DLS measurements. Figures 1d–1f show the TEM images of the respective nanoparticles exhibiting a spherical shape. The particle sizes were in the range of 130–240, 80–130, or 60–95 nm for the sample prepared at $\rho = 2$, 4, or 6, respectively. Despite the polydispersity of nanoparticles, the diameters estimated by TEM agreed roughly with those determined by DLS. It is worth noting that we have clarified the amorphous nature of PIC nanoparticles by conducting electron diffraction measurements under the TEM observations (See Supporting Information). We conclude that a series of PIC nanoparticles from several tens to hundreds nanometers could be prepared.

At $\rho = 1$, prepared nanoparticles were initially dispersed in solution; however, they are unstable to form agglomerates (or precipitates) quickly. At $\rho > 1$, that is, excess NaTPB is present in solution, the particles were observed to be stable with no precipitation. These results indicate that the PIC nanoparticles are electrostatically stabilized by the adsorption of TPB anions. Actually, we confirmed that the nanoparticle surface has negative charges by conducting a gel electrophoretic measurement; a red-colored zone including PIC nanoparticles moved toward
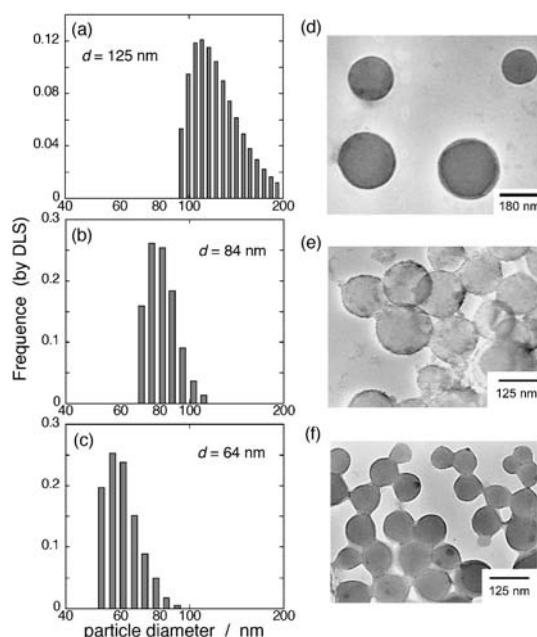

Figure 1. (a)–(c): Size distributions of PIC nanoparticles characterized by DLS. (d)–(f): Representative TEM images of the corresponding nanoparticles. The samples were prepared at different ρ; (a) and (d): $\rho = 2$, (b) and (e): $\rho = 4$, (c) and (f): $\rho = 6$.

the positive electrode when applied a voltage of 150 V. Furthermore, we found that the mean particle size of PIC nanoparticles decreased with increasing ρ, implying that the adsorption of TPB on particle surfaces would suppress the growth of nanoparticles. The size decrease caused by the surface adsorption of ions has been normally observed for metal oxide nanoparticles.[6] On the basis of Gibbs' adsorption equation, the increase in surface adsorption of ions brings about the increase in the surface charge density, yielding to the reduction of the interfacial tension of nanoparticles.[6] Similar to the case of such metal oxide nanoparticles, the increase in the surface adsorption of TPB anions would cause the reduction of interfacial tension of PIC nanoparticles, resulting in the decrease in the particle size.

Figure 2a displays the UV–vis absorption spectra of PIC nanoparticles with different sizes (or different ρ) in aqueous solution. For comparison, the spectrum of pure PIC-Br solution (0.1 mM) is also shown. From these spectra, the following three issues are discussed: (i) The spectral shapes of nanoparticles are quite similar to that of PIC monomer. This indicates that the PIC chromophore units did not aggregate themselves within nanoparticles, different from H and/or J aggregates frequently observed for the dye/anionic-site adsorption systems.[7] The observed monomeric spectrum agrees with the amorphous nature of PIC nanoparticles. (ii) The absorption peak for nanoparticles originated from π–π transition (0–0 band) of PIC chromophore is red-shifted compared to that of monomer in water (energy difference: 720–900 cm^{-1}). Such a large red shift essentially comes from the "solvent (or matrix) effect" that is related to the matrix polarizability.[8] Within the nanoparticle, it is conceivable that PIC is distributed in a hydrophobic TPB matrix with a high index of refraction due to the phenyl rings, and thus, the red shift of the 0–0 band is expected. For PIC dye, a linear relationship has been found between the 0–0 band maximum (v in cm^{-1}) and the matrix polarizability function $\phi(n^2) = (n^2-1)/(n^2+2)$ as follows:[9]

$$v \approx 19716 - 2964\phi(n^2)$$

where n is the refractive index of the matrix for Na-D line at room temperature. The energy of 19716 cm^{-1} corresponds to that of the 0–0 transition of monomeric PIC in a nonsolvated state.[9] Using this equation, for instance, $n = 1.84$ was obtained for the nanoparticle sample with the mean diameter of 64 nm. Although no n value for the TPB matrix has been published, the estimated refractive index seems to be reasonable since some organic crystals show similar value of n such as aromatic anthracene crystal of $n = 1.77$.[10] Note that we have succeeded in tuning the absorption 0–0 peak of PIC nanoparticles by changing the hydrophobic counter ions with a different matrix polarizability (or refractive index), showing a proof of the "matrix effect" (See Supporting Information). (iii) As the average nanoparticle size decreases from 125 to 64 nm, the 0–0 band slightly shifts to shorter wavelength from 549 to 543.5 nm (energy difference: 184 cm^{-1}). The result is summarized in Figure 2b. Note that the polydispersity was similar to each other. The optical size-dependent property of PIC nanoparticles differs from the quantum size effect observed in semiconductor nanoparticles whose sizes are less than the Bohr exciton diameter.[11] Similar size-dependent phenomena have been reported for perylene[12] and pyrazoline nanoparticles[1b] whose size ranges are similar to our systems. The principal reason for the optical size dependence of these organic nanoparticles is still unclear; however, the obtained in-
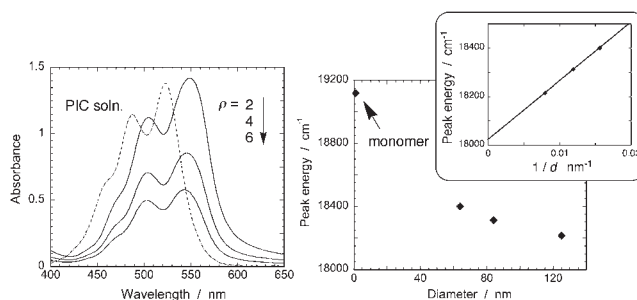
Figure 2. (a) Absorption spectra of PIC nanoparticles in aqueous solution with different sizes. The spectrum of the PIC solution (0.1 mM) is also shown. (b) Relationship between the average particle diameter (d) and the absorption peak position (0–0 band). The inset shows the inverse dependence of the peak position on d.

verse dependence of the 0–0 peak energy on the particle diameter (the inset in Figure 2b) suggests that this effect might be originated from that of the surface-to-volume ratio of nanoparticles such as matrix softening due to the increase in surface distortion.[1d,1e]

In conclusion, we prepared pseudoisocyanine (PIC) dye nanoparticles in aqueous solution based on the "ion-association technique". We believe that this technique will provide versatile syntheses for ion-based organic nanoparticles.

References and Notes
1   a) E. V. Keuren, E. Georgieva, and J. Adrian, *Nano Lett.*, **1**, 141 (2001). b) H. B. Fu and J. N. Yao, *J. Am. Chem. Soc.*, **123**, 1434 (2001). c) X. Gong, T. Milic, C. Xu, J. D. Batteas, and C. M. Drain, *J. Am. Chem. Soc.*, **124**, 14290 (2002). d) H. Kasai, H. Kamatani, S. Okada, H. Oikawa, H. Matsuda, and H. Nakanishi, *Jpn. J. Appl. Phys., Part 2*, **35**, L221 (1996). e) B. K. An, S. K. Kwon, S. D. Jung, and S. Y. Park, *J. Am. Chem. Soc.*, **124**, 14410 (2002).
2   a) B. E. Rabinow, *Nature Rev. Drug Delivery*, **3**, 785 (2004). b) E. Merisko-Liversidge, G. G. Liversidge, and E. R. Cooper, *Eur. J. Pharm. Sci.*, **18**, 113 (2003). c) R. H. Müller, C. Jacobs, and O. Kayser, *Adv. Drug Delivery Rev.*, **47**, 3 (2001).
3   D. Horn and J. Rieger, *Angew. Chem., Int. Ed.*, **40**, 4330 (2001).
4   H. Kamatani, H. Kasai, S. Okada, H. Matsuda, H. Oikawa, N. Mitani, A. Kakuta, K. Ono, A. Mukoh, and H. Nakanishi, *Mol. Cryst. Liq. Cryst.*, **252**, 233 (1994).
5   Precisely, the particles are composed of PIC and TPB moieties. We verified the binary components by measuring the FT-IR spectra of the precipitated sample. However, we call these particles "PIC nanoparticles" because their optical properties are dominated by the PIC chromophore.
6   a) L. Vayssieres, A. Hagfeldt, and S. E. Lindquist, *Pure Appl. Chem.*, **72**, 47 (2000). b) L. Vayssieres, N. Beermann, S.-E. Lindquist, and A. Hagfeldt, *Chem. Mater.*, **13**, 233 (2001).
7   a) D. Möbius, *Adv. Mater.*, **7**, 437 (1995). b) H. Yao, Y. Morita, and K. Kimura, *Surf. Sci.*, **546**, 97 (2003). c) H. Yao, S. Kitamura, and K. Kimura, *Phys. Chem. Chem. Phys.*, **3**, 4560 (2001).
8   The electrostatic interaction between PIC and counter anions might influence the electronic state of PIC chromophores; however, its contribution would be small because such interaction or related electric field is averaged in an amorphous solid.
9   I. Renge and U. P. Wild, *J. Phys. Chem. A*, **101**, 7977 (1997).
10   K. S. Sundarajan, *Z. Kristallogr.*, **93**, 238 (1936).
11   A. D. Yoffe, *Adv. Phys.*, **42**, 173 (1993).
12   H. Kasai, H. Kamatani, Y. Yoshikawa, S. Okada, H. Oikawa, A. Watanabe, O. Itoh, and H. Nakanishi, *Chem. Lett.*, **1997**, 1181.