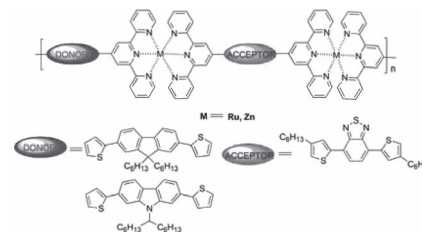


Synthesis of Main-Chain Metallo-Copolymers Containing Donor and Acceptor Bis-Terpyridyl Ligands for Photovoltaic Applications

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Two random (Zn^{II}-based **P1–P2**) and two alternating (Ru^{II}-based **P3–P4**) metallo-copolymers containing bis-terpyridyl ligands with various central donor (i.e., fluorene or carbazole) and acceptor (i.e., benzothiadiazole) moieties were synthesized. The effects of electron donor–acceptor interactions with metal (Zn^{II} and Ru^{II}) ions on their thermal, optical, and electrochemical properties were investigated. Because of the strong ICT transitions between donor and acceptor ligands in both Zn^{II}- and Ru^{II}-based metallo-copolymers and MLCT transitions in Ru^{II}-based metallo-copolymers, the absorption spectra covered a broad range of 260–750 nm with the band gaps of 1.57–1.77 eV. In addition, the introduction of Ru^{II}-based metallo-copolymer **P4** mixed with PC₆₀BM as an active layer of the BHJ solar cell device exhibited the highest PCE value up to 0.90%.



1. Introduction

The design of macromolecular structures utilizing self-recognition and self-assembly of functional structures by the interactions of transition metal ions and appropriate chelating ligands can afford many intriguing architectures that attain highly attention in modern supramolecular chemistry.^[1] Because of the chelating effect of

pyridine rings to form $d\pi-p\pi^*$ back-bonding and high binding affinities toward many metal ions, terpyridines, especially 2,2':6',2''-terpyridine (terpy) derivatives, are sufficient to support macromolecular assemblies.^[2] Combining two terpy units back-to-back through different π -conjugated spacers to form chemically and thermally stable ditopic bis-terpyridyl derivatives, various linear and rod-like polynuclear polymers could be generated via further complexation with a large variety of transition-metal ions (e.g., Ru^{II}, Zn^{II}, Fe^{II}, and Ni^{II}).^[3–5] After coordination with transition metal ions, these ligand–metal complexes could offer distorted octahedral 2:1 structures with kinetically labile or inert but nevertheless thermodynamically stable bonds.^[5] Among all transition metal ions, the availabilities and the low costs of Zn^{II} ions have also been recently attracted as novel supramolecular templates for the fabrication of structurally well-defined photoluminescent (PL) and electroluminescent metallo-cycles and metallo-polymers.^[6–10] Such systems could provide large equilibrium constants for metallo-polymers, and adjusting their π -conjugated spacers also afforded various colors from violet to yellow with high PL quantum

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yields.^[7] In our previous researches of developing light-emitting materials, Zn^{II}-based metallo-homopolymers and metallo-alt-copolymers, where bis-(terpyridines) bearing electron-donating π -conjugated spacers, were shown to possess remarkable polymer light-emitting diode (PLED) device properties.^[8]

Recently, motivations for examining the potential incorporation of conjugated polyelectrolytes into photovoltaic cell (PVC) developments, including the easy processability, the ability to be used in layer by layer (LBL) processing, and the fact that the applications in a variety of chemical and sensory schemes, have shown that they could be efficiently quenched by electron acceptors.^[11] Among all conjugated polyelectrolytes, terpyridyl Ru^{II} complexes have been found potentials to be used in PVCs, because the insertions of ruthenium metals into conjugated backbones have several advantages, such as the charge generations facilitated by the extensions of the absorption ranges because of their characteristic long-lived metal to ligand charge transfer (MLCT) transitions and to exhibit reversible Ru^{II,III} redox processes along with some ligand-centered redox processes.^[12–17]

Up to date, the solar cell applications of terpyridyl Ru^{II} complexes are limited by their low efficiency values in solar cell devices because of the lower open-circuit voltages (V_{oc}) arisen from the relatively higher highest occupied molecular orbital (HOMO) levels, smaller short circuit currents (J_{sc}) induced by less sensitization ranges, and poor morphologies caused by less solubilities in terpyridyl Ru^{II} complexes. The possible consequences for the incorporation of donor-substituted (D-substituted) bis-terpyridine with the acceptor-substituted (A-substituted) bis-terpyridine via metal ions to form main-chain metallo-copolymers, including longer absorption ranges through intramolecular charge transfer (ICT) in D-A systems, lower HOMO levels because of the insertions of electron donors, and better solubilities through the introductions of more alkyl chains, intrigued us to motivate this study. In this report, the synthesis and properties of four main-chain Zn^{II}/Ru^{II} metallo-copolymers (**P1–P4**) containing donor (fluorene or carbazole) and acceptor-substituted (benzothiadiazole) bis-terpyridyl ligands were investigated. By utilizing different polymerization methods, we are able to synthesize two random (**P1–P2**) and alternating (**P3–P4**) metallo-copolymers containing Zn^{II} and Ru^{II} ions, respectively. Characterizations of these materials were studied in detail, and the preliminary results revealed that the bulk-heterojunction PVC devices fabricated by Ru^{II} metallo-copolymers (**P3–P4**) with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as an active layer could offer the best power conversion efficiency (PCE) value up to 0.9%, which is the highest value so far in the field of conjugated polyelectrolytes.

2. Experimental Section

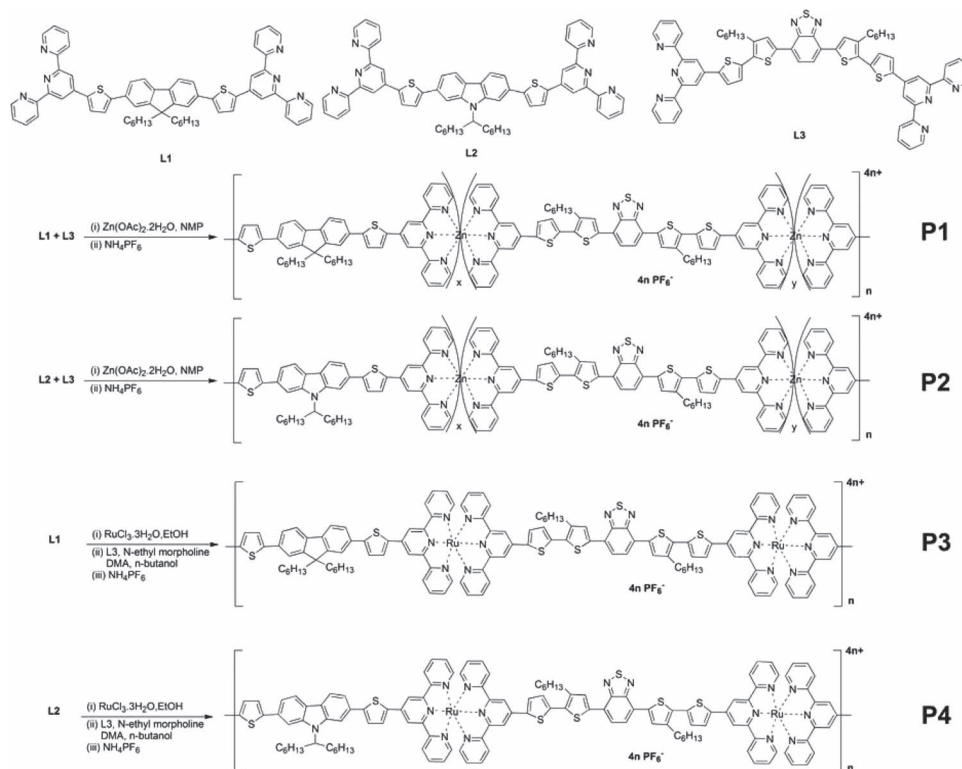
2.1. Materials

All chemicals and solvents were reagent grades and purchased from Aldrich, ACROS, Fluka, TCI, TEDIA, and Lancaster Chemical Co. Solvents were dried and distilled according to standard procedures. If not otherwise specified, the other solvents were degassed by nitrogen 1 h prior to use. Details on the synthesis of the bis-terpyridyl ligands (**L1–L3**), metallo-copolymers (**P1–P4**), the instrumentation and PVC device preparation are given in the Supporting Information.

3. Results and Discussion

3.1. Synthesis and Structural Characterization

The general synthetic routes of metallo-copolymers (**P1–P4**) are shown in Scheme 1. Zn^{II}-based random metallo-copolymers (**P1–P2**) were synthesized similar to our previous reported protocols,^[8] where the mixture of bis-terpyridine ligands **L3** and **L1** (or **L3** and **L2**) were reacted with Zn(OAc)₂ in *N*-methylpyrrolidone (NMP) for 24 h at 115 °C followed by counter ion exchange with excess NH₄PF₆. Furthermore, alternating metallo-copolymers (**P3–P4**) containing donor-acceptor bis-terpyridyl units and Ru^{II} ions were synthesized in a two-step procedure. First, ligand **L1** or **L2** was reacted with an excess of RuCl₃·3H₂O to yield the corresponding ruthenium precursor. Subsequently, another ligand **L3** was mixed with the above precursor and heated in *n*-butanol/DMA mixture for 48 h under reflux, where the reduction of Ru^{III} to Ru^{II} occurred in the presence of *n*-butanol solvent, which acted as a reducing agent in the chain growth process. The resulting highly linear-rigid polymers containing charged metal ions exhibited less solubility in common organic solvents, but were soluble in highly polar aprotic solvents, such as DMSO, DMF, NMP, and DMA. As a result of metallo-polymerization, broadened and shifted NMR signals of bis-terpyridyl ligands were observed after complexation (see Figure S1, Supporting Information). Furthermore, clear and dramatic downfield shifts of (5,5''), (4,4''), (3,3''), and (3',5'')-terpyridyl signals and upfield shifts of (6,6'')-terpyridyl signals in ¹H NMR were observed upon polymerization. To further confirm the formation of supramolecular metallo-polymers, the relative viscosity measurements of polymers to bis-terpyridyl ligands were evaluated. As shown in Table 1, P1–P4 (with $\eta = 10–11$ cp) exhibited viscosity 1.67–1.83 times larger than their corresponding bis-terpyridyl ligands **L1–L3** (with $\eta = 6$ cp), so the molar masses of **P1–P4** were expected to be higher than 30000 g mol⁻¹.^[4] Furthermore, thermogravimetric analysis revealed decomposition temperatures (T_d) (5% weight loss) of the metallo-copolymers were in the range of 413–436 °C, indicative of excellent thermal stabilities.



■ Scheme 1. Synthetic routes for metallo-copolymers (P1–P4).

3.2. Electronic Absorption

The photophysical characteristics of metallo-copolymers (P1–P4) were investigated by UV-vis absorption spectroscopy both in solutions (10^{-6} M) and solid films (see Figure 1a and b; and Table 1). The absorption spectra of Zn^{II} copolymers (P1–P2) showed three intense band regions, where the band at ca. 280 nm was associated with the characteristic π – π^* transitions of the terpyridine moieties^[10] and the low energy peaks ca. 400 and 520 nm (with tailing around 700 nm) were due to the π – π^* transitions and ICT, including both interactions of intraligand charge transfer and ligand-to-ligand charge transfer, occurred inside the overall π -conjugated D-A systems. It is known

that the Zn^{II} cores do not participate in the transitions, due to the filled d^{10} electron shell, the absorption bands at ca. 280 and 400 nm are similar to those for bis-terpyridine ligands. Furthermore, the charge transfer (CT) from electron-rich central moieties to electron-deficient terpyridyl units after metal coordination causes a red-shifted absorption in Zn^{II}-based metallo-polymers. However, as our central chromophores in ligand L3 consisting of strong electron-withdrawing (i.e., benzothiadiazole) moieties, were not able to undergo such CT processes with the terpyridyl units^[6] but having energy transfer from donor to acceptor moieties to give an ICT band at ca. 520 nm. In Ru^{II}-based metallo-polymers, self-assembly induced by metal ions is readily observed by the occurrence of an additional

■ Table 1. Optical, thermal, viscosity, and electrochemical properties of metallo-copolymers (P1–P4).

| Polymers | η^a [cp] | T_d^b [°C] | $\lambda_{\text{abs, sol}}^c$ [nm] | $\lambda_{\text{abs, film}}^d$ [nm] | $E_{\text{ox/on}}^e$ [V] | HOMO ^f [eV] | $E_{\text{red/on}}^e$ [V] | LUMO ^f [eV] | $E_g^{\text{ec g}}$ [eV] | $E_g^{\text{opt h}}$ [eV] |
|----------|------------------|-----------------|---------------------------------------|--|-----------------------------|---------------------------|------------------------------|---------------------------|-----------------------------|------------------------------|
| P1 | 11 | 413 | 278, 404, 521 | 284, 334, 462, 562 | 0.95 | –5.30 | –0.82 | –3.53 | 1.77 | 1.81 |
| P2 | 10 | 430 | 278, 412, 530 | 284, 340, 471, 567 | 0.92 | –5.27 | –0.80 | –3.55 | 1.72 | 1.78 |
| P3 | 10 | 432 | 276, 315, 409, 538 | 281, 342, 392, 560 | 0.80 | –5.15 | –0.80 | –3.55 | 1.60 | 1.82 |
| P4 | 11 | 436 | 276, 315, 414, 542 | 281, 344, 492, 565 | 0.84 | –5.19 | –0.76 | –3.59 | 1.60 | 1.76 |

^aViscosities of polymers (10 wt% in NMP); ^bDecomposition temperatures under N₂ atmosphere; ^cIn DMF (10^{-6} M) solutions; ^dSpin-coated on quartz substrates; ^eOnset oxidation and reduction potentials; ^f $E_{\text{HOMO}}/E_{\text{LUMO}} = [-(E_{\text{onset}} - 0.45) - 4.8]$ eV, where 0.45 V is the onset value for ferrocene versus Ag/Ag⁺ and 4.8 eV is the energy level of ferrocene below the vacuum level; ^g $E_g^{\text{ec}} = \text{HOMO-LUMO}$; ^h $E_g^{\text{opt}} = 1240/\lambda_{\text{edge}}$.

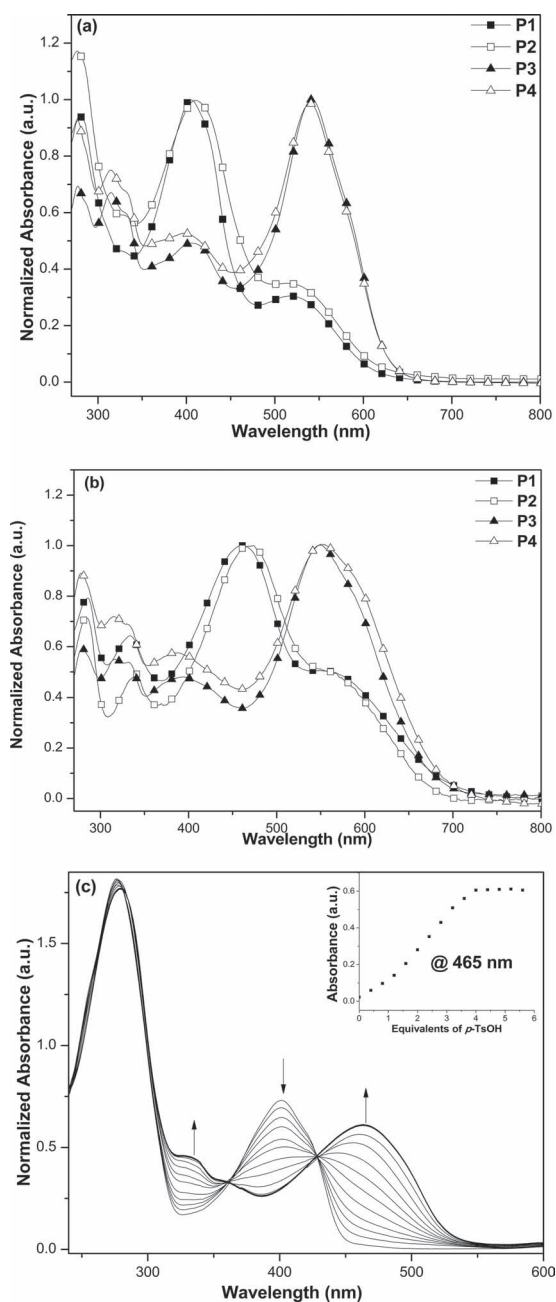


Figure 1. Normalized UV-vis spectra of (a) metallo-copolymers in dilute solutions, (b) metallo-copolymers in solid films, (c) bis-terpyridyl ligand **L1** titrated with *p*-TsOH. The inset shows the normalized absorption at 465 nm as a function of *p*-TsOH: **L1**.

absorption band (metal-to-ligand charge transfer, i.e., MLCT) at 490–560 nm,^[18,19] which were derived from the promotion of an electron from the metal (Ru^{II})-centered d-orbital to unfilled ligand-centered π^* orbitals. Compared with **P1–P2**, similar peaks were obtained in UV-vis spectra of Ru^{II} copolymers **P3–P4**, except the peak at ca. 540 nm become stronger, which could be attributed to the overlap of both ICT and MLCT bands. Furthermore, the absorption

spectra of metallo-copolymers **P1–P4** in solid films were red-shifted because of the enhancement of π - π stacking by the aggregation of neighboring chains in solid state. Besides, the bathochromic shift, a new band around $\lambda_{\text{abs}} = 340$ nm also appeared in the case of Zn^{II} copolymers (**P1–P2**) in solid films.^[17] Because of the long absorption ranges of these metallo-copolymers (**P1–P4**) containing donor- and acceptor-substituted bis-terpyridines, they possessed small optical band gaps in the range of 1.76–1.82 eV. Photoluminescence spectra and related data of the ligands (**L1–L3**) and metallo-copolymers (**P1–P4**) are depicted in the supporting information as Figure S3 and Table S1, respectively. It is evident from the data that all polymers showed emission at ca. 665 nm, but **P3–P4** have lower quantum yields than **P1–P2** because of the quenching behavior of Ru^{II} ions.

Because all bis-terpyridyl ligands **L1–L3** are basic, they can act as Lewis base to coordinate with transition metal ions or to be protonated. In either case, the electronic absorptions of the ligands would be affected because of the decreased electron densities. To understand how the protonation and metallization influence the electronic absorptions of ligands, acid-titrations with *p*-TsOH were conducted. For **L1**, upon addition of *p*-TsOH, the absorption band at 401 nm gradually decreased, accompanied by an increased absorption at 465 nm (see Figure 1c). After addition of 4 equiv. of *p*-TsOH, no further change occurred in the spectrum. The appearance of 465 nm absorption band could be attributed to two factors: first, the protonation of terpyridyl nitrogen atoms would decrease the electron density of the complex, which stabilized the π^* orbital of the complex and consequently reduce the energy of the π - π^* transition; second, the increased electron-accepting ability of the protonated terpyridine would likely induce intramolecular charge transfer from the electron-rich donor moieties to the electron-deficient protonated terpyridyl moieties. Furthermore, two isosbestic points (ca. 360 and 429 nm) were observed, which suggests that an equilibrium occurred among a finite number of spectroscopically distinct species. The similar results were obtained for **L2** and **L3** upon acid-titrations with *p*-TsOH (Figure S4, Supporting Information).

3.3. Electrochemical Properties

The redox behavior and electronic states, that is, HOMO and lowest unoccupied molecular orbital (LUMO) levels, of metallo-copolymers **P1–P4** were acquired from solid films by cyclic voltammetry measurements (see Figure S5, Supporting Information; and Table 1). Zn^{II} metallo-copolymers **P1–P2** exhibited two oxidation peaks between 1.30–1.70 V and one reduction peak at ca. 1.00 V. These peaks were attributed to the reduction of terpyridyl moieties.^[8,13] Ru^{II} metallo-copolymers **P3–P4** exhibited two reversible or quasi-reversible oxidation peaks at ca. 1.06

and 1.51 V, respectively. In agreement with the literature, these waves were attributed to the metal localized oxidation (corresponding to the II/III redox transition) and redox transitions across bridging ligands, respectively.^[5,15,18] Both polymers **P3**–**P4** also showed one reduction process at ca. 1.17 V, which was assigned to the ligand-based reduction.^[6] From the onset oxidation and reduction potentials of all metallo-copolymers (**P1**–**P4**), the estimated HOMO levels were in the range of –5.15 to –5.30 eV and LUMO levels were at ca. –3.55 eV. Apparently, LUMO levels of these metallo-polymers stayed relatively constant while HOMO levels could be tuned by varying the electron donating groups on the bis-terpyridyl ligands. The electrochemical band gaps of all metallo-copolymers (**P1**–**P4**) were in the range of 1.57–1.77 eV, which were strongly influenced by the nature of π -conjugated spacer units. All these electrochemical characteristics of Ru^{II} metallo-copolymers (**P3**–**P4**) were within the desirable range of ideal materials to be utilized in the organic photovoltaic applications.

3.4. Photovoltaic Properties

To investigate the potential use of Ru^{II} metallo-copolymers (**P3**–**P4**) in PVCs, the bulk - heterojunction solar cell devices comprising blends of these polymers as electron donors and PCBM as an electron acceptor in their active layer were fabricated with a configuration of ITO/PEDOT:PSS(30 nm)/**P3**–**P4**:PCBM blend (≈ 80 nm)/Ca(30 nm)/Al(100 nm) and measured under AM 1.5G stimulated solar light. The blended solutions were prepared from polymers and PCBM in a weight ratio of 1:1 (w/w) from DMF solutions. The current density (J) versus voltage (V) curves and EQE curves of the PVCs are shown in Figure 2, and the photovoltaic properties are summarized in Table 2. The PCE values of **P3** and **P4** devices were found to be 0.57% and 0.90%, respectively. The V_{oc} values of **P3** and **P4** devices, which are related to the difference between the HOMO level of the donor polymer and the LUMO level of the acceptor (PCBM), were found to be 0.66 and 0.70 V, respectively. The high V_{oc} value for **P4** device could be explained by the low HOMO energy level of **P4** (–5.19 eV) compared with that of **P3** (–5.15 eV). This may be attributed to the presence of a strong donor unit (carbazole) in **P4** compared with the fluorene unit in **P3**.^[20] An optimal PVC performance was observed for the **P4**:PCBM device, which reached a PCE of 0.90%, with J_{sc} of 3.50 mA cm^{-2} , V_{oc} of 0.70 V, and FF of 0.37 under AM 1.5 G irradiation (100 W cm^{-2}). The largest differences between these devices were the J_{sc} values, which generally depend on the light absorptions of the donor polymers. The EQE curves in Figure 2b show that the spectral responses of both **P3** and **P4** devices exhibited similar EQE values in the short wavelength (ca. 400 nm) region, but **P4** device displayed higher EQE values at the long wavelength (ca. 600 nm) region, which could be the main reason for the higher J_{sc} value of

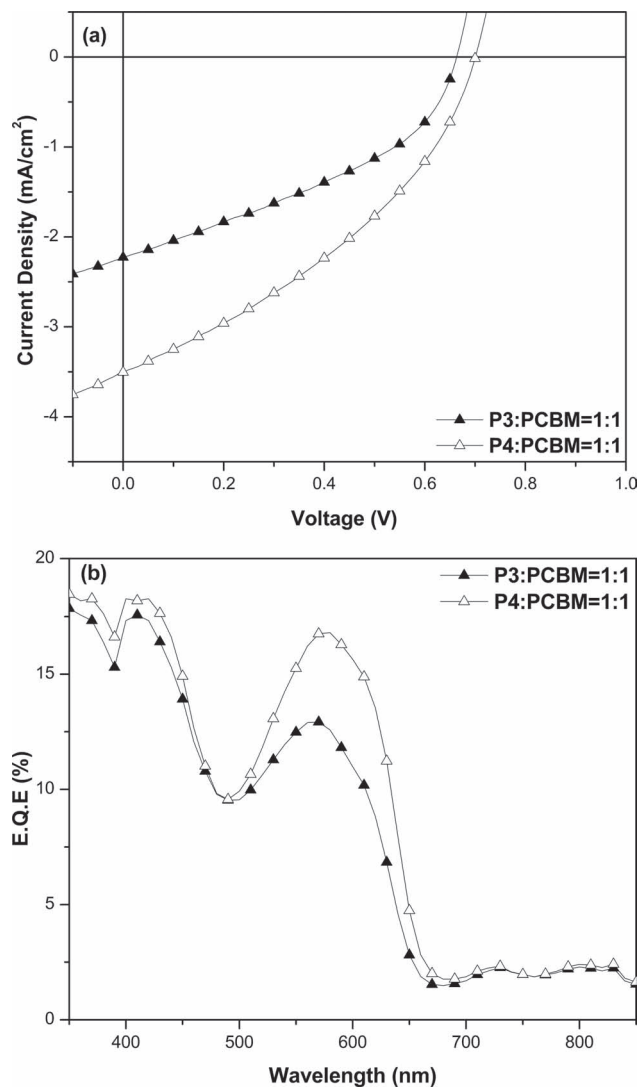


Figure 2. (a) Current–voltage curves of ITO/PEDOT:PSS/**P3**–**P4**:PC_{6i}BM (1:1 w/w)/Ca/Al under the illumination of AM 1.5G, 100 mW cm^{-2} . (b) EQE curves of PVC devices based on **P3**–**P4**/PC_{6i}BM (1:1, w/w).

the PVC cell containing **P4**. Compared with most conjugated polymers, the low EQE values of both metallo-copolymer **P3** and **P4** devices may be because of their poor dissociation of excitons. Therefore, if the EQE values of the PVC devices can be further enhanced, then the device performances can

Table 2. Photovoltaic properties of BHJ solar cell devices with a configuration of ITO/PEDOT:PSS/**P3** or **P4**:PCBM/Ca/Al.^{a)}

| Active layer ^{b)} (Polymer:PCBM) | V_{oc} [V] | J_{sc} [mA cm^{-2}] | FF [%] | PCE [%] |
|--|-----------------|-------------------------------------|-----------|------------|
| P3 | 0.66 | 2.22 | 39.0 | 0.57 |
| P4 | 0.70 | 3.50 | 37.1 | 0.90 |

^{a)} Measured under AM 1.5 irradiation, 100 mW cm^{-2} ; ^{b)} Active layer with the weight ratio of Polymer:PCBM = 1:1.

be improved significantly. Nevertheless, compared with all reported heterojunction PVC devices fabricated from terpyridyl Ru^{II}-metallo-polymers as the active layer, our device containing metallo-copolymers **P3–P4**, demonstrated the highest PCE value up to 0.90%, which probably because of the presence of electron donor and acceptor bis-terpyridyl ligands possessing higher V_{oc} values.

4. Conclusion

In summary, the synthesis and detailed characterization of four Zn^{II}- and Ru^{II}-based metallo-copolymers are described. The formation of metallo-polymers was confirmed from the broadened ¹H NMR signals, relative viscosity measurements, and UV-vis titration experiments. The electro-optical properties of Zn^{II}- and Ru^{II}-based metallo-copolymers were strongly influenced by the nature of the attached π -conjugated donor and acceptor units along with the metal ion species. In contrast to the other conjugated polyelectrolytes, an optimum PVC device (under AM 1.5G 100 mW cm⁻²) based on the blended polymer **P4**:PCBM = 1:1 (w/w) achieved the highest PCE value up to 0.90%, with V_{oc} = 0.70 V, J_{sc} = 3.50 mA cm⁻², and FF = 37.1%. Optimizations of the device performance by changing the PCBM ratio, thickness, annealing temperature are under progress, which will be targeted in the future to obtain new materials showing tailored properties for the applications of polymer solar cells.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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