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# Novel metal complexes for D- $(A-\pi-A)_2$ motif dye sensitizer: Synthesis and photovoltaic application

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#### **Funding information**

Open Project Program of Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, China, Grant/Award Number: 19HJYH10 Four metal complexes BDTT-PCd, BDTT-PZn, BDTT-PCu, and BDTT-PCo with the symmetrical structure were designed, synthesized, and characterized, which would be used as  $D-(A-\pi-A)_2$  motif dye sensitizers. These complexes adopt Cd(II), Zn(II), Cu(II), and Co(II) complexes as auxiliary electron acceptors (A), thienylbenzo[1,2-b:4,5-b']dithiophene (BDTT) as electron donor (D), and the 8-quinolinol derivative as the  $\pi$  bridge and the acceptor (A) of D- $(A-\pi-A)_2$  motif dye sensitizers. The photophysical, electrochemical, and photovoltaic properties of these complexes have been investigated. The four complexes-based dye-sensitized solar cells (DSSCs) device exhibited a shortcircuit photocurrent density  $(J_{sc})$  of 17.51, 17.02, 15.07, and 14.38 mA cm<sup>-2</sup> and an attractive power conversion efficiency ( $\eta$ ) of 8.82%, 8.32%, 8.03%, and 7.55%, respectively, under the AM 1.5 irradiation (100 mW cm<sup>-2</sup>). The photovoltaic conversion efficiency (PCE) and the short-circuit photocurrent density (J<sub>sc</sub>) of BDTT-PCd, BDTT-PZn, BDTT-PCu, and BDTT-PCo are sequentially reduced; it attributed to the difference of the electron-withdrawing ability of the auxiliary acceptor resulted by the difference of coordination abilities of metal ions Cd(II), Zn(II), Cu(II), and Co(II) with ligand. These results provide strong evidence that  $D-(A-\pi-A)_2$  motif complexes has great potential as promising photosensitizers in the applications of DSSCs.

#### K E Y W O R D S

auxiliary acceptor, coordination metal (Cd, Zn, Cu, and Co), D-(A- $\pi$ -A)<sub>2</sub> motif dye sensitizer, dye-sensitized solar cells

# **1** | INTRODUCTION

Since O'Regan and Gratzel first proposed dye-sensitized solar cells (DSSCs) in 1991,<sup>[1]</sup> they have attracted extensive attention from researchers in recent years<sup>[2,3]</sup> due to their simple manufacturing, flexible structure, low cost, and high conversion efficiency compared with the traditional silicon-based solar cells.<sup>[4,5]</sup> Dye sensitizers, as the core part of DSSCs to complete the photoelectric conversion and the breakthrough point for the greatest

improvement in efficiency, have become a hot research topic in recent years.

In the early stage of the development of the dye sensitizers, donor-acceptor (D-A) was the mainstream structure. Due to its simple structure and relatively simple synthesis, the structure of donor-acceptor binding achieved good results.<sup>[6,7]</sup> Subsequently, the D- $\pi$ -A structure of the  $\pi$  bridge was introduced between the donor and the acceptor.<sup>[8]</sup> The D- $\pi$ -A motif improves the interaction between the electron donor and the electron

acceptor, resulting in a stronger charge-transfer light absorption band, which can capture sunlight more efficiently and effectively convert sunlight into electrical energy, and the photoelectric conversion efficiency increases exponentially.<sup>[9]</sup> However, this structure has defects, such as poor performance, poor thermal stability, and narrow absorption range.

Then in 2011, Zhu et al. proposed the concept of the D-A- $\pi$ -A motif, which introduced an auxiliary electron acceptor between the  $\pi$  bridge and the donor. This structure can enhance the electron absorption capacity, reduce the reorganization of electrons, and inject more electrons into titanium dioxide, and can also adjust and ameliorate the energy level, absorption spectrum, and photovoltaic performance of the dve sensitizer.<sup>[10]</sup> In 2014. Grätzel et al. proposed a new method to synthesize the classic D-A- $\pi$ -A structure of the porphyrin dye SM315, with an efficiency of up to 13%.<sup>[11]</sup> Wu et al. put forward a view in 2015<sup>[12]</sup> that the auxiliary electron acceptor in the D-A- $\pi$ -A motif not only helps to adjust the energy level, absorption spectrum, and photovoltaic performance, but also greatly improves the photostability of the dye sensitizer.

Recently, there are several types of electronwithdrawing units, such as benzothiadiazole (BTD),<sup>[13-16]</sup> (Qu), [20–23] benzotriazole (BTZ),<sup>[17–19]</sup> quinoxaline phthalimide,<sup>[24]</sup> and diketo-pyrrolopyrrole (DPP),<sup>[25-27]</sup> that have been systematically exploited as the auxiliary electron acceptor for the D-A- $\pi$ -A structures. There is a trend to systematically add benzoxadiazole, benzothiadiazole, quinoxaline, and benzotriazole as an auxiliary electron acceptor to the D- $\pi$ -A system, and test and theoretical calculation are performed. The results show that the greater the electron-withdrawing ability of the additional acceptor unit, the greater the redshift in the light response is.<sup>[28,29]</sup> The obvious difference in energy levels and photovoltaic performance between LS-2 and WS-5<sup>[24]</sup> is a good indication that in addition to the ability to withdraw electrons, steric hindrance must also be considered when choosing an auxiliary electron acceptor.

Because of being affected by the composition and structure of the organic auxiliary electron acceptor, the electron-withdrawing ability of organic auxiliary electron acceptors such as benzoxadiazole and benzothiadiazole and the ability to adjust the electron-withdrawing capacity of the auxiliary acceptors are limited to a certain extent. Therefore, it is difficult to further drastically improve the photovoltaic performance of these organic dye sensitizers.<sup>[30,31]</sup> However, if the metal complexes are used as auxiliary electron acceptor, their electron-withdrawing ability can be changed and be controlled drastically by changing the type of coordination bond

between metal and ligand and the strength of coordination<sup>[32,33]</sup>; by this way, the push-and-pull electron balance and intramolecular electron transport ability of the dye sensitizer are improved, and the photovoltaic performance of the dye sensitizer would also be improved.<sup>[23]</sup> The structure of D-(A- $\pi$ -A)<sub>2</sub> motif is compared with that D-A- $\pi$ -A motif, the addition of one more -A- $\pi$ -A chain in the dye is in favor of the performance of the dyes; this is because of the two receptor parts that can increase the ability of the acceptor to push–pull electron and adjust the HOMO and LOMO energy level of dye molecules, so as to achieve an excellent push–pull electron balance of dye molecules.<sup>[34]</sup>

Based on the above speculation, a series of metal complex for D- $(A-\pi-A)_2$  motif dye sensitizers by using imine derivatives and metal complexes as the auxiliary electron acceptors were designed and synthesized, systematically studied of the influence of different strength coordination bond on photovoltaic performance in this paper. The research has also obtained many meaningful research results and conclusions for adopting the metal complex as the auxiliary electron acceptor of the dye sensitizer in dye-sensitized solar cells.

#### **2** | EXPERIMENTAL SECTION

### 2.1 | Materials

All starting materials in this work were obtained from the Shanghai Chemical Reagent Co. Ltd (Shanghai, China) and used as received, except that 2,6-dibromo-4,8-bis(5-(2-ethylhexyl)-thiophen-2-yl)benzo[1,2-b:4,5-b'] dithiophene (BDTT) was procured from Suzhou Ge'ao New Material Co. Ltd. *N*,*N*-Dimethylformamide (DMF) and tetrahydrofuran (THF) were dried over CaH<sub>2</sub> and freshly distilled prior to use. Other reagents and solvents were purchased commercially as analytical-grade quality and used without further purification. Column chromatography was performed on silica gel (200–300 mesh).

#### 2.2 | Instruments and measurements

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker ARX400 (400 MHz) spectrometer, using CDCl<sub>3</sub> or DMSO- $d_6$  as solvent and tetramethylsilane (TMS,  $\delta = 0.00$  ppm) as an internal standard. Elemental analyses of C, H, N, and S were taken on a Perkin-Elmer 2400 II instrument under nitrogen atmosphere. Fourier transform infrared spectra (FT-IR) were recorded on a Perkin-Elmer Spectra One with the spectral resolution of 2.0 cm<sup>-1</sup> using KBr pellets in the 4000–400 cm<sup>-1</sup> region.

Ultraviolet-visible (UV-Vis) absorption spectra of the four polymers were obtained on a Perkin-Elmer Lambada-25 spectrometer (USA). Samples were dissolved in DMF and diluted to a concentration of  $10^{-5}$ – $10^{-4}$  mol L<sup>-1</sup>. Thermogravimetric analyses (TGA) were performed on a Shimadzu TGA-7 analyzer in 25-800°C under N<sub>2</sub> atmosphere with a heating and cooling rate of 20°C/min. The average molecular weight and polydispersity index (PDI) of the four dyes were performed on PL-120 gel permeation chromatography (GPC) analysis with DMF as eluent and polystyrene as standard. Cyclic voltammetry (CV) was conducted on an electrochemistry workstation (CHI630C, Chenhua, Shanghai) in a solution of 0.1-M tetrabutylammonium tetrafluoroborate (Bu<sub>4</sub>NBF<sub>4</sub>) dissolved in acetonitrile at a scan rate of 100 mV s<sup>-1</sup> at room temperature. The working electrode was a glassy carbon electrode; the saturated calomel electrode (SCE) was used as reference electrode, and the counter electrode was a platinum wire electrode. Ferrocene/ferrocenium redox couple was used for the redox potential calibration.<sup>[17]</sup>

### 2.3 | Fabrication of DSSCs devices

The DSSCs with the sandwich structure were fabricated based on TiO<sub>2</sub> semiconductors.<sup>[18]</sup> Fluorine-doped SnO<sub>2</sub> conducting glass (FTO) was cleaned by ultrasonication in water, acetone, ethanol, and isopropanol and subjected to an O3 treatment for 10 min. The substrates were immersed in an aqueous 40 mmol  $L^{-1}$  TiCl<sub>4</sub> solution at 70°C for 30 min and then rinsed with deionized water and ethanol. The 20- to 30-nm TiO<sub>2</sub> colloidal particles were coated onto the prepared FTO glass with the sliding glass rod method and were then sintered at 450°C for 30 min. This process was repeated two more times to obtain a 15-mm-thick TiO<sub>2</sub> film. After cooling to 100°C, the TiO<sub>2</sub> film was soaked in 0.5 mmol  $L^{-1}$  dye (for BDTT-PCd, BDTT-PZn, BDTT-PCu, and BDTT-PCo) in DMF solution and kept in the dark for 24 h at room temperature. Then, the films were cleaned by anhydrous ethanol. After drying, electrolyte containing 0.5 mol  $L^{-1}$  LiI, 0.05 mol  $L^{-1}$  I<sub>2</sub>, and 0.5 mol  $L^{-1}$  4-tertbutylpyridine was dripped on the surface of the TiO<sub>2</sub> electrodes. A Pt foil used as a counter electrode was clipped onto the top of the TiO<sub>2</sub> as the working electrode. The dye-coated semiconductor film was illuminated through the conducting glass supported without a mask. The photoelectrochemical performance of the solar cell was measured using a Keithley 2602 SourceMeter controlled by a computer. The cell parameters were obtained under an incident light with intensity of 100 mW cm<sup>-2</sup>, which was generated by a 500-W Xe lamp passing through an AM 1.5-G filter with an effective area of  $0.25 \text{ cm}^2$ .

#### 2.4 | Syntheses

#### 2.4.1 | Synthesis of compound 1

About 15.6 ml of salicylaldehyde (0.15 mol) was added to the solution of concentrated hydrochloric acid (90 ml) and paraformaldehyde (9 g, 0.3 mol) was stirred at room temperature for 48 h.<sup>[19]</sup> After filtration, the crude product was washed with saturated sodium bicarbonate solution until weakly alkaline, then with distilled water until neutral, dried, and recrystallized with petroleum ether; a white needle-like solid product was collected by vacuum drying (17.8 g,70% yield), m.p. 85–86°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 11.08 (s, 1H), 9.90 (s, 1H), 7.57 (s, 1H), 7.55 (d, 1H), 7.01 (d, 1H), 4.60 (s, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 196.22, 161.63, 137.36, 133.66, 129.24, 120.37, 118.34, 45.26.

#### 2.4.2 | Synthesis of compound 2

A mixture of chloromethyl salicylaldehyde (6.96 g, 5 mmol) and triphenylphosphine (10.48 g, 40 mmol) was dissolved in 70 ml of benzene and was refluxed for 1 h.<sup>[20]</sup> After cooled to room temperature and filtration, the product was washed three times with a small amount of diethyl ether; white powdery solid (15.8 g, 91% yield) was obtained by drying in a vacuum oven for 2 days, m.p. 253-254°C. The above phosphine salt (7.785 g, 18 mmol) was dissolved in 60 ml of formaldehyde in water (37%), and NaOH solution (19.5 ml, 12.5 mol/L) was slowly added dropwise with vigorous stirring. After stirred at room temperature for 4 h, the mixture was extract with chloroform and dry with anhydrous MgSO<sub>4</sub> for 12 h. After filtration and spin off the solvent, the crude product was purified by column chromatography using petroleum ether/ethyl acetate (10/1, v): v) as eluent to obtain a light yellow solid 2 (2.1 g, 79% yield), m.p. 19–20°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 11.01 (s, 1H), 9.90 (s, 1H), 7.62 (d, 1H), 7.54 (s, 1H), 6.97 (d, 1H), 6.64-6.71 (m, 1H), 5.65-5.69 (d, 1H), 5.22-5.25 (d, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 191.04, 161.04, 136.47, 136.12, 130.84, 129.13, 127.71, 118.43, 114.30.

#### 2.4.3 | Synthesis of compound 3

About 1.48 g of 5-vinyl salicylaldehyde (10 mmol) and 0.93 g of aniline (10 mmol) were dissolved in 20 ml of anhydrous ethanol and were stirred at 80°C for 12 h.<sup>[21]</sup> After filtration, the crude product was washed with cold anhydrous. An orange-yellow solid 3 (1.82 g, 82% yield) was collected, m.p. 66–67°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 13.34 (s, 1H), 8.64 (s, 1H), 7.42–7.49 (m, Ar-H), 7.26–7.32 (m, Ar-H), 6.99–7.01 (d, 1H), 6.64–6.72 (m, 1H), 5.62–5.67

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(d, 1H), 5.16–5.19 (d, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 162.25, 161.00, 148.37, 135.64, 130.78, 130.19, 129.46, 129.04, 127.03, 121.20, 118.96, 117.53, 111.95.

#### 2.4.4 | Synthesis of PCd

A methanol solution (20 ml) of Cd (CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.585 g, 2.2 mmol) was slowly dropped into a mixture<sup>[22]</sup> of 2-cyano-3-(8-hydroxyquinolin-5-yl)acrylic acid<sup>[23]</sup> (0.446 g, 2 mmol) and compound 3 (0.48 g, 2 mmol) in dry tetrahydrofuran (50 ml) with stirring. Then the mixture was carefully adjusted by glacial acetic acid or ammonia to weak acidity and heated to reflux for 12 h. After cooled to room temperature, the crude product was collected by filtration, washed with deionized water and absolute ethanol, and then recrvstallized with anhydrous methanol. A yellow solid (0.699 g, 61% yield) was obtained by vacuum drying. FT-IR (KBr, cm<sup>-1</sup>): 3418 (O-H), 2209 (C≡N), 1603 (C=N), 1559 (C=C), 1100 (C-O-Cd), 493 (N-Cd). Anal. calcd. for [C<sub>28</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>Cd]: C, 58.60; H, 3.34; N, 7.32. Found: C, 59.30; H, 3.41; N, 7.24%.

#### 2.4.5 | Synthesis of PZn

Metal complex PZn was synthesized by the similar method that described for PCd, except that Zn  $(CH_3COO)_2 \cdot 2H_2O$  (0.42 g, 2.2 mmol) was used instead of Cd  $(CH_3COO)_2 \cdot 2H_2O$ . Am orange solid (0.547 g, 52% yield) was collected. FT-IR (KBr, cm<sup>-1</sup>): 3420 (O-H), 2207 (C=N), 1611 (C=N), 1563 (C=C), 1111 (C-O-Zn), 506 (N-Zn). Anal. calcd. for [C<sub>28</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>Zn]: C, 63.83; H, 3.63; N, 7.98. Found: C, 63.75; H, 3.52; N, 7.99%.

#### 2.4.6 | Synthesis of PCu

Metal complex PCu was synthesized by the similar method that described for PCd, except that Cu  $(CH_3COO)_2 \cdot H_2O$  (0.438 g, 2.2 mmol) was used instead of Cd  $(CH_3COO)_2 \cdot 2H_2O$ . A dark green solid (0.586 g, 56% yield) was collected. FT-IR (KBr, cm<sup>-1</sup>): 3427 (O-H), 2209 (C $\equiv$ N), 1615 (C=N), 1563 (C=C), 1113 (C-O-Cu), 515 (N-Cu). Anal. calcd. for [C<sub>28</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>Cu]: C, 64.06; H, 3.65; N, 8.00. Found: C, 64.14; H, 3.71; N, 8.12%.

#### 2.4.7 | Synthesis of PCo

Metal complex PCo was synthesized by the similar method that described for PCd, except that Co

 $(CH_3COO)_2 \cdot 4H_2O$  (0.548 g, 2.2 mmol) was used instead of Cd  $(CH_3COO)_2 \cdot 2H_2O$ . A khaki solid (0.561 g, 54% yield) was obtained. FT-IR (KBr, cm<sup>-1</sup>): 3431 (O-H), 2213 (C $\equiv$ N), 1598 (C=N), 1568 (C=C), 1114 (C-O-Co), 516 (N-Co). Anal. calcd. for [C<sub>28</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>Co]: C, 64.62; H, 3.68; N, 8.07. Found: C, 64.73; H, 3.75; N, 8.01%.

#### 2.4.8 | Synthesis of BDTT-PCd

The polymeric metal complex BDTT-PCd is synthesized according to the Heck coupling reaction.<sup>[24]</sup> A mixture of PCd (0.172 g, 0.3 mmol), 2,6-dibromo-4,8-bis(5-(2-ethyloctyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDTT) (0.11 g, 0.15 mmol), catalyst palladium acetate (Pd (CH<sub>3</sub>COO)<sub>2</sub>, 0.0021 g, 0.0094 mmol), and tris(2-tolyl)phosphine (0.018 g, 0.06 mmol) were dissolved by refined DMF solvent (8 ml) and dried triethylamine (3 ml) under nitrogen. The reactant was gradually heated to 90°C stirred for 48 h. After cooled to room temperature and filtration, the crude product was washed with anhydrous methanol. A vellow solid was obtained (0.139 g, 53% yield). FTIR (KBr,  $cm^{-1}$ ): 3405 (O-H), 2920, 2846 (C-H), 2205 (C=N), 1598 (C=N), 1557 (C=C), 1095 (C-O-Cd), 488 (N-Cd). Anal. calcd. for [C<sub>90</sub>H<sub>76</sub>N<sub>6</sub>O<sub>8</sub>S<sub>4</sub>Cd<sub>2</sub>]: C, 62.75; H, 4.45; N, 4.88; S, 7.45. Found: C, 62.98; H, 4.58; N, 4.91; S, 7.44%.  $M_n = 1.71 \text{ kg/mol.}$ 

#### 2.4.9 | Synthesis of BDTT-PZn

BDTT-PZn was obtained following the similar method that described for BDTT-PCd from a mixture of metal complex PZn, BDTT, palladium acetate, and tris(2-tolyl) phosphine, DMF, and triethylamine as a reddish brown solid (0.114 g, 46% yield). FTIR (KBr, cm<sup>-1</sup>): 3410 (O-H), 2920, 2851 (C-H), 2205 (C $\equiv$ N), 1598 (C=N), 1559 (C=C), 1108 (C-O-Zn), 497 (N-Zn). Anal. calcd. for [C<sub>90</sub>H<sub>76</sub>N<sub>6</sub>O<sub>8</sub>S<sub>4</sub>Zn<sub>2</sub>]: C, 66.37; H, 4.70; N, 5.16; S, 7.88. Found: C, 66.81; H, 4.92; N, 5.11; S, 7.93%.  $M_n = 1.64$  kg/mol.

#### 2.4.10 | Synthesis of BDTT-PCu

BDTT-PCu was obtained following the similar method that described for BDTT-PCd from a mixture of metal complex PCu, BDTT, palladium acetate and tris(2-tolyl) phosphine, DMF, and triethylamine as a black solid (0.106 g, 43% yield). FTIR (KBr, cm<sup>-1</sup>): 3418 (O-H), 2920, 2851 (C-H), 2205 (C $\equiv$ N), 1598 (C=N), 1561 (C=C), 1110 (C-O-Cu), 511 (N-Cu). Anal. calcd. for [C<sub>90</sub>H<sub>76</sub>N<sub>6</sub>O<sub>8</sub>S<sub>4</sub>Cu<sub>2</sub>]: C, 66.52; H, 4.71; N, 5.17; S, 7.89.

Found: C, 65.79; H, 4.63; N, 5.13; S, 7.62%.  $M_n = 1.63 \text{ kg/mol.}$ 

### 2.4.11 | Synthesis of BDTT-PCo

BDTT-PCo was obtained following the similar method that described for BDTT-PCd from a mixture of metal complex PCo, BDTT, palladium acetate and tris(2-tolyl) phosphine, DMF, and triethylamine as a black solid (0.115 g, 47% yield). FTIR (KBr, cm<sup>-1</sup>): 3422 (O-H), 2922, 2850 (C-H), 2206 (C=N), 1599 (C=N), 1564 (C=C), 1112 (C-O-Co), 514 (N-Co). Anal. calcd. for [C<sub>90</sub>H<sub>76</sub>N<sub>6</sub>O<sub>8</sub>S<sub>4</sub>Co<sub>2</sub>]: C, 66.90; H, 4.74; N, 5.20; S, 7.94. Found: C, 67.31; H, 4.99; N, 5.21; S, 7.93%.  $M_n = 1.60$  kg/mol.

#### 3 | RESULTS AND DISCUSSION

#### 3.1 | Synthesis and characterization

The synthesis routes of the dyes BDTT-PM are shown in Scheme 1, compound 1 attained by salicylaldehyde was reacted with paraformaldehyde in the presence of hydrogen chloride under air, compound 2 was prepared from alkenylation of 5-chloromethylsalicylic aldehyde, compound 3 was obtained by amine condensation reaction of aniline and 5-vinyl salicylaldehyde, the metal complex BDTT-PM is prepared by the coordination reaction of compound 3 and 5-vinyl-8-hydroxyquinoline with Cd(II), Cu(II), Zn(II). or Co(II) acetate, and the coupled metal complexes BDTT-PCd, BDTT-PZn, BDTT-PCu, and BDTT-PCo were gained by Heck coupling reaction of metal complexes PCd, PZn, PCu, and PCo with donor BDTT. The <sup>1</sup>H NMR spectra of compounds 1, 2, and 3 are show in Figures S1, S2, and S3. The coupled metal complexes are tested by UV-Vis absorption spectrum, thermogravimetry, cyclic voltammetry, and FT-IR spectra, and the detailed data are collected in Table 1.

The Fourier-transform infrared spectra (FT-IR) of metal complexes and metal complexes are shown in Figures S4 and S5. According to Figure S4, the peaks around 3400 cm<sup>-1</sup> are hydroxyl peaks, which are broad peaks due to the presence of hydrogen bonds;  $2209 \text{ cm}^{-1}$ , 2207 cm<sup>-1</sup>, 2209 cm<sup>-1</sup>, and 2213 cm<sup>-1</sup> are C $\equiv$ N on the auxiliary ligand absorption peak. The absorption peaks of C=N are at 1603 cm<sup>-1</sup>, 1611 cm<sup>-1</sup>, 1615 cm<sup>-1</sup>, and 1598 cm<sup>-1</sup>, and the absorption peaks of the four complexes C-O-M appear at 1100 cm<sup>-1</sup> (C-O-Cd), 1111 cm<sup>-1</sup> (C-O-Zn), 1113 cm<sup>-1</sup> (C-O-Cu), 1114 cm<sup>-1</sup> (C-O-Co); N-M absorption peaks appear at 493  $\text{cm}^{-1}$  (N-Cd), 506 cm<sup>-1</sup> (N-Zn), 515 cm<sup>-1</sup> (N-Cu), and 516 cm<sup>-1</sup> (N-Co), which is due to the absorption peak is inversely proportional to the reduced mass of coordination metal, while the reduced mass generated by Cd(II), Zn(II),



**SCHEME 1** Synthetic routes of coupled metal complex BDTT-PCd, BDTT-PZn, BDTT-PCu, and BDTT-PCo



Cu(II), and Co(II) decreases in turn. Therefore, the absorption peak wave numbers of C-O-M and N-M of metallic bonds increase in turn. From Figure S5, the C-O-M absorption peaks of BDTT-PCd, BDTT-PZn, BDTT-PCu, and BDTT-PCo appear at 1095 cm<sup>-1</sup> (C-O-Cd), 1108 cm<sup>-1</sup> (C-O-Zn), 1110 cm<sup>-1</sup> (C-O-Cu), and 1112 cm<sup>-1</sup> (C-O-Co); N-M absorption peaks appear at 488 cm<sup>-1</sup> (N-Cd), 497 cm<sup>-1</sup> (N-Zn), 511 cm<sup>-1</sup> (N-Cu), and 514 cm<sup>-1</sup> (N-Co). Compared with their respective complexes, the metal bonds have a redshift of 2-9 wavenumbers, which is due to the introduction of the donor BDTT with good planarity, increasing the degree of conjugation; 2846–2920 cm<sup>-1</sup> is the absorption peak of methyl and methylene groups on the donor alkyl chain. It can be known from FT-IR spectra and other standard data that the four target dyes have been successfully synthesized.

#### 3.2 | Photophysical properties

The higher the absorption capacity of dye sensitizers to solar energy, the higher the photoelectric conversion efficiency is. Therefore, the wavelength range of dye sensitizers excited by sunlight and generated electrons overlapped with the maximum wavelength range of solar radiation energy more and the higher the light absorption intensity, the higher the possibility of obtaining high efficiency. UV-Vis absorption of four metal complexes and four dye sensitizers was tested, their absorption spectra were summarized in Figure 1, and the relevant data were listed in Table 1.

According to the UV-Vis spectrum of PM and BDTT-PM (Figure 1), the maximum absorption wavelength of the complex PCd (384 nm) is larger than the complex PZn (375 nm), the complex PCu (369 nm),

Dyes	λ <sub>a,max</sub> (nm)	λ <sub>b,max</sub> (nm)	$\varepsilon_{ m max}$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	E <sub>red</sub> (V)	E <sub>ox</sub> (V)	HOMO (eV)	LUMO (eV)	E <sub>g</sub> (eV)	<i>T</i> <sub>d</sub> (°C)
BDTT-PCd	514	432	19,520	-1.018	1.007	-5.347	-3.322	2.025	340
BDTT-PZn	508	388	18,418	-1.052	1.026	-5.366	-3.288	2.078	323
BDTT-PCu	500	372	17,565	-1.031	1.082	-5.422	-3.309	2.113	328
BDTT-PCo	481	366	16,880	-1.028	1.126	-5.466	-3.312	2.154	309

TABLE 1 Photophysical and electrochemical property of the BDTT-PM

<sup>a</sup>The absorption peaks of metal complexes and the first absorption peaks of polymers for UV-Vis spectra in DMF solution.

<sup>b</sup>The second absorption peaks of polymers for UV-Vis spectra in DMF solution.



FIGURE 1 UV-Vis absorption spectra of PCd, PZn, PCu, and PCo and BDTT-PCd, BDTT-PZn, BDTT-PCu, and BDTT-PCo and the complex PCo (351 nm); this may be due to the radius of the Cd(II) ion that is significantly larger than that of the other three metal ions, and the electron interaction with the ligand is stronger, so the coordination bond is stronger. After coordination, it is conducive to the formation of a better planar configuration and more favorable to the electron transportation within the molecule. The maximum absorption wavelength of the complexes of the three metals in the same period PZn > PCu > PCo is affected by the electron-withdrawing ability of metal ions. The stronger the electron-withdrawing ability is, the more stable the coordination bond.

From the absorbance data in Table 1, compared with the maximum absorption peak of PM in the visible light region, BDTT-PM has a certain degree of red shift, indicating that the introduction of BDTT not only improves the electron-donating ability of the entire molecule but also improves the conjugation degree of the molecular structure. The maximum absorption wavelength of the complex BDTT-PCd (514 nm) is larger than the complex BDTT-PZn (508 nm), BDTT-PCu (500 nm), and BDTT-PCo (481 nm); this may be due to the electronic structure configuration of the coordinated metal ion that has an influence on the light absorption ability, which makes range redshift of the light absorption. All of the dye sensitizer exhibit a high molar extinction coefficient, in which the absorption coefficient of the coupled product at the maximum wavelength is all above 14,000 L mol<sup>-1</sup> cm<sup>-1</sup>; BDTT-PCd achieved the highest absorption coefficient, exceeding 19,500  $L \text{ mol}^{-1} \text{ cm}^{-1}$ .

#### **Electrochemical properties** 3.3

Applied

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are important parameters in the design of photovoltaic materials. Cyclic voltammograms (CV) can be estimated from the initial oxidation potential  $(E_{ox})$  and the initial reduction potential  $(E_{red})$ .<sup>[35]</sup> To enable the excited electrons of the dye sensitizer to be effectively injected into the conduction band of TiO<sub>2</sub>, its LUMO energy level should be higher than that of  $TiO_2$  (-4.26). While the dye sensitizer in the oxidation state can be regenerated, the HOMO energy level of the dye is required to be lower than the redox charge pair energy level (-4.83) of the electrolyte  $I^{-}/I^{3-}$ .<sup>[36]</sup> When these two conditions are met. the energy band gap of the dye sensitizer should be as small as possible to be more easily excited by sunlight.

The cyclic voltammetry curve and the HOMO and LUMO energy levels were shown in Figure 2, and the46.4881ptrelevant data are listed in Table 1. The LUMO levels of the dyes of BDTT-PCd, BDTT-PZn, BDTT-PCu, and BDTT-PCo are -3.322, -3.388, -3.309, and -3.312, respectively, which are higher than the Fermi level (-4.26 eV) of titanium dioxide, that satisfies the conditions for the dve to inject electrons into the titanium dioxide; the HOMO levels are -5.447, -5.366, -5.422, and -5.446, both lower than the redox potential of  $I^{-}/I^{3-}$  (-4.83 eV), which satisfies the conditions for dye reduction and regeneration. The energy band gaps are 2.025, 2.078, 2.113, and 2.154 eV, respectively. The narrower of the band gap means that the charge separation is easier when excited, which is the same as the result of the photophysical test.



FIGURE 2 Cyclic voltammetry curve (a) and HOMO and LUMO energy level (b) of polymers BDTT-PCd, BDTT-PZn, BDTT-PCu, and BDTT-PCo



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**FIGURE 4** IPCE spectra of BDTT-PCd, BDTT-PZn, BDTT-PCu, and BDTT-PCo

#### 3.4 | Thermal properties

Since the working environment of dye-sensitized solar cells is exposed to sunlight for a long time, the equipment will inevitably generate heat, so the thermal stability of dye-sensitized solar cells is the significant factor to improve the service life of dye-sensitized solar cells. The thermal properties of the four dyes were studied by thermogravimetric analyses (TGA). The four dyes (BDTT-PCd, BDTT-PZn, BDTT-PCu, and BDTT-PCo) show excellent thermal stability, as shown in Figure 3 and Table 1, with the onset decomposition temperatures ( $T_d$ , the temperature at which 5% weight loss under nitrogen occurs) at 340, 323, 328, and 309°C, respectively. According to the test results, it can be known that the  $T_d$ 

of the four dye sensitizers are all above 300°C, which can fully meet the requirements of dye-sensitized solar cells to work outdoors for a long time.

#### 3.5 | Photovoltaic properties

The incident photon to current conversion efficiency (IPCE) spectra and the photocurrent density-voltage curves (J-V) of DSSCs based on BDTT-PCd, BDTT-PZn, BDTT-PCu, and BDTT-PCo are shown in Figures 4 and 5, and the relevant performance parameters are summarized in Table 2.

The IPCE curves shows that the maximum external quantum efficiency of the four dyes sensitized is all above





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TABLE 2 H	Photovoltaic parameters
of devices with	sensitizers in DSSCs at
full sunlight (A	M 1.5 G, 100 mW $cm^{-2}$ )

Dyes	solvent	$J_{\rm sc}$ (mA/cm <sup>2</sup> )	$V_{\rm oc}(V)$	ff (%)	η (%)
BDTT-PCd	DMF	17.51	0.79	69.25	8.82
BDTT-PZn	DMF	17.02	0.78	66.78	8.32
BDTT-PCu	DMF	15.07	0.76	69.17	8.03
BDTT-PCo	DMF	14.38	0.74	69.53	7.55

65%, and the maximum monochromatic light efficiency of BDTT-PCd is more than 80%. The light absorption intensity of BDTT-PCd > BDTT-PZn > BDTT-PCu > BDTT-PCo shows the same trend as the absorption spectrum, and BDTT-PCd has better absorption in the long wavelength region, which is due to the influence of light absorption intensity and region; BDTT-PCd shows the highest monochromatic light photoelectric conversion efficiency 82.5%.

The J-V curves illustrate that the short-circuit current densities  $(J_{sc})$  follow the order of BDTT-PCd  $(17.51 \text{ mA/cm}^2) > \text{BDTT-PZn} (17.02 \text{ mA/cm}^2) > \text{BDTT-}$ PCu (15.07 mA/cm<sup>2</sup>) > BDTT-PCo (14.38 mA/cm<sup>2</sup>), which is consistent with the trend of increasing IPCE. The open circuit voltage  $(V_{oc})$  is 0.79, 0.78, 0.76, and 0.74 V, respectively, and the fill factor (ff) is 69.25%, 66.78%, 69.17%, and 69.53% respectively. The efficiency difference is mainly caused by short circuit current density and open circuit voltage, so the influence of different metal ion coordination ability on its performance is mainly discussed. Compared with the dye sensitizers containing metals of the same main group, the photoelectric conversion efficiency of BDTT-PCd is higher than BDTT-PZn. With containing the same cycle sensitizer comparison of three kinds of metal, the order of photoelectric conversion efficiency is BDTT-PZn > BDTT-PCu > BDTT-PCo, and BDTT-PCd achieved

the highest efficiency of 8.82%; this result is consistent with the absorption spectrum of the four dye sensitizers, which is due to the fact that BDTT-PCd has the widest absorption spectrum, so that it can produce more photocurrent.

#### CONCLUSION 4

In summary, four novel D-(A- $\pi$ -A)<sub>2</sub> motif dyes of metal complexes with Cd(II), Zn(II), Cu(II), and Co (II) of imine derivative as auxiliary acceptors, BDTT derivatives as donor (D), and 8-hydroxyquinoline derivative as  $\pi$ -bridge and acceptor were designed and synthesized. According to the results of photovoltaic test of four polymeric metal complexes, the thermogravimetric curve shows that the four dye sensitizers exhibit excellent thermal stability and can fully meet the DSSC requirements for dye sensitizers ( $T_d > 300^{\circ}$ C). The power conversion efficiency (PCE) of BDTT-PCd (8.82%) is higher than BDTT-PZn (8.32%), BDTT-PCu (8.03%), and BDTT-PCo (7.55%). This is primarily affected by the radius of the metal ion and the ability of electron-withdrawing. The more stable the coordination bond formed by the metal and the ligand, and the effect of the metal radius on the performance of the dye sensitizer is significantly higher than the effect of the electron-withdrawing ability on its performance. The properties of metal ions as radius and change number affect the stronger of coordination bonds of metal ions and ligand; the larger the radius of metal ions is, the stronger the coordination bond is in the same number of changes, which enhances the electronwithdrawing ability of the auxiliary acceptor A of metal complexes and transfer electron ability between donor (BDTT) and the electron acceptor. The strengthen of electron-withdrawing and the transfer electron ability decrease the  $E_{\rm g}$  of metal complexes that cause red shift of  $\lambda_{\text{max}}$  can increase the  $J_{SC}$  and PCE. The J-V curves shows that the short-circuit current densities  $(J_{sc})$  follow the order of BDTT-PCd  $(17.51 \text{ mA/cm}^2) > BDTT-PZn$  $(17.02 \text{ mA/cm}^2) > \text{BDTT-PCu} (15.07 \text{ mA/cm}^2) > \text{BDTT-}$ PCo (14.38 mA/cm<sup>2</sup>), which is consistent with the trend of increasing IPCE. The results shown that from BDTT-PCo, BDTT-PCu, BDTT-PZn, to BDTT-PCd, the coordination bonds were strengthened, and the electronwithdrawing of the auxiliary receptor (A) was enhanced, leading to the increase of  $J_{sc}$  and PCE. For the ligand with the same type, the stronger the metal's ability to accept electron pairs, the stronger the coordination bond, and the stronger the electron absorption ability. Of course, in addition to the composition and structure of the metal ions (charge, radius, and electron configuration), the composition and structure of the ligands also affect the strength of the coordination bonds, which is what we are studying next.

#### AUTHOR CONTRIBUTIONS

Xianming Wu: Data curation; formal analysis; software. Shiyu Tang: Data curation; formal analysis; software. Kaixuan Wang: Data curation; formal analysis; software. Yong Tian: Data curation; formal analysis; software. Chaofan Zhong: Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; resources; software; supervision; validation; visualization.

#### DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supplementary material of this article.

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#### REFERENCES

- [1] B. O'regan, M. Grätzel, Nature 1991, 353(6346), 737.
- [2] T. T. And, P. Würfel, I. U. And, J. Phys. Chem. B 1999, 103(11), 1905.
- [3] B. Lee, D. B. Buchholz, P. Guo, J. Phys. Chem. C 2016, 115(19), 9787.
- [4] L. Zhu, L. Wang, C. Pan, ACS Nano 2017, 11(2), 1894.
- [5] G. Nogay, J. Stuckelberger, P. Wyss, ACS Appl. Mater. Interfaces 2016, 8(51), 35660.
- [6] M. C. Sil, V. Sudhakar, M. K. Mele, ACS Appl. Mater. Interfaces 2017, 9(40), 34875.
- [7] H. Imahori, T. Umeyama, J. Phys. Chem. C 2009, 113(21), 9029.
- [8] H. Zhou, J. M. Ji, S. H. Kang, J. Mater. Chem. C 2018, 7(10), 2843.
- [9] M. Srikanth, G. N. Sastry, Y. Soujanya, Int. J. Quantum Chem. 2015, 115(12), 745.
- [10] W. Zhu, Y. Wu, S. Wang, Adv. Funct. Mater. 2015, 21(4), 756.
- [11] S. Mathew, A. Yella, P. Gao, Nat. Chem. 2014, 6(3), 242.
- [12] Y. Wu, W. H. Zhu, S. M. Zakeeruddin, ACS Appl. Mater. Interfaces 2015, 7(18), 9307.
- [13] Y. Z. Wu, X. Zhang, W. Q. Li, Z. S. Wang, H. Tian, W. H. Zhu, *Adv. Energy Mater.* 2012, *2*, 149.
- [14] Y. Z. Wu, M. Marszalek, S. M. Zakeeruddin, Q. Zhang, H. Tian, M. Gratzel, W. H. Zhu, *Energ. Environ. Sci.* 2012, 5, 8261.
- [15] H. B. Zhu, W. Q. Li, Y. Z. Wu, B. Liu, S. Q. Zhu, X. Li, H. Ågren, W. H. Zhu, ACS Sustainable Chem. Eng. 2014, 2, 1026.
- [16] L. Chen, X. Li, W. Ying, X. Zhang, F. Guo, J. Li, J. Hua, *Eur. J. Org. Chem.* 2013, 2013, 1770.
- [17] Y. Cui, Y. Z. Wu, X. F. Lu, X. Zhang, G. Zhou, F. B. Miapeh, W. H. Zhu, Z. S. Wang, *Chem. Mater.* **2011**, *23*, 4394.
- [18] J. Mao, F. Guo, W. Ying, W. Wu, J. Li, J. Hua, *Chem. Asian J.* 2012, 7, 982.
- [19] Y. Yen, C. Lee, C. Hsu, H. Chou, Y. Chen, J. T. Lin, *ChemAsian J.* 2013, 8, 809.
- [20] K. Pei, Y. Z. Wu, W. J. Wu, Q. Zhang, B. Chen, H. Tian, W. H. Zhu, *Chem. A Eur. J.* **2012**, *18*, 8190.
- [21] K. Pei, Y. Z. Wu, A. Islam, Q. Zhang, L. Y. Han, H. Tian, W. H. Zhu, ACS Appl. Mater. Interfaces 2013, 5, 4986.
- [22] K. Pei, Y. Z. Wu, A. Islam, S. Q. Zhu, L. Y. Han, Z. Y. Geng, W. H. Zhu, *Phys. Chem. C.* 2014, 118, 16552.
- [23] X. Chen, Dyes Pigm. 2017, 139, 420.
- [24] K. Pei, Y. Z. Wu, H. Li, Z. Y. Geng, H. Tian, W. H. Zhu, ACS Appl. Mater. Interfaces 2015, 7, 5296.
- [25] W. Q. Li, Y. Z. Wu, Q. Zhang, H. Tian, W. H. Zhu, ACS Appl. Mater. Interfaces 2012, 4, 1822.
- [26] S. Y. Qu, W. J. Wu, J. L. Hua, C. Kong, Y. T. Long, H. Tian, *Phys. Chem. C.* 2010, 114, 1343.
- [27] S. Y. Qu, C. Qin, A. Islam, J. L. Hua, H. Chen, H. Tian, L. Y. Han, *Chem. Asian J.* 2012, 7, 2895.
- [28] S. Y. Qu, C. Qin, A. Islam, Y. Z. Wu, W. H. Zhu, J. L. Hua, H. Chen, H. Tian, L. Y. Han, *Chem. Commun.* **2012**, *48*, 6972.
- [29] D. G. D. Patel, F. Feng, Y. Ohnishi, K. A. Abboud, S. Hirata, K. S. Schanze, J. R. Reynolds, *Am. Chem. Soc.* **2012**, *134*, 2599.
- [30] M. Abdul, S. Maryam, U. K. Salah, A. Naeem, Int. J. Quantum Chem. 2020, 120(15), e26253.

- [31] Z. H. Luo, R. J. Ma, Y. Q. Xiao, F. Ni, T. Liu, Q. Zhan, H. L. Sun, Y. Z. Chen, Y. Zou, X. H. Lu, H. Yan, C. L. Yang, *Small Struct.* 2020, 2000052.
- [32] X. Chen, Y. L. Liao, Y. Liu, C. X. Zhu, T. Q. Chen, C. F. Zhong, Dyes Pigm. 2017, 139, 420.
- [33] Q. Xiu, H. Huang, Y. Liu, L. R. Zhang, L. H. Guo, J. Y. Deng, G. J. Wen, S. T. Tan, C. F. Zhong, *Synth. Met.* 2011, 161, 455.
- [34] Z. D. Sun, M. F. He, C. Kadali, X. H. Ju, Mater. Chem. Phys. 2020, 248, 122943.
- [35] K. Srinivas, C. R. Kumar, M. A. Reddy, K. Bhanuprakash, Synth. Met. 2011, 161(1), 96.
- [36] K. Srinivas, C. R. Kumar, M. A. Reddy, *Synth. Met.* 2011, 161 (1), 96.

#### SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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