

# Novel Carboxylated Oligothiophenes as Sensitizers in Photoelectric Conversion Systems

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**Abstract:** Novel carboxylated oligothiophenes with different thiophene units were designed and synthesized as photosensitizers in dye-sensitized solar cells (DSSCs) for efficient opto-electric materials. The introduction of –COOH into thiophene molecules can lead to a red shift of UV-visible absorption, increase light-harvesting efficiency, and enhance photoinduced charge transport by forming efficient covalent bonds to the substrate surface. A red shift of the absorption spectrum of oligothiophene

is also achieved by the increase in the number of thiophene units. The DSSCs based on the oligomers have excellent photovoltaic performances. Under 100 mW cm<sup>–2</sup> irradiation a short-circuit current of 10.57 mA cm<sup>–2</sup> and an overall energy conversion efficiency of 3.36 % is achieved when pentathio-

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phene dicarboxylated acid was used as a sensitizer. The incident photo-to-current conversion efficiency (IPCE) has a maximum as high as 80 %. In addition, photovoltage and photocurrent transients show that slow charge recombination in DSSCs is important for efficient charge separation and excellent photoelectric conversion properties of the oligomers. These initial and promising results suggest that carboxylated oligothiophenes are efficient photosensitizers.

## Introduction

Dye-sensitized solar cells (DSSCs) have attracted much interest, since the first report from Grätzel and co-workers<sup>[1,2]</sup> because of their relatively low cost and reasonably high conversion efficiency (the maximum is 10 %) relative to conventional Si or GaAs solar cells. Photosensitizers have attracted much attention as light-harvesting species and charge-transfer media in DSSCs.<sup>[1–4]</sup> Generally, photosensitizers include inorganic materials, organic molecules, and coordination compounds,<sup>[1–5]</sup> of which ruthenium bipyridyl carboxylic acid complexes<sup>[1,2]</sup> are the most efficient sensitizers up to now. However, the expensive and rare ruthenium complexes limit their wide applications. Recently, many efforts in the area

photosensitizers have focused on conjugated polymers and oligomers due to their inexpensiveness and excellent stability. In fact, a lot of conjugated polymers and oligomers can serve as both photosensitizers and solid electrolytes in DSSCs, because they not only can absorb visible light, but also possess hole-transfer properties. The involved polymers and oligomers are polypyrrole,<sup>[6]</sup> polyaniline,<sup>[7]</sup> poly(*p*-phenylenevinylene)s,<sup>[8]</sup> phenyl-conjugated oligoene,<sup>[9]</sup> polythiophenes,<sup>[10–12]</sup> and so on. Among them, polythiophenes are studied intensively as photosensitizers in DSSCs due to their stability, low price, and excellent opto-electronic and electrochemical properties.<sup>[10–12]</sup> Yanagida et al. reported<sup>[12]</sup> the polythiophene-sensitized DSSCs with an overall conversion efficiency ( $\eta_c$ ) of ~2.4 % by introducing carboxylic acid into the polymers and ionic liquids into electrolytes; this is the best result for DSSCs based on thiophene sensitizers so far. Thiophene oligomers are not only similar to polythiophenes with respect to the above-mentioned merits, but also have better solubility and well-defined functional properties due to their precise chemical structures. Hence, they are technologically promising materials to substitute for polythiophenes. There are many efforts devoted to thiophene oligomers, which mainly focus on their physicochemical properties and applications in molecular electronic devices and in photoelectric conversion systems.<sup>[13,14]</sup> In this paper,

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two carboxyl-substituted oligothiophenes with different thiophene units [3'-amyl-5,2':5',2''-terthiophene-2,5''-dicarboxylic acid (TTDA) and 3'-amyl-5, 2':5',2'': 5'',2''':5''',2''''-pentathiophene-2,5''''-dicarboxylic acid (PTDA)] are used as photosensitizers in DSSCs, and their photoelectric properties are studied in detail.

## Results and Discussion

**UV-visible absorption and emission properties of TTDA and PTDA sensitizers:** Photophysical properties including UV-visible absorption and fluorescence are very important for evaluation of photosensitizers. Figure 1 (left-hand

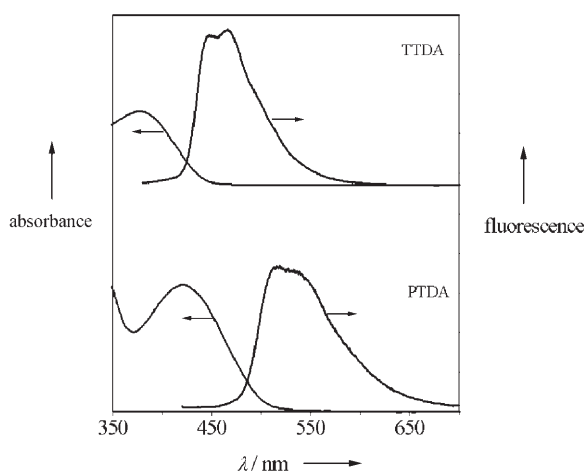


Figure 1. The normalized UV-visible spectra (left-hand curves) and fluorescence spectra (right-hand curves) of TTDA and PTDA in DMF.

curves) shows the UV-visible absorption spectra of solutions of TTDA and PTDA in *N,N*-dimethyl formamide (DMF). The  $\pi$ - $\pi$  absorptions are observed with the absorption peak ( $\lambda_{\max}$ ) located at 378 nm for TTDA and 420 nm for PTDA. Both absorption peaks shift to longer wavelengths relative to those of the unsubstituted thiophenes, terthienyl (355 nm) and pentathienyl (416 nm), respectively.<sup>[15–17]</sup> This phenomenon indicates that the introduction of -COOH group increases the conjugation length by  $\pi$ - $\pi$  interaction between carboxylic group and the thiophene rings.<sup>[9,18,19]</sup> From UV-visible spectra, the red shift of  $\lambda_{\max}$  of PTDA with respect to that of TTDA can be seen, and is ascribed to the expansion of  $\pi$ -conjugated system by the increase of thiophene units.<sup>[15–18]</sup> Meanwhile, the molar absorption coefficients ( $\epsilon$ ) are calculated from the UV-visible spectra to be  $2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for TTDA and  $4.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for PTDA, both of which are larger than the  $\epsilon$  of Ru complexes<sup>[20]</sup> used as the most efficient photosensitizers in DSSCs. The red shift of UV-visible absorption and the large  $\epsilon$  is of great benefit to the photovoltaic performance of DSSCs.

The fluorescence spectra of solutions of TTDA and PTDA in DMF are also shown in Figure 1 (right-hand

curves). These spectra have large Stokes shifts, and vibrational fine structure can be observed with the two main maxima at 446 and 465 nm for TTDA and at 514 and 538 nm for PTDA; these results suggest that the oligothiophenes adopt a more planar conformation in the first excited state due to the increased contribution of a quinoid electronic structure.<sup>[16,18,21–25]</sup> This may improve the relaxation time of excited state and be favorable for the photoelectron transfer.

In addition, the energy levels of TTDA and PTDA (see the Supporting Information) estimated by UV-visible spectra and cyclic voltammograms match well with that of  $\text{TiO}_2$  and the redox potential of  $\text{I}^-/\text{I}_3^-$  in  $\text{LiI}/\text{I}_3^-$  in acetonitrile.<sup>[26]</sup> Hence, they are employed as photosensitizers for fabrication of the dye-sensitized nanocrystalline  $\text{TiO}_2$  solar cells.

**The photoelectric conversion performance of nanocrystalline  $\text{TiO}_2$  solar cells sensitized by TTDA and PTDA:** Figure 2 shows current–voltage ( $J$ - $V$ ) characteristics of devi-

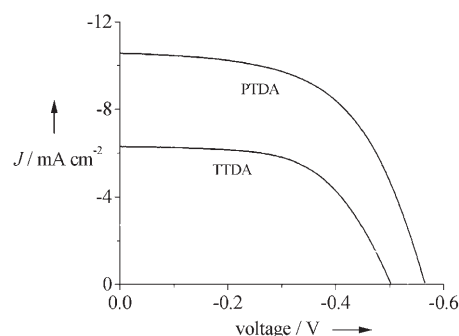


Figure 2. Current–voltage characteristics of the nanocrystalline  $\text{TiO}_2$  solar cells sensitized by TTDA and PTDA under a solar simulator irradiation of  $100 \text{ mW cm}^{-2}$ .

ces under the simulated solar irradiation of  $100 \text{ mW cm}^{-2}$ . From the  $J$ - $V$  characteristics, an open-circuit voltage ( $V_{\text{oc}}$ ) of 0.50 V, a short-circuit current density ( $J_{\text{sc}}$ ) of  $6.27 \text{ mA cm}^{-2}$ , and an  $\eta_e$  value of 1.85% are obtained for the TTDA device. However, larger values of  $V_{\text{oc}}$  (0.57 V),  $J_{\text{sc}}$  ( $10.57 \text{ mA cm}^{-2}$ ) and  $\eta_e$  (3.36%) are achieved for the PTDA-sensitized device; these results indicate that PTDA device has better photovoltaic performance than TTDA-sensitized one. It should be mentioned that, to our knowledge, the photoelectrochemical performances achieved by PTDA as a photosensitizer are the best among various photovoltaics based on thiophenes reported so far.<sup>[10–12]</sup>

Figure 3 (top) shows the spectra of the incident photon-to-current conversion efficiency (IPCE) of the solar cells in the visible light region. It matches well with the absorption spectra of the corresponding photosensitizers on  $\text{TiO}_2$  films shown in Figure 3 (middle). A maximum IPCE ( $\text{IPCE}_{\max}$ ) value of almost 80% is achieved by PTDA-sensitized device, which is close to that obtained with an Ru complex

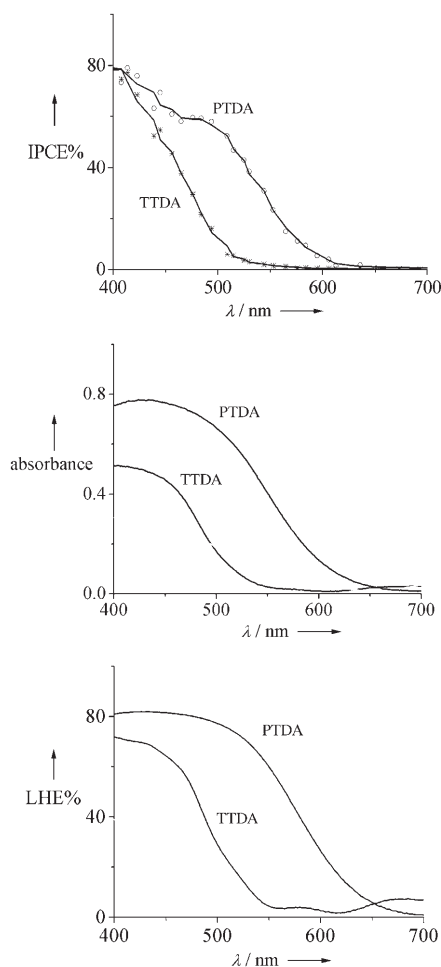


Figure 3. Top: The IPCE curves of the nanocrystalline  $\text{TiO}_2$  solar cells sensitized by TTDA and PTDA. Middle: The UV-visible spectra of TTDA- and PTDA-sensitized  $\text{TiO}_2$  films on quartz substrates. Bottom: The LHE spectra of the  $\text{TiO}_2$  films on quartz substrates sensitized by TTDA and PTDA.

system.<sup>[20]</sup> Compared with IPCE values of TTDA-sensitized device, those of PTDA-sensitized one are all larger in the visible-light region. This is consistent with the order of  $J_{\text{sc}}$ .

From UV-visible spectra of the photosensitizers on  $\text{TiO}_2$  films (Figure 3; middle), it can be seen that the visible absorbance of PTDA on  $\text{TiO}_2$  film is larger with the broader absorption band in the most part of visible light region compared with that of TTDA. Therefore, the light-harvesting efficiency (LHE) of PTDA as a photosensitizer can be predicted to be larger than that of TTDA in the visible-light region. Indeed, it can be seen from LHE spectra of TTDA and PTDA on  $\text{TiO}_2$  films in Figure 3 (bottom) that the LHE of PTDA, which is approximately 80% between 400 and 550 nm, is higher than that of TTDA; this is one reason for the optimal photovoltaic performances of the PTDA device. In addition, a red-shift absorption threshold of TTDA (600 nm) and PTDA (670 nm) on  $\text{TiO}_2$  films is observed with respect to those found in solutions of TTDA and PTDA in DMF (470 nm for TTDA and 527 nm for PTDA),

indicating that there are strong interactions between thiophene oligomers and  $\text{TiO}_2$  films. It has already been reported that carboxylic group in polythiophenes can interact with  $\text{TiO}_2$ .<sup>[11]</sup> Not only can this interaction lower energy levels and excitation energies, induce a red shift of UV-visible absorption, and increase LHE of sensitizers, but it can also accelerate injection of photoinduced electrons from sensitizers to  $\text{TiO}_2$  in the process of light excitation.<sup>[1,11,27–29]</sup> This deduction can be reflected by the complete fluorescence quenching of the photosensitizers absorbed on  $\text{TiO}_2$  films, and also suggests that the injection efficiency of photoelectrons from excited state of these sensitizers to conduction band of  $\text{TiO}_2$  is close to unity (the detailed illustration is shown in the Supporting Information).

**Photovoltage and photocurrent transients of nanocrystalline  $\text{TiO}_2$  solar cells sensitized by TTDA and PTDA:** The photovoltage and photocurrent transients of the devices based on TTDA and PTDA sensitizers were measured for investigation of the charge transport and recombination dynamics in the DSSCs, because the photovoltage or photocurrent decay is inferred as electron decay by charge recombination in circuit.<sup>[30–32]</sup> As shown in Figure 4, at the moment the sensitiz-

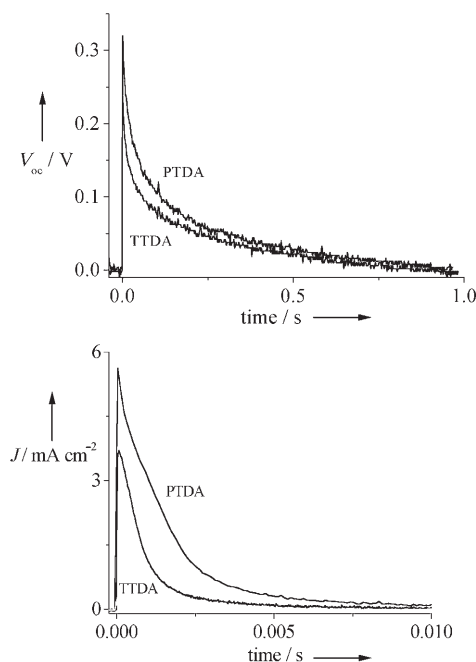


Figure 4. The photovoltage (top) and photocurrent (bottom) transients of nanocrystalline  $\text{TiO}_2$  solar cells sensitized by TTDA and PTDA.

ers are excited, the photocurrent and photovoltage responses almost instantaneously reach maxima and then decay with time following a double-exponential decay curve; however, their maximum values and decay rates are different. For the double-exponential fits of photovoltage (Figure 4, top) and photocurrent (Figure 4, bottom) transients, the two corresponding exponential time constants differ by at least a

factor of five, and the faster decay accounts for about 51–95% of the whole decay. To simplify the expression, a transit time  $\tau_{1/2}$  is defined and discussed as the time when the photovoltage or photocurrent decays to half of the peak value.<sup>[30,31]</sup> In the photovoltage transients (Figure 4, top),  $\tau_{1/2}$  is 5.9 and 39.2 ms for the TTDA and PTDA devices, respectively. In the open circuit, the voltage decay is mainly caused by interfacial recombination of injected photoelectron with the oxidized dye and electrolyte solution. Thus, the larger  $\tau_{1/2}$  value for PTDA indicates that the interfacial charge recombination rate of injected electrons with both dye cations and acceptors of redox couples in electrolyte solution of PTDA is lower; this is one of the reasons for the larger  $V_{oc}$  in the PTDA device than that in the TTDA one. In the photocurrent transients (Figure 4, bottom),  $\tau_{1/2}$  is 0.67 and 1.13 ms for the TTDA and PTDA devices, respectively; these values are coincident with the increasing trend of  $\tau_{1/2}$  in the photovoltage transient. This indicates<sup>[31]</sup> that the charge recombination and electron escape in the closed circuit decreases in the order of TTDA and PTDA. As a result, the  $J_{sc}$  of PTDA device is larger than that of TTDA one.

## Conclusion

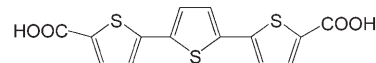
Novel carboxylated thiophene oligomers, TTDA and PTDA, were synthesized. Their UV-visible absorption properties and light-harvesting efficiencies were found to be controlled by introduction of  $-\text{COOH}$  moieties and the number of thiophene units. The photoelectric responses of DSSCs based on these sensitizers show that the oligothiophenes have efficient photoinduced charge transfer and excellent photoelectric conversion properties. The overall conversion efficiency of PTDA-sensitized DSSC is the largest (3.36%) among various photovoltaic devices based on thiophene polymers or oligomers so far, and especially, the maximum IPCE value (ca. 80%) is close to that of DSSCs based on Ru complex sensitizers. Photovoltage and photocurrent transients show that a low charge-recombination rate in DSSCs is crucial for efficient photovoltaic performance. These results strongly support the prospects for successful application of oligothiophene-sensitized DSSCs and indicate the significance of molecular design of the photosensitizer for the highly efficient DSSCs.

## Experimental Section

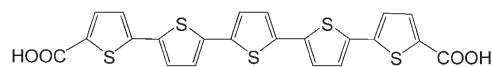
**Materials:** TTDA and PTDA were adopted as photosensitizers. Their schematic molecular formulae are shown here, and their synthesis processes are described in the Supporting Information.

**Fabrication of the nanocrystalline  $\text{TiO}_2$  solar cells sensitized by TTDA and PTDA:** The  $\text{TiO}_2$  photoelectrodes were prepared according to the method proposed by Tennakone et al.<sup>[33]</sup> with the specific surface area of  $20 \text{ m}^2 \text{ g}^{-1}$  (detected by BFHP ST-08 A specific surface system, China). The prepared  $\text{TiO}_2$  electrodes were immersed into TTDA and PTDA solutions overnight, and thus the photosensitizers were absorbed on nano-

TTDA:



PTDA:



crystalline  $\text{TiO}_2$  electrodes. The concentration of the two photosensitizers in DMF was the same, that is,  $5 \times 10^{-5} \text{ M}$ . Platinum-coated ITO glass was used as a counter electrode. Iodine (0.1 M) and lithium iodide (0.5 M) in acetonitrile were applied as electrolytes.

**Measurements:** The  $J$ - $V$  characteristics and IPCE measurements of the oligomer-sensitized solar cells were performed with an electrochemical analyzer (CHI630 A, Chenhua Instruments Co. Shanghai). A solar simulator (CMH-250, Aodite Photoelectronic Technology Ltd. Beijing) with light intensity of  $100 \text{ mW cm}^{-2}$  was used as light source.

UV-visible spectra were measured by a HITACHI U-4100 spectrophotometer. Reflectance ( $R$ , %) and transmittance ( $T$ , %) of the sensitized  $\text{TiO}_2$  films were obtained by using an integration sphere in order to calculate LHE by Equation (1):

$$\text{LHE (\%)} = 1 - T - R \quad (1)$$

The fluorescence spectra were determined by HITACHI F-4500 fluorescence spectrophotometer. The transparent  $\text{TiO}_2$  films were prepared<sup>[34]</sup> on quartz substrates for UV-visible and fluorescent spectra measurements.

Transient photovoltage and photocurrent of DSSCs based on oligothiophene sensitizers was measured. A Nd:YAG laser (NEWWAVE, Tempest 300, 5 ns, 10 Hz) with the wavelength of 532 nm was employed as a pulse source. The laser excitation beam irradiated the devices on the ITO side perpendicularly, and the irradiating area was  $0.1 \text{ cm}^2$ . The transient photovoltage and photocurrent responses were recorded by a TDS620B oscilloscope with averaging capability (Tektronix).

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