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Two-Dimensional Molecular Assembly of Bacteriochlorophyll *a* Derivatives Using Synthetic Poly(ethylene glycol)-Linked Light-Harvesting Model Polypeptides on a Gold Electrode Modified with Supported Lipid Bilayers

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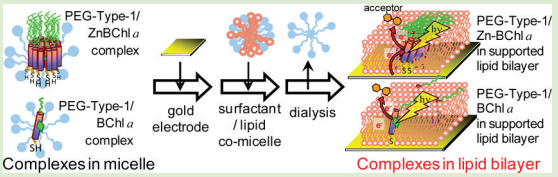
Supporting Information

ABSTRACT: The two-dimensional molecular assembly was accomplished of bacteriochlorophyll *a* (BChl *a*) and zinc-substituted BChl *a* (Zn-BChl *a*) together with synthetic poly(ethylene glycol)(PEG)-linked light-harvesting (LH) model polypeptides on a gold Au(111) electrode modified with supported lipid bilayers. Model polypeptides for LH1-*α* from *Rhodospirillum (Rs.) rubrum* were successfully synthesized and stably assembled with Zn-BChl *a* in 1,2-dioleoyl-*sn*-glycero-3-[phospho-*rac*-(1′-glycerol)] (DOPG) lipid bilayers on an electrode at room temperature, as well as in liposomal solution, in which the Zn-BChl *a* complex unlike BChl *a*, was stably assembled. The PEG moiety of the model polypeptide assisted the stable assembly with an *α*-helical conformation of the LH1-*α* model peptides together with these pigments onto the gold electrode with defined orientation. The photocurrent response depended on the combinations of the pigments and synthetic LH model polypeptides. The results presented herein will be useful for the self-assembly of these complexes on electrodes to construct efficient energy-transfer and electron-transfer reactions between individual pigments in lipid bilayers.



The lateral organization of photosynthetic membranes has been widely studied to understand the functions of the component lipids and proteins. In bacterial photosynthetic membranes, efficient energy transfer, and electron transfer occur in the lipid bilayers.[1−7] Two types of membrane protein/pigment complexes, that is, the light-harvesting complex 2 (LH2) and the light-harvesting complex 1/reaction center complex (LH1-RC), absorb light energy and transfer it to the RC, However, it is still not clear how the arrangement in these arrays affects the light-harvesting function. Artificial assembly of photosynthetic light-harvesting (LH) complexes in lipid bilayers can facilitate the study of photoenergy transfer and the subsequent electron transfer in this biological process, as well as its functional application.[3,4] On the other hand, the techniques of self-assembled monolayers (SAMs) of organic molecules on an electrode have been developed for more than 20 years.[8−10] Theses are useful for electrochemical sensing, energy conversion, and other applications. Moreover, the interactions for assembly of LH complex have been evaluated by using synthetic LH model polypeptides.[11−14] Our previous studies showed that a synthetic LH model polypeptide from *Rhodobacter (Rb.) sphaeroides*, that is, LH1-*β* with Zn-porphyrin complexes, could be used to form ordered SAMs on a gold surface to construct artificial photosynthetic LH systems that provided insight into an efficient light energy conversion and the subsequent electron transfer.[5−7,15] Here we report the two-dimensional molecular assembly of bacteriochlorophyll (BChl) *a* derivatives (Chart 1a) using poly(ethylene glycol) (PEG)-linked LH model polypeptides (Chart 1b) on a gold Au(111) electrode modified with supported lipid bilayers to gain further insight into the artificial molecular assembly of photosynthetic LH systems in lipid bilayers (Figure 1). We selected LH1-*α* from *Rhodospirillum (Rs.) rubrum* and its model polypeptides, Type-1 and PEG-Type-1, because LH1-*α* (Chart 1b) forms the native-like LH1-type complex with Zn-BChl *a*. There is axial coordination between Zn^{2+} by histidine residue in the hydrophobic core of the LH polypeptide, hydrogen bonding

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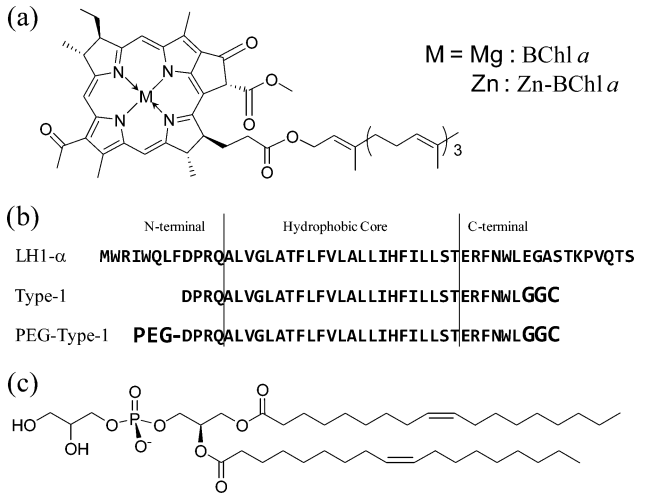
Chart 1. (a) Structure of BChl *a* Derivatives; (b) Amino Acid Sequences of *Rs. rubrum* LH1-α Model Polypeptides; (c) Structure of DOPG



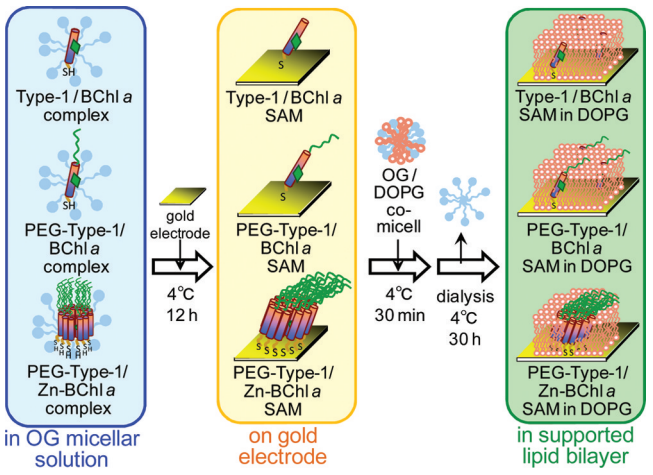


Figure 1. Schematic model of the assemblies of synthetic polypeptides (Type-1 and PEG-Type-1) with BChl *a* and Zn-BChl *a* complex in OG micellar solution and immobilization of the self-assembled monolayers (SAM) of LH model complexes onto a gold electrode and in a supported DOPG lipid bilayer assembled onto the electrode.

between carbonyl group of Zn-BChl *a* and polar amino acid residues of C-terminal LH polypeptide, hydrophobic interaction between phytol group of Zn-BChl *a* and hydorophobic amino acid residues of the hydrophobic core of the LH polypeptide, and electrostatic interaction between amino acid residues of C-terminal or N-terminal (Chart 1). The binding constant of Zn-BChl *a* with the LH1-*α* polypeptide is 100-fold higher than that of BChl *a*. Thus, interestingly, LH1-*α* forms a stable native LH1-like complex with Zn-BChl *a* in *n*-octyl-*β*-D-glucopyranoside (OG) micelles, whereas it forms a monomer-like LH complex with BChl *a*.[16] The Cys residue at the C-terminus of the model polypeptide (Chart 1) can be attached covalently to a gold surface.[5−7,15] The combinations of pigments and synthetic PEG-linked LH 1 model polypeptides will be useful for the construction of efficient energy-transfer and electron-transfer reaction systems in lipid bilayers assembled on electrodes.

Chart 1 shows the structure of the BChl *a* derivatives, the amino acid sequences of *Rs. rubrum* LH1-*α* and its synthetic model polypeptides, and the structure of 1,2-dioleoyl-*sn*-glycero-3-[phospho-*rac*-(1′-glycerol)] (DOPG). Figure 1 shows a schematic model of the immobilization of LH model complexes onto a gold electrode and formation of a bilayer around the hydrophobic moiety of the complexes on the gold electrode. The LH model complexes in OG micelles were immobilized on the gold electrode by immersing the electrode in the LH complex solution ([polypeptides] = 3.45 μM, [pigments] = 2.41 μM, [OG] = 26.7 mM) at 4 °C for 12 h. The gold electrode was then washed with Milli-Q water and dried by N_2 flow. The LH complex immobilized onto the surface was then immersed in comicelle solution containing mixed OG and anionic DOPG in 50 mM aqueous phosphate buffer (containing disodium hydrogen phosphate and sodium dihydrogen phosphate, pH = 7.5, [DOPG] = 358 μM, [OG] = 22.0 mM) at 4 °C for 30 min. The resulting gold electrode with solutions was filtered at 4 °C for 30 h through a dialysis membrane that removed substances with a molar weight smaller than 12000 g/mol to form a thin layer of the DOPG incorporating complex. All experiments were conducted in the dark.

Figure 2 shows the absorption spectra of the LH complexes in OG micellar solution. As shown in Figure 2a and b, the Q_y

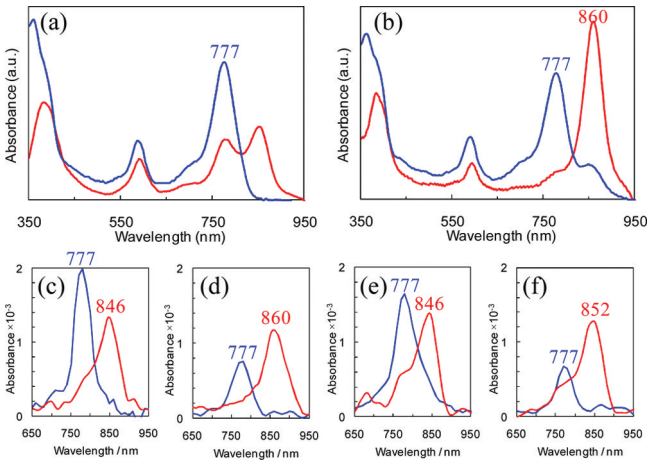


Figure 2. Absorption spectra of BChl *a* (blue line) and ZnBChl *a* (red line) in the presence of Type-1 (a, c, e) or PEG-Type-1 (b, d, f) in OG micellar solution (a, b), on a gold electrode (c, d), and in a supported lipid bilayer on a gold electrode (e, f). Experimental condition: [polypeptides] = 3.45 μM, [pigments] = 2.41 μM, [OG] = 26.7 mM in OG micellar solution. All measurements were carried out at 4 °C.

band of BChl *a* was observed at 777 nm in the presence of either PEG-Type-1 or Type-1, respectively, indicating that the formation of the BChl *a* monomer occurred with PEG-Type-1/ BChl *a* as well as with Type-1.[17] Interestingly, the Q_y band of Zn-BChl *a* was red-shifted from 777 to 860 nm with a single sharp peak owing to the presence of PEG-Type-1 polypeptide, whereas split Q_y bands of Zn-BChl *a* were observed in the presence of Type-1 polypeptide. This red-shifted peak of the Q_y band is analogous to the native LH1-type complex that was observed in the presence of LH1-*α* alone as well as in the presence of a mixture of LH1-*α* and LH1-*β*.[17] These results suggest that the PEG moiety at the N-terminal played an important role in the stable assembly of the LH1-type complex with Zn-BChl *a* in OG micellar solution.

To investigate the advantages of the process described in this study, OG micellar solutions containing the LH model complex

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were mixed with the liposome of DOPG in aqueous phosphate buffer. Each resulting solution was then filtered through a dialysis membrane that removed substances with molar weights smaller than 12000 g/mol, which resulted in the remaining solution DOPG liposomes containing the complexes. The solutions were then stored at 25 °C in the dark. The stability of BChl *a* derivatives in the LH model peptides increased in the liposome when compared to those in the OG micelles, where the Zn-BChl *a* complex was more stable than the BChl *a* complex (data not shown). For example, the time course of the absorption spectra of the complexes in DOPG liposome at 25 °C indicated that the PEG-Type-1/Zn-BChl *a* complex was stable for 241 days in the dark in the DOPG liposome and was much more stable than Type-1/Zn-BChl *a* and LH1-α/Zn-BChl *a* complexes in the DOPG liposome (Figure S1). These findings indicate that the PEG moiety of the model polypeptide assisted the stable assembly with Zn-BChl *a* in lipid bilayers as well as in OG micellar solution.

Similar absorption spectra of the Q_y bands of BChl *a* and Zn-BChl *a* in the presence of the LH model polypeptides were observed on the gold electrodes before (Figure 2c,d) and after (Figure 2e,f) modification by DOPG lipid bilayers. These findings were consistent with those obtained for the electrodes in OG micellar solution (Figure 2a,b). However, no absorption band corresponding to the Zn-BChl *a* complex obtained using LH-1α polypeptide was observed on the bare electrode (data not shown). These results indicate that BChl *a* or Zn-BChl *a* complex with LH model polypeptides containing the Cys residue at the C-terminal were covalently bound on these gold electrodes in a state that is similar to that of native LH1.

The assembly of the LH model polypeptides in the complexes on the gold electrodes modified with DOPG supported bilayers was investigated using Fourier Transform Infrared Reflection–Absorption Spectroscopy (FT-IR-RAS). The spectra of Type-l and PEG-Type-1 on the gold electrodes showed absorption bands at 1665 and 1544 cm^{-1}, as shown in Figure S2. These bands were assigned to the amide I and II bands, respectively. These results show that the LH1 model polypeptides are in an α-helical conformation when assembled together with these pigments onto the gold electrode. These bands were used to determine the tilt angle of the helices relative to the surface of the gold electrode, as previously described.[18] The tilt angles were 41, 62, 39, and 53° for the Type-1/BChl *a*, Type-1/Zn-BChl *a*, PEG-Type-1/BChl *a*, and PEG-Type-1/Zn-BChl *a* complex SAMs in DOPG lipid bilayers, respectively (Table 1, entries **3**–**6**). Interestingly, the tilt angles of PEG-Type-1 in the SAMs with both BChl *a* and Zn-BChl *a* were smaller than those of Type-1 in the SAMs. Furthermore, the tilt angles of PEG-Type-1 in the SAMs with both BChl *a* and Zn-BChl *a* on the gold electrode modified with the DOPG supported bilayer were smaller than the angles of the complex on the bare gold (Table 1, entries **1**, **2**, **3**, and **5**). These results indicated that the α-helical conformation of the LH model polypeptide increased owing to the PEG-moiety attached at the N-terminal in the supported lipid bilayers. Using the tilt angles and the lengths of the polypeptides, we determined the distances between the pigments and the gold electrode to be 19 Å (PEG-Type-1/BChl *a*) and 15 Å (PEG-Type-1/Zn-BChl *a*) for the fully helical conformation of polypeptides in the presence of PEG-Type-1 polypeptide (Table 1, entries **5** and **6**). Overall, the PEG moiety could stabilize and organize the LH complexes well via the formation

Table 1. Q_y Absorption Band, Tilt Angle, Distance between the Pigments and the Gold Electrode, and Quantum Yields (ϕ) of SAMs on the Gold Electrodes Modified with DOPG-Supported Bilayers

	SAM[a]	Q_y absorption band[b] (nm)	tilt angle (deg)	distance (Å)	quantum yields (ϕ; %)
1	Type-1/BChl *a* SAM	777	52	15	0.030
2	PEG-Type-1/BChl *a* SAM	777	57	13	0.020
3	Type-1/BChl *a* SAM in DOPG	777	41	18	0.023
4	Type-1/ZnBChl *a* SAM in DOPG	846	62	11	0.011
5	PEG-Type-1/BChl *a* SAM in DOPG	777	39	19	0.011
6	PEG-Type-1/ ZnBChl *a* SAM in DOPG	852	53	15	0.008

[a]Self-assembled monolayers. [b][Polypeptides] = 3.45 μM, [pigments] = 2.41 μM, [OG] = 26.7 mM.

of high helices of the α-helical conformation of the LH model polypeptide in the DOPG supported bilayers.[19]

Figure 3 shows the photocurrent responses of complex SAMs. Each SAM with BChl *a* generated cathodic photo-

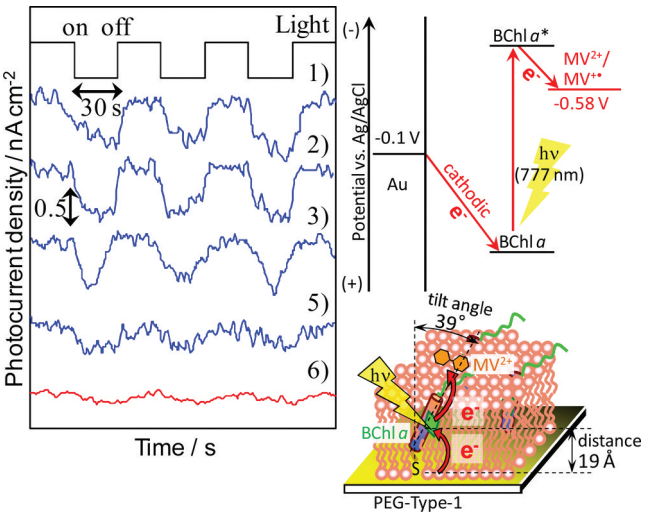

Figure 3. Cathodic photocurrent responses and schematic diagrams of electron transfer of the complexes on a gold electrode before and after modification of DOPG bilayers vs time in 50 mM phosphate buffer solution (pH = 7.5). Entry 1: Type-1/BChl *a* SAM; 2: PEG-Type-1/BChl *a* SAM; 3: Type-1/BChl *a* SAM in DOPG; 5: PEG-Type-1/BChl *a* SAM in DOPG; 6: PEG-Type-1/Zn-BChl *a* SAM in DOPG.

currents in the presence of methyl viologen (MV^{2+}) as an acceptor upon photoirradiation at 777 nm, which was the Q_y absorption maximum of the BChl *a* monomer complex (Figure 3 and Table 1, entries **1**, **2**, **3**, and **5**). These results show that BChl *a* in the SAMs sensitizes photoinduced electron transfers, indicating that one-way electron transfer from BChl *a* in the LH model polypeptide complex to MV^{2+} occurred.[5–7,15] The mechanism of cathodic photocurrent generation by the SAMs is shown schematically in Figure 3. At −0.1 V, upon photo-excitaion of BChl *a*, electron transfer occurs from the excited BChl *a* (BChl *a**) to MV^{2+}, followed by electron donation from the gold surface to the oxidized BChl *a* (the radical

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cation). The reduced MV^{2+} diffuses to the counter electrode and transfers an electron, resulting in the generation of a cathodic photocurrent. Interestingly, similar cathodic photocurrents were observed for Zn-BChl *a* in the LH model polypeptide complex when illuminated at the Q_y absorption maximum of the LH1-type Zn-BChl *a* complex in the LH model peptides as well as BChl *a*, as described above (Figure 3 and Table 1, entries **4** and **6**).

The photostability of BChl *a* derivatives in the LH model peptides assembled on the electrodes increased owing to the presence of modified lipid bilayers on the electrode, where the Zn-BChl *a* complex was more stable than the BChl *a* complex (data not shown).

The Q_y absorption band, tilt angle, distance between the pigments and the gold electrode and quantum yields (ϕ) of SAMs on the gold electrodes are summarized in Table 1. The quantum yields of the BChl *a* complexes were larger than those of the Zn-BChl *a* complexes (Figure 3 and Table 1, entries **3**−**6**). This was because more of the photoenergy absorbed by the Zn-BChl *a* complex, which was red-shifted from 777 to near 860 nm, accumulated inside the LH complexes than in the BChl *a* monomer complex. These findings are consistent with the large fluorescence quenching of Zn-BChl *a* observed in the LH complex when compared with the BChl *a* complex (data not shown).[7,20] Therefore, more photoexcited electrons from the BChl *a* complex on the electrode can be transferred to MV^{2+} when compared to the Zn-BChl *a* complex.

Further, PEG-conjugated complexes showed low quantum yield (Figure 3 and Table 1, entries **2**, **5**, and **6**) owing to the PEG-moiety attached at the N-terminal of the model polypeptides in the supported lipid bilayers. These findings are consistent with the distance between BChl *a* derivatives in the LH complex and the electrode becoming long in response to the presence of the PEG moiety. In addition, PEG moiety may hinder interactions between MV^{2+} and BChl *a* derivatives. These factors cause the quantum yield to decrease (Figure 3 and Table 1, entries **2**, **5**, and **6**)[19] because the PEG-moiety can stabilize and organize the attached complexes via the production of high helices in the DOPG supported bilayers. Taken together, the PEG-moiety and lipid bilayer could not only stabilize and organize the LH complexes well but also influence the quantum yield for photocurrent generation of BChl *a* derivatives in the LH complexes.

Moreover, the assemblies of the mixture of PEG-Type-1/BChl *a* and PEG-Type-1/Zn-BChl *a* complex in 1:1 stoichiometry on the gold electrode with DOPG bilayers showed photocurrent responses (Figure S3) that were about 10 times larger than those produced by the PEG-Type-1/BChl *a* or PEG-Type-1/Zn-BChl *a* complex alone when illuminated at the Q_y absorption maximum (Table 1 and Figure 3, entries **5** and **6**). Although the reason of this enhanced photocurrent responses are not clear at the moment, variations in the mixtures of these complexes will be of interest in the construction of a stable and efficient energy transfer and electron transfer system on the electrode. Theoretical studies and further biophysical measurements would provide the detail of this reaction.[21−27]

In conclusion, the amphiphilic compound PEG was successfully conjugated to the LH synthetic model polypeptide. The PEG moiety of the model polypeptide assisted the stable assembly of the LH model peptides together with BChl *a* and Zn-BChl *a* in supported lipid bilayers onto a gold electrode with an α-helical conformation with defined distances and orientation, as well as in the liposomal solution, where the Zn-BChl *a* complex was stably assembled when compared to BChl *a*. In this case, the photocurrent response depended on the combinations of pigments and synthetic PEG-linked LH 1 model polypeptides and these complexes. The method described herein will be useful for the self-assembly of these complexes to provide insight into energy-transfer and electron-transfer reactions between individual pigments in the photosynthetic LH complexes in lipid bilayers. These characteristics are of considerable interest for the construction of a vectorial electron transfer controlled in biological membranes and for the creation of stable electron transfer systems on electrodes for solar energy conversion devices.

EXPERIMENTAL SECTION

The detailed preparation and characterization of the LH model complexes have been described in previous studies[5−7,15] and the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures for synthesis and characterization, time-dependence, FT-IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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