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Organic Nanoparticles of Porphyrin without Self-aggregation

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Well-dispersed organic nanoparticles of porphyrin with narrow size distribution were successfully prepared in aqueous solution based on the "ion-association" method. No self-aggregation of the constituent porphyrin chromophores was confirmed. The nanoparticles exhibit interesting optical properties; a large bathochromic shift in the absorption and a remarkable resolution increase in the fluorescence compared to those for the corresponding aqueous-phase porphyrin.

Organic dyes have been widely investigated because of their interesting optical, catalytic, electronic, and biochemical properties. Among them, porphyrins are one of the most noticeable pigments that contribute to light harvesting by their strong absorption in the visible region.[1] In recent years, meso/nano-scaled materials composed of porphyrins are highly expected to exhibit chemical activities and unique photonic properties significantly different from those of free porphyrins or those immobilized onto/into supports.[2,3] So far, many studies are focused on self-assembling processes to form supramolecular nanoarchitectures.[3] Although it is undoubtedly important to design such nanoscale systems with ordered porphyrin assemblies, unfavorable aggregation that causes a large decrease in the color quality and/or photoluminescence must have been avoided.[4]

On the other hand, our group has reported a simple and versatile method for preparing organic nanoparticles in aqueous solution using "ion-association" technique.[5] This method is based on the formation of hydrophobic ion-pair nanoparticles in aqueous solution by the association of a dye cation with a hydrophobic anion. In this letter, we report the preparation of highly-dispersed porphyrin nanoparticles under controlled self-aggregation by applying this method.

In the experiments, we chose *meso*-tetrakis(1-methyl-4-pyridinio) porphine (TMPyP, Chart 1) tetra-*p*-tosylate salt as a cationic porphyrin dye. Polyvinylpyrrolidone (PVP; average $M_W = 10{,}000$) was used as a neutral stabilizer to prevent particle agglomeration. The procedure to prepare nanoparticles is as follows: Appropriate volumes of aqueous TMPyP mother solution (0.1 mM) was rapidly added into the aqueous solution containing sodium tetrakis(4-fluorophenyl) borate (NaTFPB, 0.076 mM) and PVP (0.24 mg/mL) under ultrasonication. Further sonication was continued for 10 min. The final concentration of $TMPyP^{4+}$ or $TFPB^-$ was 0.016 or 0.064 mM, respectively. Note that NaTFPB contains a hydrophobic TFPB anion, so that ion association between $TMPyP^{4+}$ cation and $TFPB^-$ anion leads to water-insoluble porphyrin nanoparticle formation.[6] The net charge ratio of the loaded $TFPB^-$ to $TMPyP^{4+}$, that is, $[TFPB^-]/(4 \times [TMPyP^{4+}])$, was 1 (neutral condition). In nanoparticle preparation, we changed the concentration of $TFPB^-$ (or net charge ratio); however, the size and dispersibility did not change. Before the measurements of dynamic light scattering (DLS), UV–vis absorption spectra, fluorescence spectra, and scanning transmission electron microscope (STEM) images, the samples were freshly prepared and filtered by a 200-nm pore size membrane filter.

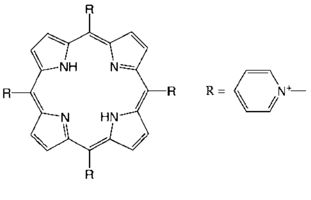

Chart 1. Chemical structure of TMPyP.

Figure 1a shows the STEM image of well-dispersed TMPyP porphyrin nanoparticles exhibiting a spherical shape in the average diameter of ca. 25 nm. The size distribution of the nanoparticles, which was obtained from a DLS measurement, is shown in Figure 1b. The mean diameter was 26 nm and the polydispersity was less than 8%. The diameter estimated by STEM agreed well with that determined by DLS. Note that the absence of PVP in solution yielded no stable TMPyP nanoparticles but formed agglomerates at the same net charge ratio (See Supporting Information). Hence, the high dispersion of nanoparticles shown in Figure 1a suggests that PVP effectively prevents agglomeration of TMPyP nanoparticles in aqueous solution.[7] Moreover, the mean size of TMPyP nanoparticles did not depend on the net charge ratio in the range between 1–3. Unlike the case of pseudoisocyanine dye nanoparticles,[5] the result indicates that adsorption of excess $TFPB^-$ anions onto nanoparticles does not play a sufficient role in stabilizing the nanoparticles.

The UV–vis absorption spectra of TMPyP nanoparticles and the aqueous TMPyP solution (0.01 mM) were shown in Figure 2. The spectrum of aqueous TMPyP solution (curve a, Figure 2) features an intense band around 420 nm known as the Soret band.[8] The Soret band of porphyrin nanoparticles largely shifted to a longer wavelength (436 nm; curve b in Figure 2) compared to that of the aqueous solution. This indicates that $TMPyP^{4+}$ electrostatically interacts with $TFPB^-$, yielding porphyrin nanoparticles. Regarding the red shift of the Soret band, four explanations have been proposed in the past:[9,10] (i) protonation of the porphyrin ring nitrogens, (ii) solvent (or matrix) effect, (iii)

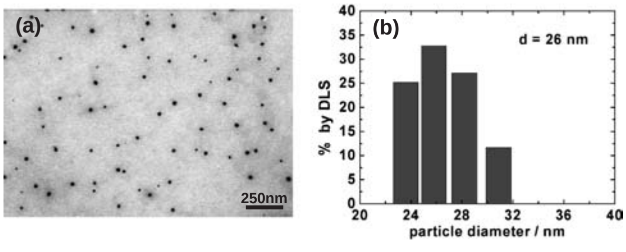

Figure 1. (a) STEM image of TMPyP porphyrin nanoparticles. (b) Size distribution of the corresponding nanoparticles characterized by DLS.

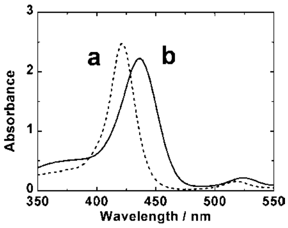

Figure 2. Absorption spectra of (a) aqueous TMPyP solution and (b) TMPyP porphyrin nanoparticles in aqueous solution.

aggregation of porphyrin molecules, and (iv) flattening of the porphyrin molecule caused by the twisting of four cationic methylpyridinium moieties. The scheme (i) is excluded because the solution pH of porphyrin nanoparticles was measured to be 7.3 (pK_a (TMPyP) $= 1.3$ in water at 25 °C).[8c] The scheme (ii) is also not the main reason because very minor spectral shifts of the Soret band are revealed for the TMPyP molecule when the solvents are varied.[11]

To confirm whether the porphyrin moieties are self-aggregated or not within the nanoparticles, fluorescence spectra were measured. Figure 3 shows the fluorescence spectrum of TMPyP porphyrin nanoparticles along with that of aqueous TMPyP solution (0.01 mM).[12a] In nanoparticles, the resolution of the Q(0,0) and Q(0,1) fluorescence bands drastically increased compared to those for the aqueous solution. Moreover, the estimated fluorescence yield of the TMPyP nanoparticle system (0.010–0.013) was similar to that of the aqueous solution.[12b] These results indicate that porphyrin molecules do not aggregate within nanoparticles (denial of the scheme (iii)). Hence, we conclude that ion-based porphyrin nanoparticles are successfully prepared without self-aggregation.

It has been revealed that resonance interaction between the π-system of porphyrin macrocycle and the pyridinium groups requires a rotation toward a coplanar conformation.[8a] The smaller the pyridinium dihedral angle is, the larger the π-conjugation between the side groups and the porphyrin core becomes.[11] Therefore, the large red shift observed in absorption spectra is ascribed to a flattening of the porphyrin molecule in the nanoparticle (scheme (iv)), that is, the four cationic methylpyridinium moieties are obliquely inclined with respect to the porphyrin ring.[13] Similar results have been reported in anionic clay–cationic porphyrin complex systems.[9]

In the coplanar conformation, strong mixing of the S_1 and a close-lying CT (charge transfer from the porphyrin to the pyridinium group) states is expected.[8a] Indeed, an increase in coplanarity of the π-systems caused by the rotation of pyridinium groups upon excitation of TMPyP in water induces a featureless or broad fluorescence (Figure 3a). However, it is known that a decrease in the dielectric constant of the solvent destabilizes the CT state of TMPyP, resulting in the reduction of electronic coupling between the unperturbed S_1 and CT states.[8a] Hence, the observed resolution increase in the fluorescence spectrum of TMPyP nanoparticles would come from the low solvent (TFPB matrix) polarity and/or immobilization of the pyridinium groups in the solid-state nanoparticles.[5,13]

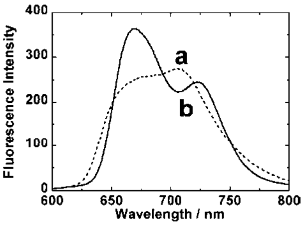

Figure 3. Fluorescence spectra of (a) aqueous TMPyP solution and (b) TMPyP porphyrin nanoparticles in aqueous solution.

In summary, well-dispersed organic nanoparticles of porphyrin are successfully synthesized in aqueous solution based on the "ion-association" technique we have developed. In the nanoparticles, no self-aggregation of the constituent porphyrin chromophores was observed. We believe that this method provides a useful way to prepare porphyrin nanoparticles under controlled aggregation, and it could be promising for constructing artificial photochemical systems.

References and Notes

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6 Precisely, the particles are composed of TMPyP^{4+} and TFPB$^-$ moieties. However, we call these particles "TMPyP (porphyrin) nanoparticles" because their optical properties are dominated by the TMPyP porphyrin chromophore. The results on the elemental analysis based on energy dispersive X-ray (EDX) spectroscopy are shown in Supporting Information.

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12 a) In Figure 3, the excitation wavelength (λ_{ex}) is 524 nm. Note that the fluorescence spectral shape did not depend on λ_{ex}. b) The fluorescence yield of the porphyrin nanoparticles was determined by comparing that of the aqueous TMPyP solution of $\phi = 0.011$ (Ref. 8b). For the estimation, absorbance at λ_{ex} was set to be almost identical and less than 0.1 with each other in both samples.

13 Theoretical calculations show that the dihedral angle of ca. 60° causes a ca. 30 nm red shift in the Soret band of TMPyP (Ref. 11a). On the basis of this estimation, pyridinium moieties would not be completely parallel to the porphyrin ring in our nanoparticles.

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