**ARTICLE**

**Photovoltaic Performance of Triphenylamine Dyes-sensitized Solar Cells Employing Cobalt Redox Shuttle and Influence of \(\pi\)-conjugated Spacers**

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Developing photosensitizers suitable for the cobalt electrolyte and understanding the structure-property relationship of organic dyes is warranted for the dye-sensitized solar cells (DSSCs). The DSSCs incorporating tris(1,10-phenanthroline)cobalt(II/III)-based redox electrolyte and four synthesized organic dyes as photosensitizers are described. The photovoltaic performance of these dye-sensitized solar cells employing the cobalt redox shuttle and the influences of the \(\pi\)-conjugated spacers of organic dyes upon the photovoltage and photocurrent of mesoscopic titania solar cells are investigated. It is found that organic dyes with thiophene derivate as linkers are suitable for DSSCs employing cobalt electrolytes. DSSCs sensitized with the as-synthesized dyes in combination with the cobalt redox shuttle yield an overall power conversion efficiency of 6.1% under 100 mW/cm² AM1.5 G illumination.

**Key words:** Dye-sensitized solar cell, Organic dye, Cobalt redox shuttle, Mass transport, Charge recombination

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**I. INTRODUCTION**

Dye-sensitized solar cells (DSSCs) have received great attention because of their low cost and great potential in large-scale applications since reported by O’Regan and Grätzel in 1991 [1–3]. To date, the ruthenium-based dyes together with an iodide/triiodide redox couple system has afforded the best power conversion efficiencies of 11.4% [4–6]. However, some disadvantages of the iodide/triiodide redox couple limit the performance of DSSCs, such as (i) its relatively high overpotential for dye regeneration has led to a noticeable potential loss [7], (ii) the halogen bonding between iodine and some electron-rich segments of dye molecules could cause a larger charge recombination rate at the titania/electrolyte interface [8–10], (iii) competitive light absorption by the triiodide has led to a light harvesting loss [11, 12], (iv) the large-scale manufacturing of DSSCs remains a challenge due to the corrosiveness of the iodide/triiodide redox couple toward most metals and sealing materials [13, 14]. Thus, research on replacing the conventional iodide/triiodide electrolyte system in DSSCs with cobalt-complex based redox couples is at present receiving great attention [15].

Recent studies have shown that cobalt redox couples can give impressively high efficiencies comparable to iodide/triiodide electrolyte by using organic dyes. By employing a combination of an zinc porphyrin dye (YD2-o-C8) and an organic dye (Y123) in conjunction with tris(2,2′-bipyridine)cobalt(II/III) redox couple, Grätzel et al. showed a 12.3% of efficiency DSSC [15]. The efficiency exceeds those obtained with today’s best ruthenium sensitizers. A cobalt complex using tridendate ligands \([\text{Co(bpy-pz)}_2]^{3+}/^{2+}\) (PF₆)₃/2 as redox mediator in combination with a cyclopentadithiophene-bridged donor-acceptor dye (Y123), adsorbed on TiO₂, yielded a power conversion efficiency of over 10% at 100 mW/cm² [16]. Wang et al. explored the tris(1,10-phenanthroline)cobalt(II/III) redox shuttles in conjunction with the triphenylamine-based organic dyes to fabricate DSSCs displaying power conversion efficiency of 5.8%–9.4% [17–20]. Boschloo and Hagfeldt et al. reported triphenylamine-based organic dyes based DSSCs employing the tris(2,2′-bipyridine)cobalt(II/III) redox shuttles displaying the best efficiency of 6.7%. An advantage of the cobalt electrolytes over iodide/triiodide redox couple is that very high open-circuit voltage (Vₜₙ₎₅) can be realized but without sacrificing short circuit photocurrent or fill factor [13]. However, simply replacing the iodide/triiodide couple in the DSSCs by cobalt redox couples may lead to poorly performing devices with low photovoltages [14, 21–24], indicating a different structure-property relationship of organic dyes in cobalt cells compared to those in iodine cells. Therefore, developing new photosensitizers suitable for DSSCs employing cobalt electrolytes is warranted. In addition, a comprehensive understanding on the structure-property relationship of organic dyes in cobalt cells will play a pivotal role in further development of iodine-free high-efficiency devices.

Herein, we report the performance of four dihexyloxy-
substituted triphenylamine dyes-sensitized solar cells XS38–40 and M12 (Scheme 1) employing cobalt or iodine electrolytes. We also investigate the influences of π-conjugated spacer of organic dyes upon the photovoltage and photocurrent of mesoscopic titania solar cells, by employing the four dyes with alkyl-substituted thieno[3,2-b]thiophene, phenylene and combined 3,4-ethylenedioxythiophene (EDOT) and methyl-substituted thieno[3,2-b]thiophene as the π-conjugated spacers.

II. EXPERIMENTS

A. Materials and methods

The synthetic routes of the XS39 and XS40 are shown in Scheme 2. XS38 and M12 were prepared according to our previous work [25, 26]. N,N-Dimethylformamide was dried over and distilled from CaH$_2$ under an atmosphere of nitrogen. Titanium(IV) isopropoxide, tertbutylpyridine, 1,10-Phenanthroline (phen), NOBF$_4$, potassium hexafluorophosphate (KPF$_6$) and Lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from J&K Scientific Ltd. All other solvents and chemicals used in this work were analytical grade and used without further purification.

Melting points of the samples were taken on an RY-1 melting point apparatus (Tianfen, China). $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM-400 spectrometer. The reported chemical shifts were against TMS. High resolution mass spectra were obtained with a Micromass GCT-TOF mass spectrometer.

B. Detailed experimental procedures and characterization

1. 4-(hexyloxy)-N-[4-(hexyloxy)phenyl]-N-[4-(6-propylthieno[3,2-b]thiophen-2-yl)phenyl]benzenamine (compound 2)

Pd(PPh$_3$)$_4$ (120 mg, 0.10 mmol) was placed to a 100 mL two-neck round-bottom flask, then air was extracted under vacuum and N$_2$ was introduced in. Compound 1 (1.00 g, 1.91 mmol) and tributyl(6-propylthieno[3,2-b]thiophen-2-yl)stannane (1.08 g, 2.29 mmol) was dissolved in 45 mL toluene. The mixture solution was added into the flask and heated to reflux. After 6 h, the result solution was cooled to room temperature. Water was added to quench the reaction, and the result mixture was extracted with CH$_2$Cl$_2$ (DCM). The combined organic layer was dried over anhydrous magnesium sulfate, then concentrated under vacuum. The residue was applied onto a silica gel column with DCM/PE (1:5) and resulted in 561 mg (47%) yellow green oil.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.53–7.31 (m, 3H), 7.20–6.97 (m, 4H), 6.97–6.68 (m, 7H), 4.08–3.84 (m, 4H) 2.71 (t, J=8.0 Hz, 2H), 1.84–1.74 (m, 6H), 1.52–1.43 (m, 4H, 1.40–1.32 (m, 8H), 1.01 (t, J=7.3 Hz, 3H), 0.95–0.89 (m, 6H), $^{13}$C NMR (100 MHz, CDCl$_3$): δ 155.8, 148.6, 146.2, 140.5, 139.5, 138.2, 135.1, 126.9, 126.5, 120.8, 120.4, 115.5, 114.4, 68.4, 32.2, 31.8, 29.5, 25.9, 22.8, 22.1, 14.2, 14.1. HRMS (ESI) calcd. for C$_{39}$H$_{47}$NO$_2$S$_2$ (M+H$^+$): 626.3126. Found: 626.3129.
Compound 2 (318 mg, 0.51 mmol) was dissolved in 50 mL of THF into a 100 mL two-neck round-bottom flask. The solution was cooled to −78 °C and n-BuLi (0.32 mL, 0.76 mmol) was added dropwise slowly. After stirring for 1 h, DMF (0.047 mL, 0.61 mmol) was added at −78 °C. Then, the reaction was warmed to room temperature smoothly overnight. Water was added to quench the reaction, and the result mixture was extracted with DCM. The combined organic layer was dried over anhydrous magnesium sulfate, then concentrated under vacuum. The residue was applied onto a silica gel column with EA/PE (1:10) and resulted in 253 mg (76%) brown oil. 

$\delta$ 10.04 (s, 1H), 7.42 (d, $J = 8.7$ Hz, 2H), 7.32 (s, 1H), 7.09 (d, $J = 8.8$ Hz, 4H), 6.92 (d, $J = 8.7$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 4H), 3.93 (t, $J = 6.5$ Hz, 4H), 3.06 (t, $J = 7.4$ Hz, 2H), 1.91 − 1.82 (m, 2H), 1.80 − 1.75 (m, 4H), 1.49 − 1.43 (m, 4H), 1.37 − 1.32 (m, 8H), 0.92 (t, $J = 7.3$ Hz, 3H), 0.93 − 0.89 (m, 6H). 

13C NMR (100 MHz, CDCl3): $\delta$ 164.4, 149.1, 143.7, 139.0, 137.9, 131.3, 127.3, 126.7, 124.3, 118.3, 115.5, 114.9, 86.4, 67.6, 31.0, 29.9, 28.7, 25.2, 22.7, 22.1, 13.9, 13.8. HRMS (ESI) calcd. for C$_{40}$H$_{47}$NO$_3$S$_2$ (M+H$^+$): 654.3075. Found: 654.3069.

Compound 3 (100 mg, 0.53 mmol) was dissolved in acetonitrile (5 mL) and chloroform (2.5 mL) in a 25 mL round-bottom flask. Then cyanoacetic acid (20 mg, 0.24 mmol) and piperidine (100 µL) was added. The solution was heated to reflux. After stirring for 5 h, water was added to quench the reaction, and the result mixture was extracted with DCM. The organic layers combined and dried over anhydrous magnesium sulfate, then concentrated under vacuum. The residue was applied onto a silica gel column with DCM/MeOH (10:1) and resulted in 93 mg (88%) red powder. M.p=45−147 °C, $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 8.27 (s, 1H), 7.79 (s, 1H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 7.8$ Hz, 4H), 6.94 (d, $J = 7.8$ Hz, 4H), 6.77 (d, $J = 8.0$ Hz, 2H), 3.94 (t, $J = 7.3$ Hz, 3H), 1.76 − 1.65 (m, 6H), 1.47 − 1.36 (m, 4H), 1.36 − 1.26 (m, 8H), 0.96 − 0.84 (m, 9H). 13C-NMR (100 MHz, DMSO-d6): $\delta$ 164.4, 149.1, 143.7, 139.0, 137.9, 131.3, 127.3, 126.7, 124.3, 118.3, 115.5, 114.9, 86.4, 67.6, 31.0, 29.9, 28.7, 25.2, 22.7, 22.1, 13.9, 13.8. HRMS (ESI) calcd. for C$_{43}$H$_{48}$N$_2$O$_4$S$_2$ (M+H$^+$): 721.3133. Found: 721.3141.

Compound 4 (100 mg, 0.53 mmol) was synthesized according to the procedure for the synthesis of compound 2, giving a yellow oil in 41% yield. $^1$H NMR (400 MHz, CDCl3): $\delta$ 7.48 − 7.28 (m, 3H), 7.19 − 6.99 (m, 4H), 6.99 − 6.75 (m, 7H), 3.94 (m, 4H), 2.37 (s, 3H), 1.83 − 1.74 (m, 4H), 1.52 − 1.43 (m, 4H), 1.39 − 1.32 (m, 8H), 0.95 − 0.91 (m, 6H). 13C NMR (100 MHz, CDCl3): $\delta$ 155.8, 148.7, 146.4, 140.5, 139.4, 139.1, 130.0, 129.5, 126.9, 119.5, 115.5, 114.3, 68.4, 31.7, 30.3, 25.9, 23.4, 22.7, 19.3, 14.2, 14.1. HRMS (ESI) calcd. for C$_{37}$H$_{45}$NO$_2$S$_2$ (M+H$^+$): 598.2813. Found: 598.2820.

Compound 5 (100 mg, 0.53 mmol) was synthesized according to the procedure for the synthesis of compound 3, giving an orange oil.
ange oil in 80% yield. ¹H NMR (400 MHz, CDCl₃): δ 10.05 (s, 1H), 7.44 (d, J = 8.7 Hz, 2H), 7.34 (s, 1H), 7.09 (d, J = 8.8 Hz, 4H), 6.92 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.8 Hz), 3.94 (t, J = 6.5 Hz, 4H), 2.68 (s, 3H), 1.83–1.74 (m, 4H), 1.51–1.43 (m, 4H), 1.39–1.31 (m, 8H), 0.93–0.90 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 182.2, 156.2, 153.0, 149.8, 145.7, 140.0, 139.9, 137.6, 127.3, 127.0, 125.2, 119.5, 115.5, 114.4, 68.4, 31.7, 29.4, 25.9, 22.8, 14.2, 13.7. HRMS (ESI) calcd for C₃₈H₃₄N₅O₅S₂ (M+H⁺): 672.2672. Found: 672.2705.

6. 3-{4-(bis(4-hexyloxy)phenyl)amino)phenyl}thieno[3,2-b]thiophen-2-yl)-2-cyanoacrylic acid (XS40)

The product was synthesized according to the procedure for the synthesis of XS39, giving a red powder in 85% yield. M.p=132–134 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 8.35 (s, 1H), 7.83 (s, 1H), 7.57 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.6 Hz, 4H), 6.94 (d, J = 8.6 Hz, 4H), 6.77 (d, J = 8.6 Hz, 2H), 3.94 (t, J = 6.3 Hz, 4H), 2.53 (s, 3H), 1.74–1.67 (m, 4H), 1.44–1.38 (m, 4H), 1.34–1.29 (m, 8H), 0.91–0.86 (m, 6H). ¹³C NMR (100 MHz, DMSO-d₆): δ 164.1, 155.8, 152.0, 149.3, 144.8, 143.4, 139.0, 138.7, 130.7, 127.3, 126.8, 124.1, 118.2, 117.2, 115.5, 115.0, 87.5, 76.7, 31.0, 28.7, 25.2, 22.1, 13.9, 13.8. HRMS (ESI) calcd for C₄₁H₄₄N₅O₅S₂ (M+H⁺): 693.2820. Found: 693.2826.

C. Photophysical and electrochemical measurements

The absorption spectra of the dye-sensitized TiO₂ films were measured by JASCO-V550 spectrophotometer. Adsorption of the dye on the TiO₂ surface was done by soaking the TiO₂ electrode in a mixture solution ethanol-dichloromethane (3:1, volume ratio) solution of the dye (standard concentration 3×10⁻⁴ mol/L) at room temperature for 24 h.

Cyclic voltammetry measurements were performed at room temperature on a computer controlled LK2005A electrochemical workstation with Pt-wires as working electrode and counter electrode, Ag/AgCl electrode as reference electrode at a scan rate of 100 mV/s. Tetra-butylammonium perchlorate (TBAP, 0.1 mol/L) and MeCN were used as supporting electrolyte and solvent, respectively. The measurements were calibrated using ferrocene as standard. The redox potential of ferrocene respectively. The measurements were calibrated using ferrocene as standard. The redox potential of ferrocene was taken as 0.63 V vs. NHE [25].

Electrochemical impedance spectroscopy (EIS) in the frequency range of 100 mHz to 10 kHz was performed with a PARSTAT 2273 potentiostat/galvanostat/FRA in the dark with the alternate current amplitude set at 10 mV.

D. Fabrication of DSSCs

TiO₂ colloid was prepared according to the literature method [27], which was used for the preparation of the nanocrystalline films. The TiO₂ paste consisting of 18% TiO₂, 9% ethyl cellulose and 73% terpinene was firstly prepared, which was printed on a conducting glass (Nippon Sheet Glass, Hyogo, Japan, fluorine-doped SnO₂ over layer, sheet resistance of 10 Ω/sq) using a screen printing technique. The thickness of the TiO₂ film was controlled by selection of screen mesh size and repetition of printing. The film was dried in air at 120 °C for 30 min and calcined at 500 °C for 30 min under flowing oxygen before cooling to room temperature. The heated electrodes were impregnated with a 0.05 mol/L titanium tetrachloride solution in a water-saturated desiccator at 70 °C for 30 min and fired again to give a ca. 5.5 μm thick mesoscopic TiO₂ film. The TiO₂ electrode was stained by immersing it into a dye solution containing 300 μmol/L dye sensitizers (ethanol-dichloromethane 3:1) for 24 h at room temperature. Then the sensitized-electrode was rinsed with dry ethanol and dried by a dry air flow.

Pt catalyst was deposited on the FTO glass by coating with a drop of H₂PtCl₆ solution (40 mmol/L in ethanol) with the heat treatment at 395 °C for 15 min to give photoanode. The dye-covered TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell according to the literature method [27]. The dye-covered TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell by a 25 μm-thick Surlyn (DuPont) hot-melt gasket and sealed up by heating. The cobalt electrolyte, CM22, is composed of 0.25 mol/L [Co(II)(phen)_3](PF₆)₂ [14], 0.05 mol/L [Co(III)(phen)_3](PF₆)₃, 0.5 mol/L 4-tetrayridine (TBP) and 0.1 mol/L LiTFSI in acetonitrile.

For comparison, an iodine electrolyte consisting of 0.25 mol/L 1,2-dimethyl-3-propylimidazolium iodide (DMPI1m), 0.1 mol/L LiTFSI, 0.05 mol/L I₂, and 0.5 mol/L tertbutylpyridine in acetonitrile, namely CM24, was formulated.

E. Characterization of DSSCs

The photocurrent-voltage (J-V) characteristics of the solar cells were carried out using a Keithley 2400 digital source meter controlled by a computer and a standard AM1.5 solar simulator-Oriel 91160-1000 (300W) SOLAR SIMULATOR 2×2 BEAM. The light intensity was calibrated by an Oriel reference solar cell. A metal mask with an aperture area of 0.16 cm² was covered on a testing cell during all measurements. The action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for solar cell were performed by using a commercial setup (QTest Station 2000 IPCE Measurement System, CROWNTECH, USA).

III. RESULTS AND DISCUSSION

A. UV-Vis absorption

The absorption and emission spectra of XS39 and XS40 in dichloromethane are shown in Fig.1(a). Ow-
TABLE I. Optical properties and electrochemical properties of the dyes.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{max}}$/nm ($\varepsilon$/$10^4$(mol/L)$^{-1}$cm$^{-1}$)</th>
<th>$\lambda_{\text{int}}^b$/nm</th>
<th>$E_{0-0}^c$/eV</th>
<th>$E(S/S^+)/V$ (vs. NHE)</th>
<th>$E(S^*/S^+)/V$ (vs. NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XS38</td>
<td>494 (37)</td>
<td>574</td>
<td>2.16</td>
<td>0.83</td>
<td>−1.43</td>
</tr>
<tr>
<td>XS39</td>
<td>474 (33)</td>
<td>565</td>
<td>2.19</td>
<td>0.82</td>
<td>−1.36</td>
</tr>
<tr>
<td>XS40</td>
<td>477 (35)</td>
<td>593</td>
<td>2.09</td>
<td>0.82</td>
<td>−1.26</td>
</tr>
<tr>
<td>M12</td>
<td>453 (14)</td>
<td>537</td>
<td>2.31</td>
<td>0.83</td>
<td>−1.48</td>
</tr>
</tbody>
</table>

$^a$ Absorption peaks of dyes measured in CH$_2$Cl$_2$, $\varepsilon$ is the extinction coefficient at $\lambda_{\text{max}}$ of absorption.

$^b$ The intersect of the normalized absorption and the emission spectra.

$^c$ $E_{0-0}$ values were estimated from the intersections of normalized absorption and emission spectra ($\lambda_{\text{int}}$): $E_{0-0}=1240/\lambda_{\text{int}}$.

$^d$ $E(S/S^+)$ was recorded by cyclic voltammograms of the dye-loaded TiO$_2$ film.

$^e$ $E(S^*/S^+)$ was calculated from $E(S/S^+)-E_{0-0}$.

FIG. 1 (a) Absorption/emission spectra of XS39 and XS40 in DCM and (b) absorption spectra of dyes-sensitized TiO$_2$ film (3 µm).

FIG. 2 Cyclic voltammogram of XS38–40 and $F_c$.##table##
TABLE II Photovoltaic performance of DSSCs using a 5.5 µm film. The parameters include short-circuit photocurrent density ($J_{SC}$), open-circuit photovoltage ($V_{OC}$), fill factor ($F_F$), and power conversion efficiency (PCE). Cobalt: 0.25 mol/L [Co(II)(phen)$_3$](PF$_6$)$_2$, 0.05 mol/L [Co(III) (phen)$_3$](PF$_6$)$_3$, 0.5 mol/L TBP and 0.1 mol/L LiTFSI in acetonitrile. Iodide: 0.25 mol/L DMPImI, 0.1 mol/L LiTFSI, 0.05 mol/L I$_2$, and 0.5 mol/L TBP in acetonitrile.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$J_{SC}$/mA/cm$^2$</th>
<th>$V_{OC}$/mV</th>
<th>$F_F$</th>
<th>PCE/%</th>
<th>Dye load /(mol/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XS38/Cobalt</td>
<td>8.6</td>
<td>810</td>
<td>0.69</td>
<td>4.8</td>
<td>$2.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>XS38/Iodine</td>
<td>10.5</td>
<td>700</td>
<td>0.68</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>XS39/Cobalt</td>
<td>9.7</td>
<td>846</td>
<td>0.71</td>
<td>5.8</td>
<td>$2.7 \times 10^{-7}$</td>
</tr>
<tr>
<td>XS39/Iodine</td>
<td>10.7</td>
<td>730</td>
<td>0.68</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>XS40/Cobalt</td>
<td>10.2</td>
<td>842</td>
<td>0.71</td>
<td>6.1</td>
<td>$3.1 \times 10^{-7}$</td>
</tr>
<tr>
<td>XS40/Iodine</td>
<td>11.3</td>
<td>725</td>
<td>0.68</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>M12/Cobalt</td>
<td>7.9</td>
<td>795</td>
<td>0.69</td>
<td>4.3</td>
<td>$2.5 \times 10^{-7}$</td>
</tr>
<tr>
<td>M12/Iodine</td>
<td>10.2</td>
<td>756</td>
<td>0.68</td>
<td>5.2</td>
<td></td>
</tr>
</tbody>
</table>

B. Photovoltaic performance of DSSCs

Using the four dyes as sensizers, we compared the photovoltaic performance of DSSCs employing a cobalt electrolyte (CM22) with those employing an iodine electrolyte (CM24). A relatively thin titania film (5.5 µm) is employed so as to avoid the mass transport limitation of tris(phen)cobalt(II/III) redox couple and to minimize interfacial charge recombination. The incident-photon-to-current conversion efficiency (IPCE) for DSSCs sensitized with the four dyes employing the cobalt electrolyte using a 5.5 µm single-layer TiO$_2$ film is shown in Fig.3(a). IPCE with more than 70% values are observed in the range of 430–580 nm for XS39- and XS40-sensitized devices. XS40-sensitized device generates the highest short-circuit photocurrent density ($J_{SC}$) among the four sensitzers (Table II), which can be attributed to its broad and intense photocurrent action spectrum. It also noted that the IPCE performance of XS40-sensitized device is higher than that of XS39, probably due to the stronger $\pi-\pi$ interaction in XS40 than that in XS39 because the longer alkyl chain can weaken the $\pi-\pi$ interaction. As presented in Fig.3(b), the absorption intensity of XS39 loaded TiO$_2$ film is slightly lower than that of XS40. By comparing the absorbance change of a dye solution (300 µmol/L) before and after dye up-taking with a titania film, the surface coverages (Γ) of XS39 and XS40 anchored on TiO$_2$ film were de-
FIG. 4  J-V characteristics of DSSCs employing (a) the cobalt electrolyte and (b) the iodide electrolyte.

determined to be $2.7 \times 10^{-7}$ and $3.1 \times 10^{-7}$ mol/cm$^2$, respectively. Obviously, the lower dye adsorption amount for XS39 on TiO$_2$ surface stems from the larger molecular size and weaker intermolecular $\pi$-$\pi$ interaction. XS38-sensitized device shows a broad IPCE in accordance with the broad absorption spectrum achieved by introduction of binary spacers of EDOT and methyl-substituted thieno[3,2-b]thiophene. In agreement with the trend in absorption spectra of dye-sensitized film (Fig.3(b)), the IPCE spectra of M12-sensitized device exhibits a narrower IPCE spectrum related to those of the XS38-XS40, leading to a relatively lower $J_{SC}$ of 8.6 mA/cm$^2$ (Table II).

The photocurrent density-voltage ($J$-$V$) curves of the devices measured under AM 1.5 irradiation (100 mW/cm$^2$) are shown in Fig.4 and the detailed photovoltaic parameters are summarized in Table II. The short-circuit photocurrent density ($J_{SC}$), open-circuit photovoltage ($V_{OC}$), and fill factor ($F_F$) of a XS40-sensitized cell with the cobalt electrolyte are 10.2 mA/cm$^2$, 842 mV, and 0.71, respectively, affording an overall power conversion efficiency (PCE) of 6.1%. In contrast, the XS40-sensitized device with the iodide electrolyte exhibits a slightly increased $J_{SC}$ of 11.3 mA/cm$^2$ and a remarkably decreased $V_{OC}$ of 725 mV, leading to a relatively lower PCE of 5.6%. The XS39-sensitized device, when combined with the cobalt electrolyte, also generates remarkably improved $V_{OC}$, resulting in an enhanced PCE of 5.8%. Evidently, XS40 is better in terms of solar cell performance, especially in $J_{SC}$, which is in agreement with the observed IPCEs. These results confirm that for XS39 and XS40, the tris(phen)cobalt(II/III) redox couple outperforms the I$^{-}$/I$_3^-$ redox couple for thin-film DSSCs. In contrast, M12- and XS38-sensitized devices exhibit better performance when employing the iodine electrolyte.

C. TiO$_2$ surface interfacial charge recombination in cobalt cells

Electrochemical impedance spectroscopy (EIS) is a powerful tool for identifying electronic and ionic transport processes in DSSCs, which provides valuable information for the understanding of photovoltaic parameters ($J_{SC}$, $V_{OC}$, $F_F$ and $\eta$). Figure 5 shows the typical EIS Nyquist and Bode phase plots of the cobalt cells measured under the dark conditions at a forward bias of $-0.75$ V. The equivalent circuit [31] presented in Fig.5(b) was used to fit the experimental data of all of the samples. $R_o$ is the series resistance accounting for the transport resistance of the TCO and the electrolyte. $C_P$ and $R_{CT}$ are the chemical capacitance and the charge recombination resistance at the TiO$_2$/electrolyte interface, respectively. $C_P$ and $R_{CT}$ are the interfacial capacitance and charge transport resistance at the Pt/electrolyte interface, respectively. The larger semi-circle at lower frequencies represents the interfacial $R_{CT}$ at the TiO$_2$/dye/electrolyte interface. The fitted $R_{CT}$ increases in the order of M12 (338 $\Omega$) < XS38 (825 $\Omega$) < XS39 (1320 $\Omega$), which is consistent with the sequence of $V_{OC}$ values in the devices. The smaller $R_{CT}$ value means the electron recombination from the conduction band to the electrolyte occurring more easily, and thus results in lower $V_{OC}$. Clearly, electron recombination in cobalt cells based on M12 is faster than that of XS38 and XS39.

D. Dependence of photovoltage on the conduction band movement and charge recombination

It is noteworthy that the dye alteration in the iodine cells from M12 to XS38/XS39 has caused a $V_{OC}$ attenuation of 56/26 mV, sharply contrasting a 15/51 mV enhancement in the cobalt cells. The $V_{OC}$ values are in the sequence of XS38 < XS39 < M12 for the iodine cells, while in the sequence of M12 < XS38 < XS39 for the cobalt cells. The opposite $V_{OC}$ variation for the iodine and cobalt cells in the case of sensitizer change from M12 to XS38/XS39 is intriguing. To scrutinize the origin of the improvement in $V_{OC}$, possible factors influencing $V_{OC}$ for DSSCs based on the three dyes involving the conduction band ($E_{CB}$) movement and the free electron density ($n_e$) in TiO$_2$ will be discussed in detail in the following sections.
be described as Eq.(1) \[32\]

\[ EOC = E_{F,\text{redox}} - E_{F,n} \] (1)

On the other hand, the \( E_{F,n} \) of TiO\(_2\) can be expressed as

\[ E_{F,n} = E_{CB} + k_B T \ln \left( \frac{n_c}{N_c} \right) \] (2)

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature (293 K in this work), \( n_c \) is the free electron density, and \( N_c \) is the density of accessible states in the conduction band [18]. Considering that \( E_{F,\text{redox}} \) would not change strongly in DSSCs with a fixed redox electrolyte, \( E_{OC} \) is intimately correlated to the \( E_{CB} \) and \( n_c \). The \( E_{F,n} \) levels can be calculated from the \( E_{F,\text{redox}} \) and \( E_{OC} \) according to Eq.(1). As presented in Fig.6, the \( E_{F,n} \) levels of XS38, XS39, and M12 are \(-0.19\), \(-0.226\), and \(-0.175\) V, respectively, taken the \( E_{F,\text{redox}} \) of Co(II)(phen)\(_3\)(PF\(_6\))\(_2\) as 0.62 V vs. NHE.

To investigate the influences of the shift in the TiO\(_2\) CB and charge recombination on \( E_{F,n} \), impedance spectra were also measured by varying the applied potential at equal intervals in the vicinity of \( V_{OC} \). The measured impedance spectra were fitted with the ZSimpWin (v 3.10) in terms of an equivalent circuit adaptable to DSSCs [33]. The chemical capacitance (\( C_\mu \)) of cells can be expressed as an exponential function of potential bias, which are shown in Fig.7. This exponential rise with the increase of forward bias is a behavior of typical \( C_\mu \) that is described by Eq.(3) [34, 35]

\[ C_\mu = \frac{e^2}{k_B T} \exp \left[ \frac{\alpha}{k_B T} (E_{F,\text{redox}} + eV_a - E_{CB}) \right] \] (3)

where \( e \) is elementary charge, \( \alpha \) is a constant related to the distribution of electronic states below the conduction. Considering that \( E_{F,\text{redox}} \) would not change strongly in DSSCs fabricated under similar conditions [36], therefore, the \( C_\mu \) is governed by the applied potential (\( V_a \)) and \( E_{CB} \).

For the cobalt cells, at a given value of \( V_a \), the \( C_\mu \) for these dyes are in the order M12 > XS38 > XS39 (Fig.7(a)), indicating a sequential positive shift of the \( E_{CB} \) [37]. Generally, positive shift of \( E_{CB} \) leads to an open-circuit photovoltage loss for DSSCs. The sequence of conduction band movement is consistent with the sequence of \( V_{OC} \) values in the devices employing the cobalt electrolyte, indicating that the movement \( E_{CB} \) for the cobalt cells is partially responsible for the variation of \( V_{OC} \). For the iodine cells (Fig.7(b)), the sequential of conduction band edge shifts for XS39 vs. M12 is in accordance with that of \( V_{OC} \) but not for XS38 vs. XS39. The increased \( V_{OC} \) is mainly ascribed to the increase in \( R_{CT} \) for XS39 compared to XS38.

The charge recombination resistance at the TiO\(_2\)/electrolyte interface (\( R_{CT} \)) was further modeled from impedance spectroscopies as a function of \( E_{F,n} \) level (Fig.8). The charge recombination resistance is related to the charge recombination rate, such that a
FIG. 7 Plots of chemical capacitance versus potential bias of (a) the cobalt cells and (b) the iodine cells.

smaller $R_{CT}$ means the larger charge recombination rate. As presented in Fig.8(a), for the cobalt cells, the fitted $R_{CT}$ increases in the order of M12<XS38<XS39, indicating the same order of decreased charge recombination rate. On the other hand, the cobalt-to-iodine electrolyte alteration has caused a contrary consequence: the fitted $R_{CT}$ increases in the order of XS38<XS39<M12. It is noted that, the sequence of $R_{CT}$ values is consistent with the sequence of $V_{OC}$ values in the devices employing iodine electrolyte, implying that it is charge recombination, rather than the position of CB, that governs $V_{OC}$.

We suspect that the $R_{CT}$ variation of the three dyes in different electrolytes is probably due to the following reasons: it is known that the halogen bonding between iodine and some electron-rich segments of dye molecules could cause a larger charge recombination rate at the titania/electrolyte interface [8, 10, 37, 38]. Therefore, the $R_{CT}$ variation of the dyes in different electrolytes is probably related to the adverse impact of possible halogen bonding on interfacial charge recombination in DSSCs. XS38 and XS39 containing methyl-substituted thiieno[3,2-b]thiophene and EDOT with more interaction sites (sulfur atom) prefers formation of dye-iodine complexes in comparison with M12. Thereby, the increasing $I_3^-$ concentration at the vicinity of the TiO$_2$ decreases the electron lifetimes, leading to a lower $R_{CT}$ for XS38 and XS39-sensitized devices. Apart from the adverse impact of possible halogen bonding, the linker length also has an important impact on the surface blocking effect of dyes, which is correlated to the $R_{CT}$ values. Recent studies have shown that the surface blocking of the dye layer as well as the electron lifetime would suffer from an extension of the linker conjugation [9]. Clearly, XS38 showed enhanced electron recombination in comparison to XS39 when used in the iodine cells due to the cumulative adverse effects arising from the possible halogen bonding and extension of the linker conjugation. In cobalt cells, higher $R_{CT}$ of XS39-sensitized device related to that of M12 can be partially ascribed to the absence of this non-covalent interaction between the dyes and electrolytes. These results provide a new clue to understand the halogen-bonding issue in DSSCs, suggesting that organic dyes with thiophene derivates as linkers are suitable for DSSCs employing cobalt electrolytes.

We further compare the dependencies of $R_{CT}$ on the $E_{F,n}$ level for cells with the cobalt and iodine electrolytes. It can be found from Fig.8 that, compared to the iodine cells, the employment of the cobalt electrolyte brings forth smaller $R_{CT}$, i.e., an acceleration of charge recombination at the titania/electrolyte interface, leading to shorter electron lifetime. This adverse impact of a shorter electron lifetimes upon photovoltage partially compensates for the positive effect of the...
cobalt electrolyte correlated interfacial energetics, resulting in a less improvement of the voltage by using the cobalt electrolyte compared to the theoretical value.

E. Dependence of photocurrent on the mass transport limitations and charge recombination

It is noteworthy that the iodine-to-cobalt electrolyte alteration has caused a $J_{SC}$ attenuation of about 1 mA for XS39/XS40-sensitized devices. On the other hand, for the XS38- and M12-sensitized devices, the electrolyte alteration has caused significant a $J_{SC}$ reduction of 1.9 and 2.3 mA/cm$^2$, respectively, leading to decreased PCEs. From the results mentioned above, the sequential negative shift of the $E_{CB}$ are in the order M12<XS38<XS39 for the cobalt cells. Generally, negative shift of $E_{CB}$ leads to a driving force reduction for electron injection as well as an open-circuit photovoltage improvement for DSSCs. Considering the $J_{SC}$ reduction order of M12>XS38>XS39, it can be concluded that the $E_{CB}$ movement is not the main reason for the low $J_{SC}$ of XS38- and M12-sensitized devices employing cobalt electrolyte. Assuming that driving force for electron injection is constant, $J_{SC}$ will be determined by the mass transport and recombination limitations associated with the cobalt redox shuttle, which is varied with different dyes. The origin of the observed $J_{SC}$ trend will be discussed according to these two parameters.

It is known that the mass transport limitation, which results from the larger size of the cobalt complex and greater viscosity of cobalt complex solution, prominently deteriorates the photovoltaic performance of DSSCs employing cobalt electrolytes [39]. To gain insight into the mass transport limitation clearly, photocurrent transients were recorded for cobalt cells under AM 1.5 irradiation (100 mW/cm$^2$). The photocurrent transients were measured by using an on/off modulation of the incident light. As presented in Fig.9(a), for XS38-, XS39- and M12-sensitized devices, a spike in the photocurrent is observed when the light is switched on, followed by a decrease in photocurrent, eventually reaching a lower stationary value after a few seconds of illumination time. This behavior has been attributed to mass transport limitation of the electrolyte, which limits the photocurrent [40, 41]. This limitation arising from the mass transport is one of the main reasons for the $J_{SC}$ attenuation during iodine-to-cobalt electrolyte alteration.

In addition, a discrepancy in the ratio of the initial peak current to steady state current can be observed between DSSCs sensitized with different dyes. The photocurrent of the XS38 and M12-sensitized devices decreased by around 20% during 0.6 s after light-on. In contrast, the photocurrent of the XS39-sensitized device decreased only by 16%. The discrepancy is more easily distinguished in Fig.9(b), where the current densities are normalized. This indicates that the current depends not only on the slower mass transport of the bulky redox species but also on the recombination of photoinjected electrons with the oxidized form of the redox mediator [13], as discussed above. In other words, the significant $J_{SC}$ reduction for XS38 and M12-sensitized devices can be ascribed to the mass transport limitation of the electrolyte and faster interfacial charge recombination related to XS39-sensitized cobalt cell.

IV. CONCLUSION

In conclusion, four triphenylamine dyes, XS38, XS39, XS40, and M12, that incorporating combined EDOT and methyl-substituted thiieno[3,2-b]thiophene, propyl-substituted thiieno[3,2-b]thiophene, methyl-substituted thiieno[3,2-b]thiophene and phenylene as the π-conjugated spacers, respectively, were used as organic dyes for DSSCs employing tris(phen)cobalt(II/III) redox shuttle. The results from photovoltaic performance confirm that for XS39 and XS40, the tris(phen)cobalt(II/III) redox couple outperforms the $I^-/I_3^-$ redox couple for thin-film DSSCs. In contrast, M12 and XS38-sensitized devices exhibit better performance when employing iodine electrolyte. EIS measurements show that iodine-to-cobalt electrolyte alteration has caused a different order of charge recombination.

FIG. 9 Photocurrent transients of XS38, XS39 and M12-sensitized devices that utilized the cobalt redox electrolyte (a) without and (b) with normalization of the current density.
rate, which is related to the adverse impact of possible halogen bonding, giving an explanation of the opposite $V_{OC}$ variation for the iodine and cobalt cells. Organic dyes with thiophene derivates as linkers are suitable for DSSCs employing cobalt electrolytes. DSSCs sensitized with XS40 in combination with the cobalt redox shuttle yield a DSC with high $V_{OC}$ values reaching 884 mV and an overall power conversion efficiency (PCE) of 6.1% under 100 mW/cm$^2$ AM1.5 G illumination.

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