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# New Morphology-Controlled Poly(aniline) Synthesis Using Anionic Porphyrin Aggregate as a Template and Proton-Driven Structural Changes in the Porphyrin Aggregate

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It was found that 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS), which is known to aggregate in a one-dimensional fashion in water, acts as a template for the electropolymerization of aniline on an ITO electrode. Examinations using cyclic voltammetry (CV) and UV–vis spectroscopy established that J-aggregated TPPS molecules are entrapped in the resultant poly(aniline). Scanning electron microscopy (SEM) observations established that poly(aniline) grows to a nanosized rod-like structure, reflecting the aggregation structure of TPPS. The chemical oxidative polymerization of aniline in the presence of TPPS also gave a poly(aniline) rod-like structure containing the TPPS J-aggregate. It was found that the J-aggregation mode in the poly(aniline)/TPPS composite disappears when the medium pH is shifted from acidic to basic, but is regenerated when the medium pH is shifted from basic to acidic. This interconversion could be visually recognized by changes in the color and the fluorescence intensity.

Poly(aniline) is a conductive polymer, that is easily obtained by the electrochemical polymerization of aniline. In spite of the convenient preparation method and cheapness of the monomer, the applications have been rather limited.[1–3] One reason for the limited number of applications is a serious disadvantage related to a difficulty in controlling the morphology in the polymerization process. Thus, there has been increased interest in synthesizing oriented poly(aniline) and/or morphology-controlled poly(aniline), such as a fibrous structure and a helical structure. To synthesize those polymers, it is known that the presence of certain polymers,[4] camphorsulfonic acid,[5] or amphiphile,[6] which is considered to act as a template in the polymerization process, is effective. However, there was no preceding report, in which the organic superstructure acting as the template is strictly compared with that of the resultant polymer morphology to clarify whether or not fine transcription is really induced. Recently, we and others explored a method to transcribe a variety of organic superstructures into inorganic materials by a sol–gel reaction of metal alkoxides ("sol–gel transcription"), by which one can control the morphology of inorganic compounds and create various new superstructural inorganic materials.[7–13] The driving force operating in this sol–gel transcription is considered to be electrostatic and/or hydrogen-bonding interactions between silica nanoparticles and organic assemblies acting as the templates. Thus, it occurred to us that the film structure of poly(aniline) would also be controllable, by applying the concept of the template method to the electropolymerization process: that is, as aniline is protonated under acidic conditions, the anionic assemblies should act as an appropriate template because of the mutual electrostatic interaction. Here, we employed the assembly of an anionic porphyrin (TPPS) as a template, because the porphyrin tends to aggregate in a one-dimensional direction and the aggregate structure is well characterized by microscopic methods.[14,15] We here report, for the first time, that the electropolymerization of aniline results in a novel rod-like structure due to the template effect of the one-dimensionally-stacked TPPS aggregate[16] and their application as a proton sensor.

## Results and Discussion

**Electro and Chemical Oxidative Polymerization of Aniline in the Presence of TPPS Aggregate.** An aqueous solution containing aniline sulfate (5.0 mmol dm$^{-3}$), $H_2SO_4$ (50 mmol dm$^{-3}$), and $Na_2SO_4$ (50 mmol dm$^{-3}$) was subjected to electropolymerization in both the absence and presence of TPPS (0.11 mmol dm$^{-3}$). Figure 1 shows a UV–vis spectrum of a polymerization solution containing TPPS. Absorption peaks were observed at 490 nm and 430 nm, which are assigned to an exciton band and a red-shifted Soret band, respectively.[17,18] This spectral pattern indicates that TPPS molecules

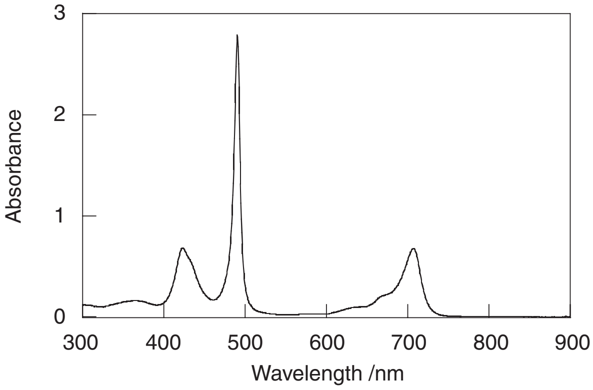

Fig. 1. UV–vis spectrum of TPPS J-aggregate under the polymerization conditions (cell length: 1 mm).

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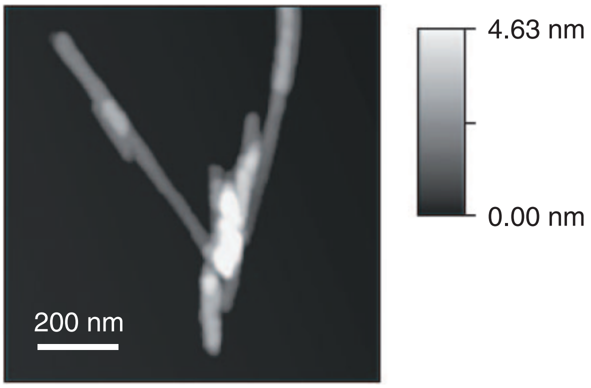

Fig. 2. AFM image of the TPPS J-aggregate prepared from 0.11 mmol dm$^{-3}$ of TPPS aqueous solution on mica.

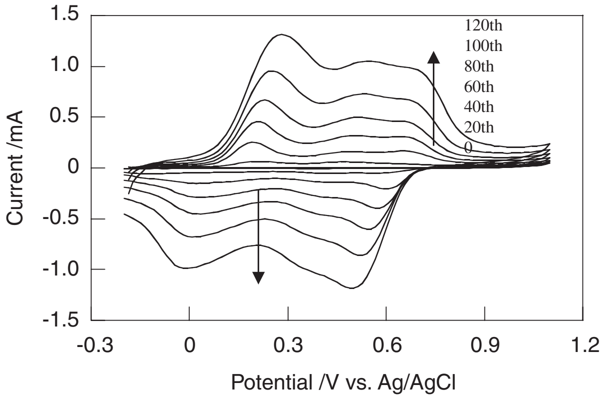

Fig. 3. Electropolymerization of aniline in the presence of the TPPS J-aggregate.

are assembled into a J-aggregate in the polymerization solution.

As shown in Fig. 2, an AFM measurement established that this TPPS J-aggregate forms a rod-like structure with ca. 1 µm length and 2–3 nm height. This image indicates that the TPPS molecules tend to grow to a one-dimensional aggregate, and several aggregates are assembled to form a bundle that can be recognized as a rod on mica.

The electropolymerization cell consisted of an ITO electrode as the working electrode, a Pt counter electrode, and an Ag/AgCl reference electrode. The redox was repeated in a voltage range of −0.2 to 1.1 V (vs Ag/AgCl) with a scan rate of 0.1 V s$^{-1}$ at 25 °C. Three redox peaks at $E_{\text{ox}}/E_{\text{red}} =$ 0.2/0.0, 0.5/0.35, and 0.65/0.5 V (vs Ag/AgCl) increase during the successive potential sweeping in the presence of TPPS (Fig. 3), corresponding to the growth of an electroactive polymer film on the ITO electrode.

Figure 4 shows the UV–vis absorption spectra of the film obtained at potentials from 0 to 0.6 V (vs Ag/AgCl) electropolymerized after 120 cycles on the ITO electrode. One can clearly recognize an exciton-coupling band (491 nm) as well as a Soret band (426 nm) and Q bands (660–730 nm), indicating that TPPS molecules are deposited in this thin film layer. This spectral pattern establishes that the J-aggregate formed in solution is still maintained even after deposition in the poly(aniline) film. To obtain unambiguous evidence that this thin film is made from poly(aniline), the UV–vis absorption spectra were measured in a 50 mmol dm$^{-3}$ of $H_2SO_4$ aqueous solution containing 50 mmol dm$^{-3}$ of $Na_2SO_4$ under various voltages (Fig. 4). As expected, the absorbance at the visible wavelength region increases with an increase in the applied voltage, which is a characteristic property of the poly(aniline) film.[19] The foregoing findings consistently support the view that the oxidative polymerization of aniline on the ITO electrode proceeds under the influence of the electrostatic interaction with anionic TPPS aggregates to form a poly(aniline)/TPPS composite film.

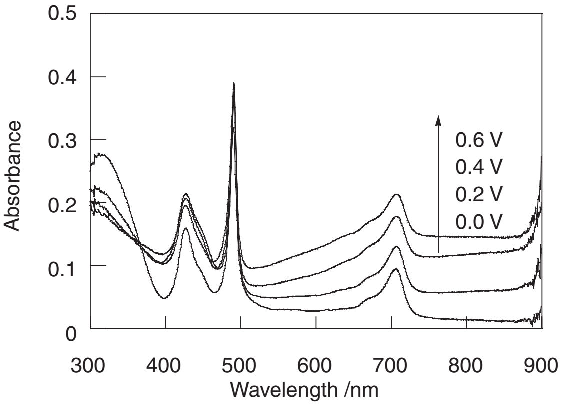

Fig. 4. UV–vis absorption spectra of the poly(aniline) film in 50 mmol dm$^{-3}$ $H_2SO_4$ at potentials from 0 to 0.6 V electropolymerized after 120 cycles in a voltage range of −0.2 to 1.1 V.

To obtain a visual image of this composite film, we took SEM pictures (Fig. 5). The electropolymerization of aniline in the presence of TPPS (after 120 cycles) affords a rod-like structure with 200–1000 nm length and 30–50 nm diameter (Figs. 5a and 5b). When the redox treatment was stopped after 30 cycles, the resultant nanorods were "thinner" (with 20–40 nm diameter: Fig. 5c) than those obtained after 120 cycles (Fig. 5b). This morphological difference implies that the nanorods are adsorbed onto the ITO electrode surface in its incipient stage, and then grow to "fat" nanorods on the surface. As a reference experiment, we confirmed that electropolymerization of aniline results in a film with a smooth surface in the absence of TPPS (Fig. 5d).

**Structural Evaluation of Poly(aniline)/TPPS Composites.** We estimated the influence of the TPPS concentration on the morphology and the CV. The SEM images obtained after 120 cycles at various TPPS concentrations are shown in Fig. 6. As long as the aniline concentration is kept constant, the size of the nanorods is not very different among Figs. 6a, 6b, and 6c. However, the "density" of the nanorods was significantly dependent on the TPPS concentration: that is, the network becomes more crowded with an increase in the TPPS concentration. In other words, the "density" reflects the "number" of nanorods formed in solution. This is raised as further evidence that the TPPS aggregates act as a template for nanorod formation by the electropolymerization of aniline.

Figure 7 shows CV charts after 120 cycles normalized at 0.5 V. Two peaks at 0.2/0.0 (peak I) and 0.65/0.5 V (peak II) (vs Ag/AgCl), which are caused by the oxidation of poly(aniline), increase with increasing TPPS concentration.[19] The middle peak III is usually assigned to the cross-linking unit in the

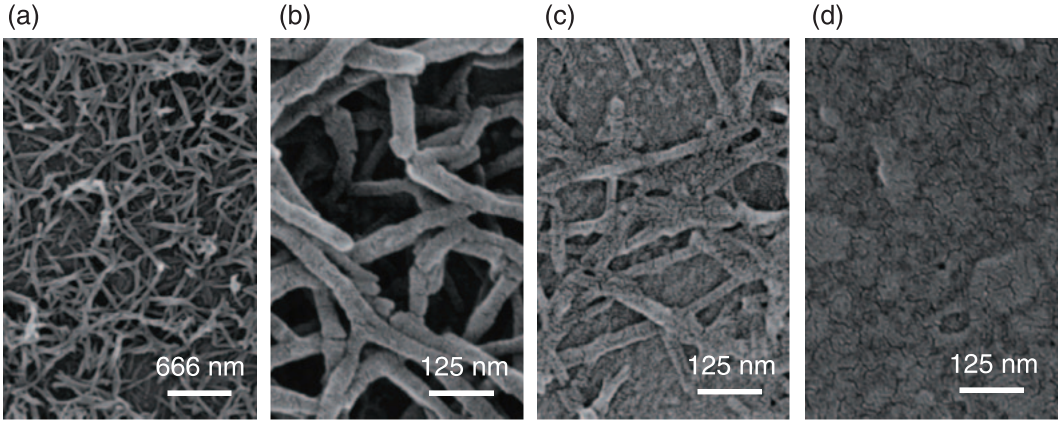

Fig. 5. SEM images of poly(aniline) films electropolymerized after various cycles: (a) and (b) 120 cycles in the presence of TPPS, (c) 30 cycles in the presence of TPPS, (d) 120 cycles in the absence of TPPS.

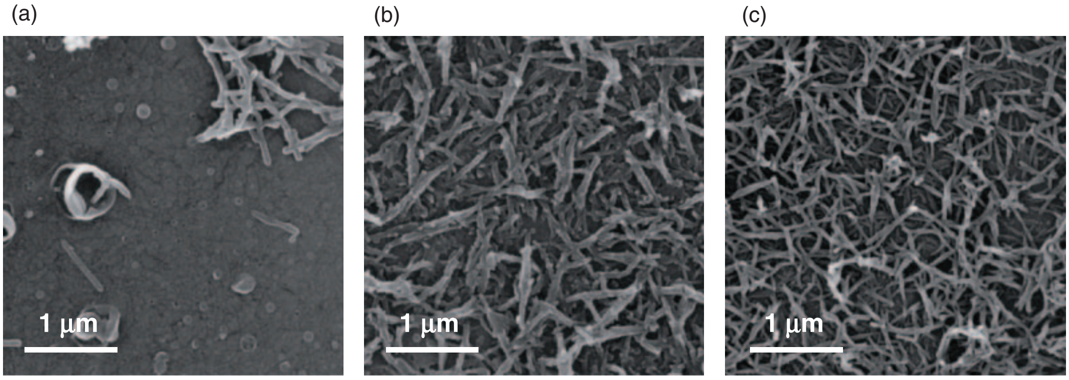

Fig. 6. SEM images of poly(aniline) films electropolymerized after 120 cycles at various TPPS concentrations: (a) 0.011 mmol dm$^{-3}$, (b) 0.032 mmol dm$^{-3}$, (c) 0.11 mmol dm$^{-3}$. The flat background is the poly(aniline) film formed without the template effect.

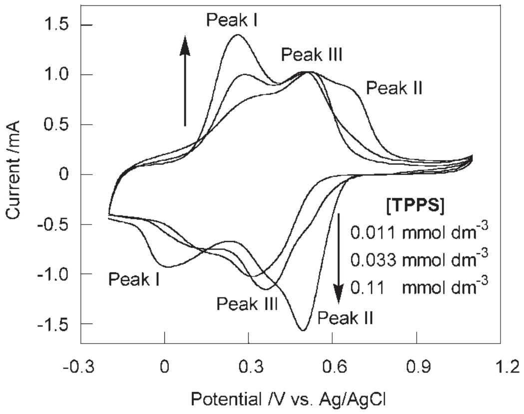

Fig. 7. Cyclic voltammograms of poly(aniline) films electropolymerized at various concentrations of TPPS normalized at 0.5 V.

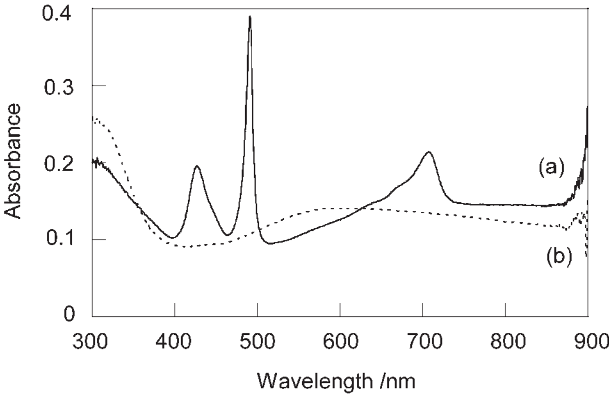

Fig. 8. UV–vis spectra of poly(aniline) films at 0.6 V electropolymerized in (a) the presence and (b) the absence of TPPS, at 25 °C.

poly(aniline), yielded by some side reaction and/or overoxidation.[19,20] The increase of this peak is rather suppressed by TPPS addition, and the peak intensity is significantly weaker than that of the poly(aniline) film obtained in the absence of TPPS. These results indicate that the presence of the TPPS J-aggregate facilitates the electropolymerization of aniline to yield more redox-active poly(aniline) films, and inhibits the generation of cross-linking and/or overoxidation products of poly(aniline) through the templating effect.

UV–vis spectra of poly(aniline) films electropolymerized in both the presence and absence of TPPS were measured at 0.6 V (Fig. 8). The poly(aniline) film prepared in the absence of TPPS had an absorption band at around 570 nm (Fig. 8b), whereas the poly(aniline)/TPPS composite film had an absorption band near to the IR region, assignable to the conventional poly(aniline) film (Fig. 8a). This result indicates that the poly(aniline)/TPPS composite features a longer conjugate length: that is, the template effect of the TPPS J-aggregate is valid not only for the reaction of a novel fibrous poly(aniline) bundle, but also for the facilitation of electropolymerization and suppression of side reactions.

To obtain the ratio of poly(aniline) vs TPPS composition, X-ray photoelectron spectroscopy (XPS) measurements were performed on electropolymerized poly(aniline) films. To exclude any contribution of sulfur coming from the electrolyte and acid, a HCl aqueous solution and NaCl were used instead of $H_2SO_4$ and $Na_2SO_4$. The final concentrations of the reagents are mentioned as follows: $[\text{TPPS}] = 0.11\ \text{mmol dm}^{-3}$, $[\text{aniline}] = 10\ \text{mmol dm}^{-3}$, $[\text{HCl}] = 0.11\ \text{mol dm}^{-3}$, and $[\text{NaCl}] = 50\ \text{mmol dm}^{-3}$. An electropolymerization solution containing chloride ion was obtained performed under the same conditions as that containing sulfate ion. A redox active poly(aniline) film was also yielded, and the CV responses were similar to those shown in Fig. 3. One may, therefore, consider that a similar poly(aniline) film was obtained from the polymerization solution containing chloride ion. Figure 9 shows the XPS spectra of poly(aniline) films electropolymerized in both the presence and absence of TPPS. New peaks (shown with allow marks) assignable to sulfur were observed only for the poly(aniline)/TPPS film. This result provides another evidence that the TPPS J-aggregate is deposited as counteranions in the film (Fig. 9a). The molar ratio of TPPS to the aniline unit was calculated from the elemental ratio of C/N/S in the poly(aniline)/TPPS film, resulting in the molar ratio of TPPS to the aniline unit being 1:16.

To obtain a TEM image of the poly(aniline)/TPPS composite film, one has to peel the film out of the electrode surface. However, this treatment may damage the superstructural morphology of the polymeric bundle. We thus prepared a sample for a TEM observation by chemical oxidative polymerization in homogeneous solution. This experiment was also significant to confirm whether chemical oxidative polymerization results in the same morphology as electropolymerization. The chemical oxidative polymerization of aniline in the presence of TPPS was performed using ammonium peroxodisulfate (APS) as an oxidizing reagent. APS was added to the polymerization solution, the reaction mixture was kept for 60 min, and then dialysis (MW: 10000) of the reaction mixture yielded a poly(aniline)/TPPS composite as a greenish-black precipitate. Figure 10 shows a UV–vis spectrum of the poly(aniline)/TPPS composite dispersed in $50\ \text{mmol dm}^{-3}$ $H_2SO_4$ aqueous solution. One can clearly recognize an exciton-coupling band (491 nm) as well as a Soret band (426 nm) and Q bands (660–730 nm), indicating that TPPS molecules still maintain a J-aggregate in the obtained poly(aniline), and are not removed from the composite even after dialysis. This finding indicates that the TPPS J-aggregate is strongly entrapped in the poly(aniline).

Figure 10 shows TEM images of the thus-obtained poly(aniline)/TPPS composite. Since they were observed without a staining treatment, one may consider that the contrast can be attributed to the presence of poly(aniline). As shown in Fig. 11, poly(aniline)/TPPS composite forms a rod-like structure which is similar to that observed for the poly(aniline) film prepared by electropolymerization (see Fig. 5). Interestingly, one can recognize the presence of a hollow inside some rod-like poly(aniline) bundles, the size of which (ca. 20 nm) is

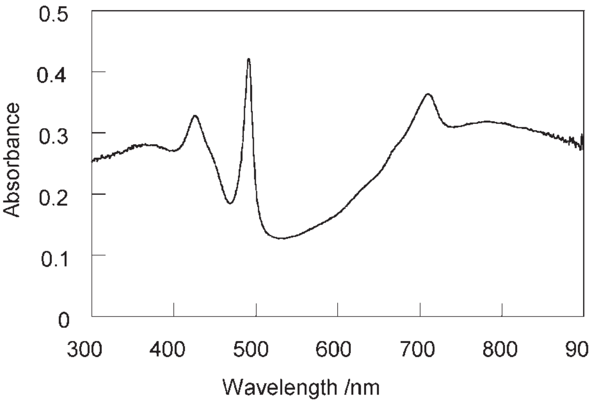

Fig. 10. UV–vis spectrum of the poly(aniline)/TPPS composite dispersed in a $50\ \text{mmol dm}^{-3}$ $H_2SO_4$ aqueous solution, at 25 °C.

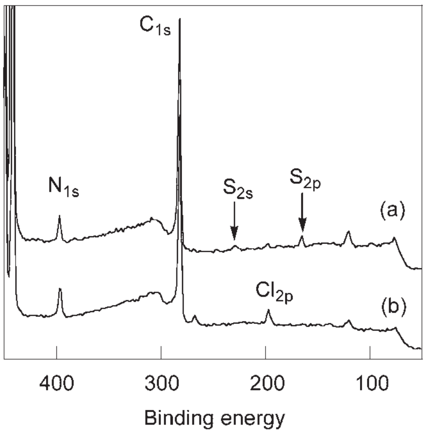

Fig. 9. XPS spectra of the poly(aniline) films electropolymerized in (a) the presence and (b) the absence of TPPS.

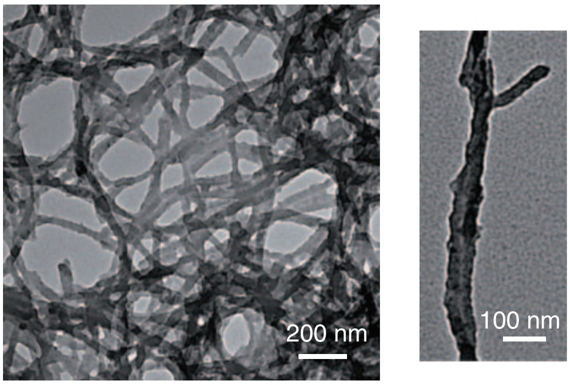

Fig. 11. TEM images of a poly(aniline)/TPPS composite obtained from the chemical oxidative polymerization of aniline in the presence of TPPS (without a staining treatment).

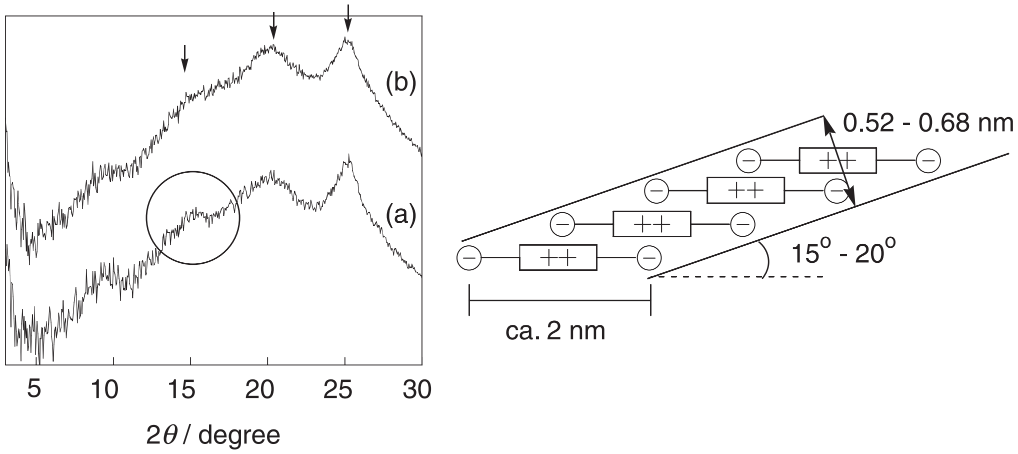

Fig. 12. XRD patterns of poly(aniline)s obtained from chemical oxidation in (a) the presence and (b) the absence of TPPS, and a schematic representation of the porphyrin packing mode in the J-aggregate.

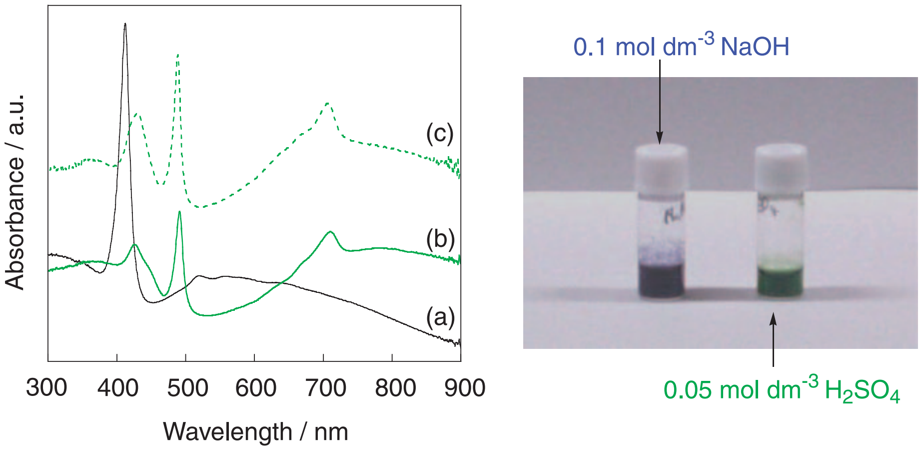

Fig. 13. UV–vis spectra and color change of the poly(aniline)/TPPS composite: (a) poly(aniline)/TPPS composite dispersed in a 0.1 mol dm$^{-3}$ NaOH aqueous solution, (b) poly(aniline)/TPPS composite dispersed in a 50 mmol dm$^{-3}$ $H_2SO_4$ aqueous solution, (c) after the addition of a $H_2SO_4$ aqueous solution to the solution of (a) until it reaches to an acidic condition (ca. pH 2.5).

comparable to that of the TPPS J-aggregate formed in solution. It is, therefore, undoubted that the TPPS J-aggregate acts as a template.

The X-ray diffraction (XRD) pattern was measured for the poly(aniline) and the poly(aniline)/TPPS composite prepared by chemical oxidative polymerization. The typical XRD patterns of the poly(aniline) and poly(aniline)/TPPS composites are shown in Fig. 12. The poly(aniline) prepared by chemical oxidative polymerization has three diffraction angles ($2\theta =$ 15°, 20°, and 25°: arrow marks in Fig. 12), which are in accord with those reported in a reference.[21] The poly(aniline)/TPPS composite has a similar diffraction pattern to that of the poly(aniline), except for an increase in the peak intensity at 15° (circle in Fig. 12). It is known that the TPPS J-aggregate is constructed by an intermolecular association between the positively charged porphyrin ring and negatively charged sulfonate groups (see Fig. 12).[17] Taking this orientation into account, the diameter of one fiber is estimated to be ca. 0.6 nm. This value is compatible to a diffraction angle of 15°, the intensity of which increases in the poly(aniline)/TPPS composite. Thus, the XRD data also support the view that the TPPS J-aggregate is included in the composite.

**Fluorescence Changes in the Poly(aniline)/TPPS Composite Induced by Alignment Changes in TPPS.** The color change of a poly(aniline)/TPPS composite prepared by chemical oxidation was monitored under an acidic condition or a basic condition. Figure 13 shows its UV–vis spectra and color change; the sample was dispersed in a 50 mmol dm$^{-3}$ $H_2SO_4$ aqueous solution or a 0.1 mol dm$^{-3}$ NaOH aqueous solution. The poly(aniline)/TPPS composite gave a green turbid solution under an acidic condition and a bluish purple, turbid solution under a basic condition (Fig. 13).[5] This color change was the same as that already reported in a reference.[5] It can be seen from Fig. 13a that under a basic condition, the Soret band appears very strongly, while the exciton-coupling band is considerably suppressed. This spectral change implies that TPPS molecules are no longer oriented according to the J-aggregation mode.[22] When the solution was returned to the acidic condition by the addition of $H_2SO_4$, the original spectral pattern having a stronger exciton-coupling band and a red-shifted Soret band was reproduced (Fig. 13c). According to the TEM observation, the rod-like morphology of the poly(aniline)/TPPS was scarcely affected by the pH change. As a summary of the foregoing findings, one can propose that the spectral

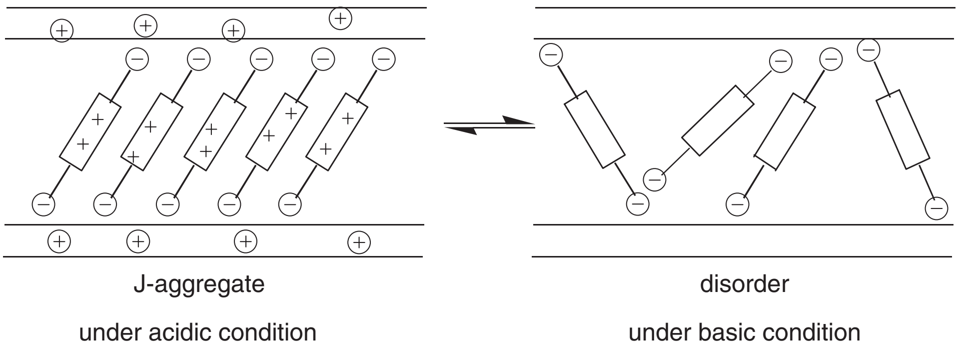

Fig. 14. Reversible J-aggregation/disorder interconversion of TPPS molecules induced by a pH change.

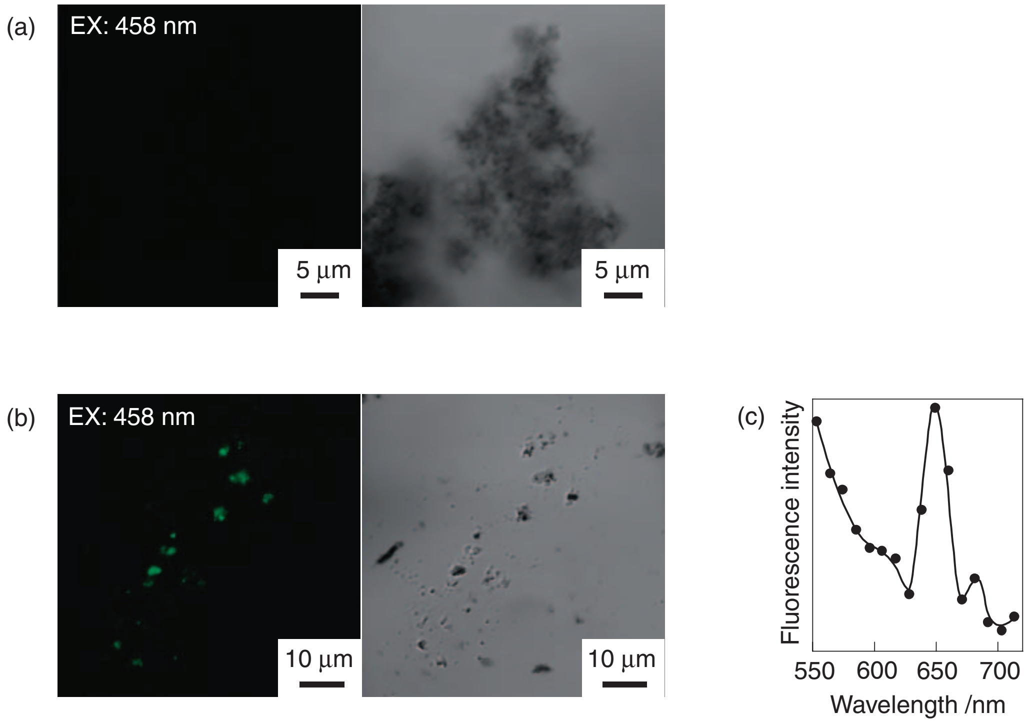

Fig. 15. CLSM images and light transmission images of poly(aniline)/TPPS composite dispersed in (a) 50 mmol dm$^{-3}$ $H_2SO_4$ aqueous solution, (b) 0.1 mol dm$^{-3}$ NaOH aqueous solution, and (c) fluorescence spectrum of poly(aniline)/TPPS obtained from fluorescence spot in CLSM image: excitation wavelength, 458 nm.

change is due to a change in the aggregation mode of TPPS molecules deposited in the poly(aniline). Under an acidic condition, the poly(aniline) carries the cationic charges due to partial protonation, and anionic TPPS molecules are assembled into the J-aggregate through an electrostatic interaction (Fig. 14a). Under a basic condition, these cationic charges almost disappear, and there is no direct interactive force enforcing TPPS molecules to arrange in the J-aggregate. Important is the finding that the J-aggregate can be regenerated by protonation of the poly(aniline). We, therefore, consider that the nitrogen base near the sulfonate group is protonated more easily or the poly(aniline) bundle keeps the memory for the J-aggregation mode.

The pH-induced interconversion of the TPPS assembly was monitored in situ using confocal laser scanning microscopy (CLSM) in a 50 mmol dm$^{-3}$ $H_2SO_4$ aqueous solution or a 0.1 mol dm$^{-3}$ NaOH aqueous solution. Under an acidic condition, fluorescence emission is not observed, even for the spots where the presence of the poly(aniline)/TPPS composite is recognized by a light transmission image (Fig. 15a). In general, protonated porphyrins are weakly fluorescent. Under an acidic condition, these porphyrins are assembled, so that the fluorescence emission from the J-aggregate is scarcely detectable. Under a basic condition, the bright fluorescence spots are clearly observed, overlapping with those of the light-transmission image (Fig. 15b). This implies that TPPS molecules exist almost discretely as fluorescence-active species in the poly(aniline). In fact, the fluorescence maximum (650 nm) obtained by excitation of the bright spot is attributed to the fluorescence of a monomeric porphyrin (Fig. 15c). These results indicate that the poly(aniline)/TPPS composite shows fluorescence only under a basic condition, due to the monomeric dispersion of TPPS molecules in the rod-like poly(aniline) structure.

## Conclusion

In conclusion, the present study has demonstrated, for the first time to the best of our knowledge, that the morphology of poly(aniline) can be controlled by using anionic TPPS aggregates as a template. One may regard, therefore, that this is a novel transcription process of anionic templates to poly(aniline) through electropolymerization as well as chemical oxidative polymerization. So far, it has been believed that the difficulty in the structure control is a serious demerit in the oxidative polymerization of aniline in spite of its easiness of preparation. This demerit has hampered broad applications of poly(aniline) as functional materials. The present study would solve this demerit (at least partially) and stimulate further utilization of poly(aniline) as new functional materials. In addition, the finding that the aggregation mode of TPPS can be controlled by the pH is very novel. We now consider that, in principle, the various polymeric superstructures can be created from poly(aniline) as long as appropriate "anionic" assemblies suitable for the template and the orientation can be controlled by stimuli from the outside world.

## Experimental

**General Methods.** Cyclic voltammometry (CV) experiments were performed with a one-compartment, three electrode electrochemical cell driven by an electrochemical analyzer (BAS 100B) in an aqueous solution. UV–vis spectroscopy measurements were performed on a Shimadzu UV-2500. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a Perkin-Elmer ESCA 5300 spectrometer. Scanning electron microscopy (SEM) studies were carried out on a Hitachi S-5000. Transmission electron microscopy (TEM) studies were carried out on a JEOL JEM-2010. Confocal laser scanning microscopy (CLSM) studies were carried out on a BIO-RAD Radiance 2000 AGR3. The excitation wavelength was 458 nm. X-ray diffractograms (XRD) were recorded on an imaging plate using Cu radiation ($\lambda = 1.54178$ Å at a distance of 15 cm).

**Materials.** TPPS (Tokyo Kasei Kogyo), aniline (Wako Chemicals), $H_2SO_4$ (Kishida Chemicals), and $Na_2SO_4$ (Kishida Chemicals) were used as received.

**Synthesis of TPPS/Poly(aniline) by Electropolymerization.** An aqueous solution containing aniline sulfate (5.0 mmol dm$^{-3}$), $H_2SO_4$ (50 mmol dm$^{-3}$), and $Na_2SO_4$ (50 mmol dm$^{-3}$) was subjected to electrochemical polymerization in the presence of TPPS (0.11 mmol dm$^{-3}$). The cell consisted of an ITO electrode as the working electrode, a Pt counter electrode, and an Ag/AgCl reference electrode. The redox was repeated in a voltage range of $-0.2$ to 1.1 V (vs Ag/AgCl) with a scan rate of 0.1 V s$^{-1}$ at 25 °C.

**Synthesis of TPPS/Poly(aniline) by Chemical Oxidative Polymerization with APS.** An aqueous solution containing aniline sulfate (5.0 mmol dm$^{-3}$), $H_2SO_4$ (50 mmol dm$^{-3}$), and $Na_2SO_4$ (50 mmol dm$^{-3}$) was subjected to chemical oxidative polymerization in the presence of TPPS (0.11 mmol dm$^{-3}$). APS (12 mg) was added to 10 mL of the polymerization solution, the reaction mixture was kept for 60 min at 25 °C, and dialysis (MW: 10000) of the reaction mixture yielded the poly(aniline)/TPPS composite as a greenish-black precipitate.

## References

1 P. N. Bartlett and J. H. Wang, *J. Chem. Soc., Faraday Trans.*, **92**, 4137 (1996).

2 E. Pringsheim, E. Terpetschnig, S. A. Piletsky, and O. S. Wolfbeis, *Adv. Mater.*, **11**, 865 (1999).

3 E. Shoji and M. S. Freund, *J. Am. Chem. Soc.*, **123**, 3383 (2001).

4 J. M. Liu and S. C. Yang, *J. Chem. Soc., Chem. Commun.*, **1991**, 1529.

5 J. Huang and R. B. Kaner, *J. Am. Chem. Soc.*, **126**, 851 (2004); W. Li and H.-L. Wang, *J. Am. Chem. Soc.*, **126**, 2278 (2004).

6 M. Kanungo, A. Kumar, and A. Q. Contractor, *J. Electroanal. Chem.*, **528**, 46 (2002); Z. Zhong and M. Wan, *Synth. Met.*, **128**, 83 (2002); Z. Wei and M. Wan, *Adv. Mater.*, **14**, 1314 (2002).

7 J. H. Jung, Y. Ono, K. Hanabusa, and S. Shinkai, *J. Am. Chem. Soc.*, **122**, 5008 (2000); J. H. Jung, Y. Ono, K. Sakurai, M. Sano, and S. Shinkai, *J. Am. Chem. Soc.*, **122**, 8648 (2000); Y. Ono, K. Nakashima, M. Sano, J. Hojo, and S. Shinkai, *J. Mater. Chem.*, **11**, 2412 (2001).

8 S. Kobayashi, N. Hamasaki, M. Suzuki, M. Kimura, H. Shirai, and K. Hanabusa, *J. Am. Chem. Soc.*, **124**, 6550 (2002), and reference cited therein.

9 A. M. Seddon, H. M. Patel, S. L. Burkett, and S. Mann, *Angew. Chem., Int. Ed.*, **41**, 2988 (2002).

10 K. Katagiri, R. Hamasaki, K. Ariga, and J. Kikuchi, *J. Am. Chem. Soc.*, **124**, 7892 (2002).

11 J. H. Jung, S. Shinkai, and T. Shimizu, *Nano Lett.*, **2**, 17 (2002).

12 K. Sugiyasu, S. Tamaru, M. Takeuchi, D. Berthier, I. Huc, R. Oda, and S. Shinkai, *Chem. Commun.*, **2002**, 1212.

13 For a recent review, see: K. C. J. van Bommel, A. Friggeri, and S. Shinkai, *Angew. Chem., Int. Ed.*, **42**, 980 (2003).

14 M. Kimura, T. Shiba, M. Yamazaki, K. Hanabusa, H. Shirai, and N. Kobayashi, *J. Am. Chem. Soc.*, **123**, 5636 (2001); S. Tamaru, M. Takeuchi, M. Sano, and S. Shinkai, *Angew. Chem., Int. Ed.*, **41**, 853 (2002).

15 A. Miura, Y. Yanagawa, and N. Tamai, *J. Microsc.*, **202**, 401 (2001).

16 Preliminary communication: T. Hatano, M. Takeuchi, A. Ikeda, and S. Shinkai, *Chem. Lett.*, **32**, 314 (2003).

17 R. Rubires, J.-A. Farrera, and J. M. Ribo, *Chem.—Eur. J.*, **7**, 436 (2001).

18 M. Shirakawa, S. Kawano, N. Fujita, K. Sada, and S. Shinkai, *J. Org. Chem.*, **68**, 5037 (2003).

19 A. Abd-Elwahed and R. Holze, *Synth. Met.*, **131**, 61 (2002).

20 E. M. Genies, M. Lapkowski, and J. F. Penneau, *J. Electroanal. Chem.*, **249**, 97 (1988).

21 X. Sui, Y. Chu, S. Xing, and C. Liu, *Mater. Lett.*, **25**, 1255 (2004); R. Murugesan and E. Subramanian, *Mater. Chem. Phys.*, **80**, 731 (2003).

22 The XRD pattern had been measured for the poly(aniline)/TPPS composite treated under basic conditions. It is, however, difficult to obtain the data for the poly(aniline)/TPPS composite because inorganic materials complicated the XRD measurement and analyses.