

# Photocurrent Generation Enhanced by Charge Delocalization over Stacked Perylenediimide Chromophores Assembled within DNA

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**S** Supporting Information

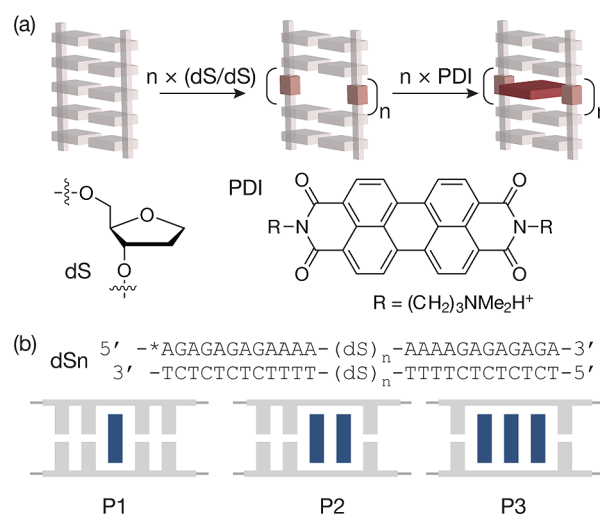
**ABSTRACT:** We now report the photocurrent generation and charge transfer dynamics of stacked perylenediimide (PDI) molecules within a  $\pi$ -stack array of DNA. The cofacially stacked PDI dimer and trimer were found to strongly enhance the photocurrent generation compared to an isolated PDI monomer. Femtosecond time-resolved transient absorption experiments revealed that the excitation of the stacked PDI dimer and trimer provided the broad transient absorption band, which was attributed to the charge delocalization of a negative charge over the PDI chromophores. The lifetime of the charge delocalization of the PDI dimer and trimer (nearly 1 ns) was much longer than that of the charge separated state of the PDI monomer. A comparison between the photocurrent measurements and time-resolved transient absorption measurements demonstrated that the cofacially stacked structure could possibly lead to the charge delocalization and increase the lifetime of the charge-separated state that is essential to enhancing the photocurrent generation.

Chromophores in a  $\pi$ -stacked or conjugated system show unique photophysical properties, such as energy and charge transfer through the strong electronic coupling interaction between the chromophores, and various types of supramolecular structures realizing efficient light-harvesting and charge conduction properties have been designed and characterized.<sup>1–4</sup> The characteristic features of DNA as building blocks and a platform for incorporating functional molecules at desirable positions through chemical modification allow one to construct a one-dimensional or helical array of the functional molecules along the DNA strands.<sup>5–8</sup> In addition, DNA can serve as conductive molecules based on the hole/electron transporting properties through the  $\pi$ -stack array of the base pairs.<sup>9–12</sup> Therefore, DNA is considered to be a prospective biomolecule for designing molecular-based optoelectronics<sup>13–17</sup> and an electrochemical biosensor system.<sup>9,18–21</sup>

Perylenediimide (PDI) derivatives have been extensively used to design functional materials due to their excellent physical, optical, and assembling properties.<sup>22</sup> DNA molecules functionalized with PDI covalently or noncovalently have been prepared, and their photophysical properties have been investigated.<sup>23–25</sup> In order to realize a photovoltaic device or optoelectronics constructed using DNA, it is essential to

understand the photoelectrochemical properties of DNA functionalized with photoactive chromophores. We now report our investigation of the charge transfer dynamics of a stacked PDI assembly constructed inside DNA and the photocurrent generation of the electrode modified with the PDI assembly.

We have previously shown that water-soluble cationic PDI chromophores can bind to an artificial pocket created by replacing nucleosides with deoxyribospacers (dS) within DNA (dSn) and form stacked assemblies depending on the size of the pocket (Figure 1a).<sup>26</sup> Based on this approach, we prepared PDI/dSn complexes (Pn) in which the PDI chromophores were bound to the pocket as a monomer (P1), or cofacially stacked as a dimer (P2) or trimer (P3) (Figure 1b). The Pn



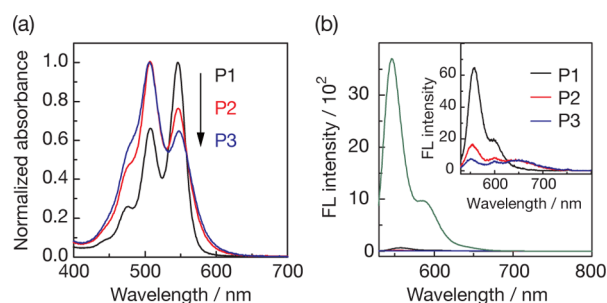
**Figure 1.** (a) Schematic of formation of PDI/DNA complexes constructed by specific binding of PDI to a pocket created by dS/dS pairs. Chemical structures of basic site analogue (deoxyribospacer, dS) and perylenediimide (PDI). (b) DNA sequences (dSn) and the complex of dSn with the PDI chromophores (Pn, n = 1, 2, 3). The number of dS/dS pairs determined the number of PDI chromophores (blue) bound to the pocket. A hexyl thiol linker (represented by asterisk) was attached to DNA in order to prepare DNA-modified gold electrodes for photocurrent measurements.

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complexes were prepared by mixing an equal amount of PDI versus the number of dS/dS pairs.

The UV/vis absorption spectra of the  $P_n$  complexes are shown in Figure 2a. The **P1** complex shows the characteristic

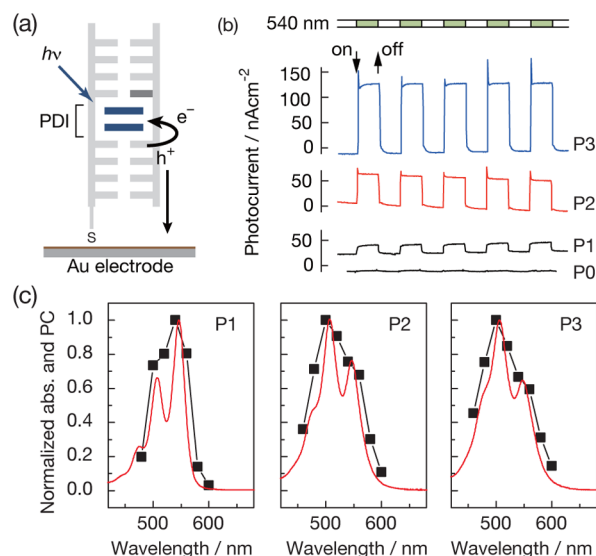


**Figure 2.** (a) UV/vis spectra normalized at absorption maximum and (b) fluorescence spectra for  $P_n$  complexes (**P1**, black; **P2**, red; and **P3**, blue) and for PDI in the absence of DNA (green). The solution was prepared in a Na phosphate buffer solution (pH 7.0, 20 mM) containing 2.5  $\mu$ M PDI. The excitation wavelength was 520 nm. Inset shows magnified fluorescence spectra of  $P_n$ .

absorption maxima at 507 and 546 nm. For the **P2** complex, the decrease in the absorption intensity at 546 nm ( $A_{546}$ ) and the increase in the intensity at 507 nm ( $A_{507}$ ) were observed. Further spectral changes were observed for **P3**, which are consistent with our previous observations for the PDI trimer–DNA complex.<sup>26</sup> Moreover, the value of  $A_{546}/A_{507}$  of the **P3** complex (PDI trimer) is larger than that of the **P2** complex (PDI dimer), supporting that the third PDI molecule is stacked with the first two PDI molecules.<sup>23,27,28</sup> Titration experiments and circular dichroism spectra of  $P_n$  confirmed the specific binding of PDI to the pocket and the formation of stacked PDI chromophores in the pockets (see Supporting Information (SI)). PDI in the excited state is known to work as a strong photooxidant and induce electron transfer between PDI and purine bases.<sup>24</sup> Compared to the fluorescence of PDI in the absence of DNA, the fluorescence of PDI in the pocket was strongly quenched, confirming the electron transfer reaction (Figure 2b). The broad emission appearing around 650 nm can be assigned to the excimer emission of the PDI chromophores, showing the formation of the stacked dimer for **P2** and trimer for **P3** (Figure 2b, inset).

Photocurrent generation of the electrodes modified with DNA possessing the stacked PDI chromophores were investigated. The  $P_n$  complexes were immobilized on a gold electrode surface according to a well established procedure.<sup>29</sup>  $P_n$  with a hexylthiol linker was directly deposited to a gold surface, and then, the surface was backfilled with 6-mercapto-1-hexanol. The photocurrent generated by the excitation of the PDI chromophores leading to charge separation and charge transfer was examined (Figure 3a). In the DNA sequence, the PDI chromophores were separated from a guanine base by four A–T base pairs to prevent the rapid charge recombination with the guanine.<sup>30–32</sup> The photocurrent response of the electrode upon irradiation at 540 nm is shown in Figure 3b. All three complexes showed a prompt on/off photocurrent response upon irradiation, indicating the charge separation induced by the excitation of PDI and following charge transfer through DNA to the electrode.<sup>19</sup>

Despite the similar photon absorption efficiency ( $rA_{540}$ ) at the excitation wavelength (Table 1), the photocurrent intensity was strongly dependent upon the number of PDIs in the



**Figure 3.** (a) Schematic of photocurrent generation of gold electrodes modified with  $P_n$  complexes. Photocurrent is generated through charge separation and charge transfer initiated by the excitation of PDI chromophores inside DNA. (b) Photocurrent response observed upon irradiation at 540 nm with a repetition time of 10 s for the  $P_n$  complexes and the complex of PDI and DNA without the pocket (**P0**). (c) Photocurrent action spectra (black) of the  $P_n$  complexes and corresponding normalized absorption spectra (red).

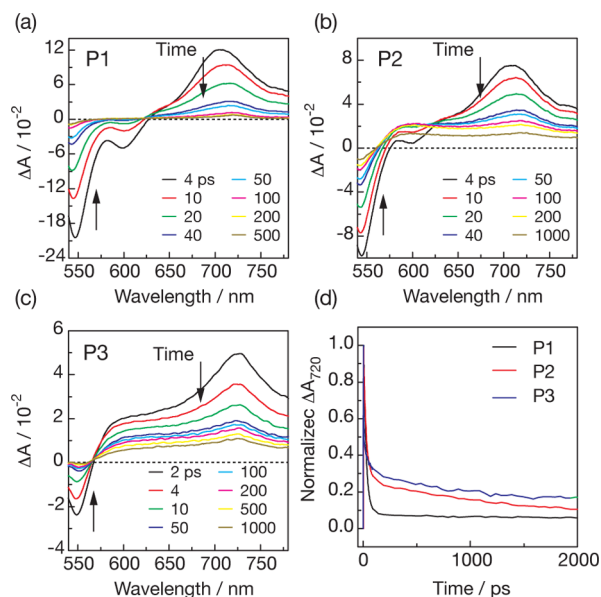
**Table 1. Comparison of Kinetic Parameter and Photocurrent (PC) Intensity for the  $P_n$  Complexes**

	PC <sup>a</sup> /nAcm <sup>-2</sup>	$rA_{540}$ <sup>b</sup>	$k_d$ <sup>c</sup> /ps
<b>P1</b>	18 ± 4	1	22
<b>P2</b>	63 ± 10	0.9	19, 807
<b>P3</b>	145 ± 12	1.2	2.5, 850

<sup>a</sup>Photocurrent intensity of the DNA-modified electrode with irradiation at 540 nm. <sup>b</sup>Relative absorbance ( $rA_{540}$ ) of the  $P_n$  complexes at 540 nm. <sup>c</sup>Decay rate constants ( $k_d$ ) obtained from time profiles monitored at 720 nm.

complex. **P2** and **P3** possessing the stacked PDI chromophores inside DNA showed much stronger photocurrents than **P1**. The PDI dimer of **P2** and the trimer in **P3** showed nearly 4- and 8-fold enhanced photocurrents compared to **P1**, respectively (Table 1), implying that the stacked form of the chromophore generated the charge separated state different from the monomer and led to an efficient conversion of the photon to the photocurrent signal. To confirm that the photocurrent generation originated from the excitation of the stacked PDI chromophores of  $P_n$ , the photocurrent action spectra of these modified electrodes were measured (Figure 3c). As shown in Figure 3c, the shape of the photocurrent action spectrum for the electrode bound to the  $P_n$  complex is consistent with that of the absorption spectrum for the corresponding the  $P_n$  complex in solution. The results show that the photocurrent is generated by the excitation of the PDI monomer for **P1**, dimer for **P2**, and trimer for **P3**, respectively. Importantly, when the mixture of PDI and DNA possessing no dS/dS pairs (**P0**) was immobilized on the electrode, little or no photocurrent responses were observed upon irradiation (Figure 3b). Therefore, we can preclude the effect of the PDI chromophore(s) bound to the groove of DNA on photocurrent generation.

In order to understand how the charge separation and charge transfer initiated by the excitation of PDI are related to the photocurrent generation of the DNA-modified electrode, we carried out femtosecond time-resolved transient absorption measurements (Figure 4). As for **P1**, the ground state bleaching



**Figure 4.** Transient absorption spectra for (a) **P1**, (b) **P2**, and (c) **P3** in a Na phosphate buffer solution (20 mM, pH 7.0) after excitation with a 540 nm laser pulse (150 fs). (d) Time profiles of the **P<sub>n</sub>** complexes monitored at 720 nm.

of the PDI around 540 nm stimulated emission at 600 nm, and  $S_1-S_n$  absorption of PDI in the singlet excited state was observed.<sup>24</sup> At 10 ps after the pulse excitation, the transient absorption spectrum with a peak around 710 nm was shifted ca. 10 nm to a longer wavelength, which was assigned to the formation of the PDI radical anion ( $\text{PDI}^{\bullet-}$ ) produced by electron transfer between PDI in the excited state and the adjacent adenine base.  $\text{PDI}^{\bullet-}$  with a peak at 720 nm decayed within 100 ps. The decay profiles monitored at 720 nm showed a rapid charge separation between  $^1\text{PDI}^*$  and A (<10 ps), and charge recombination in the contacted ion pair ( $\text{PDI}^{\bullet-}/\text{A}^{\bullet+}$ ) was observed. These results were consistent with previous studies of the PDI–DNA conjugates reported by Lewis, Wasielewski and co-workers.<sup>24,33</sup> Similarly, the PDI dimer in **P2** showed a transient absorption spectrum attributed to the singlet-excited state of PDI and the following formation of  $\text{PDI}^{\bullet-}$ . However, unlike the case of **P1**, a broadened transient absorption spectrum appeared after the rapid decay of  $\text{PDI}^{\bullet-}$  within several tens of picoseconds and slowly decayed in a time scale of 0.8 ns (Figure 4b). A similar broad transient absorption spectrum with a slightly different shape was also observed for the PDI trimer of **P3** (Figure 4c). It has been reported that the one-electron reduction of the stacked PDI assembly showed a broad spectrum assigned to the delocalization of the negative charge on the PDI chromophores.<sup>34–37</sup> Therefore, transient species in **P2** and **P3** were assigned to the delocalized state of the negative charge over the PDI chromophores.

Recently, Lewis and Wasielewski et al. reported the charge transfer dynamics of the stacked PDI assembly covalently incorporated into DNA. They show that the electron hopping or delocalization occurs over the two to three PDI

chromophores,<sup>28</sup> and the transient decay of the PDI dimer is depended upon the ground state geometry.<sup>38</sup> Consistent with their findings, the stacked PDI chromophores with conformational freedom in the pocket of the **P2** and **P3** complex led to the charge delocalization which contributed to the longer lifetime relative to the **P1** complex (Figure 4d and Table 1). The enhanced photocurrent generation observed for **P2** and **P3** can be explained by the charge-delocalized state in **P2** and **P3** with a longer lifetime than that for **P1**. The **P2** and **P3** complexes showed similar decay constants ( $\sim 0.8$  ns). However, the shape in the transient absorption spectra were different between **P2** and **P3**, and the residual component of the **P3** complex after 1 ns (the absorption intensity of the **P3** complex at 720 nm) was larger than that of the **P2** complex (Figure 4c). The transient absorption intensity should relate to the formation and amount of the charge-delocalized state that contribute to the difference in photocurrent response.

We demonstrated the enhanced photocurrent generation of electrodes modified with DNA possessing face-to-face  $\pi$ -stacked PDI chromophores. Time-resolved transient absorption measurements showed the formation of long-lived intermediates attributed to the charge delocalization of the  $\pi$ -electron over the stacked PDI chromophores leading to the longer lifetime of the initial charge separated state in these complexes. These results support the idea that the cofacial arrangement of functional chromophores in the  $\pi$ -stacked array is essential for the hole/electron transfer pathway and generation of the long-lived state leading to an enhanced photocurrent response, which enables us to develop molecular optoelectronics based on the DNA sequence and structure.<sup>1</sup>

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Detailed DNA preparation, modified electrode preparation, and characterization of DNA/PDI complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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