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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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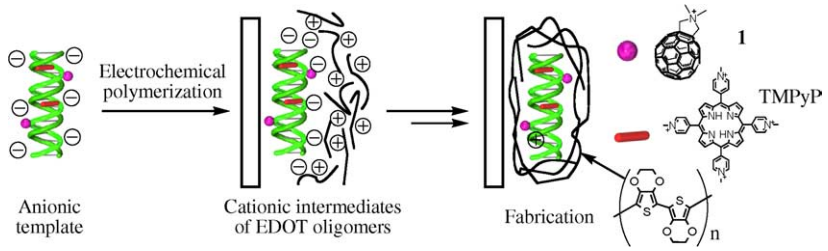

Figure 1. Schematic illustration of the **1**/TMPyP/DNA-poly(EDOT) film.

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/

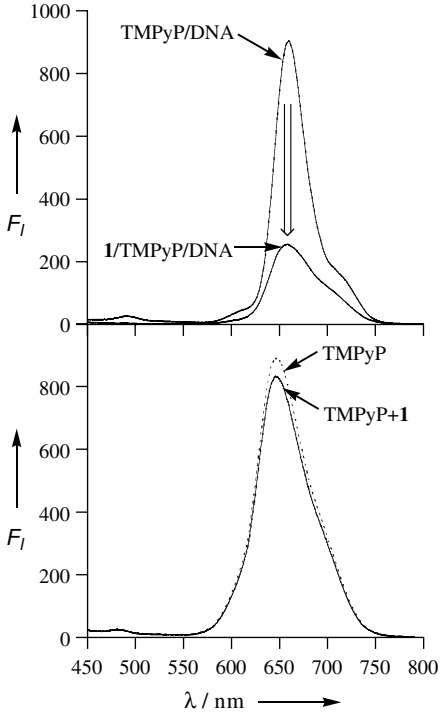

Figure 3. Fluorescence spectra of the TMPyP/DNA and **1**/TMPyP/DNA complexes in aqueous solution at 25 °C, excitation 410 nm.

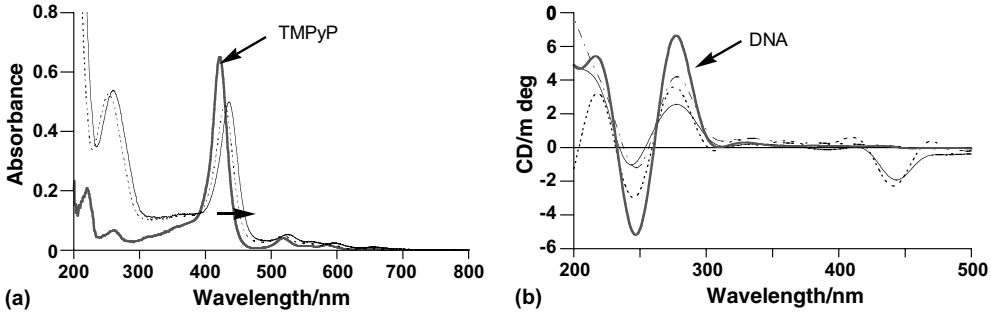

Figure 2. (a) UV–vis absorption spectra of TMPyP/DNA (· · · · · ·) and **1**/TMPyP/DNA (—) in aqueous solution and (b) CD spectra of **1**/DNA (– –), TMPyP/DNA (· · · · · ·), and **1**/TMPyP/DNA (—) in aqueous solution: 25 °C, [**1**] = 0.034 mM, [TMPyP] = 0.034 mM, [DNA] = 1.95 mM (base unit).

DNA complex. The cell consisted of an ITO electrode as the working electrode (working area = 16.8 cm^2), a Pt counter electrode, and an Ag/AgCl reference electrode. The redox cycle was repeated in a voltage range of 0–1.1 V (vs Ag/AgCl) with a scan rate of 0.05 V s^{-1} at 25 °C. In the electrochemical polymerization, the value of electric current increased with the increase in the number of the successive potential sweeping (Fig. S1), indicating that a poly(EDOT) film is generated on the ITO electrode.

The oxidized and reduced states of the obtained poly(EDOT) film deposited on the ITO electrode were characterized by UV–vis spectroscopy. The oxidized state of this film showed a weak absorption band in the visible region and a strong absorption band in the near-IR region, whereas the reduced state showed a broad absorption band at 480–510 nm because of the π–π^* electronic transition (Fig. S2). To confirm the deposition of DNA-bound **1** in the poly(EDOT) film, we measured the cyclic voltammetry (CV), because it is known that [60]fullerenes have a characteristic redox peak at −0.49 V (vs Ag/AgCl).[10] From the oxidation peak area (Fig. S3), the amount of deposited **1** was estimated to be 4.5×10^{-10} mol cm^{-2}.[11] The deposition of DNA-bound TMPyP in the poly(EDOT) film was evidenced by the differential UV–vis absorption spectra in the absence and the presence of the **1**/TMPyP/DNA complex. As shown in Figure S4, the differential spectrum of the **1**/TMPyP/DNA-poly(EDOT) film and the poly(EDOT) film displays an absorption maximum at λ_{max} 436 nm, which is assignable to a Soret band in the **1**/TMPyP/DNA complex ($Abs_{436} = 0.198$). From the TMPyP absorption band ($\varepsilon_{436} = 7.34 \times 10^8$ M^{-1} cm^{-1}), the surface concentration of TMPyP was estimated to be 2.7×10^{-10} mol cm^{-2}. The results indicate that **1** and TMPyP are deposited in the poly(EDOT) film in a molar ratio of 5:3. We confirmed that these concentrations are scarcely reduced by rinsing the ITO electrode in aqueous solution. Since neither **1** nor TMPyP was deposited on the ITO electrode by oxidative polymerization of EDOT in the absence of DNA, one can regard that DNA is also present in the poly(EDOT) film. However, to obtain direct evidence for inclusion of DNA was more difficult, because the absorption band of DNA overlaps with that of poly(EDOT). We thus carried out XPS analysis (Fig. S5). The XPS spectra clearly exhibit the peaks assignable to the P element arising from DNA in the **1**/TMPyP/DNA-poly(EDOT) film. On the basis of the foregoing findings, one can conclude that the **1**/TMPyP/DNA ternary complex can be efficiently fabricated by poly(EDOT) through electrochemical polymerization and deposited on the ITO electrode. After electrochemical polymerization of EDOT, unreacted DNA was not detected at all in the cell (confirmed by UV–vis spectroscopy). Assuming DNA is entirely included in the poly(EDOT) film, it follows that one **1** and one TMPyP are bound per 57 and 34 nucleobase units, respectively: that is, these molecules exist approximately in every 3 pitches of DNA.[12]

Photocurrent measurements were carried out for the poly(EDOT) film including DNA, TMPyP/DNA, **1**/DNA, and **1**/TMPyP/DNA systems deposited on an ITO electrode as the working electrode.[13] The solution was adjusted to pH 7.3 with 0.01 M phosphate buffered saline (PBS). When the **1**/TMPyP/DNA-poly(EDOT) film was photoirradiated, a photocurrent wave with ca. 52 nA appeared (Fig. 4). This photocurrent intensity is 12 times stronger than that obtained from the TMPyP/DNA-poly(EDOT) film and 4.3 times stronger than that obtained from the **1**/DNA-poly(EDOT) film.

To specify the photoexcited species and to clarify the electron transfer mechanism, we measured action spectra for the poly(EDOT), **1**/DNA-poly(EDOT), and **1**/TMPyP/DNA-poly(EDOT) films between 375 and 650 nm (Fig. 5). The poly(EDOT) film generates only a weak photocurrent at 440–650 nm. It is clearly seen from Figure 5 that in the **1**/TMPyP/DNA-poly(EDOT) film a large maximum appears at 400 nm, which is assignable to a Soret band of TMPyP. In the **1**/DNA-poly(EDOT) film, on the other hand, the photocurrent

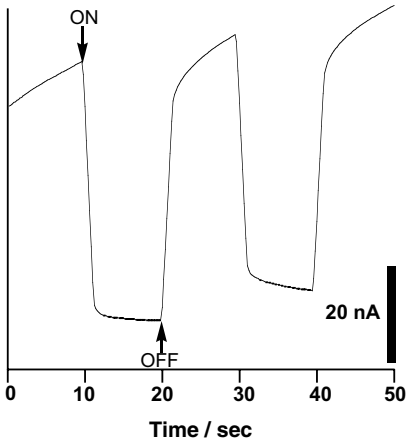

Figure 4. Photochemical response of the **1**/TMPyP/DNA-poly(EDOT) film: excited at 400 nm.

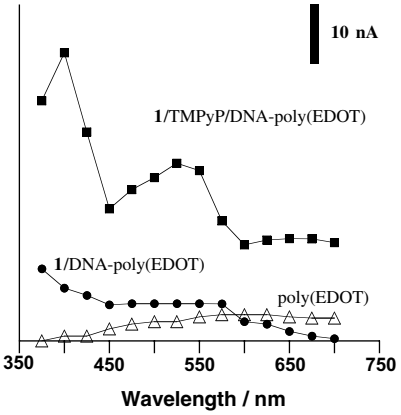

Figure 5. Action spectra of the poly(EDOT) (–△–), **1**/DNA-poly(EDOT) (–●–), and **1**/TMPyP/DNA-poly(EDOT) (–■–) films: 50 mM LiCl + 50 mM AsA aqueous solution, bias voltage −0.1 V versus Ag/AgCl, 25 °C. The broad band at 500–560 nm in the **1**/TMPyP/DNA-poly(EDOT) film is ascribed to the exciton of poly(EDOT) and/or Q-bands of TMPyP.

intensity becomes stronger in the shorter wavelength region and the spectral shape is similar to that of **1**. In all wavelengths, the photocurrent intensity for the **1**/TMPyP/DNA-poly(EDOT) film is stronger than that of the **1**/DNA-poly(EDOT) film. The increased photocurrent density for the **1**/TMPyP/DNA system shows that a significant amount of photocurrent is streaming according to a route of TMPyP → **1** → ITO electrode.

To obtain clearer evidence that the increased photocurrent intensity is ascribable to the presence of both **1** and TMPyP, we photoirradiated several reference electrodes at 400 nm (Fig. 6). As shown in Figure 5, poly(EDOT) itself is not photoexcited at 400 nm. As expected, we could not detect any photocurrent for the DNA-poly(EDOT) film. The TMPyP/DNA-poly(EDOT) and **1**/DNA-poly(EDOT) films gave weak photocurrent intensities less than 10 nA. TMPyP has a large extinction coefficient at this wavelength, but the excited-state life time is relatively shorter than that of C[60],[14] making it difficult to attain an efficient electron transfer to the ITO electrode, whereas C[60] can act as an excellent electron mediator because of the long excited-state life time,[15] but the extinction coefficient of **1** is small. In the **1**/TMPyP/DNA-poly(EDOT) film, these drawbacks are compensated by the electron transfer from TMPyP* to **1** and the cation hole is efficiently transferred from $TMPyP^{+\cdot}$ to ascorbic acid (AsA) via the electron-conducting poly(EDOT) film (Fig. S6). Thus the particularly large photocurrent intensity is observable only for the **1**/TMPyP/DNA-poly(EDOT) film. The quantitative quantum yield[14] can be estimated to be 3.8%, which is sufficiently high compared with several similar systems.[12,16]

In conclusion, the present paper demonstrated that DNA is useful as a one-dimensional scaffold to arrange photochemically redox-active species and that the complexes are readily fabricated and deposited by oxidative polymerization of EDOT on an ITO electrode. Since this polymer film is stable and generates photocurrent with a moderate quantum yield, one may regard that this is a new type of light-harvesting device.

Experimental: The synthesis of **1** was reported previously.[7]

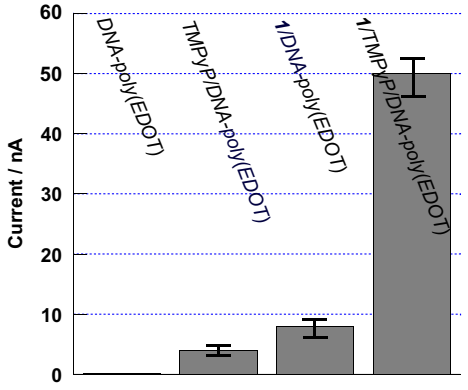

Figure 6. Comparison of the photocurrent intensities: excited at 400 nm.

[60]Fullerene (>99.5%) was purchased from MER Corporation. Ethylenedioxythiophene (EDOT, Aldrich), 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-porphine (TMPyP, Tokyo Kasei Kogyo), and lithium chloride (LiCl, Kishida Co. Japan) were used as received. Cyclic voltammetry (CV) experiments were performed with a one-compartment, three electrode electrochemical cell driven by an electrochemical analyzer (Autolab PGSTAT12 potentiostat/galvanostat) in aqueous solution containing supporting electrolyte (LiCl, 50 mM). The oxidative polymerization of EDOT was carried out in a CV cell using 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 0–1.1 V (vs Ag/AgCl) with scan rate of 0.05 mV s^{-1} at 25 °C. After polymerization, five redox cycles in a corresponding voltage range were performed in 50 mM LiCl aqueous solution to wash the film. A 500 W Xe arc lamp (Ushio XB-50101AAA, XS-50102AAA) was used as a light source in the photoelectrochemical studies and a monochrometer (Shimadzu SPG 120IR) was used to obtain desired wavelengths. The intensity of the light was measured with an energy and power meter (Advantest TQ8210). Photocurrent measurements were carried out in an aqueous LiCl (50 mM) solution by using a three-electrode photoelectrochemical cell, consisting of the modified ITO electrode. Quantum efficiency was calculated based on the number of photons absorbed by chromophore on the ITO electrode at each wavelength using the input power. The photocurrent density and the absorbance were determined from the amount of deposited **1** and TMPyP. UV–vis and CD spectroscopic studies were performed on a Shimadzu UV-2500 PC spectrophotometer and a Jasco J-720WI spectrometer, respectively. Fluorescence spectral measurements were performed using a Hitachi F-4500 spectrometer. XPS spectra were measured on a Physical Electronics PHI 5800 ESCA system.

Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.tetlet.2005.03.059.

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12. We first prepare the poly(EDOT) film in the presence of 10% of **1** and TMPyP. From this film, we could not detect any photocurrent generation. It is expected that the quantum yield is enhanced by further introduction of **1** and TMPyP. However, when the concentrations were further increased than those in the present system, they were precipitated with DNA. We now consider, therefore that the present system is very close to an optimum condition.
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