

# Efficient Panchromatic Organic Sensitizers with Dihydrothiazole Derivative as $\pi$ -Bridge for Dye-Sensitized Solar Cells

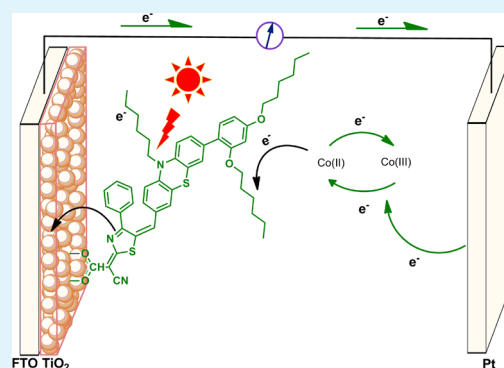
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## S Supporting Information

**ABSTRACT:** Novel organic dyes CC201 and CC202 with dihydrothiazole derivative as  $\pi$ -bridge have been synthesized and applied in the DSSCs. With the synergy electron-withdrawing of dihydrothiazole and cyanoacrylic acid, these two novel dyes CC201 and CC202 show excellent response in the region of 500–800 nm. An efficiency as high as 6.1% was obtained for the device fabricated by sensitizer CC202 together with cobalt electrolyte under standard light illumination (AM 1.5G, 100 mW cm<sup>-2</sup>). These two novel D- $\pi$ -A panchromatic organic dyes gave relatively high efficiencies except common reported squaraine dyes.



**KEYWORDS:** sensitizers, dye-sensitized solar cells, D- $\pi$ -A organic dyes, panchromatic organic dyes, phenothiazine, triphenylamine

## INTRODUCTION

Dye-sensitized solar cells (DSSCs) have attracted considerable attention because of their relatively high solar energy conversion efficiency, low fabrication cost, and eco-friendly specialty since the report by O'Regan and Grätzel in 1991.<sup>1</sup> The energy of the near-infrared region accounts for 52% of the total solar energy, thus making full use of the near-infrared region is very important to improve the efficiency of DSSCs. At present, for DSSCs sensitized by Ru complexes exhibiting relatively broad response to solar spectrum and favorable photovoltaic properties, power conversion efficiencies of almost 12% at standard global air mass AM 1.5G have been achieved.<sup>2</sup> However, the containing of noble metal and complicated purification steps for these Ru complexes have limited the development of DSSCs in large scale.<sup>3</sup> Therefore, the design and development of near-infrared and panchromatic metal-free organic dyes have become significant to make full use of solar energy due to their low cost and easy fabrication. Until now, only a few kinds of photosensitizers, such as porphyrin,<sup>4–8</sup> phthalocyanine,<sup>9–13</sup> perylene,<sup>14–16</sup> and squaraine<sup>17–20</sup> dyes, which have efficient response in the near-infrared region have been reported. To the best of our knowledge, except for the several kinds of dyes mentioned above, there has rarely been a strong response to near-infrared spectrum among the traditional donor- $\pi$ -bridge-acceptor (D- $\pi$ -A) sensitizers. This is mainly due to the withdrawing ability of an acceptor being too weak to reduce the band gap of sensitizer. As an electron-deficiency unit, thiazole with a significant electron-withdrawing

ability and a good coplanarity, has been widely applied in many fields.<sup>21–23</sup> Herein, with the introduction of dihydrothiazole derivatives into the dyes as  $\pi$ -bridge, we envisioned the synergy electron-withdrawing of dihydrothiazole and cyanoacrylic acid may increase spectral response through lengthening  $\pi$ -conjugation and increasing the withdrawing ability while maintaining good charge injection. Therefore, we designed two novel organic dyes CC201 and CC202, and applied them in dye-sensitized solar cells (DSSCs). The specific structures of dyes CC201 and CC202 are shown in Figure 1.

In this series of dyes, 2,4-dibutoxy-N-(2,4-dibutoxyphenyl)-N-phenylaniline and 3-(2,4-bis(hexyloxy)phenyl)-10-hexyl-10H-phenothiazine, which are widely employed as donor in DSSCs and present unique electronic and optical properties,<sup>24–28</sup> are adopted as donor part. The spatial structure in the ground state and the introduction of long alkyl chains in these two donors can restrict dye aggregation and the recombination of electron with electrolyte. Carbon–carbon double bond along with dihydrothiazole derivative showing withdrawing ability are used as conjugated  $\pi$ -bridge, cyanoacrylic acid is utilized as acceptor. It is very interesting that these two dyes exhibit panchromatic response to solar spectrum and gain relatively good photovoltaic properties. This is very different from traditional D- $\pi$ -A organic dyes. The detailed synthesis of dyes

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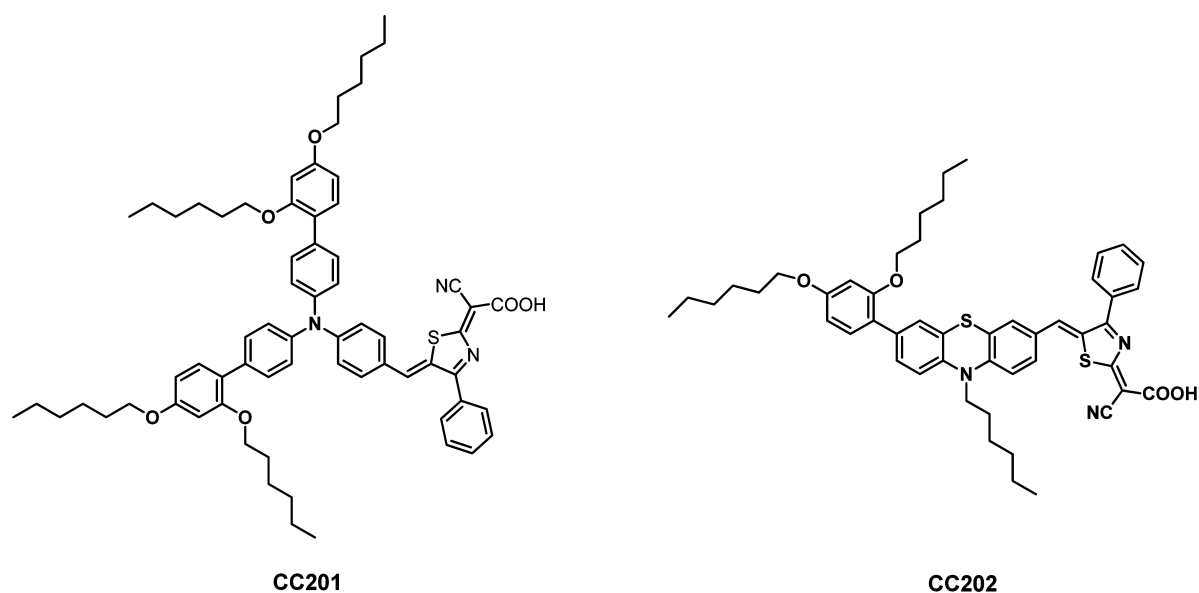


Figure 1. Structure of sensitizers CC201 and CC202.

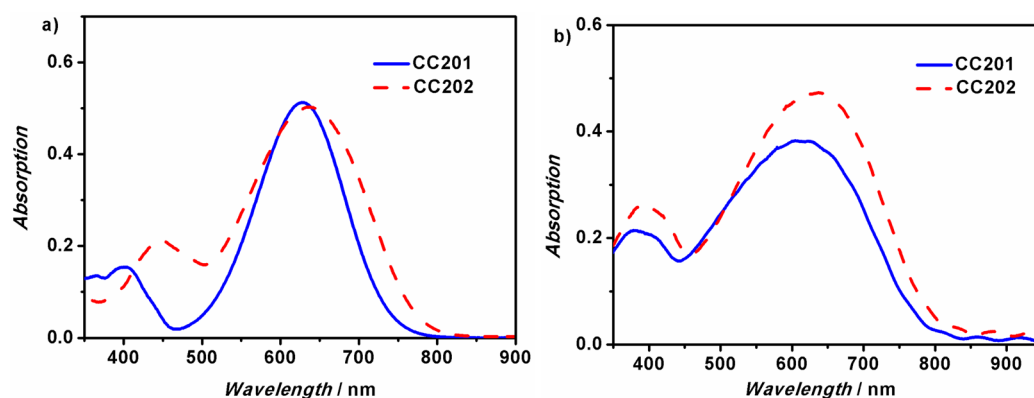


Figure 2. Absorption spectra of CC201 and CC202 dyes (a) in  $\text{CH}_2\text{Cl}_2$  solution and (b) on  $\text{TiO}_2$  films.

CC201 and CC202 and the details of DSSCs fabrication process are described in the Supporting Information.

## RESULTS AND DISCUSSION

Absorption spectra of dyes CC201 and CC202 in  $\text{CH}_2\text{Cl}_2$  solution and on  $\text{TiO}_2$  film are shown in Figure 2. The corresponding spectroscopic parameters extracted are summarized in Table 1.

Table 1. Photophysical and Electrochemical Properties of CC201 and CC202

dye	$\lambda_{\text{max}}^a$ in $\text{CH}_2\text{Cl}_2$ (nm)	$\epsilon$ at $\lambda_{\text{max}}$ ( $\text{M}^{-1} \text{cm}^{-1}$ )	$\lambda_{\text{max}}^b$ on $\text{TiO}_2$ (nm)	$E_{0-0}^c$ (V)	$E_{\text{S}_2^+/S}^d$ (V) (vs NHE)	$E_{\text{S}_2^+/S^*}^e$ (V) (vs. NHE)
CC201	628	25630	621	1.57	0.86	-0.71
CC202	638	25132	633	1.55	0.72	-0.83

<sup>a</sup>Absorption spectra were measured in  $\text{CH}_2\text{Cl}_2$  solution ( $2 \times 10^{-5}$  M). <sup>b</sup>Absorption spectra on  $\text{TiO}_2$  film were measured with dye-loaded  $\text{TiO}_2$  films immersed in  $\text{CH}_2\text{Cl}_2$  solutions. <sup>c</sup> $E_{0-0}$  was determined from intersection of the tangent of absorption on  $\text{TiO}_2$  film and the X axis by  $1240/\lambda$ . <sup>d</sup>The oxidation potentials of the dyes were measured in  $\text{CH}_2\text{Cl}_2$  solutions with  $\text{LiClO}_4$  (0.1 M) as electrolyte, ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) as an internal reference and converted to NHE. <sup>e</sup> $E_{\text{S}_2^+/S^*}$  was calculated by  $E_{\text{ox}} - E_{0-0}$ .

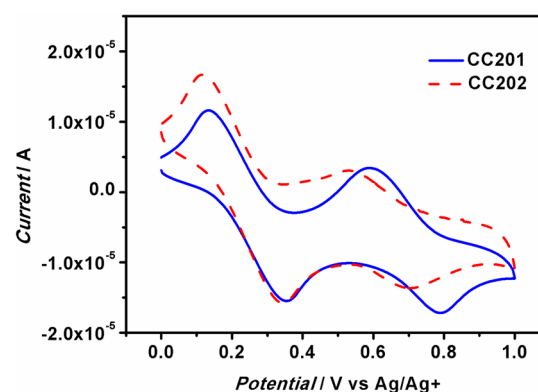


Figure 3. Cyclic voltammetry of CC201 and CC202 dyes in  $\text{CH}_2\text{Cl}_2$  solution.

ized in Table 1. Very different from traditional D- $\pi$ -A organic dyes in which heteroaromatic compounds (such as thiophene derivative, furan derivative, thiazol derivative, benzene, benzothiadiazole and so on) are widely employed as  $\pi$ -bridge in metal-free sensitizers and the  $\pi$ -bridge usually connect with cyanoacrylic acid through single carbon-carbon bond, for these two novel dyes CC201 and CC202, the electron-withdrawing conjugation unit of dihydrothiazole connect directly with

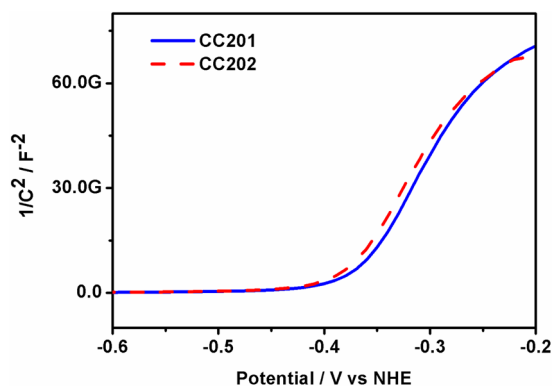


Figure 4. Mott-Schottky curves of dye-sensitized TiO<sub>2</sub> film.

Table 2. Calculation Results of Dyes CC201 and CC202 with DFT on a B3LYP/6-31G(d) Level

Dye	HOMO	LUMO
CC201		
CC202		

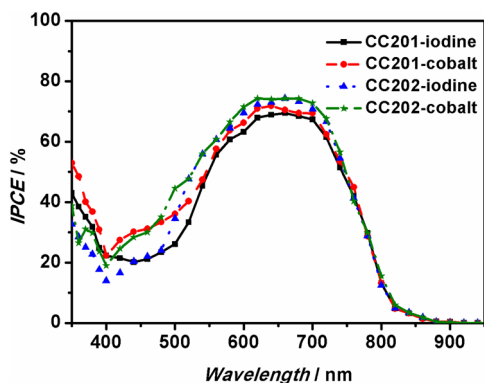


Figure 5. IPCE spectra of the DSSCs sensitized by CC201 and CC202.

Table 3. Photovoltaic Performance of DSSCs Sensitized by CC201 and CC202

dye	electrolyte	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	η (%)
CC201	iodine	560	12.6	72.3	5.1
	cobalt	633	13.4	68.8	5.8
CC202	iodine	540	13.9	71.5	5.4
	cobalt	615	14.5	67.0	6.1

cyanoacrylic acid. At the same time, most of the reported sensitizers (such as TPC1,<sup>29</sup> DS,<sup>30</sup> T2-2,<sup>31</sup> JK46,<sup>32</sup> JK303,<sup>33</sup> WS-2,<sup>34</sup> RD-I,<sup>35</sup> RD-II,<sup>35</sup> CC103,<sup>36</sup> and so on) show maximum absorption around 450–530 nm. For these two novel dyes CC201 and CC202, a panchromatic response to solar spectrum both in CH<sub>2</sub>Cl<sub>2</sub> solution and on TiO<sub>2</sub> film was

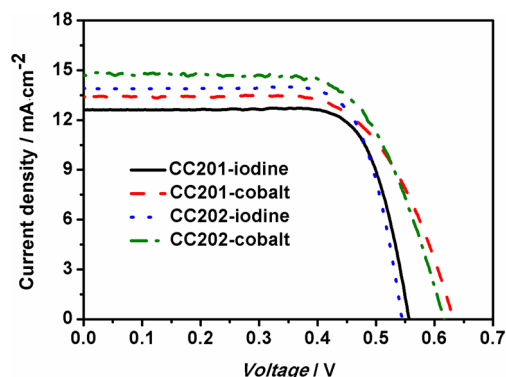


Figure 6. J–V curves of the DSSCs sensitized by CC201 and CC202.

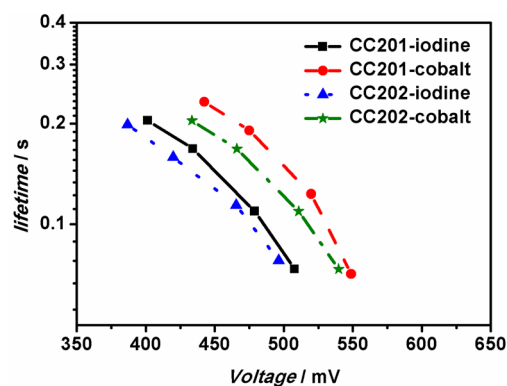


Figure 7. Electron lifetimes for DSSCs based on CC201 and CC202 with iodine or cobalt electrolyte.

achieved. The maximum absorption ( $\lambda_{\max}$ ) of dyes CC201 and CC202 in CH<sub>2</sub>Cl<sub>2</sub> solution are 628 nm ( $\epsilon = 25630 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 638 nm ( $\epsilon = 25132 \text{ M}^{-1} \text{ cm}^{-1}$ ), respectively. Compared to the spectra in CH<sub>2</sub>Cl<sub>2</sub> solution, the absorption peaks for CC201 and CC202 on transparent TiO<sub>2</sub> film are all blue-shifted to a small extent (see Table 1), which can be ascribed to H aggregation for both dyes.

Cyclic voltammetry (CV) was employed to evaluate the electrochemical properties of dyes CC201 and CC202 (see Figure 3), and the examined  $E_{S+/S}$  and  $E_{S+/S^*}$  are collected in Table 1. From the test results we can see that the  $E_{S+/S}$  of dyes CC201 and CC202 are 0.86 and 0.72 V vs NHE, respectively, which are sufficiently positive than the redox potential value (0.4 V vs NHE for  $\text{I}^-/\text{I}_3^-$ , 0.56 V vs NHE for  $[\text{Co}(\text{bpy})_3]^{2+}/\text{Co}(\text{bpy})_3]^{3+}$ ),<sup>26</sup> indicating that the oxidized dyes could be regenerated efficiently with the action of redox couple thermodynamically.<sup>37</sup> The  $E_{S+/S^*}$  is calculated from  $E_{\text{ox}} - E_{0-0}$ . The  $E_{S+/S^*}$  of dyes CC201 and CC202 are  $-0.71 \text{ V}$  and  $-0.83 \text{ V}$  vs NHE, respectively. The conduction-band-edge energy level ( $E_{\text{cb}}$ ) of the TiO<sub>2</sub> electrode is about  $-0.5 \text{ V}$  vs NHE. While a substantial charge rearrangement takes place upon dye or 4-*tert*-butylpyridine (TBP) adsorption onto the semiconductor surface. This charge redistribution can cause significant modifications on the TiO<sub>2</sub> electronic structure.<sup>38,39</sup> Thus we tested the conduct band (CB) of TiO<sub>2</sub> sensitized by these two dyes CC201 and CC202. The test results are shown in Figure 4. The CB of TiO<sub>2</sub> sensitized by CC201 and CC202 are  $-0.40$  and  $-0.39 \text{ V}$  vs NHE, respectively, which are comparable. The LUMOs of these two dyes are more negative than that of  $E_{\text{cb}}$  of TiO<sub>2</sub> indicating that the electrons can be injected into the CB of TiO<sub>2</sub>.<sup>37</sup> The LUMO level of CC202 is

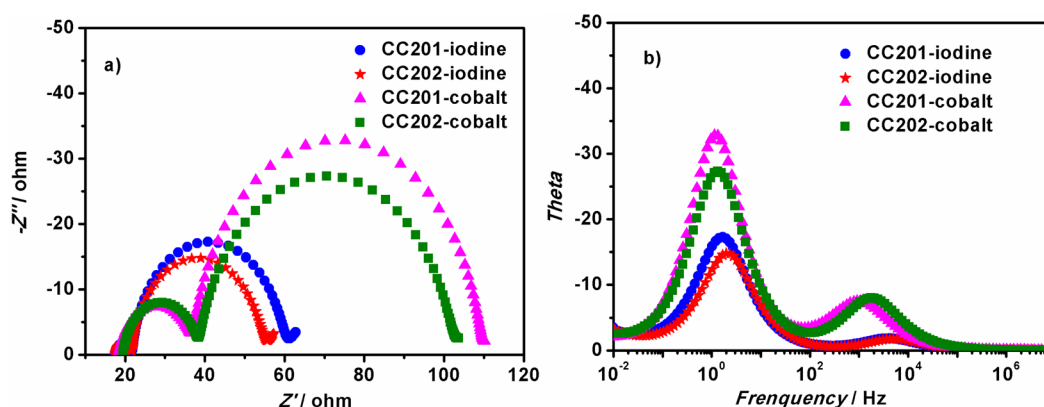


Figure 8. Electrochemical impedance spectroscopy of DSSCs based on CC201 and CC202 (a) Nyquist plots and (b) Bode plots.

Table 4. EIS Parameters of DSSCs Sensitized by CC201 and CC202 with Different Electrolytes

dye	electrolyte	$R_s$ (ohm)	$R_{rec}$ (ohm)	$R_{ce}$ (ohm)
CC201	iodine	17.5	39.4	4.2
	cobalt	18.4	74.3	17.4
CC202	iodine	17.5	34.0	4.0
	cobalt	19.5	65.2	18.9

more negative than that of CC201, which is mainly due to the donating ability of CC202 with electron donating group phenothiazine derivative is much stronger than that of CC201 with triphenylamine derivative considering the similar band gap of the two dyes.

From density functional theory (DFT) calculation results (see Table 2) we can see that the HOMO levels of dyes CC201 and CC202 are mainly distributed on the donor part (triphenylamine ring and phenothiazine ring), while the

LUMO levels are mainly distributed on cyanoacrylic acid and dihydrothiazole. It is illustrated that the HOMO–LUMO excitation can efficiently transfer the electron from the donor part to the acceptor part. Furthermore, the HOMO levels of dyes are hardly distributed on the long alkyl chain, which efficiently impeded the recombination with electrolyte.

The incident photon-to-current efficiency (IPCE) spectra of DSSCs based on the dyes CC201 and CC202 are shown in Figure 5. The IPCE values of dyes CC201 and CC202 exceed 50% in a broad range from 525 to 750 nm, reaching the maximum of 69% at 660 nm and 74% at 660 nm, respectively, when iodine electrolyte was employed. It is implied that dyes CC201 and CC202, with the introduction of dihydrothiazole derivative into the dyes as  $\pi$ -bridge, extend spectra response to the near-infrared region, and present a relatively high IPCE values. The change trend of IPCE are exactly in agreement with the UV–vis spectra of these dyes on TiO<sub>2</sub> film. Moreover, the IPCE value of dye CC202 is a little higher than that of dye

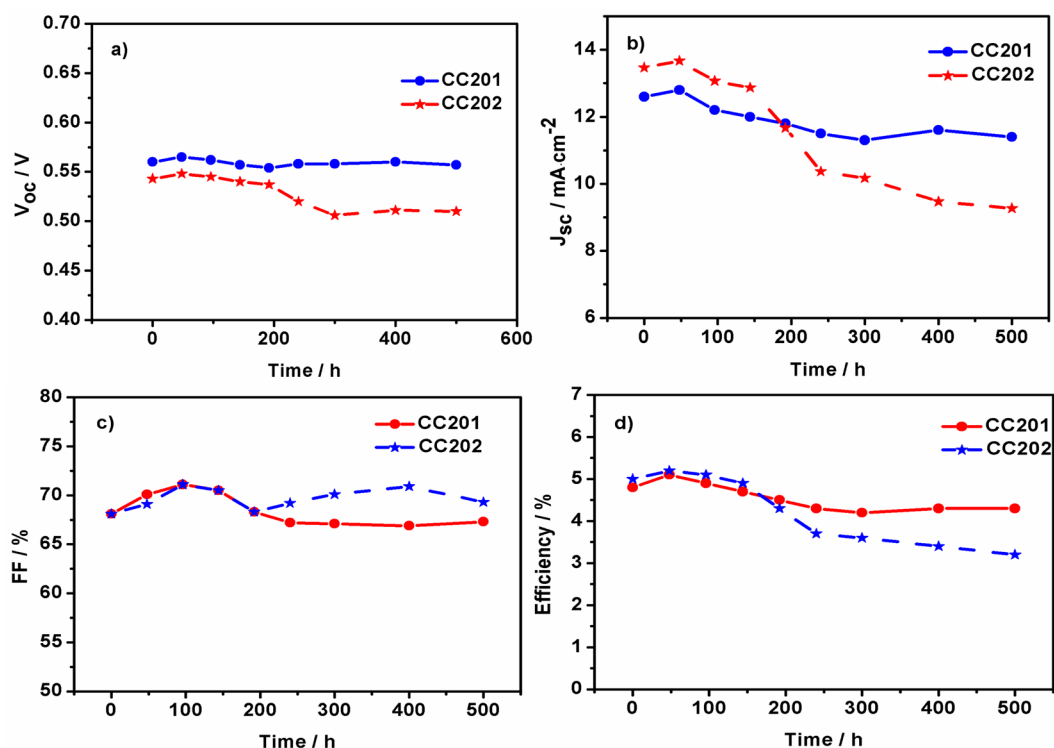


Figure 9. Stability tests of DSSCs based on CC201 and CC202.



CC201, because of the electron-donating ability of dye CC202 with the donor unit of phenothiazine derivative is stronger than that of dye CC201 with the donor unit of triphenylamine derivative. When cobalt electrolyte was employed, the devices showed higher IPCE values in the region 350–500 nm compared to those of the devices employing iodine electrolyte. This phenomenon could be attributed to the much weaker absorption of cobalt electrolyte compared to that of iodine electrolyte in the region of 350–500 nm.

The  $J$ - $V$  properties of DSSCs based on the dyes CC201 and CC202 are shown in Table 3 and Figure 6. The DSSC device sensitized by the dye CC201 showed an efficiency of 5.1%, with a short-circuit photocurrent density ( $J_{sc}$ ) of 12.6 mA/cm<sup>2</sup>, an open-circuit photovoltage ( $V_{oc}$ ) of 560 mV, and a fill factor (FF) of 72.3%, when iodine electrolyte was employed. When the donor unit of triphenylamine derivative was replaced by phenothiazine derivative, the efficiency of the DSSC device based on dye CC202 was improved to 5.4% ( $V_{oc}$  = 540 mV,  $J_{sc}$  = 13.9 mA/cm<sup>2</sup>, FF = 71.5%) under the same conditions. Dye CC202 has higher a  $J_{sc}$  than dye CC201, because dye CC202 has a much stronger response to solar spectrum than dye CC201, which is supported by the IPCE test results. The  $V_{oc}$  of the device based on CC201 is larger than that of CC202. This is mainly because the two more alkyl chains in CC201 are beneficial to restrict recombination. This is in accordance with the electron-lifetime test results. (see Figure 7). The devices fabricated with CC201 showed longer electron lifetimes than that of CC202 when the same electrolyte was employed. When cobalt electrolyte was employed to fabricate DSSCs, the  $J_{sc}$ ,  $V_{oc}$ , and  $\eta$  were improved, but the FF become much lower. Correspondingly, the efficiencies of DSSCs were improved but in a small degree. An efficiency of 6.1% was achieved by CC202 together with cobalt electrolyte.

The electrochemical impedance spectroscopy (EIS) was employed to get further study on the interface charge transfer process of the DSSCs. The test results are shown in Figure 8 and the corresponding data are collected in Table 4. From the test results we can see that with the iodine electrolyte, the  $R_{rec}$  of dye CC201 and CC202 decreases in the order of CC201 ( $R_{rec}$  = 39.40  $\Omega$ ) > CC202 ( $R_{rec}$  = 34.04  $\Omega$ ), indicating that the electron recombination is much more efficiently resisted for the device sensitized by CC201 compared with that of CC202. Correspondingly, much higher  $V_{oc}$  was achieved for the devices sensitized by CC201. Similar results can be detected when cobalt electrolyte was employed. However, when cobalt electrolyte was employed, both of the  $R_{rec}$  and  $R_{CE}$  increase a lot. The increase of  $R_{CE}$  value when cobalt electrolyte was employed reflects a slower electronic transmission rate at counter electrode, correspondingly, much lower FF was achieved.

For future applications, we tested the stability of DSSCs fabricated with CC201 and CC202 with iodine electrolyte (0.6 M DMPII, 0.2 M LiI, 0.02 M I<sub>2</sub>, 0.05 M TBAI in methoxy propionitrile). The results are showing in Figure 9. After 500 h of light soaking, for the devices sensitized by CC201, just the  $J_{sc}$  decreased by 1.2 mA cm<sup>-2</sup>, correspondingly, the efficiency become a little lower (from 4.8% to 4.3%). While for the devices sensitized by CC202, both of the  $J_{sc}$  and  $V_{oc}$  decreased a lot. In our just published study, we found that double carbon-carbon bond as  $\pi$ -bridge has little effects on stability. While with the synergy between water and UV light, the sensitizer could desorb from the TiO<sub>2</sub> surface and the cyanoacrylic acid unit of the sensitizer was transformed into the aldehyde group.<sup>40</sup> After

500 h illumination, the devices fabricated with CC201 maintain 90% of the initial efficiency. The relatively better long-term stability of CC201 can be attributed to the good hydrophobic properties of substituted hexyloxy group on TPA units and the stability of TPA unit. While for the devices fabricated with CC202, the stability is poor and the efficiency declined dramatically. This is mainly due to instability of phenothiazine through hexyloxy group was introduced to weaken the action between dyes and water.

## EXPERIMENTAL SECTION

The CV tests, EIS, IPCE,  $J$ - $V$  measurement, Mott-Schottky curves and fabrication of DSSCs devices were conducted according to the previous literature with modification.<sup>39,41</sup> The expatiation is shown in the Supporting Information.

## CONCLUSION

In conclusion, efficient novel organic dyes CC201 and CC202, with dihydrothiazole as  $\pi$ -bridge and cyanoacrylic acid as acceptor, have been designed and applied in the DSSCs. Very different from traditional D- $\pi$ -A dyes, the synergy withdrawing ability of dihydrothiazole and cyanoacrylic acid makes the sensitizers show a panchromatic response to solar spectrum. When applied to DSSCs, an efficiency as high as 6.1% was achieved by sensitizer CC202 cooperating with cobalt electrolyte under standard light illumination (AM 1.5G, 100 mW cm<sup>-2</sup>). We believed that this work can diversify the dyes for the sensitization in the visible and near-infrared region with high conversion efficiency.

## ASSOCIATED CONTENT

### Supporting Information

The detailed synthesis of dyes CC201 and CC202, test conditions, and DSSCs fabrication process were described in Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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