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# Rational Design and Creation of Novel Polymeric Superstructures by Oxidative Polymerization Utilizing Anionic Templates

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Conjugate polymers assemble into novel superstructures when they are prepared by chemical or electrochemical oxidation of ethylenedioxythiophene, pyrrole or aniline in the presence of 'anionic' templates. The 'anionic' templates used are the [60]fullerene/anionic calix[8]arene complex, anionic porphyrin J-aggregate, anionic synthetic lipids, DNA, DNA/single-walled carbon nanotube complex, etc. Thus, dots, fibers, helical tapes, circles, etc. can be created from the assemblies of these conjugate polymers. We confirm that these conjugate polymers have a sufficient level of electroconductivity. In several systems, interesting redox properties were observed: when the [60]fullerene/conjugate polymer composite was deposited on an indium tin oxide (ITO) electrode, a significant amount of photocurrent was generated. The composite including DNA acted as a DNA sensor. We thus believe that the present templating system is useful as a new method to rationally design and conveniently create novel polymeric superstructures having interesting photochemical and redox properties.

*Keywords:* Templating polymerization; Conductive polymers; Superstructures; Helical structures; DNAs

## INTRODUCTION

Oriented polymers and polymer nanostructures have recently attracted wide attention [1–3]. In particular, such structures consisting of conjugate polymers have potential application to electrochemical switches, electric devices, sensors, and so on [4–7]. Poly(ethylenedioxythiophene) (PEDOT), poly(pyrrole) (PP) and poly(aniline) (PANI) are typical examples of such conjugate polymers easily obtained by chemical or electrochemical oxidative polymerization of the corresponding monomers.

So far, several attempts have been made to construct oriented polymers and polymeric nanostructures: for example, they have been prepared in oriented environments such as LB membranes [8], surfactant aggregates [9–13], liquid crystals [14–15], and so on [16–21]. It is known, however, that in these systems the prediction of the resultant superstructures and the fine-tuning of the polymer assemblies are very difficult, and in most cases these superstructures are in fact obtained by accident.

More recently, we and others have explored a new method to transcribe a variety of organic superstructural assemblies into inorganic materials by a sol–gel reaction of metal alkoxides ('templating sol–gel reaction'), by which we can fine-tune the morphology of inorganic compounds and create various new superstructural inorganic materials [22–41]. The driving force operating in these templating sol–gel reactions is considered to be electrostatic and/or hydrogen-bonding interactions between silica nanoparticles and organic assemblies acting as templates [32–33]. Thus, it occurred to us that the morphology of the aggregates constructed by assembling these conjugate polymers would also be controllable, applying this templating concept: that is, as oxidative polymerization of these monomers produces cationic intermediates, the anionic assemblies should act as a potential template due to the mutual electrostatic attractive force (Fig. 1). In fact, we found that when single-walled carbon nanotubes (SWNTs) dispersed into aqueous solution by sodium dodecylsulfate are used as a template, the conjugate polymers are produced by electrochemical polymerization on the ITO electrode [42–43].

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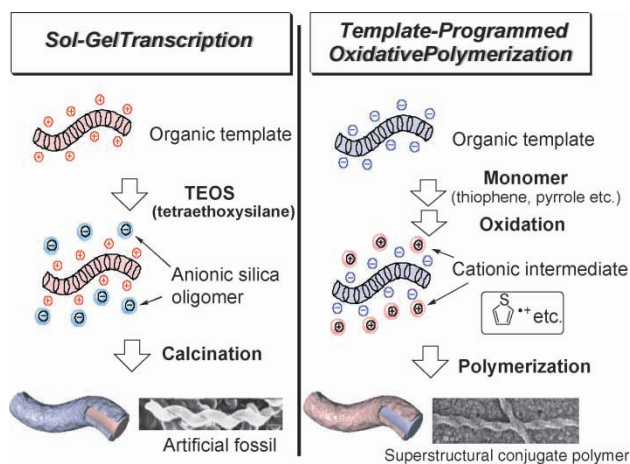


FIGURE 1 Conceptual illustrations of sol-gel transcription using a cationic template (left) and template-programmed oxidative polymerization using an anionic template (right).

Scanning electron microscopy (SEM) established that the resulting conjugate polymers assemble into a fibrous superstructure similar to that of the original template. This implies that the structure of the SWNTs is transcribed into the polymeric assembly structure. These novel findings prompted us to apply this concept to a variety of anionic templates bearing unique superstructures.

#### FACILE DEPOSITION OF [60]FULLERENE INSULATED BY A HOST-GUEST INTERACTION ON THE ITO ELECTRODE

The ready availability of [60]fullerene and its homologues as novel electron-pool  $\pi$ -systems has increasingly invited exploration of their outstanding new physical and chemical properties. In particular, the preparation of superstructural fullerenes is of great interest from both a fundamental and a practical point of view [44–45]. However, the challenge is to overcome the high aggregation tendency inherent to these carbon spheres [46–47]. One approach to overcome this problem is to introduce either thin-layer-forming substituents (such as long aliphatic groups [48–51]) or surface-adsorptive substituents (such as trimethoxysilyl or mercapto groups [52–58]) into these carbon spheres. These derivatives may be deposited on electrode surfaces as monolayers by means of Langmuir–Blodgett (LB) techniques and self-assembly. In the case of fullerene derivatives, monolayer systems composed of covalently linked donor–acceptor molecules can result in high light-to-photocurrent conversion values, because the fullerene layers tend to generate long-lived charge-separated species [59–61]. However, only a few studies have so far been reported for these systems because of the synthetic difficulty in covalently linking all of the thin-layer-forming substituents in one molecular system

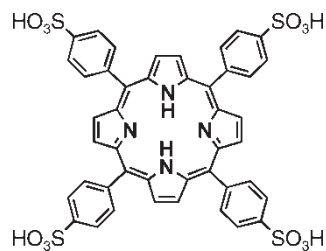
[59–61]. It thus occurred to us that a self-assembly method, which is easily prepared by alternate adsorption of donor and acceptor layers [62–65], will offer a promising prospect for formation of new multilayer photocurrent generation systems on the electrode. Previously, we reported that a hexacationic homooxacalix[3]arene-[60]fullerene 2:1 complex can be deposited on anion-coated gold surfaces as a monolayer or as a component of a bilayer with a porphyrin-containing anionic polymer [66–69]. As expected, these membranes showed an efficient redox response in cyclic voltammetry (CV) and a photoelectrochemical response under visible light irradiation [68–69]. Taking these results into consideration, we designed a photocurrent generation system in which [60]fullerene encapsulated in anionic *p*-sulfonatocalix[8]arene (**1**) is deposited on the electrode through fabrication by conjugate polymers [42–43].

It was found that [60]fullerene encapsulated in **1** can be readily deposited on the ITO electrode by electrochemical oxidative polymerization of ethylenedioxythiophene (EDOT) without chemical modification of this carbon sphere. The driving force for the deposition is an electrostatic interaction between the anionic charges in the [60]fullerene **1** complex and the cationic charges of PEDOT formed in the oxidative polymerization process. The surface morphology was thoroughly characterized by SEM: the [60]fullerene/PEDOT film is covered by nanoparticles of diameter 20–100 nm. The results indicate that the anionic complexes act as nuclei of the polymer growth in the oxidative polymerization. Interestingly, when this modified ITO electrode was photoirradiated, photocurrent generation was observed. The action spectrum is similar to the absorption spectrum of [60]fullerene, indicating that the photoexcited energy of [60]fullerene is efficiently collected by the electroconductive PEDOT film and eventually transferred to the ITO electrode. The main characteristics of the present system are: (1) as unmodified [60]fullerene can be assembled as a film because of the encapsulation effect by anionic calix[8]arenes, sufficient  $\pi$ -conjugate systems necessary for efficient electron transfer are retained; (2) as all [60]fullerene molecules are insulated from each other by encapsulation, undesired self-quenching is avoidable; and (3) the photoexcited state energy is efficiently transduced to the electrode through the electroconductive PEDOT [42–43].

#### CREATION OF PANI WITH A FIBRILLAR STRUCTURE USING A PORPHYRIN J-AGGREGATE AS A TEMPLATE

PANI is a conductive polymer easily obtained by electrochemical polymerization of aniline. Despite

the convenient method of preparation and the use of an inexpensive monomer, the application has been limited [70–72]. One reason for this is the serious disadvantage related to the difficulty in controlling the morphology in the polymerization process. Thus, there has been increased interest in controlling the morphology of PANI, for example, into a fiber or a sheet. To synthesize this kind of polymer, the presence of certain polymers [73], camphorsulfonic acid [74–75] or amphiphile [10–13], which are considered to be effective as templates in the polymerization process, is indispensable. However, there was no preceding report in which the organic superstructure acting as the template is strictly compared with that of the resultant polymeric assembly to clarify whether or not the fine transcription is achieved. As aniline is protonated under acidic conditions, the anionic assemblies should act as the appropriate template because of the mutual electrostatic interaction. Here we used the assembly of an anionic porphyrin 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS 2) as a template, because TPPS tends to aggregate in a one-dimensional direction and the J-aggregate structure is well characterized by microscopic methods [76–78]



TPPS was found to act as a template for electropolymerization of aniline on the ITO electrode [79–81]. Examinations using CV and UV–visible spectroscopy established that the J-aggregated TPPS molecules are entrapped in the resultant PANI. SEM observation established that PANI grows up to a nanosized rod-like structure, reflecting the aggregation mode of TPPS (Fig. 2). Chemical oxidative polymerization of aniline in the presence of TPPS also gave the PANI rod-like structure containing the J-aggregated TPPS. Very interestingly, the J-aggregation mode in the PANI/TPPS composite disappears when the pH of the medium is shifted from acidic to basic, but it is regenerated when the pH is shifted from basic to acidic. This interconversion could be visually recognized by changes in the color and the fluorescence intensity [79–81]. This behavior, which may be regarded as a sort of the memory effect, implies that when shifted from basic to acidic, the protonation of PANI occurs in the sites energetically favorable to the J-aggregate construction.

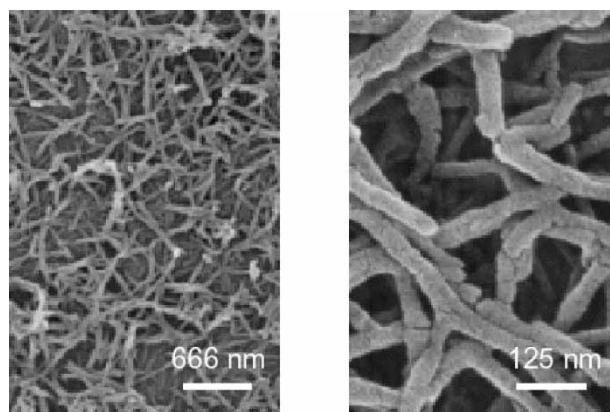


FIGURE 2 SEM images of PANI films electropolymerized (120 cycles) in the presence of TPPS.

### CREATION OF CONJUGATED POLYMERIC ASSEMBLIES WITH A HELICAL SUPERSTRUCTURE

As mentioned above, the morphology of conjugate polymers (such as PEDOT, PP and PANI) is controllable by applying the concept of the templating method to oxidative polymerization. As these monomers produce cationic intermediates in their polymerization processes, the anionic assemblies can act as potential templates due to electrostatic attractive forces. We found that when oxidative polymerization of EDOT, pyrrole and aniline was carried out using a helical superstructure of synthetic chiral lipid assemblies (3 and 4) as templates, oxidative polymerization resulted in novel polymeric aggregates such as a helical tape structure and an intertwined helical structure. Furthermore, both the right- and left-handed helical structures can be created by a change in the hydrophilic head groups (Fig. 3) [82–83]. This is the first example that the helical superstructures composed of conjugate polymers are designed using a convenient templating method [84]. As these lipid/conjugate polymer composites tend to grow into one-dimensional

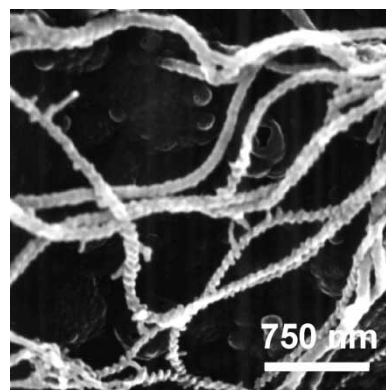


FIGURE 3 PP with a left-handed helical motif created by electropolymerization in the presence of 3.



architectures, they can bridge the interdigitated electrodes separated on the micromolar scale. This has enabled us to estimate the electroconductivity of these helical conjugate polymers, which was found to be moderate when the EDOT units in PEDOT were partially oxidized [82–83].

### DNAs AS TEMPLATES FOR OXIDATIVE POLYMERIZATION

To design and creation functional materials at a nanosized level is a major research target in the field of nanotechnology. When we apply such functional materials to practical materials, immobilization by a fabrication technique based on the template method seems to be most convenient and most promising. Here we noted that a polymeric template that is not yet used in this system but would be the most suitable and attractive candidate is a ‘polynucleotide’. Among these biological molecules, DNAs exhibit various unique higher-order structures, so that they should act as fascinating templates to create novel PP-based superstructures [85–86]. However, DNAs are highly water-soluble and biochemically unstable, making them difficult to use as functional materials and devices. To use DNAs as attractive templates, we have to overcome these drawbacks. We thus used a few DNAs as templates and carried out oxidative polymerization of pyrrole by chemical and electrochemical methods [87–88].

It was found that DNAs can act as attractive templates for oxidative polymerization of pyrrole and result in novel higher-order superstructures composed of the DNA and conjugate polymers [87–88]. Furthermore, the resultant DNA/PP composites can be deposited on an ITO electrode. Transmission electron microscopy (TEM) and SEM observations have shown that when plasmid DNA is used as a template, PP grows into nanosized rod-like, circular or supercoiled structures, depending on the higher-order conformations of DNA (Fig. 4). From several lines of evidence, it became clear that the DNA is

included inside these polymeric superstructures. The findings establish that the polymer structures obtained are controlled by a change in the DNA morphologies used as their templates. Furthermore, we found that salmon testes DNA is deposited on an ITO electrode as a stable composite with a PP film. The deposition of the DNA onto the electrode was evidenced by (1) attenuated total reflection infrared (ATR IR) absorption bands assignable to the DNA, (2) X-ray photoelectron spectroscopy (XPS) binding energy of the phosphate group assignable to the DNA, and (3) binding of ethidium bromide (EB) as detected by UV–visible spectroscopy and confocal laser scanning microscope (CLSM). Interestingly, the electrode modified by the DNA/PP composite showed CV responsiveness to the DNA intercalators, indicating a potential to apply this system to a new amperometric DNA sensor. To the best of our knowledge, this is the first example of a variety of higher-order DNA conformers being successfully transcribed into conjugate polymers, which are shown to be useful as novel functional materials.

### DEPOSITION OF SWNT/DNA COMPOSITES ON THE ITO ELECTRODE

The foregoing findings led us to consider that ‘anionic’ superstructures would also be useful as templates to transcribe them into ‘cationic’ polymer-forming materials. PEDOT is a well-known conductive polymer easily obtained by electrochemical polymerization of EDOT [89–91]. Although the presence of anionic micelles is known to affect the resultant PANI morphology [10,92–93], the concept has never been applied to EDOT. In fact, the morphology of the superstructure acting as the template had never been strictly compared with that of the resultant polymeric assemblies in order to clarify whether the fine transcription is attained or not.

Very recently, Nakashima *et al.* demonstrated that double-stranded DNA is capable of wrapping

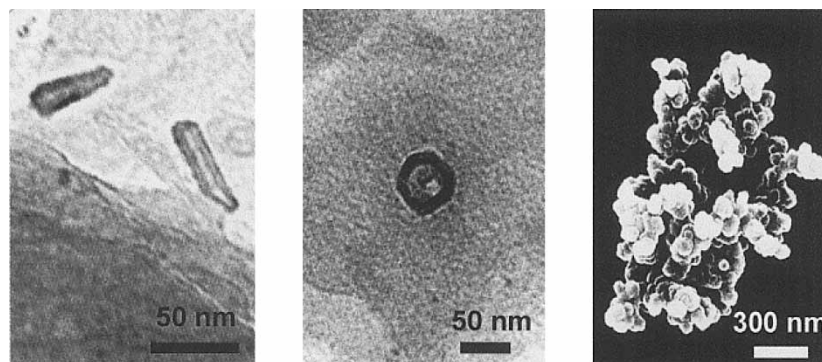


FIGURE 4 TEM images of PP obtained in the presence of coiled (left), circular (middle) and supercoiled (right) plasmid DNA.

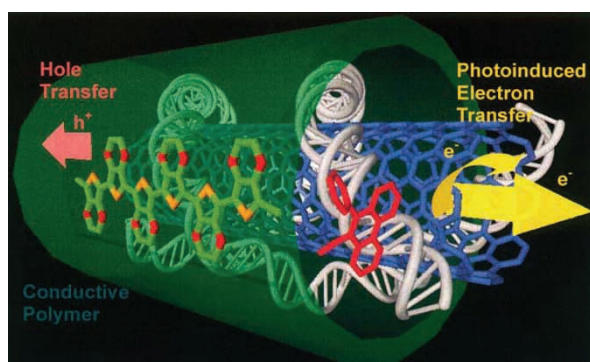


FIGURE 5 Schematic representation of photocurrent generation occurring in a cascade of DNA-bound EB → SWNT → conductive polymer → ITO electrode.

SWNTs to dissolve them into aqueous solution [94]. Because of the rigid nature of the complex, it should be suitable as a template of the present system and for estimation of the transcription reality. We predicted that the complex would also be useful as a new template because of the DNA-originated anionic charges. It was found that SWNTs solubilized in water by complexation with DNA (salmon testes) can be readily obtained on the ITO electrode by electrochemical oxidative polymerization of EDOT [95]. The driving force for this novel deposition is an electrostatic interaction between the anionic charges of wrapping DNA and the cationic charges of PEDOT formed in the oxidative polymerization process. The presence of PEDOT, SWNTs and DNA in the composite was confirmed by measurements of UV–visible, IR and resonance Raman spectra, CV and CLSM. The composite adsorbed DNA intercalators (for example, EB) very efficiently, which is regarded to be further evidence for inclusion of DNA. The surface morphology, characterized by CLSM, SEM and AFM, featured the network structure consisting of 0.5–10 μm nanorods. Very interestingly, we found that photoexcitation of EB bound to DNA generates a photocurrent, indicating that the excited energy of EB is injected into SWNTs, which is collected by the electroconductive PEDOT film on the ITO electrode (Fig. 5). We believe, therefore, that the present system is a very convenient method to explore new materials related to redox and photochemical functions, retaining the basic character of DNAs [95]. Furthermore, we expect that these polymeric assemblies would show novel functions inherent to their unique superstructures. These investigations are currently being continued in our laboratory.

## CONCLUSIONS

This work is concerned with the new concept that oxidative polymerization of EDOT, pyrrole and

aniline proceeds along the anionic template, owing to the efficient electrostatic force operating between the conjugate polymers and the templates. The templates shown to be effective so far are host–guest complexes, supramolecular aggregates, amphiphile aggregates and DNAs. We further expect that proteins, nanoparticles, block copolymers, etc. would also be useful as templates as long as they have an ‘anionic’ surface. The results obtained have three important aspects: (1) control of the morphology of conjugate polymers, which has been very difficult or nearly impossible, has become possible by using appropriate anionic templates; (2) this process is useful as a new fabrication or immobilization method for labile, temporarily associated assemblies; and (3) the composites produced show new redox and photochemical properties. We believe, therefore, that this concept is very interesting not only from a structural viewpoint but also from a functional viewpoint.

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