Metallo-homopolymer and metallo-copolymers containing light-emitting poly(fluorene/ethynylene/(terpyridyl)zinc(II)) backbones and 1,3,4-oxadiazole (OXD) pendants

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Abstract

A series of novel metallo-polymers containing light-emitting poly(fluorene/ethynylene/(terpyridyl)zinc(II)) backbones and electron-transporting 1,3,4-oxadiazole (OXD) pendants (attached to the C-9 position of fluorene by long alkyl spacers) were synthesized by self-assembled reactions. The integrated ratios of $^1$H NMR spectra reveal a facile result to distinguish the well-defined main-chain metallo-polymeric structures which were constructed by different monomer ligand systems (i.e. single, double, and triple monomer ligands with various pendants). Furthermore, UV–vis and photoluminescence (PL) spectral titration experiments were carried out to verify the metallo-polymeric structures by varying the molar ratios of zinc(II) ions to monomers. As a result, the enhancement of thermal stability ($T_d$) and quantum yields were introduced by the metallo-polymerization, and their physical properties were mainly affected by the nature of the pendants. The photophysical properties of these metallo-polymers exhibited blue PL emissions (around 418 nm) with quantum yields of 34–53% (in DMF). In contrast to metallo-polymers containing alkyl pendants, the quantum yields were greatly enhanced by introducing 1,3,4-OXD pendants but reduced by carbazole (CAZ) pendants. Moreover, electroluminescent (EL) devices with these light-emitting metallo-polymers as emitters showed green EL emissions (around 550 nm) with turn-on voltages of 6.0–6.5 V, maximum efficiencies of 1.05–1.35 cd A$^{-1}$ (at 100 mA/cm$^2$), and maximum luminances of 2313–3550 cd/m$^2$ (around 15 V), respectively.

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1. Introduction

Recently, the use of transition or rare earth metal complexes to build up polymeric light-emitting diode (PLED) devices has attracted much attention because of the enhancement in EL efficiency [1–5]. Chan and co-workers demonstrated that the construction of conjugated polymers made of ruthenium bipyridyl complexes can enhance the light-emitting performance by utilizing energy transfer from the triplet excited state [6–8]. A whole set of coordination polymers consisting of ditopic electro- and photo-active terpyridyl ligands complexed with zinc ions were recently published by Che and co-workers [9]. These coordination polymers exhibit different emission wavelengths ranging from violet to yellow colors with high PL quantum yields, and these polymers were successfully applied to PLED devices. Hence, tuning electroluminescent (EL) properties could be achieved through the incorporation of different transition metal complexes into polymer main chains [6–14]. Moreover, it is confirmed that due to the d$^{10}$ zinc(II) species the phenomena of intraligand charge transfers (ILCTs) happen between terpyridine/zinc(II) complexes and chromophores even in fully conjugated metallo-polymers [9–12]. Therefore, the incorporation of terpyridine/zinc(II) moieties into metallo-polymers with fine-tuned chromophores can provide good quantum yields.
and thermal stabilities, and thus to have the potential to become high-performance emissive or host materials in PLED applications [15–17].

However, some important and fundamental challenges remain to solve, including the maximization of luminescence and power efficiency, the designs and syntheses of new materials for purer colors, and the modes of addressing devices for full-color displays with optimized resolutions. A major factor responsible for poor device performance is that the charge injection and transportation in emissive materials are generally unbalanced. This imbalance arises because the energy barrier between the indium tin oxide (ITO) anode and the highest occupied molecular orbital (HOMO) level of an emissive material is different from that between the metal cathode and its lowest unoccupied molecular orbital (LUMO) level [18]. In previous studies, molecular and polymeric 1,3,4-oxadiazole (OXD) derivatives are one of the most widely studied classes of electron injection and/or hole-blocking materials, mainly because of their electron deficiencies, high photoluminescence quantum yields, and chemical stabilities [18–22]. Therefore, the introduction of electron-deficient OXD groups into the C-9 position of the fluorene units increase the electron affinities of resulting polymers and lead to more balanced charge injection and transporting properties as well as better recombination behavior [23–25].

In this context, various electron- and hole-transporting substituents, i.e. 1,3,4-oxadiazole (OXD) and carbazole (CAZ) pendants, were incorporated into poly(fluorene/ethynylene/terpyridyl)zinc(II)-based metallo-copolymers (as shown in Scheme 1). In addition, the $^1$H NMR, thermal, photophysical, and electrochemical properties were investigated as well. Furthermore, the PLED applications of metallo-copolymers as emitters in multilayer EL devices with two different heterojunction configurations of ITO/PEDOT:PSS/polymer/TPBI[2,2',2''-(1,3,5-benzenetriyl)tris(1-phenyl-1H-benzimidazole)/LiF/Al and ITO/PEDOT:PSS/polymer/BCP(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)/AlQ(tris(8-hydroxyquinoline)-aluminium)/LiF/Al were studied.

2. Experimental

2.1. Measurements

$^1$H NMR spectra were recorded on a Varian Unity 300 MHz spectrometer using CDCl₃ and DMSO-d₄ solvents. Elemental analyses were performed on a HERAEUS CHN-OS RAPID elemental analyzer. Phase transition temperatures were determined by differential scanning calorimetry (DSC, model: Perkin Elmer Diamond) with a heating and cooling rate of 10 °C/min. Thermogravimetric analysis (TGA) was conducted on a Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen. Melting points were determined by a Buchi SMP-20 capillary melting point apparatus. Viscosity measurements were proceeded by 10% weight of polymer solutions (in NMP) in contrast to those proceeded by the same condition of monomer solutions (with viscosity $\eta = 6 \text{ cP}$) on a BROOKFILEL DV-III+RHEOMETER system (100 rpm, spindle number: 4) at 25°C. UV–visible (UV–vis) absorption spectra were recorded in dilute DMF solutions (10$^{-3}$ M) on a HP G1103A spectrophotometer, and fluorescence spectra were obtained on a Hitachi F-4500 spectrophotometer. Fluorescence quantum yields were determined by comparing the integrated photoluminescence (PL) intensity of coumarin-1 in ethanol with a known quantum yield (ca. 5 × 10$^{-6}$ M, quantum yield = 0.73). Cyclic voltammetry (CV) was performed at a scanning rate of 100 mV/s on a BAS 100 B/W electrochemical analyzer, which was equipped with a three-electrode cell. Pt wire was used as a counter electrode, and an Ag/AgCl electrode was used as a reference in the CV measurements. The CV experiments were performed by solid samples immersed into electrochemical cell containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) solutions (in DMF) with a scanning rate of 100 mV/s at room temperature under nitrogen. UV–vis and PL titrations were performed by the 1.0 × 10$^{-5}$ M of monomer solutions in the solvent of CH₃CN/CHCl₃ (2/8 in vol.) were titrated with 50 μl aliquots of 3.9 × 10$^{-4}$ M of Zn(OAc)$_2$ solutions in the same solvent composition as described. The addition was done stepwise and the formation of Zn(II)-coordination polymers was monitored by UV–vis spectroscopy. Polymer thin solid films in UV–vis and PL measurements were prepared by spin-coating polymers on quartz substrates from DMF solutions with a concentration of 10 mg/ml. A series of EL devices with two device configurations of ITO/PEDOT:PSS/polymer/TPBI-(2,2',2''-(1,3,5-benzenetriyl)tris(1-phenyl-1H-benzimidazole))/LiF/Al and ITO/PEDOT:PSS/polymer/BCP(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)/AlQ(tris(8-hydroxyquinoline)-aluminium)/LiF/Al were made, where TPBI and AlQ were used as electron-transporting layers, and BCP was used as a hole-blocking layer collocated to AlQ. ITO substrates were routinely cleaned by ultrasonic treatments in detergent solutions and diluted water, followed by rinsing with acetone and then with ethanol. After drying, ITO substrates were kept in oxygen plasma for 4 min before being loaded into the vacuum chamber. The solutions (10 mg/ml) of light-emitting materials in DMF were spin-coated on glass slides precoated with indium tin oxide (ITO) having a sheet resistance of 25 Ω/square and an effective individual device area of 3.14 mm$^2$. The spin coating rate was 5278 rpm for 60 s with PEDOT:PPS, 4000 rpm for 60 s with resulting polymers, and the thicknesses of PEDOT:PPS and polymers were measured with an Alfa Step 500 Surface Profiler (Tencor). TPBI, BCP, and AlQ were thermally deposited at a rate of 1−2 Å/s under a pressure of ~2 × 10$^{-5}$ Torr in an Ulvac Cryogenic deposition system. Under the same deposition conditions and systems, one layer of LiF was thermally deposited as a cathode at a rate of 0.1−0.2 Å/s, which was followed by capping with aluminum.

2.2. Materials

Chemicals and solvents were reagent grades and purchased from Aldrich, ACROS, TCI, and Lancaster Chemical Co. Solvents were purified and dried according to standard
procedures. Chromatography was performed with Merck silica gel (mesh 70–230) and basic aluminum oxide, which was deactivated with 4 wt% of water. 4′-[[Tri(2,4,6-trifluoromethyl)sulfonyl]oxy]-2,2′:6′,6′-terpyridines and compounds 1a, 4b (M2), and 4c (M3) were prepared and purified according to literature procedures [11,12,25–27]. The synthetic routes of monomers 4a–4c (M1–M3) and metallo-polymers P1–P4 are illustrated in Schemes 1 and 2.

2.3. Synthetic procedures of monomers

2.3.1. Compound 2a

To a solution of compound (1a) (28 mmol) in 60 mL of THF/Et3N (1/1), 3-methyl-1-butyn-3-ol (84 mmol) was added. After the solution was degassed with nitrogen for 30 min, Pd(PPh3)2Cl2 (0.28 mol), PPh3 (11 mol), and CuI (2.8 mmol) were added. The reaction was then refluxed at 70 °C under N2 for 12 h. The solvent was removed under reduced pressure. The resulting solid was extracted with CH2Cl2/H2O then dried over MgSO4. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate = 4/1) to afford a white solid; mp 76–77 °C. 1H NMR (300 MHz, CDCl3): δ 8.01–8.05 (m, 8H), 7.60 (d, J = 7.8 Hz, 2H), 7.39–7.42 (m, 4H), 6.94 (d, J = 9 Hz, 4H), 3.90 (t, J = 6.3 Hz, 4H), 2.44 (s, 6H), 2.04 (s, 2H), 1.95 (br, 4H), 1.59–1.66 (m, 16H), 1.13–1.18 (m, 12H). Yield: 77%. FABMS: m/e 996; C65H66N4O6 requires m/e 998.50.

2.3.2. Compound 3a

A mixture of 2a (1.63 mmol) and KOH (6.5 mmol) in 60 mL of 2-propanol was heated to reflux under N2 with a vigorous stirring for 3 h. The solvent was then removed and crude product was purified by column chromatography (silica gel, hexane) to afford a white solid; mp 82–83 °C. 1H NMR (300 MHz, CDCl3): δ 7.99–8.04 (m, 8H), 7.64 (d, J = 7.8 Hz, 2H), 7.47–7.50 (m, 4H), 7.32 (d, J = 8.4 Hz, 4H), 6.95 (d, J = 9 Hz, 4H), 3.91 (t, J = 6.3 Hz, 4H), 1.76 (s, 2H), 1.97 (br, 2H), 1.59–1.66 (m, 4H), 1.13–1.20 (m, 12H). Yield: 77%. FABMS: m/e 882; C59H54N4O4 requires m/e 882.41.

2.3.3. Monomer 4a (M1)

Compound 3a (0.5 mmol) and 4′-[[Tri(2,4,6-trifluoromethyl)sulfonyl]oxy]-2,2′:6′,6′-terpyridine (1.1 mmol) were dissolved in nitrogen-degassed benzene, then [Pd0(PPh3)4] (70 mg, 0.06 mmol) was added followed by the addition of 20 mL of nitrogen-degassed iPr2NH. The solution was then heated to 70 °C. After complete consumption of starting materials, the solvent was evaporated and the product was purified by column chromatography (alumina, hexane/dichloromethane = 10/1 in vol.) to afford a white solid; mp 115–116 °C. 1H NMR (300 MHz, CDCl3): δ 8.7 (d, J = 5.1 Hz, 4H), 8.60–8.64 (m, 8H), 7.93–7.97 (m, 8H), 7.86 (t, J = 7.8 Hz, 4H), 7.75 (d, J = 8.7 Hz, 2H), 7.58–7.61 (m, 4H), 7.33–7.37 (m, 4H), 7.30 (d, J = 8.1 Hz, 4H), 6.93 (d, J = 8.7 Hz, 4H), 6.92 (t, J = 6.6 Hz, 4H), 2.43(s, 6H), 2.08 (br, 4H), 1.64 (br, 4H), 1.22 (br, 12H). Yield: 75%. FABMS: m/e 1343; C89H72N10O4 requires m/e 1344.57. Anal. Calcd for C89H72N10O4: C, 79.44; H, 5.39; N, 10.42; O, 4.76. Found: C, 80.15; H, 5.77; N, 10.22; O, 4.41.

2.4. Synthetic procedures of metallo-polymers

2.4.1. Metallo-homopolymer P1

To monomer 4a (M1) (0.52 mmol) in 30 mL of NMP solution, zinc acetate (0.52 mmol) in NMP (10 mL) was added
dropwise. The resulting solution was heated at 105 °C under nitrogen atmosphere. After stirring for 24 h, excess KPF₆ (1.2 mmol) was added into the hot solution. The resulting solution was poured into methanol and the precipitate obtained was purified by repeated precipitations using NMP and ether. The polymers were dried under vacuum at 60 °C for 24 h and collected as yellow solids. Yields: 78–82%.

2.4.2. Metallo-alt-copolymer P₂

To zinc acetate (1.25 mmol) in 20 ml of NMP (N-methylpyrrolidinone) solution, monomer 4b (M₂) (0.61 mmol) in NMP (20 ml) was added dropwise. After stirring at r.t. for 2 h, monomer 4a (M₁) (0.64 mmol) was also added dropwise. The resulting solution was heated at 105 °C under nitrogen atmosphere. After stirring for 24 h, excess KPF₆ (2.6 mmol) was added into the hot solution. The resulting solution was poured into methanol and the precipitate obtained was purified by repeated precipitations using NMP and ether. The polymers were dried under vacuum at 80 °C for 24 h and collected as yellow solids. Yields: 74–80%.

2.4.3. Metallo-alt-copolymer P₃

The procedure is analogous to that described for P₂. Yield: 80–84%.

2.4.4. Metallo-copolymer P₄

To zinc acetate (0.92 mmol) in 20 ml of NMP (N-methylpyrrolidinone) solution, monomer 4b (M₂) (0.45 mmol) in NMP (20 ml) was added dropwise. After stirring at r.t. for 2 h, mixture monomers 4a (M₁) and 4c (M₃) (0.42 mmol, 4a (M₁):4c (M₃) = 1:1) was also added dropwise. The resulting solution was heated at 105 °C under nitrogen atmosphere. After stirring for 24 h, excess KPF₆ was added into the hot solution. The resulting solution was poured into methanol and the precipitate obtained was purified by repeated precipitations using NMP and ether. The polymer was dried under vacuum at 80 °C for 24 h and collected as a yellow solid. Yield: 80%.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes of monomers 4a, metallo-homopolymer P₁ and metallo-copolymers P₂–P₄ are illustrated in Schemes 1 and 2. Metallo-homopolymer P₁ was obtained by refluxing monomer 4a (M₁) with Zn(OAc)₂ at a ratio of 1:1 in NMP solution and followed by subsequent anion exchange [11,12]. The key steps in the syntheses of metallo-alt-copolymers were first to functionalize two end terpyridyl units of
monomers 4b (M2) and 4c (M3) with Zn(OAc)$_2$, at a ratio of 1:2 to afford complexes 5b and 5c, respectively. Then, complexes 5b and 5c as initiators were coordinated with monomer 4a (M1) (see Scheme 2) at a ratio of 1:1 (as a sequential-coupling method), respectively, to obtain metallo-alt-copolymers P2 and P3 [11]. Moreover, metallo-copolymer P4 was obtained by reacting the mixture of monomers 4a (M1) and 4c (M3) (at a ratio of 1:1) with complex 5b (monomer mixture:complex 5b = 1:1). In contrast to other polymerization methods, i.e. the Witting or Heck coupling reactions, there are three points worthy to be noted. First, the reactive lability of zinc(II) ions and the stability of six-coordinate bis-terpyridine zinc(II) moieties allow self-assembled reactions to take place under refluxing conditions [3–5,9]. Second, the present procedure does not need any catalysts. Third, the chemical structures of metallo-copolymers can be controlled by proper stoichiometries of metals and monomers [11,12].

3.2. Structural characterization with $^1$H NMR

$^1$H NMR spectra of monomers 4a–4c (M1–M3), complexes 5b and 5c and metallo-polymers P1–P4 were recorded in DMSO-$d_6$, as shown in Fig. 1. Compared with $^1$H peaks of monomers 4b (M2) and 4c (M3) in our previous study [11], those in terpyridyl units of complexes 5b and 5c show the same downfield shift effect in proton peaks of (6,6'-), (5,5'), (4,4'), (3,3'), and (3,3')-H. Furthermore, proton peaks of (4,4')-H in terpyridyl units of complexes 5b and 5c overlap with $^1$H peaks of fluorene units. It appears that the formation of complexes 5b and 5c can be, respectively, proven by the disappearance of original $^1$H peaks in terpyridyl units of monomers 4a and 4b (M1 and M2) in the mixture of zinc ions and monomers at a ratio of 2:1 [11]. The formation of homopolymer P1 is clearly indicated by the appearance of a new set of $^1$H peaks and the absence of the original $^1$H peaks in terpyridyl units, which belong to the uncomplexed monomer 4a (M1). (The assignments of $^1$H peaks of the terpyridyl units for all polymers are made by asterisks with respect to 4-chloro-terpyridine Zn$^{2+}$ complexes). In terms of $^1$H peaks of 1,3,4-OXD and carbazole (CAZ) pendants, there are no obvious changes in chemical shifts among monomers 4a (M1), 4c (M3) and polymers P3, P4. Therefore, the most up-shifted $^1$H peaks in the terpyridyl units of polymers P3 and P4 could be overlapped with the $^1$H peaks of these pendants. To distinguish the structural differences among these main-chain metallo-polymers P1–P4, it is feasible to compare the relative integrated ratios of the $^1$H peaks. As a result, the integrated ratios of the $^1$H peaks in the terpyridyl units (A for P1, A1 for P2, A2 for P3, and A3 for P4) and the $^1$H peaks of the alkyl chains (spacer –CH$_2$–) attached to 1,3,4-OXD (B for P1, B1 for P2, B2 for P3, and B3 for P4) and CAZ units (C2 for P3 and C3 for P4) of these polymers are compared. It reveals that the relative integrated ratios are $\text{A}/\text{B} = 0.5$, $\text{A1}/\text{B1} = 1$, $\text{A2}/\text{B2} = 1$, and $\text{A3}/\text{B3} = 2$ for metallo-polymers P1, P2, P3, and P4, respectively, which suggests that the integrated ratios of polymers were consistent with the monomer amounts containing pendant 1,3,4-OXD units [11].

In contrast to the relative integrated ratio of B2/C2 (=1.1) in polymer P3, that of B3/C3 was 1 for polymer P4. According to these results, the input ratios (molecular ratios) of monomers for polymerization were very similar to the output ratios (the relative integrated ratios of $^1$H NMR) of the metallo-polymers. Consequently, the amounts of monomer ligands incorporated in the monomer ligand-based metallo-polymers can be confirmed by $^1$H NMR [28–30].

3.3. Thermal and viscosity properties

The thermal and viscosity properties of monomers 4a–4c (M1–M3) and metallo-polymers P1–P4 were studied by thermogravimetric analysis (TGA) and rheometry as summarized in Table 1. The decomposition temperatures ($T_d$) (5%
weight loss measured by TGA of monomers under nitrogen atmosphere were ranged from 221 to 351 °C, and those of polymers were ranged from 355 to 389 °C. In contrast to monomers, polymers exhibited slightly enhanced thermal stability due to the increased rigidity of the main-chain structures [8]. As the bulky OXD and CAZ pendants are attached to the backbones of the metallo-polymers, it leads to reduced rigidity of the polymers [31,32]. Hence, compared with polymers P1, P3, and P4 containing more bulky OXD and CAZ pendants, P2 shows the highest Td value among these metallo-polymers due to its higher molar ratio of less bulky alkyl pendants. This behavior was also confirmed by that the Td value (422 °C) of metallo-homopolymer containing M2 (with alkyl pendants) is larger than that (399 °C) of metallo-homopolymer containing M3 (with CAZ pendants) in our previous report, [11] and both Td values are larger than that (355 °C as shown in Table 1) of metallo-homopolymer P1 containing M1 (with OXD pendants). Moreover, the same trend of the pendant size effect on the Tg values were also observed in the monomers, i.e., 4b (M2 with alkyl pendant) = 103 °C > 4c (M3 with CAZ pendant) = 92 °C > 4a (M1 with OXD pendant) = 67 °C, so molecular structures with larger pendant groups have lower Tg values. This obviously indicates that the presence of OXD and CAZ pendants in these metallo-polymers suppresses the crystallinity (and chain aggregation) of the polymers effectively. Similar results were also observed in poly(fluorene)-based copolymers containing various 1,3,4-oxadiazole dendritic pendants [25]. However, all metallo-polymers P1–P4 did not show any phase transition temperatures, including Tg.

It suggested that the fully aromatic conjugated main-chain structures may induce the aggregation in metallo-polymers P1–P4 by π–π stacking and thus to reduce the phase transition behavior [11]. In conclusion, the thermal properties were truly affected by the nature of different pendants incorporated into the polymers.

To further confirm the structures of metallo-polymers, molecular weights of these metallo-polymers should be investigated. However, these polymers showed poor solubilities in THF, CH2Cl2, and alcoholic solvents, so standard measurements of molecular weights by GPC (gel permeation chromatography) could not be proceeded. Therefore, the relative viscosities of polymers to monomers were carried out to support the formation of polymeric structures. Solutions of monomers 4a, 4b (M1, M2) (10% weight ratio) in NMP with viscosities η = 6–7 cP at 25 °C were used as references to determine the viscosities of metallo-polymers.

d Values are larger than that (355 °C), 351 °C (> 354 °C), and 354 °C for 4c (M3), respectively.

d Reduction peaks in N2-purged DMF, r in parentheses means reversible.

e LUMO energy levels were calculated from the measured optical band gaps.

Table 1

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Td (°C)</th>
<th>η (cP)b,c</th>
<th>E_onset (V) d</th>
<th>E_LUMO (eV) e</th>
<th>E_HOMO (eV) f</th>
<th>Band gap (eV) g</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>355</td>
<td>11</td>
<td>−1.54 (r)</td>
<td>−3.10</td>
<td>−6.26</td>
<td>3.16</td>
</tr>
<tr>
<td>P2</td>
<td>389</td>
<td>10</td>
<td>−1.54 (r)</td>
<td>−3.04</td>
<td>−6.20</td>
<td>3.16</td>
</tr>
<tr>
<td>P3</td>
<td>366</td>
<td>10</td>
<td>−1.54 (r)</td>
<td>−2.88</td>
<td>−6.03</td>
<td>3.15</td>
</tr>
<tr>
<td>P4</td>
<td>356</td>
<td>9</td>
<td>−1.55 (r)</td>
<td>−2.87</td>
<td>−6.02</td>
<td>3.15</td>
</tr>
</tbody>
</table>

a The decomposition temperatures (Td) (5% weight loss) were determined by TGA with heating rates of 20 °C/min under N2 atmosphere. The Td values were 221 °C for 4a (M1), 351 °C for 4b (M2), and 354 °C for 4c (M3), respectively.

b Solutions of monomers 4a–4c (M1–M3) (10% in weight) in NMP (with viscosities η = 6–7 cP, 25 °C) were used as references to determine the viscosities of metallo-polymers.

d Reduction peaks in N2-purged DMF, r in parentheses means reversible.

e LUMO energy levels were calculated from the absorption spectra in solutions by extrapolating the tails of the lower energy peaks.

3.4. Electrochemical properties

The electrochemical behavior of polymers were studied by cyclic voltammetry (CV), and the electrochemical properties are summarized in Table 1. The lowest unoccupied molecular orbital (LUMO) energy levels were estimated from reduction potentials by the reference energy level of ferrocene (4.8 eV below the vacuum level) according to the following equation:

\[ E_{\text{LUMO}} = \left[ -E_{\text{onset}} - 0.45 \right] - 4.8 \text{ eV} \]

However, the oxidation potentials of all metallo-polymers were not detectable, so the highest occupied molecular orbital (HOMO) energy levels can be estimated by the sums of LUMO energy levels and optical band gaps. All metallo-polymers exhibit reversible reduction peaks around −1.54 V in cathodic scans (up to −2.5 V). These peaks are attributed to the reduction of terpyridyl-based moieties [9,11]. The absence of oxidation peaks in the anodic scans (up to 1 V) of these polymers are due to the metal oxidation of d10 zinc(II) ion species being extremely difficult to be observed [33–35]. The optical band gaps were estimated from absorption spectra in DMF solutions by extrapolating the tails of the lowest energy peaks, and the optical band gaps of these polymers were ranged from 3.15 to 3.16 eV. Since metallo-polymers P1–P4 possess similar backbone structures, there are no obvious differences in the optical band gaps. The electrochemical results indicate that the incorporation of 1,3,4-OXD pendant groups into the backbones of metallo-polymers will efficiently reduce the LUMO energy levels, and thus to reduce the electron injection barrier between the cathode and the emitters [36–37].
3.5. UV–vis and photoluminescence titration

To characterize the formation of metallo-homopolymer P1 and complexes 5a and 5b, the UV–visible (UV–vis) and photoluminescence (PL) titration experiments are clear ways to investigate their stepwise changes. Fig. 2 described that upon addition of Zn$^{2+}$ ions to monomer 4a (M1) reaching a ratio of Zn$^{2+}$:4a (M1) = 1:1, the spectra revealed clear shifts of three absorption bands at 364, 379, and 405 nm along with one isosbestic point, which suggests that an equilibrium occurred between a finite number of spectroscopically distinct species. The titration curve (in the inset of Fig. 3) showed a linear increase and a sharp end point at a ratio of Zn$^{2+}$:4a (M1) = 1:1, indicating the formation of metallo-homopolymer P1. The syntheses and characterization of metallo-homopolymers by adding Zn$^{2+}$ ions to monomers 4b (M2) or 4c (M3) to the ratio of Zn$^{2+}$:4b (M2) = 1:1 or Zn$^{2+}$:4c (M3) = 1:1 have also been investigated [11]. Beyond this point (Figs. 3 and 4), the subsequent addition of Zn$^{2+}$ ions induced new peaks at 279, 285, 348, and 394 nm for complex 5b (332, 348, and 393 nm for 5c) as well as new isosbestic points to form, which points out that an equilibrium arose between spectroscopically distinct species. Thus, Figs. 5 and 6 depicted that the ratios of Zn$^{2+}$ ions to monomers 4b (M2) or 4c (M3) are above 1:1, and the depolymerization is driven by the formation of chain-terminating complexes 5b or 5c [11,38]. All of the UV–vis titration spectra showed the lowest absorption around $\lambda_{abs} = 394-404$ nm, which corresponds to a charge transfer occurring between the electron-rich central fluorenyl

Fig. 2. UV–vis spectra acquired in the process of 4a (M1) to P1 upon the titration of monomer 4a (M1) in CH$_3$CN/CHCl$_3$ (2/8 in vol.) with Zn(OAc)$_2$. The spectra are shown at selected ranges of Zn$^{2+}$:4a (M1) = 0–1. The inset shows the normalized absorption at 380 nm as a function of Zn$^{2+}$:4a (M1) ratio.

Fig. 3. UV–vis spectra acquired (in the process of 4b (M2) to 5b) upon the titration of monomer 4b (M2) in CH$_3$CN/CHCl$_3$ (2/8 in vol.) with Zn(OAc)$_2$. The spectra are shown at selected ranges of Zn$^{2+}$:4b (M2) = 0–2. The inset shows the normalized absorption at 274 nm as a function of Zn$^{2+}$:4b (M2) ratio.

Fig. 4. UV–vis spectra acquired (in the process of 4c (M3) to 5c) upon the titration of monomer 4c (M3) in CH$_3$CN/CHCl$_3$ (2/8 in vol.) with Zn(OAc)$_2$. The spectra are shown at selected ranges of Zn$^{2+}$:4c (M3) = 0–2. The inset shows the normalized absorption at 315 nm as a function of Zn$^{2+}$:4c (M3) ratio.

Fig. 5. PL spectra acquired upon the titration of monomer 4a (M1) in CH$_3$CN/CHCl$_3$ (2/8 in vol.) with Zn(OAc)$_2$. The spectra are shown at selected ranges of Zn$^{2+}$:4a (M1) = 0–1. The inset shows the quantum yields as a function of Zn$^{2+}$:4a (M1) ratio.
components and the electron-deficient metal-coordinated terpyridyl moieties [38,39]. In Fig. 5, monomer 4a (M1) showed an emission band around 429 nm. As the ratio of Zn$^{2+}$:4a (M1) reached 1:1, a new emission band at 456 nm was induced. The PL quantum yields of medium complexes, i.e. the ratio of Zn$^{2+}$:4a (M1) gradually approached 1:1 in the inset of Fig. 5, scarcely increased followed by increasing molar ratio of Zn$^{2+}$ ions. Therefore, the PL quantum yields of metallo-homopolymer P1 can be marginally enhanced by attaching 1,3,4-OXD pendant groups to the polymer backbones. Furthermore, the monomer 4b (M2) exhibited a similar PL result by the formation of metallo-homopolymer reaching the ratio of Zn$^{2+}$:4b (M2) = 1:1, except for the metallo-homopolymer synthesized from monomer 4c (M3) with CAZ pendants possessing a much lower quantum yield (in solution) than its monomer 4c [11]. In titration experiments, not only different complexed situations could be confirmed by various stoichiometries, but also the alteration of photophysical properties between the monomers and polymers were also observed during the coordination processes.

3.6. Photophysical properties

The photophysical measurements of monomers 4a–4c (M1–M3) and metallo-polymers P1–P4 were carried out by UV–vis absorption and photoluminescence (PL) experiments in both dilute DMF (N,N-dimethylformamide) solutions (with some solubility problems) and solid films, and their photophysical properties are presented in Table 2. In Fig. 6, similar absorption features of polymers P1–P4 were observed at 286, 320, and 377 nm. In general, other absorption peaks can be assigned to pendant groups (i.e. $\lambda_{abs} = 295$ and 300 nm for CAZ and OXD pendants, respectively) and these absorption peaks attributed to pendant groups also can assist to confirm the metallo-copolymer structures. PL emissions of all monomers and polymers are assigned to intraligand ($\pi^*-\pi$) fluorescence. They showed purple-blue emission colors in DMF solutions, where the values of PL emission peaks ($\lambda_{max,PL}$) were around 414 nm (in DMF) with quantum yields (\(\Phi\)) of 20–33% for monomers 4a–4c (M1–M3) and $\lambda_{max,PL} \sim 417$ nm (in DMF) with quantum yields ($\Phi$) of 34–53% for metallo-polymers P1–P4. The enhancement of the quantum yields in metallo-polymer was attributed to the polymerization procedure and similar results were reported in literature [9,11,12]. Nevertheless, PL emissions from the OXD pendants were not observed, even when metallo-polymers were excited at the absorption peaks of the OXD pendants. This indicates the existence of efficient energy transfer from the OXD pendants to the polymer backbones [26]. Comparing PL quantum yields of metallo-copolymers P2–P4 with the same molar ratio (50%) of OXD pendants, the order of PL quantum yields (in solutions) is P2 > P4 > P3, which is reverse to the order of the molar ratio of CAZ pendants in metallo-polymers P2–P4, i.e. P2 (0% CAZ) < P4 (25% CAZ) < P3 (50% CAZ). It suggests that of the metallo-polymers containing M2 (with alkyl pendants) have larger PL quantum yields than those containing M3 (with CAZ pendants). This behavior fits well with the PL quantum yield (53%) of metallo-homopolymer P1 containing M1 (with OXD pendants) being larger than that (23%) [11] of metallo-homopolymer containing M2 (with alkyl pendants), and also larger than that (11%) [11] of metallo-homopolymer containing M3 (with CAZ pendants). Overall, in contrast to metallo-polymers containing alkyl pendants, the quantum yields were greatly enhanced by introducing 1,3,4-OXD pendants but reduced by carbazole (CAZ) pendants. Hence, PL quantum yields of metallo-polymers were truly affected by incorporating different monomer ligands into main-chain polymeric structures.

Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{abs, sol}$ (nm)$^a$</th>
<th>$\lambda_{max, PL, sol}$ ($\Phi_{PL, sol}$) (nm)$^{b,c}$</th>
<th>$\lambda_{abs, film}$ (nm)</th>
<th>$\lambda_{max, PL, film}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a (M1)</td>
<td>292, 363, 378</td>
<td>414/0.33</td>
<td>298, 298, 337, 399</td>
<td>416/0.35 (401)</td>
</tr>
<tr>
<td>4b (M2)</td>
<td>285, 319, 363, 373</td>
<td>415/0.20</td>
<td>299, 354, 413</td>
<td>502</td>
</tr>
<tr>
<td>4c (M3)</td>
<td>287, 294, 319, 347, 364, 374</td>
<td>414/0.25</td>
<td>283, 354, 408</td>
<td>502 (472, 533)</td>
</tr>
<tr>
<td>P1</td>
<td>288, 327, 361, 377</td>
<td>418/0.53</td>
<td>289, 354, 413</td>
<td>500</td>
</tr>
<tr>
<td>P2</td>
<td>287, 317, 361, 378</td>
<td>416/0.51</td>
<td>297, 353, 410</td>
<td>502</td>
</tr>
<tr>
<td>P3</td>
<td>287, 294, 316, 348, 361, 377</td>
<td>416/0.34</td>
<td>297, 353, 410</td>
<td>502</td>
</tr>
<tr>
<td>P4</td>
<td>288, 295, 316, 348, 361, 378</td>
<td>416/0.35 (401)</td>
<td>297, 353, 410</td>
<td>502 (473)</td>
</tr>
</tbody>
</table>

$^a$ Concentration of $1 \times 10^{-6}$ M in DMF.

$^b$ Coumarin-1 in ethanol (ca. $5 \times 10^{-6}$ M, quantum yield = 0.73) used as a reference to determine the quantum yields of PL in solutions.

$^c$ The PL emission shoulders are shown in the parentheses.
Fig. 7. Normalized PL spectra of metallo-polymers P1–P4 in solutions and solid films.

Regarding solid films of these metallo-polymers, they emitted blue to green colors with PL values of $\lambda_{\text{max, PL}}$ in the range 509–520 nm (Fig. 7). According to PL emissions of polymer films, all polymers showed large Stokes shifts (ca. 83–104 nm) in contrast to their PL emissions in solutions, which were attributed to the excimer formation resulting from $\pi$–$\pi$ stacking of aromatic interaction in solid films [40,41]. When the bulky pedants (i.e. CAZ) were attached to the C-9 position of fluorene units, they were able to suppress the excimer formation as shown in our previous result [9]. However, metallo-copolymers P3 and P4 only showed small shoulders around 472 nm (see Fig. 7), which correspond to the emissions of polymer backbones, and metallo-polymers P1 and P2 even with dominant excimer emissions around 500 nm. Nevertheless, compared with our previous result of metallo-homopolymers containing CAZ pendants, OXD pendants in all metallo-polymers P1–P4 did not suppress the excimer formation efficiently, which might be due to more flexible pendant configurations (with lower $T_g$ values) of metallo-polymers containing 1,3,4-OXD pendants in comparison with those containing CAZ pedants.

3.7. Electroluminescence (EL) properties

Two device configurations were applied in the EL measurements, where the metallo-polymers were used as an emission layer and PEDOT:PSS was utilized as a hole-transporting layer. Either TPBI or BCP/ALQ was used as a hole-transporting layer, and the results are separately discussed as follows:

(a) ITO/PEDOT:PSS/polymer(P1–P2)/TPBI/LiF/Al devices. Good photoluminescence properties exhibited by solutions of metallo-polymers P1 and P2 suggest both polymers are suitable candidates for fabrication of PLED devices, and devices with configurations of ITO/PEDOT:PSS (40–55 nm)/polymer(P1–P2) (50–65 nm)/TPBI (40 nm)/LiF (1 nm)/Al (150 nm) were fabricated. Fig. 8 shows normalized EL spectra of metallo-polymers P1 and P2, and an emission band around 570 nm and a small shoulder around 400 nm originated from TPBI emissions were observed [42,43]. It is worthy of noting that the EL spectra of PLED devices do not resemble their corresponding PL spectra in solid films (as shown in Fig. 7). This is presumably due to the EL and PL emissions originating from different excited states and/or ground states [11,44]. In comparison with the HOMO values of polymers P1 (−6.26 eV) and P2 (−6.20 eV), TPBI (−6.20 eV) layer could not block holes from emitters sufficiently for polymers P1 and P2 in the PLED devices [42,43], so they exhibited very similar results to each other. Hence, no further investigation has been done in the other TPBI-based PLED devices regarding polymers P3 and P4.

(b) ITO/PEDOT:PSS/polymer/BCP/ALQ/LiF/Al devices. Green EL emissions were obtained for all metallo-polymers with configurations of ITO/PEDOT:PSS (40–55 nm)/polymer(P1–P4) (50–65 nm)/BCP (10 nm)/ALQ (30 nm)/LiF (1 nm)/Al (150 nm), and the electroluminescence properties are listed in Table 3. Fig. 9 illustrates the normalization EL spectra of metallo-polymers P1–P4 with emission bands around 550 nm. Similarly, the EL spectra of BCP/ALQ devices do not resemble their corresponding PL spectra in solid films due to the same reason as explained in the TPBI-based PLED devices. At a bias voltage of 10 V, all PLED devices in Fig. 9 show green emissions with $\lambda_{\text{max, EL}}$ values around 550 nm and their EL intensities were enhanced by increasing the bias voltages. The turn-on voltages of all PLED devices based on BCP/ALQ were approximately 6.0–6.5 V. The power efficiency and maximum luminance of PLED devices for all polymers were ranged from 1.05 to 1.35 cd A$^{-1}$ (at 100 mA/cm$^2$) and 2313–3550 cd/m$^2$ (at 14–15 V), respectively. The current density–voltage ($I–V$) and luminance–voltage ($L–V$) characteristic curves of PLED devices containing metallo-polymers P1–P4 are shown in Figs. 10 and 11, and similar turn-on voltages for both current density and luminance demonstrate that a matched balance of both injection and transportation
in charges were achieved [26], which were much improved in contrast to TPBI-based PLED devices. The BCP layer (HOMO = −6.70 eV, LUMO = −3.20 eV) can offer a large hole barrier between BCP and the emitter but shows no influence on electron-transporting behavior of ALQ (HOMO = −6.00 eV, LUMO = −3.30 eV) [45]. As shown in Fig. 11, it indicates that no ALQ emission band was observed. The EL spectra of BCP/ALQ-based devices (polymers P1 and P2) revealed less Stocke shifts (ca. 20 nm) than those of TPBI-based devices. The different timing for the charge arriving at the emitter region may be related to different electron mobilities for these two transporting materials [43,45,46]. From this result, it can be concluded that the incorporation of electron-transporting (OXD) or hole-transporting (CAZ) pendants into polymer backbones can improve the EL performance of the PLED devices [47].

4. Conclusions

In summary, a series of novel poly(fluorene/ethynylene/(terpyridyl)zinc(II))-based metallo-polymers containing 1,3,4-OXD pendants were obtained by different stoichiometric ratios of complexes. Furthermore, the thermal, photophysical, and electroluminescence properties are greatly affected by the nature of the pendant groups in the C-9 position of fluorene via long alkyl spacers. The incorporation of various pendants into polymer backbones will change the rigidities and the thermal stability (as well as the $T_d$ and $T_v$ values) of the metallo-polymers. In comparison with metallo-polymers containing alkyl pendants, the quantum yields were greatly enhanced by introducing 1,3,4-OXD pendants but reduced by carbazole (CAZ) pendants. The enhancement of PL quantum yields by the introduction of 1,3,4-OXD pendants into metallo-polymers is due to the energy transfer happened between pendants and polymer backbones. By utilization of these metallo-polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max}, \text{EL}}$ (nm)</th>
<th>$V_{\text{on}}$ (V)$^b$</th>
<th>Max. luminescence (cd/m$^2$) (V)</th>
<th>Power efficiency (cd A$^{-1}$)$^c$</th>
<th>CIE coordinates (x and y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>549</td>
<td>6.5</td>
<td>2913 (14.5)</td>
<td>1.12</td>
<td>(0.41, 0.52)</td>
</tr>
<tr>
<td>P2</td>
<td>549</td>
<td>6.5</td>
<td>3550 (15)</td>
<td>1.35</td>
<td>(0.41, 0.52)</td>
</tr>
<tr>
<td>P3</td>
<td>551</td>
<td>6.0</td>
<td>3220 (15)</td>
<td>1.25</td>
<td>(0.41, 0.55)</td>
</tr>
<tr>
<td>P4</td>
<td>550</td>
<td>6.5</td>
<td>2313 (14.5)</td>
<td>1.05</td>
<td>(0.41, 0.52)</td>
</tr>
</tbody>
</table>

$^a$ Device structure: ITO/PEDOT:PSS/polymer (P1–P4)/BCP/ALQ/LiF/Al, where the metallo-polymer (P1–P4) is an emitting layer.

$^b$ $V_{\text{on}}$ is the turn-on voltage.

$^c$ Power efficiencies were obtained at 100 mA/cm$^2$. 

![Normalized EL spectra of PLED devices with configurations of ITO/PEDOT:PSS/polymer (P1–P4)/BCP/ALQ/LiF/Al at 10 V.](image1)

![Current density–voltage (I–V) curves of PLED devices with configurations of ITO/PEDOT:PSS/polymer (P1–P4)/BCP/ALQ/LiF/Al.](image2)

![Electroluminescence (EL) properties of PLED devices containing a layer of emitting metallo-polymers P1–P4.](image3)
as emitting materials to fabricate PLED devices, green EL emissions and high EL performance can be obtained in the double-heterojunction device structures with PEDOT as the hole-transporting material and either TPBI or BCP/ALQ as the electron-transporting material.

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References