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Supramolecular design of a porphyrin–[60]fullerene photocurrent generation system on a DNA scaffold fabricated by a conjugate polymer film

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Abstract—DNA which binds monocationic [60]fullerene (**1**) and tetracationic porphyrin (TMPyP) was readily fabricated by electrochemical oxidative polymerization of 3.4-ethylenedioxythiophene (EDOT) and the resultant poly(EDOT) composite was deposited on an ITO electrode as a stable thin film. Spectral and CV analyses established that one **1** and one TMPyP are bound per 57 nucleobase units, that is, every three pitches of DNA. Photoirradiation of this **1**/TMPyP/DNA-poly(EDOT) film generated a photocurrent in 3.8% quantum yield, which was much higher than those obtained from **1**/DNA and TMPyP/DNA systems. One can conclude, therefore that the photoexcited energy of TMPyP is transferred to **1**, which is collected by the electron-conducting poly(EDOT) film. The present paper shows that DNA is useful as a scaffold to arrange redox-active couples in a one-dimensional matrix.

The conversion of light to chemical energy is a subject of interest not only in the field of basic research but also as a target of practical applications. Recently, researchers have paid much attention to artificial photosynthetic systems in terms of nanoscience and nanotechnology as well as energy and environmental problems.[1] The key process of photosynthesis is a cascade of photoinduced energy transfer (PET) steps between donors and acceptors embedded in the antenna complexes and reaction centers.[2] One potential approach is to deposit such functionalized molecular systems on electrode surfaces by means of self-assembled monolayers (SAMs) or Langmuir–Blodgett (LB) membranes.[3,4] However, the challenges have lain in overcoming the synthetic difficulty to integrate all of such functional units within one molecular system. This situation suggests an alternative system, in which the knowledge accumulated in a supramolecular chemistry field plays a central role for this purpose. Recently, we and others have explored a very convenient method to transcribe a variety of organic superstructures into conjugate polymers by a templating method: that is, anionic superstructures can act as templates in oxidative polymerization of thiophenes, pyrroles, anilines, etc., which generate cationic charges in their polymerization processes.[5] In fact, we found that when DNA or its carbon nanotube (CNT) complex is used as a template, oxidative polymerization results in the composites with conjugate polymers, the fibrous morphology of which resembles that of the used templates.[6] It is well known that DNA is capable of binding various intercalators and side binders. It thus occurred to us that DNA might be useful as a one-dimensional "scaffold" to arrange redox couples necessitated for designing a light harvesting system and that immobilization of this system by fabrication with the conjugate polymer on an ITO electrode would lead to an efficient photocurrent generation system. Here, we report a facile deposition method for a [60]fullerene/porphyrin/DNA ternary complex through oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT) on the ITO electrode and an efficient photocurrent generation system induced by light excitation of the porphyrin.

C[60]-*N*,*N*-dimethylpyrrolidinium iodide (**1**) was prepared according to Ref. 7. The **1**/DNA complex was prepared by mixing a salmon tests DNA aqueous solution

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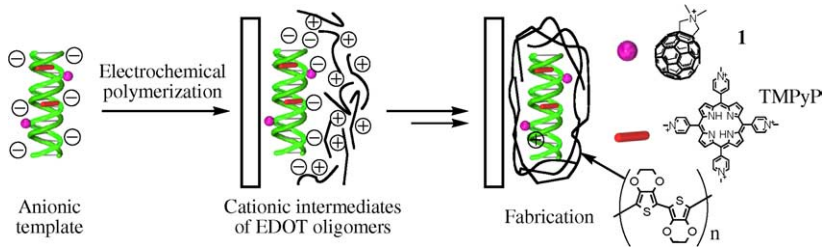

Figure 1. Schematic illustration of the **1**/TMPyP/DNA-poly(EDOT) film.

with a DMSO solution of **1**. This mixed solution was dialyzed (100 Da) for 24 h to remove DMSO. The **1**/DNA aqueous solution thus obtained was a transparent light-yellow solution, but it was difficult to estimate the concentration of the complexed **1** from a spectroscopic method because **1** does not have any characteristic absorption band. Thus, the concentration of **1** in the complex was estimated after deposition on an ITO electrode (vide post) (Fig. 1).

It is known that DNA binds 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-porphine (TMPyP) as an intercalator.[8] A TMPyP aqueous solution was injected into an aqueous solution containing the **1**/DNA complex. To obtain concrete evidence that TMPyP is intercalated into this complex, UV–vis absorption and CD spectra of this solution were measured (Fig. 2). In the UV–vis absorption spectra the Soret band shifts from 424 to 439 nm. In the CD spectra a negative CD band appears at the Soret band region and the exciton-coupling-type band at around 260 nm is also changed by the interaction with TMPyP.[9] These results support the view that TMPyP is bound to DNA by intercalation and the electronic state is affected by the chiral environment of DNA.

Furthermore, we confirmed the binding of both **1** and TMPyP to the DNA scaffold by using fluorescence spectroscopy. The fluorescence spectrum of the TMPyP/DNA complex shows an emission peak at 660 nm, characteristic of TMPyP. On the other hand, the fluorescence intensity of the **1**/TMPyP/DNA complex was drastically decreased (Fig. 3). As a reference, we mixed **1** and TMPyP in the absence of DNA. We confirmed that the fluorescence intensity of TMPyP is scarcely decreased by added **1**. These results clearly show that TMPyP and **1** are entrapped by the DNA scaffold and the photoexcited energy of TMPyP is efficiently transferred therein to **1**.

An aqueous solution containing EDOT (10 mM) and LiCl (50 mM) was subjected to electrochemical polymerization in the absence and the presence of the **1**/TMPyP/

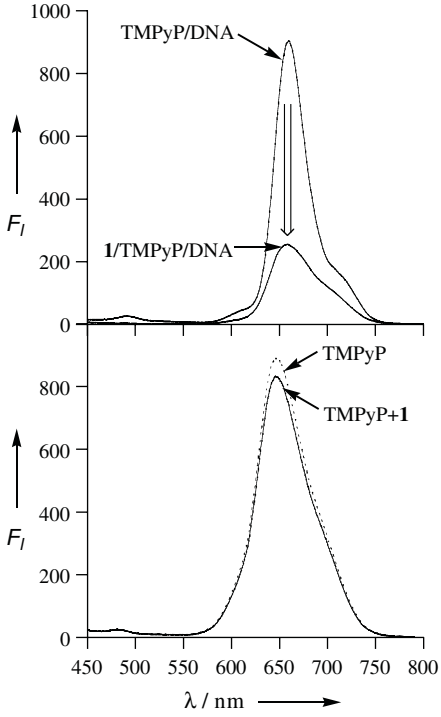

Figure 3. Fluorescence spectra of the TMPyP/DNA and **1**/TMPyP/DNA complexes in aqueous solution at 25 °C, excitation 410 nm.

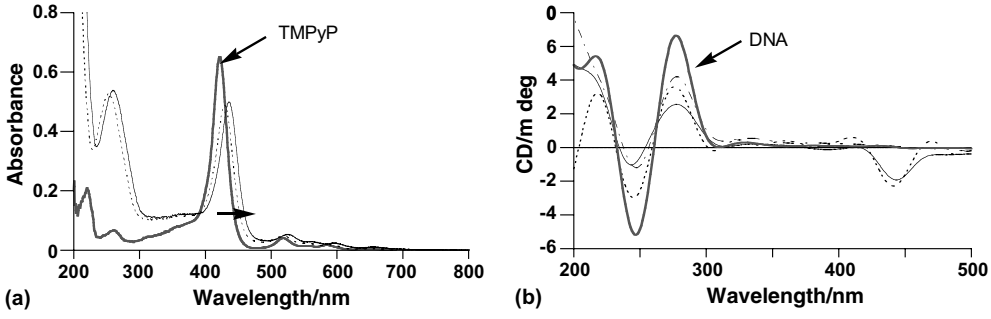

Figure 2. (a) UV–vis absorption spectra of TMPyP/DNA (· · · · · ·) and **1**/TMPyP/DNA (—) in aqueous solution and (b) CD spectra of **1**/DNA (– –), TMPyP/DNA (· · · · · ·), and **1**/TMPyP/DNA (—) in aqueous solution: 25 °C, [**1**] = 0.034 mM, [TMPyP] = 0.034 mM, [DNA] = 1.95 mM (base unit).