PAPER

Synthesis and properties of Zn^{2+}/Cd^{2+}-directed self-assembled metallo-supramolecular polymers based on 1,4-diketo-pyrrolo[3,4-c]pyrrole (DPP) derivatives

Xuegang Chen,* Kai Guo, Fanchao Li, Li Zhou and Hongbin Qiao

New building blocks based on 1,4-diketopyrrolo[3,4-c]pyrrole (DPP), 2,5-bis(2-ethylhexyl)-3,6-bis(5-[p-(2,2':6',2''-terpyridine-4'-yl) phenyl]thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**M1**) and 2,5-bis(2-ethylhexyl)-3,6-bis(4-[p-(2,2':6',2''-terpyridine-4'-yl) phenyl]phenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**M2**) were synthesized by the Suzuki Pd-catalyzed cross-coupling reaction. Under moderate conditions, directed self-assembly polymerizations by the transition metal ions Zn^{2+} and Cd^{2+}, respectively, were carried out. The metallo-supramolecular polymers **P1Zn**, **P1Cd**, **P2Zn** and **P2Cd** were obtained and fully characterized. The supramolecular polymers **P2Zn** and **P2Cd**, containing DPP modified by a phenyl unit, showed absorption maxima at about 504 and 506 nm in films. In contrast, the polymers **P1Zn** and **P1Cd**, in which the thiophene moiety-modified DPP was introduced, exhibited strong and broad visible absorption over 300–800 nm with maxima at about 601 and 598 nm and shoulder peaks at about 665 and 671 nm, respectively. The low band gaps estimated from CV of 1.52, 1.51, 1.58 and 1.58 eV for **P1Zn**, **P1Cd**, **P2Zn** and **P2Cd**, respectively, are also reported.

1 Introduction

There has been much interest in the development of conjugated polymers for their various applications, such as in light-emitting devices, organic field effect transistors and photovoltaic devices.[1,2] Recently, high performance pigments, such as diketopyrrolopyrroles (DPPs),[3–5] quinacridones,[6] benzodifuranones,[7] benzodipyrrolidones[8] and others,[9] were incorporated into the main chain of conjugated polymers to obtain promising fascinating properties. Among the compounds, diketopyrrolopyrroles (DPPs) are a class of commercial and easily synthesized dyes with exceptional photochemical, mechanical and thermal stabilites.[3–5] Because of its strong fluorescence performance, absorption in the visible region, strong electron withdrawing properties and exceptional stability, the diketopyrrolopyrrole (DPP) unit is expected to be a promising building block for low band gap with other electron-donating moieties.[10–12] Small molecules and polymers based on diketopyrrolopyrrole (DPP) have now gained much attention for their promising applications in organic thin-film transistors (OTFTs),[13,14] organic solar cells (OSCs) or polymer solar cells (PSCs).[15–19]

In the past two decades, the supramolecular chemistry and architectures, which are obtained *via* self-assembly of designed building blocks, have made rapid and significant progress.[20,21] Among this filed, the supramolecular polymers (SP), in which the monomeric units that are brought assembly together by non-covalent interactions such as hydrogen bonding, metal coordination, electrostatic interactions, hydrophobic interactions and π–π (or arene–arene) interactions, play a vital role in modern supramolecular chemistry and many novel and interesting structures and systems with fascinating properties are designed and synthesized.[22,23] The metallo-supramolecular polymers, based on the metal-ligand coordination, have attracted much interest for their easy tuning of photophysical properties resulting from their varying metal–ligand combination.[24] Polypyridyl compounds have ring nitrogen atoms serving as the multiple interaction sites, and form the stable coordination complexes with various metal ions.[25–27] Among the best studied complexes, Ru(II)(bpy)$_3$ (bpy = 2,2'-bipyridine) is the most popular.[28–30] The focus of rapid development of supramolecular chemistry, however, has shifted onto the metal–ligand interaction chemistry and materials based on 2,2':6',2''-terpyridine (tpy) due to this tridentate ligand offers more strong binding strength, prevention of Δ/Λ-chirality and synthetic advantages than the bidentate bpy (2,2'-bypyridine).[31–35] Many supramolecular polymers containing terpyridine-based complexes were reported presently.[36–43] Würthner reported zinc(II)-directed polymerization of highly fluorescent perylene

Key Laboratory of Rubber-Plastic of Ministry of Education (QUST), School of Polymer Science and Engineering, Qingdao University of Science and Technology, 53 Zhengzhou Road, Qingdao 266042, China. E-mail: xgchen@qust.edu.cn

bisimide dye connected to bis(terpyridyl) and their optical properties.[40] Che and coworkers have synthesized a new class of Zn-terpyridyl based polymer *via* self-assembly reactions, which are promising light-emitting materials for polymer light-emitting diodes (PLEDs).[41] Schubert introduced electron-rich units and electron-withdraw units into bis(terpyridine) building block as the spacers to form metallo-supramolecular polymers.[42] We reported a series of supramolecular polymers prepared *via* cadmium(II) ion directed self-assembled polymerization of bis(2,2′:6′,2″-terpyridine)-based ligand monomers where oligofluorenes was introduced as spacers and electron-rich triphenylamine was introduced into the backbone of the supramolecular polymers in order to further tune the emission color.[43]

With the above considerations in mind, the combination of DPP and terpyridine units are expected to provide the promising novel supramolecular polymers with fascinating properties such as physical properties and electrochemical properties. Through molecular design, the molecular orbital can be tuned, as well as the performances. To the best of our knowledge, there have been no examples of introducing high performance pigment DPP into the backbones of supramolecular polymers *via* the coordination chemistry bonds of 2,2′:6′,2″-terpyridine and transition metals. Therefore, in this paper, two novel building block monomers, 2,5-bis(2-ethylhexyl)-3,6-bis(5-[*p*-(2,2′:6′,2″-terpyridine-4′-yl) phenyl]thiophen-2-yl)pyrrolo[3,4-*c*]-pyrrole-1,4(2*H*,5*H*)-dione (**M1**) and 2,5-bis(2-ethylhexyl)-3,6-bis(4-[*p*-(2,2′:6′,2″-terpyridine-4′-yl) phenyl]phenyl)pyrrolo[3,4-*c*]-pyrrole-1,4(2*H*,5*H*)-dione (**M2**), were designed and synthesized (Scheme 1). Then directed by transition ion zinc(II) and cadmium(II) ion, the building blocks were self-assembly polymerized to form the corresponding metallo-supramolecular polymers **P1Zn**, **P2Zn**, **P1Cd** and **P2Cd** (Scheme 2). The thermal stability, optical absorption, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the obtained polymers were studied systematically.

2 Experimental section

2.1 Materials

Reagents. All starting organic compounds were commercially purchased and used without further purification. The reaction solvents were distilled prior to use. The compounds 3,6-bis(4-bromophenyl)-pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**4**) and 2,5-bis(2-ethylhexyl)-3,6-bis (4-bromophenyl)pyrrolo[3,4-*c*] pyrrole-1,4(2*H*,5*H*)-dione (**5**) were prepared as the similar procedure described in publications.[44] 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**3**) was synthesized as literature.[45] The important intermediate 4′-(4-pinacolatoboronphenyl)-2,2′:6′,2″-terpyridine (**6**) was synthesized according to reported method.[46] All other compounds were synthesized following the procedures described below.

2,5-Dihydro-3,6-bis(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (1). Metallic sodium (1.73 g, 75 mmol) and ferric chloride were dissolved in 2-methyl-2-butanol (30 ml) and heated at 90 °C for 2 hours, then cooled to 50 °C and 2-

thiophenecarbonitrile (3 g, 27.5 mmol) was added. While the mixture was heated to 90 °C again, diisopropyl succinate (3.03 g, 15 mmol) in 2-methyl-2-butanol (5 ml) was added to the system dropwise and heated at 90 °C for 20 hours. The reaction system was cooled down to 50 °C, then acetic acid was added to the mixture and refluxed for 10 minutes, the precipitate was filtered off. The precipitate was washed with water and methanol, and dried *in vacuo* to yield a red solid (2.56 g, 62.0%). ^{1}H NMR (500 MHz, DMSO-d6, ppm): 11.25 (s, 2H), 8.21 (s, 2H), 7.95 (d, $J = 4.5$ Hz, 2H), 7.29 (t, $J = 7.5$ Hz, 2H).

2,5-(2-Ethylhexyl)-3,6-bis(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrolo-1,4(2*H*,5*H*)-dione (2). Compound (**1**) (3.0 g, 10.0 mmol) was dissolved in anhydrous DMF (100 ml), potassium carbonate (5.52 g, 40.0 mmol) was added to the solution under nitrogen atmosphere, then the mixture was heated to 120 °C and kept for 1.5 hours. 2-Ethylhexyl bromide (4.83 g, 25 mmol) was added to the system *via* a syringe. After heated to 130 °C and kept for 24 hours, the resulting mixture was cooled down to room temperature, extracted with dichloromethane, washed with distilled water, and dried over anhydrous Na_2SO_4. After the solvent was removed, the crude product was purified on silica gel with hexane–dichloromethane = 1 : 1 as the eluent. A purple brown powder was obtained (3.72 g, yield 70.9%). ^{1}H NMR (500 MHz, CDCl3, ppm): 8.91 (d, $J = 4.0$ Hz, 2H), 7.64 (d, $J = 5.0$ Hz, 2H), 7.29 (t, $J = 5.0$ Hz, 2H), 4.04 (m, 4H), 1.87–0.87 (m, 30H).

2,5-Bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (3). *N*-Bromosuccinimide (0.23 g, 1.68 mmol) was added to the solution of compound (**2**) (0.40 g, 0.71 mmol) in dichloromethane (20 ml). After stirred for 24 hours at room temperature, the resulting mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After the solvent was removed, the crude product was purified on silica gel with hexane–dichloromethane = 1 : 1 as the eluent. A dark purple solid was obtained (0.32 g, 61.7%). ^{1}H NMR (500 MHz, CDCl3, ppm): 8.67 (d, $J = 4.5$ Hz, 2H), 7.24 (d, $J = 4.0$ Hz, 2H), 3.94 (m, 4H), 1.37–0.87 (m, 30H).

2,5-Bis(2-ethylhexyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]-pyrrole-1,4(2*H*,5*H*)-dione (5). 3,6-Bis(4-bromophenyl)-pyrrolo [3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**4**) (1.11 g, 2.5 mmol) and potassium *tert*-butylate (0.62 g, 5.5 mmol) were dissolved in dry NMP (20 ml), then heated to 60 °C. After 1.5 hours, 2-ethylhexyl bromide (2.67 ml 15 mmol) was added to the system dropwise, and the reaction system was kept at 60 °C for another 24 hours. After cooled down to room temperature, the mixture was poured into dichloromethane and washed with water, then dried over anhydrous Na_2SO_4. After the solvent was removed, the crude product was purified on silica gel with hexane–dichloromethane = 2 : 1 as the eluent. A light yellow solid was obtained (1.13 g, yield 67.7%). ^{1}H NMR (500 MHz, CDCl3, ppm): 7.65 (m, 8H), 3.71 (m, 4H), 1.55–0.67 (m, 30H).

2,5-Bis(2-ethylhexyl)-3,6-bis(5-[*p*-(2,2′:6′,2″-terpyridine-4′-yl) phenyl]thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (M1). Compound (**3**) (0.2 g, 0.3 mmol) and 4′-(*p*-pinacolatoboronylphenyl)-2,2′:6′,2″-terpyridine (0.288 g, 0.66 mmol) were added to dry THF (40 ml), then sodium carbonate in water (2 M, 5 ml)
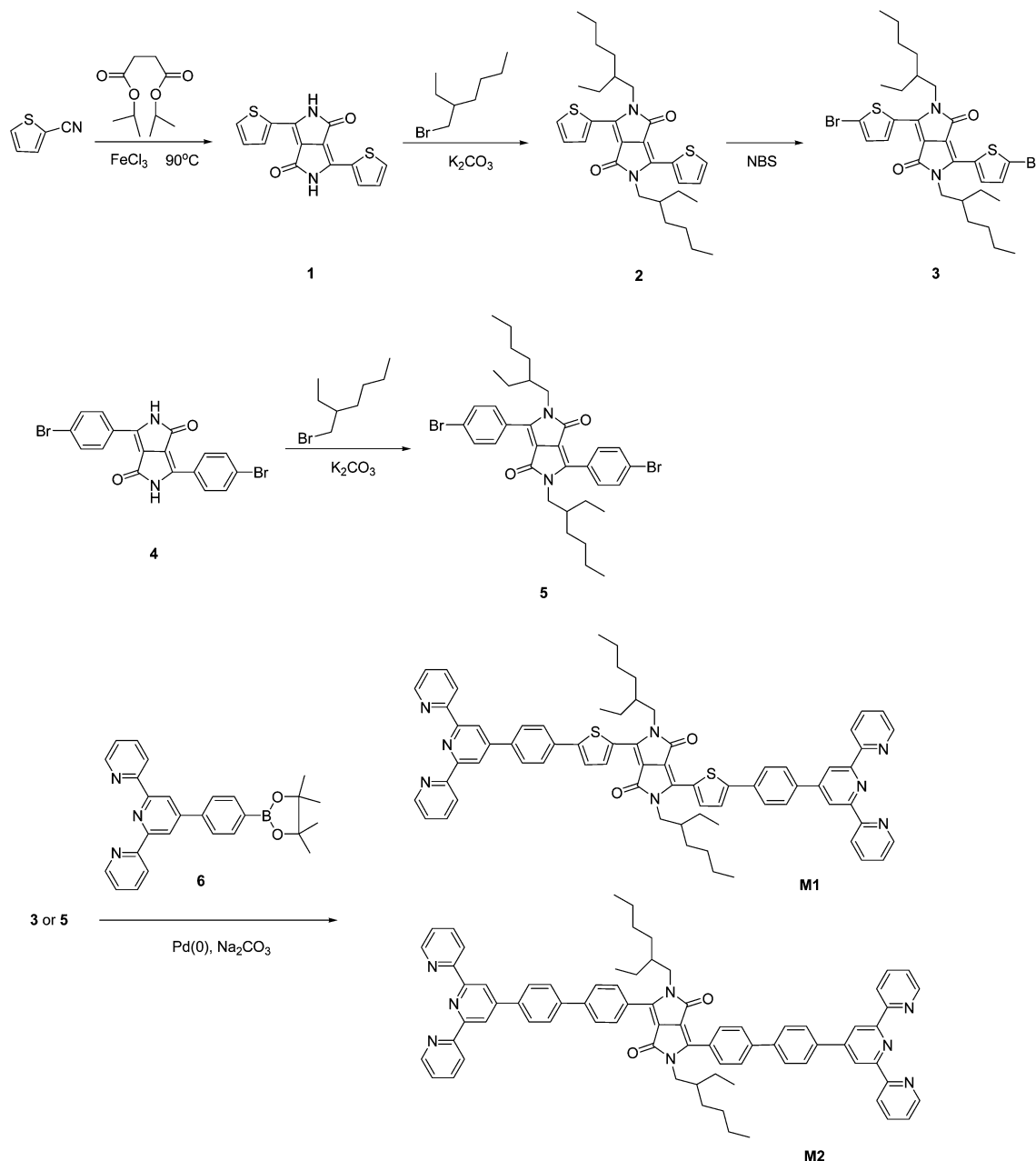
Scheme 1 Synthesis of building block monomers **M1** and **M2**.

was added to the system dropwise under nitrogen atmosphere within 30 minutes. To the resulting mixture was added Pd(PPh$_3$)$_4$ (0.017 g, 0.015 mmol) and refluxed for 30 hours. Then the mixture was cooled to room temperature and extracted with dichloromethane, the organic layer was washed with water and dried over anhydrous Na$_2$SO$_4$. After the solvent was removed, the crude product was purified on silica gel with hexane–chloroform = 1 : 1 as the eluent. A dark purple solid was obtained (0.221 g, yield 64.6%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): 9.03 (d, J = 4.5 Hz, 2H), 8.76 (m, 8H), 8.68 (d, J = 8.0 Hz, 4H), 7.97 (d, J = 8.0 Hz, 4H), 7.91 (t, J = 8.5 Hz, 4H), 7.79 (d, J = 8.0 Hz, 4H), 7.56 (d, J = 4.0 Hz, 2H), 7.38 (t, J = 6.0 Hz, 4H), 4.11 (m, 4H), 1.45–0.89 (m, 30H). ^{13}C NMR (500 MHz, CDCl$_3$, ppm): 159.21, 153.69, 153.60, 146.65, 146.29,

137.28, 136.16, 134.36, 131.28, 126.80, 125.48, 123.95, 122.39, 121.35, 118.88, 115.99, 105.96, 74.73, 74.48, 74.22, 43.57, 36.89, 27.96, 26.11, 21.30, 20.61, 14.00. Anal. calc. for C$_{72}$H$_{66}$N$_8$O$_2$S$_2$: C, 75.89; H, 5.84; N, 9.83. Found: C, 76.32; H, 5.73; N, 9.96.

2,5-Bis(2-ethylhexyl)-3,6-bis(4-[*p*-(2,2′:6′,2″-terpyridine-4′-yl) phenyl]phenyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (M2). Following the same procedure as **M1**, **M2** was prepared from compound (**5**) and a deep red solid was obtained (0.435 g, yield 71.4%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): 8.80 (s, 4H), 8.75 (d, J = 4.0 Hz, 4H), 8.68 (d, J = 8.0 Hz, 4H), 8.05 (d, J = 8.0 Hz, 4H), 7.93 (d, J = 8.0 Hz, 4H), 7.90 (t, J = 7.5 Hz, 4H), 7.82 (d, J = 8.5 Hz, 4H), 7.80 (d, J = 8.5 Hz, 4H), 7.38 (t, J = 6.0 Hz, 4H), 3.85 (m, 4H), 1.45–0.89 (m, 30H). ^{13}C NMR (500 MHz, CDCl$_3$, ppm):
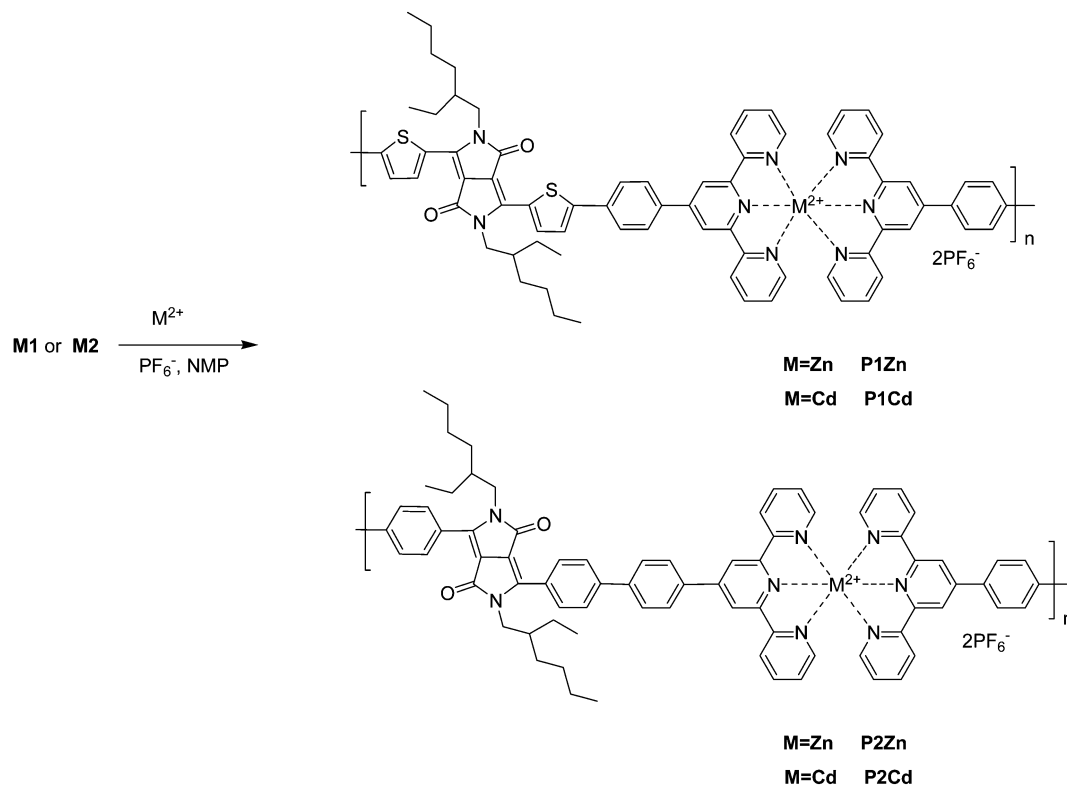
Scheme 2 Synthesis of metallo-supramolecular polymers directed by transition metal ions.

167.33, 160.56, 153.76, 145.06, 142.57, 141.52, 134.19, 132.45, 132.24, 131.74, 128.56, 125.91, 123.02, 82.88, 82.63, 82.40, 45.24, 45.08, 44.92, 44.75, 44.59, 44.43, 43.19, 35.16, 33.05, 28.66, 27.53, 18.71, 15.27. Anal. calc. for $C_{76}H_{70}N_8O_2$: C, 80.96; H, 6.26; N, 9.94. Found: C, 80.18; H, 6.15; N, 10.06.

Preparation of zinc-directed and cadmium-directed supramolecular polymers. The transition metal ion-directed polymerization of building blocks **M1** and **M2** was carried out using similar methods. A typical synthesis procedure can be described for the preparation of polymer **P1Zn**. To a monomer **M1** (0.05 g, 0.044 mmol) in NMP (10 ml) was added $Zn(OAc)_2 \cdot 2H_2O$ (0.0096 g, 0.044 mmol), then the reaction system was heated to 105 °C and kept for 20 hours. After reaction, a saturated methanol solution of KPF_6 (0.04 g, 0.22 mmol) was added to the system and stirred for another 0.5 hour. The resulting mixture was pour into methanol (100 ml), and the residue was filtered off and washed with methanol. A deep dark red solid was obtained (0.046 g, yield 87.1%).

2.2 Methods

^{1}H NMR/^{13}C NMR spectra were recorded using a Bruker AV500 in deuterated chloroform or dimethyl sulfoxide solution at 298 K, with tetramethylsilane (TMS) as the internal standard. And chemical shifts are quoted in ppm relative to the solvent residual peak, with peak multiplicity (bs, broad singlet; s, singlet; d, doublet; t, triplet), integration, and coupling constants (J) quoted in Hz (uncorrected) as appropriate. Inherent viscosities were measured in NMP at 30 °C using a

Ubbelohde viscometer. Elemental analysis was performed with a VarioEL analysis system. The thermal behaviors were monitored with a Universal V2.6 TA instrument under a nitrogen atmosphere with the heating rate of 10 °C min^{-1}. The optical properties of the supramolecular polymers were investigated using UV-vis absorption via F-4600 Hitachi UV-vis spectrometer. Cyclic voltammetry (CV) measurements were carried out using a Autolab PGSTAT204 analyzer equipped with a three-electrode system, in which a Pt electrode, a Pt wire coil and an Ag/AgCl electrode were used as working electrode, auxiliary electrode and reference electrode, respectively. Voltammograms were recorded using CH_2Cl_2 solutions with 0.1 mol L^{-1} of tetrabutylammonium hexafluorophosphate as the supporting electrolyte, at a scan rate of 0.1 V s^{-1}. Column chromatography was carried out on silica (silica gel 80–120 mesh).

3 Results and discussion

3.1 Synthesis and characterization of monomers and supramolecular polymers

The preparation of building blocks 2,5-bis(2-ethylhexyl)-3,6-bis(5-[p-(2,2′:6′,2″-terpyridine-4′-yl)phenyl]thiophen-2-yl)pyrrolo-[3,4-c]pyrrole-1,4(2H,5H)-dione (**M1**) and 2,5-bis(2-ethylhexyl)-3,6-bis(4-[p-(2,2′:6′,2″-terpyridine-4′-yl)phenyl]phenyl)pyrrolo-[3,4-c]pyrrole-1,4(2H,5H)-dione (**M2**) and supramolecular polymers **P1Zn**, **P1Cd**, **P2Zn** and **P2Cd** is outlined in Scheme 1 and Scheme 2. The alkylation reaction was realized by treating 1,4-diketo-3,6-bis(4-bromophenyl)-pyrrolo[3,4-c]pyrrole (**4**) with

alkyl bromide in the presence of potassium carbonate to give 1,4-diketo-2,5-(2-ethylhexyl)-3,6-bis (4-bromo-phenyl)pyrrolo [3,4-c]pyrrole (**5**). The introducing of 2-ethylhexyl group at the 2,5-positions of the DPP moiety resulted into the improved

solubility. 1,4-diketo-2,5-(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole (**3**) was synthesized in multistep procedures as literature.[45] From compounds thiophene-2-carbonitrile and dibutyl succinate in *tert*-amyl alcohol catalyzed by FeCl$_3$, 1,4-
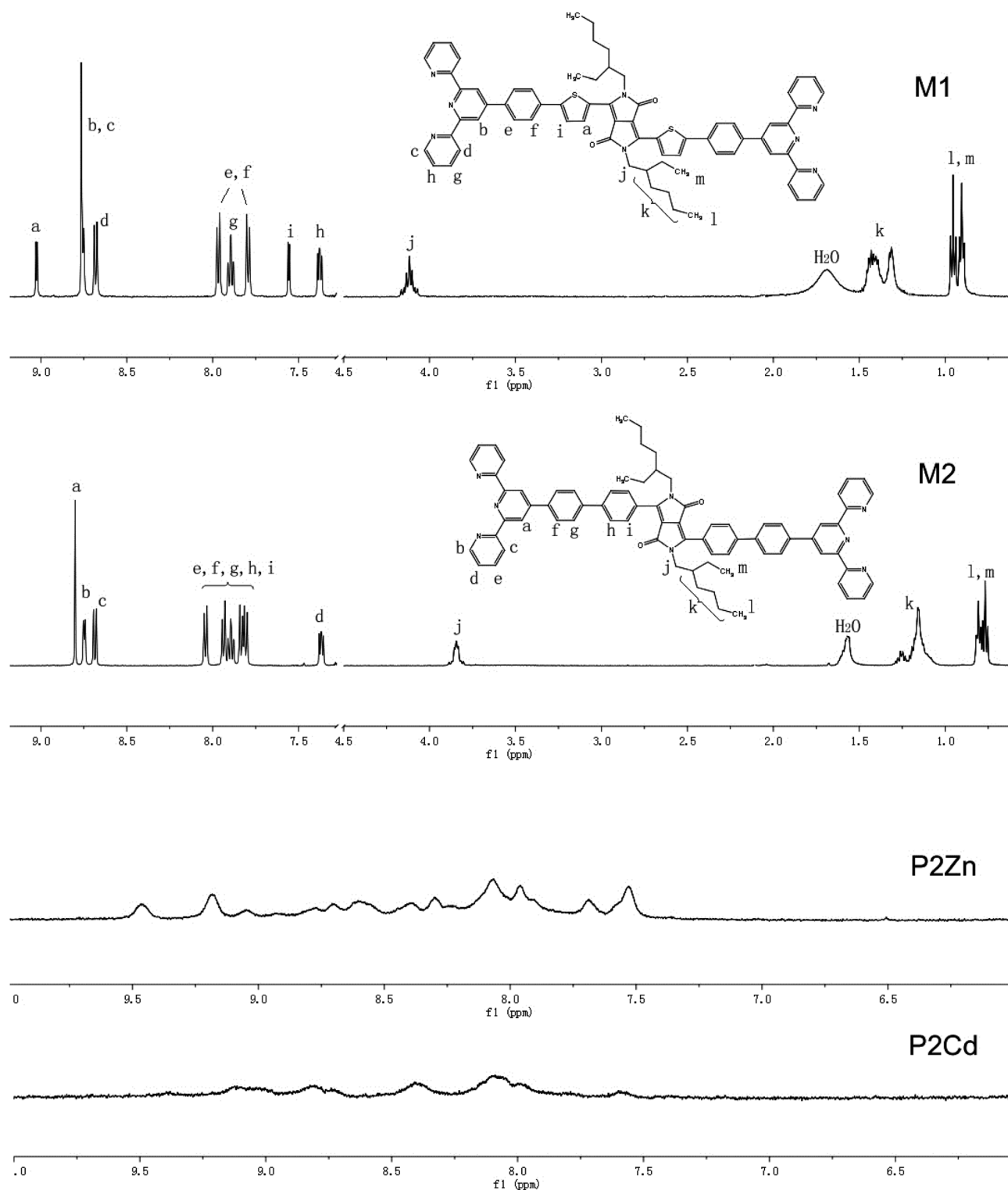
Fig. 1 ^{1}H-NMR spectra (500 MHz) of monomers **M1** and **M2** in chloroform-d and supramolecular polymers **P2Zn** and **P2Cd** in DMSO-d$_6$ at 298 K.

diketo-3,6-di(thiophen-2-yl)pyrrolo[3,4-c] pyrrole (**1**) was obtained. And with the similar procedure as the synthesis of compound (**5**), after the introduction of alkyl group 2-ethylhexyl group by alkylation and subsequent bromination with NBS in chloroform, the most important intermediate brominated compound 1,4-diketo-2,5-(2-ethylhexyl)-3,6-di(thiophen-2-yl) pyrrolo[3,4-c]pyrrole (**3**) was obtained. As outlined in Scheme 1, monomers **M1** and **M2** were synthesized by the means of palladium-catalyzed Suzuki reaction. The boronate ester-substituted terpyridine ligand, 4′-(4-pinacolatoboronphenyl)-2,2′:6′,2″-terpyridine (**6**), was prepared according to literature procedure.[46] The palladium catalyzed Suzuki–Miyaura cross-coupling reactions used have the advantages that competitive homo-coupling of the aryl halide is usually minimal.[47] Condensation of (**3**) and (**5**) with two equivalents of 4′-(4-pina-colatoboronphenyl)-2,2′:6′,2″-terpyridine (**6**) afforded **M1** and **M2** after column chromatographic purification in moderate yields. The bis(2,2′:6′,2″-terpyridine) based building blocks **M1** and **M2** containing DPP moiety were easily soluble in common organic solvents such as chloroform and their structures were determined by means of ^{1}H NMR, ^{13}C NMR, elemental analysis. As depicted in Fig. 1, the **M1** and **M2** displayed all expected resonances without discernible peaks corresponding to impurities. For both monomers, the chemical shifts located on about 8.6–8.8 ppm where one singlet signal and two double signals can be ascribed to the typical resonances signal of protons H3′, H5′, H3, H5, H3″, H6″ for 2,2′:6′,2″-terpyridine. The other two protons H4 and H5 showed two triplet signals were found at about 7.4 and 7.9 ppm, respectively.[48] For **M1**, the double signal at 9.01 ppm originates from one proton of thiophene moiety. The signal with a chemical shift at about 4.0 ppm for **M1** and **M2** was from the protons of –CH2– attached N position of DPP core directly. And the other protons of alkyl groups can be found at about 0.8–1.5 ppm.

Modifying DPP with tridentate moieties 2,2′:6′,2″-terpyridine endue the building blocks **M1** and **M2** the abilities to self-assembly polymerization to form supramolecular polymers with directing action of zinc(II) and cadmium(II) ions (Scheme 2). In NMP solution, the monomers and one mole equivalent zinc(II) or cadmium(II) ion were stirred at 105 °C for about 24 hours, followed by subsequent anion exchange with potassium hexafluorophosphate to give corresponding metallo-supramolecular polymers **P1Zn**, **P1Cd**, **P2Zn** and **P2Cd** in good yield. Obviously, unlike the procedure widely used to synthesize conjugated polymers such as Yamamoto, Wittig and Heck coupling reaction, the self-assembly polymerization can be performed in mild condition. Self-assembly polymerization was confirmed by comparing the ^{1}H NMR spectra of monomers and polymers. As depicted in Fig. 1, polymerization of monomers led most resonances of the terpyridine moiety shift downfield and the spectra signals of the polymers became more broad compared with that of the monomers.[40–42,48] Additionally, there was no exclusive chemical shift characteristic of free monomers in the ^{1}H NMR spectra of the polymers, revealing that coordination polymerization was complete. Furthermore, the polymerization degree of the resulting supramolecular polymers were estimated by studying their inherent viscosities

in NMP solution using a Ubbelohde viscometer and the inherent viscosity ranged from 0.89 to 1.35 dL g^{-1} at 30 °C (Table 1). Moreover, all of the polymers displayed good thermal stabilities and the decomposition temperatures of the polymers exceeded 400 °C.

3.2 Optical properties

Fig. 2 showed the UV-vis absorption spectra of the DPP-based supramolecular polymers in solution and in thin films. All the polymers had the low band gaps with absorption maxima between 500 and 700 nm (Table 2). As a strong electron-withdrawing moiety, DPP has been coupled with a variety of electron-rich groups to provide low band gap polymers and small molecules.[49] Polymers **P2Zn** and **P2Cd**, in which the DPP unit was coupled with phenyl, exhibited the absorption band at 498 and 490 nm, respectively, in chloroform solution due to the characteristic electronic neutrality of phenyl moiety. When the phenyl was replaced by thiophene, the thiophene-modified DPP-based polymers **P1Zn** and **P1Cd** were obtained. As depicted in Fig. 2, their lowest energy absorption bands were observed with the maxima at 586 and 588 nm which were about 88 and 98 nm red-shifts compared with **P2Zn** and **P2Cd**, respectively. Obviously, due to the electron deficient nature of the DPP unit, coupling with electron-donating thiophene moiety resulted in the strong electron donor–acceptor structures in the backbone of supramolecular polymers, and subsequently the longer wavelength absorption. Furthermore, the onset of the absorptions of the polymers red-shifted in a certain

Table 1 The physical properties of metallo-supramolecular polymers

Polymers	$\eta_{in}h^a$ (dL g^{-1})	Yield (%)	T_d (°C)
P1Zn	1.18	87	431
P1Cd	0.89	82	419
P2Zn	1.35	85	412
P2Cd	1.05	78	427

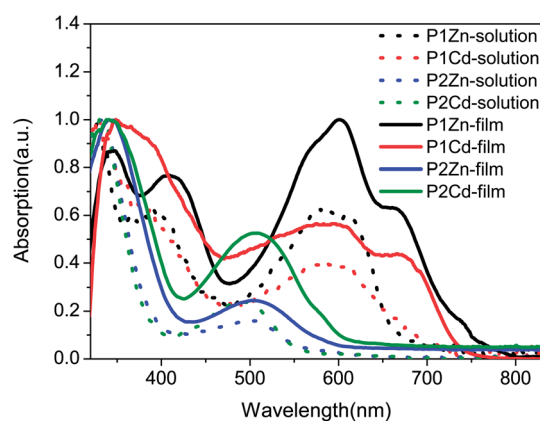^{a} Inherent viscosity measured in NMP at 30 °C using a Ubbelohde viscometer.

Fig. 2 UV-vis absorption of supramolecular polymers in solution and film.

Table 2   Optical and electrochemical properties of the DPP-based supramolecular polymers

Polymers	Solution[a]	Film	$E_g^{opt\,b}$ (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_g^{CV\,c}$ (eV)
P1Zn	586	601, 665	1.65	−5.24	−3.72	1.52
P1Cd	588	598, 671	1.68	−5.19	−3.68	1.51
P2Zn	498	504	2.07	−5.19	−3.61	1.58
P2Cd	490	506	2.04	−5.16	−3.58	1.58

[a] Determined from absorption spectra in chloroform solution. [b] Optical bandgap E_g^{opt} was determined from the onset of absorption spectra in thin film. [c] E_g^{CV} = electrochemical band gap (LUMO−HOMO).
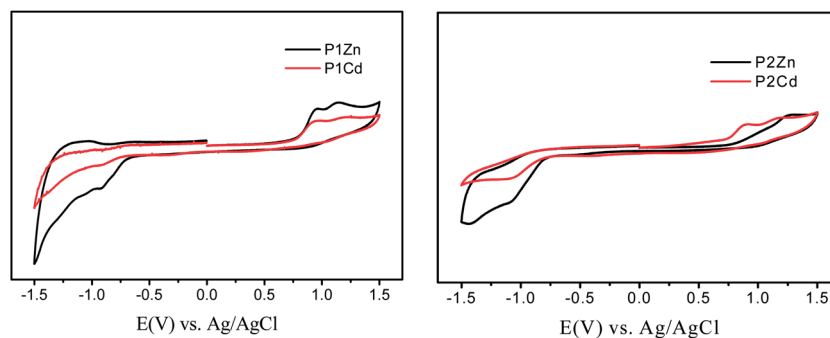

Fig. 3   Cyclic voltammograms of supramolecular films recorded in CH_2Cl_2/0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) electrolyte at a scan rate of 100 mV s^{-1}.

extent from the solution to the film. As seen in Fig. 2, the **P1Zn** and **P1Cd** in film exhibited the absorption maxima at about 601 and 598 nm with the shoulder peaks at about 665 and 671 nm, respectively. Moreover, broadened absorption band within the range from about 300 to 800 nm was shown. Obviously, the longer wavelength absorption resulted from a decrease in rotation angle along the backbone and an enhanced packing in solid or condensed state. Similarly, the **P2Zn** and **P2Cd** showed the absorption maxima at about 504 and 506 nm, a slight bathochromic shift of 6 and 16 nm with regard to the solution absorption (Table 2). The phenyl-coupled DPP monomer resulted in a significantly wider band gap due to the twist of the phenyl ring and then the loss of conjugation. Both in the solution and solid state, the absorption spectra of **P1Zn** and **P1Cd** containing thiophene showed the bimodal absorptions while **P2Zn** and **P2Cd** containing phenyl unit showed the single broad absorptions, which was likely led by the result of vibronic coupling. As seen in Fig. 2, these vibronic structures of **P1Zn** and **P1Cd** were more pronounced in the solid state than in solution which could be a result of aggregation occurring in the thin film.

3.3   Electrochemical properties

Cyclic voltammetry was carried out in the presence of an electrolyte (0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate in CH_2Cl_2) at a scan rate of 0.1 V s^{-1}. As depicted in Fig. 3, oxidation peaks of the polymers showed an irreversible process while reduction peaks exhibited a quasi-reversible process, and for **P1Zn** and **P2Zn** reduction peaks were stronger than the oxidation ones, indicating that these polymers were more easily

deoxidized. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the polymers were estimated from the onset of the oxidation and reduction curves, respectively.[50] All HOMO, LUMO and band gap data were summarized in Table 2. As listed in Table 2, the LUMO level of **P1Zn** (−3.72 eV) and **P1Cd** (−3.68 eV) were positioned 0.11 and 0.10 eV below the LUMO level of **P2Zn** (−3.61 eV) and **P2Cd** (−3.58 eV), respectively. On the other hand, the HOMO level of **P1Zn** (−5.24 eV) and **P1Cd** (5.19 eV) is positioned 0.05 and 0.03 eV below the HOMO level of **P2Zn** (−5.19 eV) and **P2Cd** (−5.16 eV), respectively. This result suggested that the introducing of thiophene moiety instead of phenyl into the DPP-based supramolecular polymer backbone had a more pronounced influence on the LUMO levels than HOMO levels. On the other hand, as seen in Table 2, the band gap of **P1Zn** and **P1Cd** was lower than that of **P2Zn** and **P2Cd**, which was led by the formation of well-defined D–A structure in which the HOMO to LUMO transition was a donor to acceptor intramolecular charge transfer (ICT).[51] And this can explain the red-shifted absorption of **P1Zn** and **P1Cd** compared with **P2Zn** and **P2Cd**, respectively. Furthermore, the low band gaps estimated from CV were 1.52, 1.51, 1.58 and 1.58 eV for **P1Zn**, **P1Cd**, **P2Zn** and **P2Cd**, respectively, which are lower than those of optical band gaps.

4   Conclusions

In conclusion, the novel building blocks based on electro-deficient core DPP have been designed and synthesized by Pd-catalyzed Suzuki cross-coupling reaction and well characterized. Four transition metal ion directed metallo-supramolecular

polymers, **P1Zn**, **P1Cd**, **P2Zn** and **P2Cd**, containing electro-deficient unit core DPP, which possess acceptable solubility and thermal stability as well as good film-forming ability, have been designed and synthesized. By changing the modified neighboring groups of DPP, the optical and electrochemical properties of the resulting metallo-supramolecular polymers can be tuned. Also, a deep look on the differences between the metallo-supramolecular polymers containing thiophene-modified DPP and phenyl-modified DPP to study the structure–property relationship has been taken on. Incorporating thiophene or phenyl unit in the DPP-based metallo-supramolecular polymer backbone lowered the bandgap of the polymer to 1.51–1.58 eV and broadened the absorption band to the range from about 300 to 800 nm. Our work presented a new promising metallo-supramolecular polymeric material for potential application in high-performance photovoltaic materials. Further modifications to the building blocks for metallo-supramolecular polymers are under progress in an effort to achieve better performances.

Acknowledgements

References

1 Y.-J. Cheng, S.-H. Yang and C.-S. Hsu, *Chem. Rev.*, 2009, **109**, 5868–5923.

2 A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.*, 2009, **109**, 897–1091.

3 D. G. Farnum, G. Mehta, G. G. I. Moore and F. P. Siegel, *Tetrahedron Lett.*, 1974, **29**, 2549–2552.

4 O. R. Lenz, *Macromol. Symp.*, 2002, **187**, 617–629.

5 (*a*) S. Qu and H. Ti, *Chem. Commun.*, 2012, **48**, 3039–3051; (*b*) H. Zhang, I. Welterlich, J.-M. Neudorfl, B. Tieke, C. Yang, X. Chen and W. Yang, *Polym. Chem.*, 2013, **4**, 4682–4689.

6 C. Wang, W. Chen, S. Chen, S. Zhao, J. Zhang, D. Qiu and Y. Wang, *New J. Chem.*, 2012, **36**, 1788–1797.

7 (*a*) C. W. Greenhalgh, J. L. Carey, N. Hall and D. F. Newton, *J. Soc. Dyers Colour.*, 1994, **110**, 178–184; (*b*) H. Zhang, S. Ghasimi, B. Tieke, A. Schade and S. Spanger, *Polym. Chem.*, 2014, **4**, 3817–3823.

8 J. W. Rumer, M. Levick, S.-Y. Dai, S. Rossbauer, Z. Huang, L. Biniek, T. D. Anthopoulos, J. R. Durrant, D. J. Procter and I. McCulloch, *Chem. Commun.*, 2013, **49**, 4465–4467.

9 (*a*) H. Zhang, J.-M. Neudorfl and B. Tieke, *Macromolecules*, 2013, **46**, 5842–5849; (*b*) H. Zhang, J.-M. Neudorfl and B. Tieke, *Polym. Chem.*, 2014, **5**, 3754–3757; (*c*) H. Zhang, S. Ghasimi, B. Tieke, A. Schade and S. Spanger, *Polym. Chem.*, 2014, **4**, 4682–4689; (*d*) H. Zhang, J. Zhang and B. Tieke, *Polym. Chem.*, 2014, **5**, 646–652.

10 L. Dou, J. Gao, E. Richard, J. You, C.-C. Chen, K. C. Cha, Y. He, G. Li and Y. Yang, *J. Am. Chem. Soc.*, 2012, **134**, 10071–10079.

11 Y. Li, P. Sonar, S. P. Singh, M. S. Soh, M. V. Meurs and J. Tan, *J. Am. Chem. Soc.*, 2011, **133**, 2198–2204.

12 S. Qu, C. Qin, A. Islam, Y. Wu, W. Zhu, J. Hua, H. Tian and L. Han, *Chem. Commun.*, 2012, **48**, 6972–6974.

13 J. S. Ha, K. H. Kim and D. H. Choi, *J. Am. Chem. Soc.*, 2011, **133**, 10364–10367.

14 S. Subramaniyan, F. S. Kim, G. Ren, H. Li and S. A. Jenekhe, *Macromolecules*, 2012, **45**, 9029–9037.

15 G. D. Sharma, J. AMikroyannidis, S. S. Sharma, M. S. Roy and K. R. J. Thomas, *Org. Electron.*, 2012, **13**, 652–666.

16 J.-Y. Pan, L.-J. Zuo, X.-L. Hu, W.-F. Fu, M.-R. Chen, L. Fu, X. Gu, H.-Q. Shi, M.-M. Shi, H.-Y. Li and H.-Z. Chen, *ACS Appl. Mater. Interfaces*, 2013, **5**, 972–980.

17 W. Shin, T. Yasuda, G. Watanabe, Y. S. Yang and C. Adachi, *Chem. Mater.*, 2013, **25**, 2549–2556.

18 W. Li, W. S. C. Roelofs, M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2012, **134**, 13787–13795.

19 J. C. Bijleveld, R. A. M. Verstrijden, M. M. Wienk and R. A. J. Janssen, *J. Mater. Chem.*, 2011, **21**, 9224–9231.

20 J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995.

21 J.-M. Lehn, *Science*, 2002, **295**, 2400–2403.

22 L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071–4097.

23 F. Huang and O. A. Scherman, *Chem. Soc. Rev.*, 2012, **41**, 5879–5880.

24 H. Hofmeiera and U. S. Schubert, *Chem. Soc. Rev.*, 2004, **33**, 373–399.

25 J.-P. Sauvage, J. P. Collin, J.-C. Chambron, S. Guillerez and C. Coudret, *Chem. Rev.*, 1994, **94**, 993–1019.

26 V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759–834.

27 L. Blackmore, R. Moriarty, C. Dolan, K. Adamson, R. J. Forster, M. Devocelle and T. E. Keyes, *Chem. Commun.*, 2013, **49**, 2658–2660.

28 V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Acc. Chem. Res.*, 1998, **31**, 26–34.

29 M. Lopez-Lopez, F. Montilla, M. Olivares, J. A. Lebron, M. L. Moya and P. Lopez-Cornejo, *Dalton Trans.*, 2013, **42**, 6171–6181.

30 E. Lebon, S. Bastin, P. Sutra, L. Vendier, R. E. Piau, I. M. Dixon, M. Boggio-Pasqua, F. Alary, J.-L. Heully, A. Igau and A. Juris, *Chem. Commun.*, 2011, **48**, 741–743.

31 J.-P. Collin, S. Guillerez, J.-P. Sauvage, F. Barigelletti, L. D. Cola, L. Flamigni and V. Balzani, *Inorg. Chem.*, 1991, **30**, 4230–4238.

32 P. D. Benny, G. A. Fugate, A. O. Barden, J. E. Morley, E. Silva-Lopez and B. Twamley, *Inorg. Chem.*, 2008, **47**, 2240–2242.

33 L.-Z. Sui, W.-W. Yang, C.-J. Yao, H.-Y. Xie and Y.-W. Zhong, *Inorg. Chem.*, 2012, **51**, 1590–1598.

34 A. Li, H. Ma and J. L. Huang, *Organometallics*, 2013, **32**, 7460–7469.

35 H. Y. He, M. Lipowska, X. L. Xu, A. T. Taylor, M. Carlone and L. G. Marzilli, *Inorg. Chem.*, 2005, **44**, 5437–5446.

36 H. Hofmeier, A. El-ghayoury, A. P. H. J. Schenning and U. S. Schubert, *Chem. Commun.*, 2004, 318–319.

37 S. Kelch and M. Rehahn, *Macromolecules*, 1999, **32**, 5818–5828.

38 K. Zhang, Y. Zha, B. Peng, Y. Chen and G. N. Tew, *J. Am. Chem. Soc.*, 2013, **135**, 15994–15997.

39 J.-L. Wang, X. Li, X. Lu, I.-F. Hsieh, Y. Cao, C. N. Moorefield, C. Wesdemiotis, S. Z. D. Cheng and G. R. Newkome, *J. Am. Chem. Soc.*, 2011, **133**, 11450–11453.

40 R. Dobrawa and F. Würthner, *Chem. Commun.*, 2002, 1878–1879.

41 S. C. Yu, C. C. Kwok, W. K. Chan and C. M. Che, *Adv. Mater.*, 2003, **15**, 1643–1647.

42 F. Schlütter, A. Wild, A. Winter, M. D. Hager, A. Baumgaertel, C. Friebe and U. S. Schubert, *Macromolecules*, 2010, **43**, 2759–2771.

43 X. Chen, L. Ma, Y. Cheng, Z. Xie and L. Wang, *Polym. Int.*, 2007, **56**, 648–654.

44 (*a*) D. R. Cao, Q. L. Liu, W. J. Zeng, S. H. Han, J. B. Peng and S. P. Liu, *Macromolecules*, 2006, **39**, 8347–8355; (*b*) Y. Zhu, K. Zhang and B. Tieke, *Macromol. Chem. Phys.*, 2009, **210**, 431–439.

45 G.-Y. Chen, C.-M. Chiang, D. Kekuda, S.-C. Lan, C.-W. Chu and K.-H. Wei, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 1669–1675.

46 C. J. Aspley and J. A. G. Williams, *New J. Chem.*, 2001, **25**, 1136–1147.

47 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457–2483.

48 N. W. Alcock, P. R. Barker, J. M. Haider, M. J. Hannon, C. L. Painting, Z. Pikramenou, E. A. Plummer, K. Rissanen and P. Saarenketo, *J. Chem. Soc., Dalton Trans.*, 2000, 1447–1461.

49 (*a*) I. Welterlich and B. Tieke, *Polym. Chem.*, 2013, **4**, 3755–3764; (*b*) H.-J. Yun, H. H. Choi, S.-K. Kwon, Y.-H. Kim and K. Cho, *Chem. Mater.*, 2014, **26**, 3928–3937; (*c*) Y. Suna, J. Nishida, Y. Fujisaki and Y. Yamashita, *Org. Lett.*, 2012, **14**, 3356–3359; (*d*) S. Subramaniyan, F. S. Kim, G. Ren, H. Li and S. A. Jenekhe, *Macromolecules*, 2012, **45**, 9029–9037; (*e*) L. Dou, J. Gao, E. Richard, J. You, C.-C. Chen, K. C. Cha, Y. He, G. Li and Y. Yang, *J. Am. Chem. Soc.*, 2012, **134**, 10071–10079; (*f*) S. Qu and H. Tian, *Chem. Commun.*, 2012, **48**, 3039–3051; (*g*) P. Sonar, J.-M. Zhuo, L.-H. Zhao, K.-M. Lim, J. Chen, A. J. Rondinone, S. P. Singh, L.-L. Chua, P. K. H. Hob and A. Dodabalapur, *J. Mater. Chem.*, 2012, **22**, 17284–17292; (*h*) A. B. Tamayo, X.-D. Dang, B. Walker, J. Seo, T. Kent and T.-Q. Nguyen, *Appl. Phys. Lett.*, 2009, **94**, 103301–103304; (*i*) T. L. Nelson, T. M. Young, J. Liu, S. P. Mishra, J. A. Belot, C. L. Balliet, A. E. Javier, T. Kowalewski and R. D. McCullough, *Adv. Mater.*, 2010, **22**, 4617–4621; (*j*) H. Zhang, I. Welterlich, J.-M. Neudoerfl, B. Tieke, C. Yang, X. Chen and W. Yang, *Polym. Chem.*, 2013, **4**, 4682–4689.

50 (*a*) J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch and J. Daub, *Adv. Mater.*, 1995, **7**, 551–554; (*b*) S. Ranjan, S.-Y. Lin, K.-C. Hwang, Y. Chi, W.-L. Ching, C.-S. Liu, Y.-T. Tao, C.-H. Chien, S.-M. Peng and G.-H. Lee, *Inorg. Chem.*, 2003, **42**, 1248–1255.

51 (*a*) S. Leroy, T. Soujanya and F. Fages, *Tetrahedron Lett.*, 2001, **42**, 1665–1667; (*b*) C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319–2358.