Enhanced Photocurrent via π-Bridge Extension of Perylenemonoimide-Based Dyes for p-Type Dye-Sensitized Solar Cells and Photoelectrochemical Cells

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ABSTRACT: Two dyes TB and TSB containing triphenylamine as the donor and perylenemonoimide as the acceptor, with and without bithiophene as π-bridge, respectively, were successfully prepared and characterized for p-type dye-sensitized solar cells (p-DSSCs) and dye-sensitized photoelectrochemical cells (DS-PECs). As a result, TSB with bithiophene π-bridge exhibited a broader absorption spectrum and a higher molar extinction coefficient than TB. Furthermore, the photocurrents of p-DSSCs and DS-PECs for the dye TSB were increased by 26.9 and 32.9%, respectively, compared with those of the dye TB. Meanwhile, the electrochemical impedance spectroscopy of the TSB-based p-DSSC showed the smaller charge-transfer resistance and larger hole lifetime because the longer π-bridge facilitated charge transfer and separation within the dye molecule and effectively prevented the hole recombination process at the NiO/dye interface, resulting in improvement of photoelectric performance. Hence, these results show that the π-bridge extension of dyes has a promising effect on the photocurrent improvement of p-DSSCs and DS-PECs.

1. INTRODUCTION

Severe challenges in balancing the energy utilization, economic development, and environmental protection have impelled scientists and technicians continuously to investigate solar power and sustainable and clean energy.1–5 Fortunately, dye-sensitized solar cells (DSSCs)6–14 and dye-sensitized photoelectrochemical cells (DS-PECs) have emerged,15–19 as a means of converting solar energy into green fuels and electrical energy, respectively.20,21 which really leads a comprehensive viable approach to use highly efficient solar energy. Enhancing light-harvesting ability by broadening the absorption spectrum of dyes is the effective way to improve the photoelectric conversion performance. In general, the tandem p-/n-type device can achieve it by the two dyes whose spectral responses are complementary to each other adsorbed on the photoanode and the photocathode, respectively, which can avoid competitive adsorption between dyes adsorbed on the same semiconductor substrate. It is worth mentioning that the theoretical efficiency of a single photoelectrode device is around 30% for DSSCs, whereas the theoretical conversion efficiency of the tandem p-/n-type device reaches 43%. The greatest advantage is that the absorption spectrum can be broadened by two dyes whose spectral responses are complementary to each other.

As He et al. first reported a NiO-based p-type dye-sensitized photocathode and constructed a tandem p-/n-DSSC,26,27 research on tandem p-/n-DSSCs has gradually made progress in the past 20 years.12,17,28 However, the overall power conversion efficiency of tandem p-/n-DSSCs is much lower than that of n-DSSCs.29–31 The reason is mainly attributed to the lower photocurrent rooted in the p-type electrode, causing the mismatch photocurrent generated by the counterpart n-type electrode. As an antenna for capturing light energy, the spectral absorption range and molar extinction coefficient of a dye sensitizer have the most important influence on the photocurrent.32–36 Currently, perylenemonoimide (PMI)-6T-TPA is the most efficient dye applied in p-DSSCs and p-DSPEC devices.37,38 Among them, 3-hexyl-substituted sexithiophene groups as π-bridge are a bright spot of the dye structure, which not only broadens the spectral absorption but also increases the distance between the holes and the electrons in the NiO and dye, reducing the recombination between electrons and holes, resulting in further improved photoelectric performance. In previous report, compounds YK-1 and YK-2 were constructed by our group, and the effects of anchoring groups on p-DSSCs and DS-PECs were discussed.38 In addition, triphenylamine is widely used in photovoltaic materials because of its easy generation of holes and high hole mobility.39–41 Therefore, our group synthesized two new dyes TB and TSB based on the dye YK-1 with triphenylamine as the donor and the bithiophene group as the π-bridge for further improving the photoelectric performance of the device.

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Hence, we studied the influence of π-bridge on dye absorption and photovoltaic and photoelectric properties for the two dyes TB and TSB. Because of the introduction of bisphenol, the absorption spectrum of the dye was red-shifted by 5 nm, and the molar absorption coefficient was increased to 40 100 ε/M cm−1 for TSB. The photocurrents of p-DSSCs and DS-PECs for the dye TSB were increased by 26.9 and 32.9%, respectively, compared with those of the dye TB. Electrochemical impedance spectroscopy (EIS) was employed to further investigate the influence of extending π-bridge on the charge-transfer and recombination processes in the p-DSSCs. The linear scan voltammetry (LSV) and the transient photocurrent responses were also employed to estimate the photovoltaic performances of the dye-sensitized photocathodes. A schematic view of the molecular structure of two dyes TB and TSB and Co-1 is shown in Scheme 1.

Scheme 1. Structures of Dyes TB and TSB and Cocatalyst Co-1

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. All solvents and chemicals were commercially available and were used without further purification unless otherwise stated. All chemical reactions were performed under nitrogen. Compound 4 was obtained according to previous report.28 Co-1 (Co(dmgBF2)2(H2O)2), was synthesized according to the reference report.29

2.2. Characterization Method. 1H NMR and 13C NMR spectra were acquired at 400 and 100 MHz, respectively, with tetramethylsilane as an internal standard. The high-resolution spectra were acquired at 400 and 100 MHz, respectively, with a Varian-600 MHz spectrometer.

2.3. Preparation of TB and TSB. 2.3.1. Preparation of Co-1. To a solution of compound 2 (250 mg, 0.46 mmol) in DCM (20 mL) was added NaOH aqueous solution (10 mL, 2 mol/L) was well mixed in THF (50 mL). The solution was stirred at 60 °C for 30 min. Then (4-ethoxyacetyl)phenylboronic acid was added to the solution, which was stirred at 60 °C under N2 for 12 h. After examining the procedure of the reaction using thin-layer chromatography (TLC), water was poured into the solution, and then the mixture was extracted with dichloromethane (DCM). Organic layers were collected and dried over anhydrous Na2SO4. After removing the organic solvent in vacuum, the crude product was then purified by silica gel column chromatography to get compound B. Yield: 88%. 1H NMR (400 MHz, chloroform-d): δ 8.12–8.07 (m, 4H), 7.68–7.62 (m, 4H), 7.57–7.52 (m, 4H), 7.32 (m, J = 8.5, 7.3 Hz, 2H), 7.24–7.17 (m, 6H), 7.11 (t, J = 7.4 Hz, 1H), 4.40 (q, J = 7.1 Hz, 4H), 1.42 (t, J = 7.1 Hz, 6H). HRMS (m/z): [M − H+] calc for C36H21NO4, 564.2151; found, 564.2141.

2.3.2. Preparation of 3. To a solution of compound 2 (250 mg, 0.46 mmol) in DCM (20 mL) was added NaOH aqueous solution (10 mL, 2 mol/L) was well mixed in THF (50 mL). The solution was stirred at 60 °C for 30 min. Then (4-ethoxyacetyl)phenylboronic acid was added to the solution, which was stirred at 60 °C under N2 for 12 h. After examining the procedure of the reaction using TLC, water was poured into the solution, and then the mixture was extracted with DCM. Organic layers were collected and dried over anhydrous Na2SO4. After removing the organic solvent in vacuum, the crude product was then purified by silica gel column chromatography to get compound C. Yield: 48%. 1H NMR (400 MHz, chloroform-d): δ 8.03 (d, J = 8.3 Hz, 4H), 7.67 (d, J = 8.3 Hz, 2H), 7.58 (m, J = 8.5, 3.5 Hz, 4H), 7.47 (t, J = 8.0 Hz, 4H), 7.15 (m, J = 9.2, 2.5 Hz, 4H), 7.08 (d, J = 8.3 Hz, 2H), 4.33 (q, J = 7.1 Hz, 4H), 1.35 (t, J = 7.1 Hz, 6H), 1.18 (s, 12H).

2.3.3. Preparation of 5. A mixture of compound 4 (100 mg, 0.117 mmol), Pd(dpa)4 (10 mg, 0.01 mmol), and K2CO3 aqueous solution (10 mL, 2 mol/L) was well mixed in THF (60 mL). The solution was stirred at 50 °C for 30 min, and then 2-{[(2, 2′-bithiophen)-5-yl]-4,4,5,5-tetramethyl-1, 3,2-dioxaborolare (50 mg, 0.175 mmol) was added. Then the mixture solution was stirred at 60 °C under N2 for 12 h. After examining the procedure of the reaction using TLC, water was poured into the solution, and then the mixture was extracted with DCM. Organic layers were collected and dried over anhydrous Na2SO4. After removing the organic solvent in vacuum, the crude product was then purified by silica gel column chromatography to get compound 6. Yield: 54%. 1H
NMR (400 MHz, DMSO-d$_6$): $\delta$ 9.33 ($d$, $J = 12.4$, 8.1 Hz, 2H), 8.45 ($d$, $J = 8.3$ Hz, 1H), 8.08 ($d$, $J = 3.3$ Hz, 2H), 7.89–7.76 ($m$, 2H), 7.59 ($d$, $J = 4.3$ Hz, 1H), 7.50 ($d$, $J = 9.0$, 4.1 Hz, 3H), 7.43 ($dq$, $J = 6.9$, 3.0 Hz, 3H), 7.31 ($d$, $J = 7.8$ Hz, 2H), 7.22–7.17 ($m$, 4H), 7.15 ($d$ ($d$, $J = 5.0$, 3.6 Hz, 1H), 1.29 ($d$, $J = 1.5$ Hz, 18H), 1.03 ($d$, $J = 6.8$ Hz, 12H). HRMS (m/z): [M + H$^+$] calc for C$_{62}$H$_{56}$NO$_4$S$_2$, 942.3651; found, 942.3654.

2.3.4. Preparation of 6. To a solution of compound 5 (60 mg, 0.064 mmol) in DCM (20 mL) was added N-bromosuccinimide (15 mg, 0.084 mmol) at 0 °C. The solution was stirred at room temperature under dark for 3 h and evaporated to dryness to get crude product. Then the crude product was used without further purification.

2.3.5. Preparation of 7. A mixture of compound 4 (200 mg, 0.23 mmol), Pd(dpa)$_4$ (10 mg, 0.01 mmol), and K$_2$CO$_3$ aqueous solution (10 mL, 2 mol/L) was well mixed in THF (60 mL). The solution was stirred at 50 °C for 30 min, and then compound 3 (156 mg, 0.23 mmol) was added. Then the solution was stirred at 60 °C under N$_2$ for 12 h. After examining the procedure of the reaction using TLC, water was poured into the solution, and then the mixture was extracted with DCM. Organic layers were collected and dried over anhydrous Na$_2$SO$_4$. After removing the organic solvent in vacuum, the crude product was then purified by silica gel column chromatography to get compound 5. Yield: 45%. $^1$H NMR (400 MHz, chloroform-d): $\delta$ 9.41–9.35 (m, 2H), 8.34 (s, 2H), 8.16 (m, 1H), 8.14–8.09 (m, 4H), 7.71–7.65 (m, 4H), 7.64–7.56 (m, 6H), 7.50–7.45 (m, 2H), 7.45–7.39 (m, 5H), 7.35–7.28 (m, 8H), 7.12–7.06 (m, 4H), 4.41 (q, $J = 7.1$ Hz, 4H), 2.73 (m, $J = 6.9$ Hz, 2H), 1.42 ($t$, $J = 7.1$ Hz, 6H), 1.34 (s, 18H), 1.15 (d, $J = 6.9$ Hz, 12H). HRMS (m/z): [M + H$^+$] calc for C$_{95}$H$_{80}$N$_2$O$_8$, 1317.5993; found, 1317.5988.

2.3.6. Preparation of TB. Compound 7 (100 mg, 0.076 mmol) was well mixed in a solution of 10 mL THF, 5 mL ethanol, and 5 mL 20% K$_2$CO$_3$ aqueous solution. The solution was stirred at 60 °C under N$_2$ for 12 h. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 9.34 to 8.56 (m, 2H), 8.45 (s, 1H), 8.08 (s, $J = 2.3$ Hz, 2H), 8.01 ($d$, $J = 8.4$ Hz, 4H), 7.95 (s, 1H), 7.86 ($d$, $J = 8.3$ Hz, 1H), 7.20 ($d$, $J = 8.4$ Hz, 4H), 7.75 ($d$, $J = 8.5$ Hz, 4H), 7.69 ($d$, $J = 8.4$ Hz, 2H), 7.53–7.47 (m, 6H), 7.44 ($d$, $J = 4.0$ Hz, 2H), 7.31 ($d$, $J = 7.8$ Hz, 2H), 7.22–7.19 (m, 7H), 7.19–7.14 (m, 3H), 2.66 ($d$, $J = 8.3$ Hz, 2H), 1.29 ($d$, $J = 1.5$ Hz, 18H), 1.03 ($d$, $J = 6.8$ Hz, 12H). $^{13}$C NMR (101 MHz, DMSO-d$_6$): $\delta$ 172.08, 129.94, 127.96, 127.16, 126.09, 34.01, 31.03, 30.99, 30.36, 28.94, 23.65, 20.99. HRMS (m/z): [M + H$^+$] calc for C$_90$H$_{80}$N$_2$O$_8$, 1452.5112; found, 1452.5107.

2.4. Preparation of NiO Films. A precursor solution of copolymer F68 (2 g), deionized water (H$_2$O, 6 g), nickel(II)-chloride (NiCl$_2$ 2 g), and ethanol (EtOH, 12 g) was obtained according to the previous report. The NiO film was formed on a fluorine-doped tin oxide (FTO) glass by a spin-coating method at 500 rpm for 9 s and then 2000 rpm for 30 s. The film was obtained after heating in an oven at 450 °C for 30 min. For p-DSSC, the four-layer NiO film with a thickness of 2 μm for each layer was acquired after four repetitions of spin-coating and heating procedure. The three layers for DS-PEC were obtained by the same method.

2.5. Fabrication of the DSSCs. The prepared NiO films were immersed in 3 × 10$^{-4}$ M dye solution in a mixture of MeOH/toluene (v/v = 7/3) at room temperature for 12 h. The Pt-counter electrodes were obtained by heating at 400 °C for 15 min after spin-coating 20 mM H$_2$PtCl$_6$ isopropanol solution onto the FTO glass. The dye-sensitized NiO WE was acquired after washing with EtOH and was then assembled with the Pt-counter electrode together employing a 25 μm thick Surlyn gasket. The electrolyte consisted of 0.03 M I$_2$, 0.1 M GuaSCN, 0.6 M BMII, and 0.5 M TBP in acetonitrile (GuaSCN = guanidine thiocyanate, BMII = 1-butyl-3-methylimidazolium iodide, and TBP = tert-butylpyridine).

2.6. Fabrication of the Photoelectrochemical Cells. An Ag/AgCl reference electrode, a Pt counter electrode, and the dye-sensitized NiO WE were employed to prepare a traditional three-electrode system according to the above method. A catalyst was introduced onto dye-sensitized NiO films by drop-casting the acetonitrile (CH$_3$CN) solution of Co(1) (100 μL, 2 mM) onto the surface of NiO and then drying with air flow. The electrolyte was an aqueous solution of 10 mM phosphate at pH = 7. All DS-PEC cells were
Scheme 2. Reagent and Conditions: (a) (4-(Ethoxycarbonyl)phenyl)boronic Acid, Pd(PPh₃)₄, K₂CO₃, THF, H₂O, 60 °C, 12 h, 80%; (b) NBS, DCM, 0 °C, 3 h, 88%; (c) 4,4',4,5,5',5'-Octamethyl-2,2'-bi(1,3,2-dioxaborolane), AcOK, Pd(dppe)₂Cl₂, 1,4-Dioxane, 80 °C, 5 h, 48%; (d) 2-(2,2'-Bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, Pd(PPh₃)₄, K₂CO₃, THF, H₂O, 60 °C, 12 h, 54%; (e) NBS, CH₂Cl₂, 0 °C, 3 h, 92%; (f) Pd(PPh₃)₄, K₂CO₃, THF, H₂O, 60 °C, 12 h, 45%; (g) 20% KOH, THF, EtOH, 60–70 °C, 12 h, 89%; (h) Pd(PPh₃)₄, K₂CO₃, THF, H₂O, 60 °C, 12 h, 66%; (i) 20% KOH, THF, EtOH, 60–70 °C, 12 h, 90%

Figure 1. (a) UV–vis absorption spectra of TB and TSB in THF (3 × 10⁻⁴ M). (b) Normalized absorption spectra of dyes TB and TSB on 2 μm NiO films.

Table 1. Photophysical Properties and Photovoltaic Properties of p-DSSC Iodide/Triiodide Redox Electrolyte of TB, TSB, and YK-1

| dye | λmaxd/a (nm) | λmaxb/b (nm) | Eₐ/ε ∆ (V vs NHE) | Eₑ/s/s⁺d (V vs NHE) | Eₑ/s/s⁻d (V vs NHE) | Eₑ/s/s⁺e (V vs NHE) | Voc (mV) | Jsc (mA cm⁻²) | FF (%) | PCE (%) |
|-----|-------------|-------------|-------------------|-------------------|-------------------|-------------------|---------|-------------|--------|--------|
| TB  | 528 (27 900) | 522         | 2.09              | 1.22              | −0.77             | 1.32              | −0.97   | 129.30      | 2.83   | 29.47   |
| TSB | 533 (40 100) | 534         | 2.02              | 0.98              | −0.80             | 1.22              | −1.04   | 130.70      | 3.59   | 28.12   |
| YK-1| 556 (34 600) | 547         | 2.00              | 0.87              | −1.13             | 102.00            | 2.33    | 27.90       | 0.10   | 0.13    |

*Absorption maximum of dyes dissolved in THF. **Absorption maximum of dyes adsorbed on 2 μm NiO films. The zero–zero transition energy (E₀,₀) was calculated from the absorption threshold from the absorption spectra of dyes in solution. All potentials are given versus NHE converted by adding E_Fc/Fc⁰ = 0.69 V vs NHE. The excited-state potentials were estimated from E₀,₀ and the recorded potentials by using CV, according to the following:

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deoxygenated by N₂ for at least 15 min before the measurements.

3. RESULTS AND DISCUSSION

3.1. Dye Synthesis. In this work, the main point of the molecular structure design was the addition of the π-bridge. Hence, TB and TSB were both synthesized with modified triphenylamine and PMI as the electron donor and the electron acceptor part for building a large conjugate unit, respectively. Dithiophene π-bridge was introduced into TSB to increase the distance between the donor and the acceptor, reduce the charge recombination, and enhance the light-capturing ability.\textsuperscript{13,14} Two dyes were synthesized through a series of chemical reactions of bromination, carboxyester hydrolysis, Suzuki coupling, and Williamson ether synthesis, and the synthetic route is shown in Scheme 2. First, compound 2 was obtained by the Suzuki coupling reaction of 1 and 4-((ethoxycarbonyl)phenyl)boronic acid and then by bromination with N-bromosuccinimide (NBS) and coupling to provide the key intermediate 3. In addition, another important intermediate 6 was obtained by alkylation reaction, Suzuki–
and TSB nm with a high molar extinction coe
the maximum absorption peak of
the maximum absorption peaks attributed to the intramolecular
the light absorption capacity of two dyes. As a result, the
dissolved in THF and adsorbed on NiO
shows the UV
TB than
TB solution, the maximum absorption peaks of
amine donor. Compared with the absorption spectra in
the corresponding data are listed in Table 1 . First, the
potentials
E_{*+/*} = E_{0+/0} - E_{0-0} = E_{*+/*} = E_{0-0}
Unlike conventional optoelectronic devices, light absorption
and charge transfer are separated in dye-sensitized photocathodes. The dye acts as a photosensitizer that can capture photons from the sunlight and stimulate to an excited state (dye*) through photoexcitation. The holes transfer from the highest occupied molecular orbital (HOMO) of dye* to the valence band (VB) of NiO to form the charge-separated state dye*/NiO (h+), and then the holes (h+) divert to glass coated with FTO through NiO. The reduced dye is regenerated by transferring electrons to redox couples (usually I3-/I-) or hydrogen-producing catalyst (typically used with Co-116) in p-DSSCs and p-DS-PECs, respectively. In order to investigate the feasibility of charge-transfer process, CVs of reduction dyes TB and TSB were tested in DCM solution (Figure 2b), and the corresponding data are listed in Table 1 . First, the potentials $E_{*+/*}$ (corresponding to the HOMO energy levels of TB and TSB) were located at 1.32 and 1.22 V versus NHE, respectively, and were much lower than the VB of NiO (0.54 V vs NHE). It guaranteed sufficient driving force for hole metastasis from the dye to NiO. In addition, the zero−zero transition energy $E_{0-0}$ values (corresponding to band gap), estimated from the absorption threshold from the absorption spectra of dyes in solution, were 2.09 eV for TB and 2.02 eV for TSB (Table 1 ), respectively. The potential $E_{*+/*}$ values (corresponding to the lowest unoccupied molecular orbital

3.2. Optical and Electrochemical Properties. Figure 1 shows the UV−vis absorption spectra of TB and TSB dissolved in THF and adsorbed on NiO films, respectively, and their corresponding parameters are listed in Table 1 . With the push−pull structure, both dyes in the THF solution exhibited major absorption bands in wavelength ranges of 500−550 nm in Figure 1a. Meanwhile, the π-bridge between triphenylamine donor and PMI acceptor leads to a difference in the light absorption capacity of two dyes. As a result, the maximum absorption peaks attributed to the intramolecular charge transfer are located at $\lambda_{\text{max}}$ = 528 and 534 nm for TB and TSB, respectively, indicating that the π-bridge was beneficial for broadening the absorption spectra. Meanwhile, the π-bridge also has a great influence on the molar extinction coefficient, in which the dye TSB with dithiophene π-bridge has a higher molar extinction coefficient (40 100 ε/M−1 cm−1) than TB (27 900 ε/M−1 cm−1). In addition, compared to TB, the maximum absorption peak of YK-1 is located at $\lambda_{\text{max}}$ = 547 nm with a high molar extinction coefficient (34 600 ε/M−1 cm−1) because of strong electron-donating ability of diphenylamine donor. Compared with the absorption spectra in solution, the maximum absorption peaks of TB showed a blue shift by 6 nm on the NiO film, whereas in TSB, it barely shifted (Figure 1b). When sensitzers adsorbed onto the NiO surface, the carboxyl group of dyes undergoes a deprotonation reaction, and its electron-withdrawing ability is greatly reduced.

As the intramolecular electron push−pull effect is weakened, the charge polarization energy increases, so the absorption of TB exhibits a sharp blue shift. As for TSB, the intramolecular electron push−pull effect has not weakened because of the introduction of the π-bridge, so the absorption spectrum of TSB is basically not blue-shifted.44,45

$$E_{*+/*} = E_{0+/0} = E_{0-0}$$

Miyaura cross-coupling, and regioselective bromination of 4. Then Suzuki coupling reactions were performed between 3 and 4 and 3 and 6 to connect the donor and acceptor, respectively. The target products TB and TSB were obtained by the carboxyester hydrolysis of 7 and 8, respectively. All the new compounds were confirmed with 1H NMR, 13C NMR, and HRMS.

Figure 6. Transient current responses to on−off cycles under an applied potential of −0.1 V vs Ag/AgCl (light intensity 100 mW cm−2), operated in a three-electrode PEC cell with Pt as the counter electrode and 100 mM PBS (pH = 7.0) as the electrolyte.

Figure 5. LSV measurements of the (a) TB + Co-I@NiO and (b) TSB + Co-I@NiO WE s under 100 mW cm−2 light illumination (scan rate = 50 mV s−1), operated in a three-electrode PEC cell with Ag/AgCl as the reference electrode, Pt as the counter electrode, and 100 mM PBS (pH = 7.0) as the electrolyte.
energy levels of TB and TSB) were −0.77 and −0.80 V versus NHE for TB and TSB, respectively (Table 1). These values were much higher than the redox potential of the iodide/triiodide system (∼−0.40 V vs NHE) in DSSCs and cocatalyst Co-1 (∼−0.43 V vs NHE) in DS-PECs, indicating significant thermodynamic force for electron transfer between the excited dyes and the redox couple, cocatalyst. The schematic diagram of energy levels and charge divert processes in p-DSSCs and p-DS-PECs is shown in Figure 2c. In addition, from the CV of TB and TSB for 20 cycles (Figure 2a), we can easily infer that both dyes have excellent photoelectrochemical stability.

3.3. Photovoltaic Properties. The performances of p-DSSCs based on the two dyes (TB and TSB) were obtained under AM 1.5G irradiation (100 mW cm⁻²). Figure 3a shows the photocurrent density—voltage curves (J−V) of the p-DSSCs, and the corresponding data are listed in Table 1. It was found that the device based on TSB with dithiophene π-bridge showed higher J_{oc} compared to TB. Generally speaking, the J_{oc} value is related to the light-capturing ability of photosensitizers. J_{oc} of p-DSSCs based on TSB with the larger molar extinction coefficient is higher than that of TB. In addition, the higher IPCE values of the TSB-based p-DSSCs in the visible light range of 350−660 nm (Figure 3b) also support this result. It is worth noting that the IPCE values of TB- and TSB-based p-DSSCs were also much higher than those of YK-1 and YK-2 in our previous report. Although it has better light-trapping ability than TB, YK-1 has an energy level similar to TSB and the cell performance of the YK-1-based device is lower than those of TB- and TSB-based devices. This is because the hole mobility of triphenylamine donor in p-DSSCs is higher than that of diphenylamine.

3.4. Electrochemical Impedance Spectroscopy. In general, V_{oc} is correlated to the hole recombination rate and the VB (E_{VB}) position at the electrolyte/dye/NiO interface. Here, EIS was employed to understand the difference of V_{oc} between TB- and TSB-based p-DSSCs. The charge-transfer resistances (R_{ct}), chemical capacitances (C_{chem}), and the hole lifetimes (τ_{h}) of the p-DSSCs based on TB and TSB were investigated (Figure 4). Figure 4a shows the charge-transfer resistance (R_{ct}) between the NiO films and the electrolyte, where the R_{ct} of p-DSSCs based on TSB was larger than that based on TB under the voltage range, indicating that the introduction of dithiophene π-bridge efficiently inhibited charge recombination at the NiO/dye/electrolyte interface.

In addition, V_{oc} is positively correlated to the quasi-Fermi level (E_{FF}) of NiO. An increase in V_{oc} was observed under the conditions of the TSB-based device compared to TB, and the result is further confirmed by the hole lifetime (τ_{h}) and chemical capacitance (C_{chem}) for TSB-based p-DSSCs in Figure 4b, indicating the lower NiO VB energy and hole state density, thereby leading to an improved V_{oc}. The τ_{h} was used to evaluate the hole recombination between the injected holes in the NiO film and the sensitizer or redox couple. The values of the TSB-based p-DSSCs were higher than that of TB-based p-DSSCs as shown in Figure 4c, further indicating that the extended dithiophene π-bridge effectively inhibits hole recombination, resulting in an improved V_{oc} and a higher PCE.

3.5. Photoelectrochemical Properties of Dye-Sensitized NiO Films. In order to study the photocatalytic performance of the dye-sensitized photocathode, we constructed DS-PEC based on TB and TSB, respectively. After illumination of the photocathode, the excited dyes acted as photosensitizers to inject holes into the VB of NiO, and then the molecular catalyst Co-1 was reduced by the dye for eventual hydrogen and photocurrent generation. The schematic diagram of charge divert processes in p-DS-PECs is shown in Scheme 3.

Here, we investigated the photoelectrochemical performance of dye-sensitized NiO membranes. In a traditional three-electrode cell system, the dye-sensitized NiO photocathode was used as the WE and Pt plate and Ag/AgCl were used as the counter electrode and reference electrode, respectively. LSV and transient photocurrent responses (I−t) were employed to study the interfacial electron-transfer kinetics.

As shown in Figure 5, LSV of TB + Co-1@NiO and TSB + Co-1@NiO showed the relationship between the applied bias potential and the photocurrent, respectively. Under illumination, the photocurrent of TB + Co-1@NiO obviously increased from −0.25 to −0.1 V (vs Ag/AgCl), and then at E > −0.1 V (Figure 5a), it reached a plateau with a photocurrent density of 50 µA cm⁻². Meanwhile, TSB + Co-1@NiO showed similar trends, whose photocurrent rapidly increased with the applied bias from −0.25 to −0.1 V (vs Ag/AgCl) and then reached a plateau at E > −0.1 V with a photocurrent density of 75 µA cm⁻² (Figure 5b). These values are higher compared to the current densities under dark conditions, revealing that the dye-sensitized photocathode is photoactive. It is worth noting that the photocurrent of TSB + Co-1@NiO is higher than that of TB + Co-1@NiO, which may be attributed to the broader absorption and higher molar extinction coefficient of TSB because of the introduction of dithiophene π-bridge.

According to the relationship between the applied bias potential and the photocurrent from LSV, we chose −0.1 V as the applied bias and then measured the photocurrent of the dye + Co-1@NiO WE. The transient photocurrent responses to on−off cycles under illumination were then investigated, and the results are shown in Figure 6. As shown in Figure 6a, for the TB + Co-1@NiO photocathode, it showed a low photocurrent of −10 µA cm⁻² in dark and it can produce a much higher photocurrent once illuminated, and then the photocurrent gradually decreases. Finally, it reached a final photocurrent of −12.75 µA cm⁻². On the other hand, the TB + Co-1@NiO photocathode excluded Co-1 only displaying low photocurrent under the same conditions. Meanwhile, for the TSB + Co-1@NiO photocathode in Figure 6b, it shows similar photoelectrochemical properties and can give an average photocurrent of −16.94 µA cm⁻². It can be obviously found that the TSB + Co-1@NiO photocathode showed higher photocurrent than the TB + Co-1@NiO photocathode, which may be attributed to the higher molar extinction coefficient of TSB and better photovoltaic properties of TSB@NiO including lower charge recombination data. It is worth noting that the photocurrent values of the TB- and TSB-based photocathodes were both much higher than those of YK-1 in our previous report.

4. CONCLUSIONS

In summary, two novel organic PMI-based dyes TB and TSB with and without bithiophene π-bridge were successfully prepared and applied in p-DSSCs and DS-PECs, respectively. The effect of π-bridge on the photocurrent of p-DSSCs and DS-PECs was discussed. The UV−vis absorption spectra showed that TSB with bithiophene π-bridge had a broadened absorbance spectrum and a higher molar extinction coefficient.
compared to TB. As a result, the maximum absorption peaks were located at $\lambda_{\text{max}} = 528$ nm ($27 \, 900 \, eV/\text{cm}^2$) and 534 nm ($40 \, 100 \, eV/\text{cm}^2$) for TB and TSB, respectively. Furthermore, the photocurrents of p-DSSCs and DS-PECs for the dye TSB were increased by 26.9 and 32.9%, respectively, compared with those of the dye TB. In addition, the TSB-based cell showed the highest PCE of 0.1326% with the iodide-

EIS indicated that the introduction of bithiophene $\pi$-bridge led to higher hole lifetime and lower charge–hole recombination data. In the research of p-type dye-sensitized photocathodes, prolonging the $\pi$-bridge chain of the photosensitizer contributes to the improvement in the photoelectrochemical properties of the device, which provides strategies for the rational design of the molecular structure.

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The authors declare no competing financial interest.

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