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Terpyridine-based donor—acceptor metallo-supramolecular polymers with tunable band gaps: Synthesis and characterization



PIGMENTS

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ABSTRACT

Three new building blocks containing the electron-donor fused-ring motifs carbazole, dithienosilole (DTS) and dithienopyrrole (DTP) and the 2,2':6',2"-terpyridine electron-acceptor motif were designed and synthesized. Directed by transition metal ions, the self-assembly of the building blocks triggered polymerization to form the corresponding metallo-supramolecular polymers **PCzTPY**, **PSiTPY** and **PNTPY**, respectively. The UV–vis absorption maxima of the building blocks occur at long wavelengths (351, 368 and 430 nm for **CzTPY**, **SiTPY** and **NTPY**, respectively), which arises from intramolecular charge transfer (ICT) transitions. However, the absorption maxima of their corresponding metallo-supramolecular polymers are clearly red-shifted (to 394, 431 and 509 nm for **PCzTPY**, **PSiTPY** and **PNTPY**, respectively), which is caused by the incorporation of the transition metal ion into the backbones of the target polymers. Based on the above strategies, the resulting metallo-polymers exhibit reduced energy gaps, which are 2.07, 1.97 and 1.56 eV for the **PCzTPY**, **PSiTPY** and **PNTPY** metallo-supramolecular polymers.

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1. Introduction

Over the past few decades, the design and study of π -conjugated organic semiconductors has attracted increasing attention. One of the important advantages of organic/polymer semiconductor materials is that the levels of their frontier orbitals and energy gaps of the organic and polymer molecules can be tuned easily by molecular design; consequently, the resulting photoelectronic and electrochemical properties can be finely tailored. Presently, conjugated polymers with alternating electron-donating (D) and electronaccepting (A) units along the same backbone have become especially useful in optoelectronics, such as OLEDs [1], photovoltaic devices [2], chemical sensors [3], field-effect transistors (FETs) [4], and NLOs [5]. Such donor–acceptor organic/polymers exhibit

** Corresponding author. College of Optoelectronic Technology, Chengdu University of Information Technology, No. 24 Block 1, Xuefu Road, Chengdu, 610225, China. *E-mail addresses:* xgchen@qust.edu.cn (X. Chen), lijie@quit.edu.cn (J. Li). narrow energy gaps and strong dipoles resulting from intramolecular charge transfer (ICT). Further, these molecules possess the ability to span the optical absorption spectrum across the visible and near-IR range. The strength, nature and type of the donor and acceptor motifs heavily influence the energy levels of the frontier orbitals; hence, the optical and electronic properties of the organic light-emitting, light-absorbing and semiconducting materials. Although many studies exist concerning the synthesis, properties and the relationship between structure and properties, many phenomena in such push—pull systems of D/A materials have not been sufficiently clarified, and a broad understanding of the electronic and photophysical properties and energetic alignment of the frontier orbitals remains unclear.

Electron-rich units such as triphenylamines [6], carbazole [7], benzodithiophene [8], dithieno[3,2-b:2',3'-d]silole (DTS) [9–11], and dithieno[3,2-b:2',3'-d]pyrrole (DTP) [12–15] and their derivatives have been developed as donor units in D/A polymer materials. One approach to their synthetic modification is to introduce fused aromatic units into the conjugated backbone, which results in materials that exhibit enhanced carrier mobilities, delocalized π -conjugated organic and polymer semiconductors and reduced



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energy gaps. Among the electron-rich units, carbazole, dithieno [3,2-b:2',3'-d]silole (DTS) and dithieno[3,2-b:2',3'-d]pyrrole (DTP) contain fused planar tricyclic systems and possess low-lying LUMO energy levels and enhanced carrier mobilities. Further, because of their good molecular planarity and their capacity to be easily modified, the introduction of these fused-ring donor motifs into various π -conjugated polymeric and molecular materials is desirable for providing high carrier mobilities, enhanced fluorescence and reduced band gaps [16–18].

2,2':6',2"-Terpyridine and its derivatives are well-studied, though they remain fascinating because of their outstanding favorable geometry and because they can be used in metallomacrocycles [19], terpyridine-ruthenium(II) complexes for their photovoltaic performance [20], and supramolecular materials and chemistry [21–23]. Interest in supramolecular polymers (SP), in which the monomeric building blocks are held together via noncovalent interactions, such as hydrogen bonding, metal coordination, electrostatic interactions, hydrophobic interactions and $\pi - \pi$ interactions, has been stimulated because of the vast of progresses in modern supramolecular chemistry [24]. The so-called metallosupramolecular polymers, which are based on metal-ligand coordination, have recently made rapid progress in supramolecular systems and materials [25,26]. The introduction of metal ions into the backbones of the supramolecular polymers results in some very interesting photophysical and electrochemical properties. At the same time, pyridine rings, especially terpyridine, can be used as the electron-withdrawing units, and monomeric building blocks incorporated with 2,2':6',2"-terpyridine can be used to generate D-A π -conjugated organic/polymers materials [27.28].

Based on the above considerations, we report herein the details of the synthesis of novel building blocks based on π -conjugated 2,2':6',2"-terpyridine. Using Suzuki coupling reactions with Pdcatalysts, the electron-acceptor π -conjugated 2,2':6',2"-terpyridine was coupled with the electron-donor moieties carbazole, DTS and DTP, which have good molecular planarity because of their fused-rings, to synthesize the monomeric building blocks **CzTPY**, **SiTPY** and **NTPY**, respectively (Scheme 1). Directed by the transition metal ion Zn²⁺, three new donor–acceptor metallosupramolecular polymers were synthesized *via* self-assembly polymerization under moderate conditions (Scheme 2). The effects of the D-A molecular structures and the transition metal ions on the photophysical, electrochemical properties and the energy gaps of the resulting metallo-polymers were fully investigated in this paper.

2. Experimental section

2.1. Synthesis of the monomeric building blocks and metallosupramolecular polymers

2.1.1. 3,3',5,5'-tetrabromo-2,2'-bithiophene (1)

To a solution of 2,2'-bithiophene (2.78 g, 16.7 mmol) in the mixed solvent of glacial acetic acid (20 mL) and CHCl₃ (23 mL) at 0 °C was added dropwise bromine (9.8 g, 61.3 mmol) in 20 mL CHCl₃. The mixture was stirred at room temperature overnight and then heated under reflux for 24 h. After cooling to room temperature, 50 mL of 10% KOH aqueous solution was added, followed by extraction with CHCl₃. The organic layer was dried over anhydrous MgSO₄ and the solvent was removed by evaporation. After recrystallization from ethanol, colorless crystals were obtained (7.50 g, 93%). ¹H NMR (CDCl₃), δ (ppm): 7.04 (s, 2H).

2.1.2. 3,3'-dibromo-2,2'-bithiophene (2)

Compound **1** (25.00 g, 51.8 mmol) was added to a refluxing dispersion of zinc powder (13.00 g, 0.3 mol) in a mixing solution of

150 mL ethanol, 30 mL water, 60 mL glacial acetic acid and 5 mL 3 M HCl. After refluxing for an additional 6 h and then cooling to room temperature, the mixture was filtered and washed three times with ethanol. The solvent was then removed by evaporation and water was added. The mixture was then extracted with diethyl ether and then dried over anhydrous MgSO₄. The solvent was removed by evaporation, and the crude product was recrystallized in hexane to afford colorless crystals (14.54 g, 86.3%). ¹H NMR (CDCl₃), δ (ppm): 7.41 (d, J = 5.5 Hz, 2H), 7.09 (d, J = 5.0 Hz, 2H).

2.1.3. N-dodecyldithieno[3,2-b:2',3'-d]pyrrole (3)

A mixture of **2** (7.50 g, 23.3 mmol), NaO^tBu (5.38 g, 56.0 mmol) and BINAP (1.45 g, 2.2 mmol) in 65 mL dry toluene was purged with N₂ for 30 min. A catalytic amount of Pd₂dba₃ and dodecylamine (4.54 g, 24.5 mmol) were added to the above mixture and the reaction mixture was stirred and heated under reflux overnight. After cooling to room temperature, water was added to the mixture. The mixture was extracted with diethyl ether and then dried over anhydrous MgSO₄. The solvent was removed by evaporation. The crude product was purified by silica gel column chromatography (hexane) to give the product as a light yellow oil (6.69 g, 82.6%). ¹H NMR (CDCl₃), δ (ppm): 7.13 (d, J = 5.0 Hz, 2H), 7.00 (d, J = 5.5 Hz, 2H), 4.20 (t, J = 7.0 Hz, 2H), 1.86 (m, 2H), 1.30–1.24 (m, 18H), 0.88 (t, J = 6.5 Hz, 3H).

2.1.4. 2,6-Dibromo-N-dodecyldithieno[3,2-b:2',3'-d]pyrrole (4)

To a solution of **3** (3.15 g, 9.1 mmol) in 300 mL THF was added NBS (3.23 g, 18.1 mmol) at 0 °C. Water was added after the solution was stirred for 2 h. The mixture was extracted with CH_2Cl_2 , dried over anhydrous MgSO₄, and the solvent was removed under reduced pressure. The crude product was recrystallized from CH_2Cl_2 /methanol to give light yellow crystals (3.71 g, 81.2%). ¹H NMR (CDCl₃), δ (ppm): 6.91 (s, 2H), 4.08 (t, J = 7.0 Hz, 2H), 1.80 (m, 2H), 1.28–1.24 (m, 18H), 0.88 (t, J = 7.0 Hz, 3H).

2.1.5. 3,3'-dihexylsilylene-2,2'-bithiophene (5)

2.2 M n-BuLi in hexane (7.32 mL, 16.2 mmol) was added dropwise to a solution of **2** (2.49 g, 7.7 mmol) in anhydrous THF (55 mL) under vigorous stirring at -78 °C. The mixture was then stirred at -78 °C for 1 h. Then, a solution of dichlorodihexylsilane (2.50 mL, 8.1 mmol) in THF (100 mL) was added dropwise. The reaction mixture was stirred at -78 °C for an additional 5 h. The mixture was allowed to warm to room temperature overnight with stirring. The reaction mixture was quenched and a saturated aqueous NH₄Cl solution was added. The mixture was extracted with diethyl ether and then dried over MgSO₄. The solvent was removed by evaporation, and the crude product was purified by silica gel column chromatography (hexane) to yield a light yellow liquid (1.84 g, 66.6%). ¹H NMR (CDCl₃), δ (ppm): 7.19 (d, J = 4.5 Hz, 2H), 7.05 (d, J = 4.5 Hz, 2H), 1.41–0.85 (m, 26H).

2.1.6. 5,5'-dibromo-3,3'-dihexylsilylene-2,2'-bithiophene (6)

To a solution of **5** (0.26 g, 0.7 mmol) in 10 mL DMF was added NBS (0.28 g, 1.6 mmol) in one portion. The mixture was stirred at room temperature for 10 min, and then water was added. The mixture was extracted with diethyl ether. The combined organic phase was washed with water and dried over MgSO₄. The solvent was removed, and the product was purified by silica gel column chromatography (hexane) to afford a green liquid (0.31 g, 89.1%). ¹H NMR (CDCl₃), δ (ppm): 6.99 (s, 2H), 1.34–0.88 (m, 26H).

2.1.7. 2,7-Dibromo-N-octylcarbazole (7)

To a solution of 2,7-dibromocarbazole (1.63 g, 50.0 mmol) in 10 mL DMSO were added 1-bromooctane (1.45 g, 75.0 mmol) and 5 mL of a 50% NaOH solution. The mixture was stirred at room



Scheme 1. Synthesis and molecular structures of the terpyridine-based monomeric building blocks CZTPY, SiTPY and NTPY.

temperature for 4 h. The reaction mixture was extracted with diethyl ether and then dried over MgSO₄. After evaporation of the solvent, the resulting crude solid was purified by silica gel column chromatography (hexane) to obtain a white solid (1.77 g, 81.3%). ¹H NMR (CDCl₃), δ (ppm): 7.83 (s, 2H), 7.46 (d, J = 2.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.28 (t, J = 7.0 Hz, 2H), 1.83 (m, 2H), 1.50–1.20 (m, 8H), 0.86 (m, 2H), 0.82 (t, J = 7.0 Hz, 3H).

2.1.8. 2,7-Bis(p-(2,2':6',2"-terpyridine-4'-yl)phenyl)-N-octylcarbazole (**CzTPY**)

The intermediate 4'-(4-pinacolatoboronphenyl)-2.2':6'.2"-terpyridine (8) was synthesized according to published methods [29]. To a mixture of **7** (0.50 g, 1.2 mmol) and **8** (1.03 g, 2.4 mmol) in 50 mL THF was added a solution of sodium carbonate (0.88 g, 8.34 mmol) in 5 mL H_2O . The solution was purged with N_2 for 30 min and then a catalytic amount of Pd(dppf)Cl₂ was added. The mixture was refluxed for 36 h. After cooling to room temperature, the mixture was extracted with CH₂Cl₂ and washed with water, dried over with MgSO₄ and concentrated via rotary evaporation. The crude product was purified by silica gel column chromatography (petroleum ether/acetone, 2:1 v/v) to give the product as a white solid (0.834 g, 81.2%). ¹H NMR (CDCl₃), δ (ppm): 8.82 (s, 4H), 8.76 (d, J = 5.0 Hz, 4H), 8.69 (d, J = 8.0 Hz, 4H), 8.22 (d, J = 8.0 Hz, 4H), 8.18 (d, J = 8.5 Hz, 4H), 7.93-7.88 (m, 8H), 7.69 (s, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.38 (m, 2H), 4.48 (t, J = 7.0 Hz, 2H), 1.99 (m, 2H), 1.50-1.39 (m, 8H), 0.95 (m, 2H), 0.84 (t, J = 7.0 Hz, 3H). ¹³C NMR $({\rm CDCl}_3):\delta$ 156.29, 155.98, 149.82, 149.15, 142.88, 141.60, 138.37, 136.89, 128.04, 127.74, 123.84, 123.79, 122.18, 121.40, 120.78, 118.68, 118.60, 107.24, 77.26, 77.01, 76.75, 43.14, 31.82, 29.21, 27.37, 22.62. Anal. Calc. for $C_{62}H_{51}N_7$: C, 83.28; H, 5.75; N, 10.97. Found: C, 83.02; H, 5.51; N, 10.80.

2.1.9. 5,5'-bis(p-(2,2':6',2"-terpyridine-4'-yl)phenyl)-3,3'dihexylsilylene-2,2'-bithiophene (**SiTPY**)

Compound **SiTPY** was prepared following a similar procedure to give the product as yellow crystals (72.1%). ¹H NMR (CDCl₃), δ (ppm): 8.79 (s, 4H), 8.75 (d, J = 4.0 Hz, 4H), 8.69 (d, J = 8.5 Hz, 4H), 7.95 (t, J = 7.5 Hz, 4H), 7.89 (t, J = 7.0 Hz, 4H), 7.75 (d, J = 4.0 Hz, 4H), 7.46 (s, 2H), 7.38 (d, J = 8.0 Hz, 4H), 1.42–1.11 (m, 20H), 0.89 (t, J = 7.0 Hz, 6H). ¹³C NMR (CDCl₃), δ (ppm): 156.01, 155.86, 149.50, 149.42, 149.17, 136.92, 136.88, 127.85, 126.33, 126.08, 124.02, 123.87, 121.48, 121.42, 118.59, 118.55, 77.29, 77.04, 76.79, 33.08, 23.12, 16.18. Anal. Calc. for C₆₂H₅₆N₆S₂Si: C, 76.19; H, 5.78; N, 8.60. Found: C, 76.94; H, 5.47; N, 8.41.

2.1.10. 2,6-Bis(p-(2,2':6',2"-terpyridine-4'-yl)phenyl)-N-dodecyldithieno[3,2-b:2',3'-d]pyrrole(**NTPY**)

Compound **10** was prepared following a similar procedure to give the product as an orange-red solid (75.6%). ¹H NMR (CDCl₃), δ (ppm): 8.80 (s, 4H), 8.76 (d, J = 4.0 Hz, 4H), 8.70 (d, J = 8.0 Hz, 4H), 7.97 (d, J = 8.5 Hz, 4H), 7.90 (t, J = 7.5 Hz, 4H), 7.80 (d, J = 8.5 Hz, 4H), 7.38 (d, J = 7.0 Hz, 4H), 7.37 (s, 2H), 4.28 (t, J = 7.0 Hz, 2H), 1.97 (m,



Scheme 2. Synthesis of the donor-acceptor metallo-supramolecular polymers PCzTPY, PSiTPY and PNTPY.

2H), 1.28–0.92 (m, 18H), 0.85 (t, J = 7.0 Hz, 3H). 13 C NMR (CDCl₃), δ (ppm): 156.26, 155.94, 149.47, 149.14, 149.08, 136.96, 136.94, 127.77, 125.58, 123.91, 123.88, 121.47, 121.43, 118.45, 118.40, 115.05, 77.32, 77.07, 76.82, 51.04, 47.45, 31.95, 30.50, 29.67, 29.37, 27.11, 22.72, 14.17. Anal. Calc. for C_{62}H_{55}N_7S_2: C, 77.39; H, 5.76; N, 10.19. Found: C, 78.21; H, 5.58; N, 10.07.

2.1.11. Synthesis of the metallo-supramolecular polymers **PCzTPY**, **PSiTPY** and **PNTPY**

The metallo-polymers **PCzTPY**, **PSiTPY** and **PNTPY** were obtained through similar methods. A typical polymerization process is described for the synthesis of the polymer **PCzTPY**. To a solution of the monomer **CzTPY** (0.0896 g, 0.1 mmol) in NMP (10 mL) was added Zn(OAc)₂·2H₂O (0.022 g, 0.1 mmol). The reaction was allowed to proceed at 105 °C for approximately 20 h. An excess saturated methanol solution of KPF₆ was added and stirred for 30 min at 105 °C. After cooling to room temperature, the reaction solution was poured into methanol (100 mL). The precipitates were filtered off and washed with methanol, resulting in a solid yellow polymer (yield 94.0%).

2.2. Characterization

All reagents and chemicals were used as commercially supplied unless otherwise noted. ¹H and ¹³C NMR spectra were measured using a Bruker AV500 spectrometer. Chemical shifts are quoted in parts per million (ppm) with tetramethylsilane (TMS) as the internal standard. Inherent viscosities were measured in NMP at 30 °C using an Ubbelohde viscometer. UV–vis spectra were recorded on a HITACHI U-4100 UV–vis spectrophotometer, and PL spectra were recorded on a HITACHI F-4600 fluorescence spectrophotometer. The electrochemical cyclic voltammetry (CV) was performed on an Autolab PGSTAT 204 (Metrohm, Switzerland) with a standard three-electrode cell at a scan rate of 100 mV s⁻¹. The system consists of a platinum disk as the working electrode, platinum wire as the auxiliary electrode, an Ag/AgCl electrode (saturated KCl) as the reference electrode and tetrabutylammonium hexafluorophosphate (0.1 M) in acetonitrile solution as the supporting electrolyte. The solutions were deoxygenated by sparging with argon for 10 min prior to each measurement.

3. Results and discussion

3.1. Synthesis and characterization of monomers and supramolecular polymers

A selective debromination reduction of 3,3',5,5'-tetrabromo-2,2'-bithiophene (1) with zinc powder as the catalyst was performed to give compound 2. The resulting compound was treated with dodecylamine with Pd₂dba₃ as the catalyst under basic conditions to obtain compound 3. After bromination with NBS in a THF solution, the brominated compound 2,6-dibromo-N-dodecyldithieno[3,2-b:2',3'-d]pyrrole (4) was obtained. In another experiment, the intermediate compound 2 was treated with 2.0 equivalents of n-BuLi in THF at -78 °C and cyclized with dichlorodihexylsilane to produce compound 5. This compound was then brominated with NBS to give 5,5'-dibromo-3,3'-dihexylsilylene-2,2'-bithiophene (6). 2,7-Dibromo-N-octylcarbazole (7) was easily obtained from 2,7-dibromocarbazole in good yield. The monomeric building blocks CzTPY, SiTPY and NTPY were synthesized by Suzuki coupling [30,31] between 4'-(4-pinacolatoboronphenyl)-2,2':6',2"terpyridine (8) and the corresponding dibrominated compounds 2,7-dibromo-*N*-octylcarbazole 5,5'-dibromo-3,3'-dihex-(7), ylsilylene-2,2'-bithiophene (6) and 2,6-dibromo-N-dodecyldithieno[3,2-*b*:2',3'-*d*]pyrrole (**4**), respectively, in refluxing anhydrous THF after stirring for 36 h. All of these building blocks are soluble in a wide range of common organic solvents such as dichloromethane, chloroform and tetrahydrofuran. Under moderate conditions and directed by the transition metal ion Zn²⁺, the monomeric building blocks CzTPY, SiTPY and NTPY polymerized to form the metallo-supramolecular polymers PCzTPY, PSiTPY and PNTPY, respectively (Scheme 2). The resulting polymers can be simply purified through washing in methanol. The polymerization of the monomeric building blocks can be confirmed through the distinct ¹H NMR spectra of the monomers and polymers. As seen in Fig. 1, after polymerization, the characteristic peaks of the terpyridine moiety shift downfield and the peaks broaden [32,33]. Further, their inherent viscosities were characterized using an Ubbelohde viscometer in an NMP solution to estimate the degree of polymerization of the resulting metallo-supramolecular polymers. The polymers exhibit inherent viscosities that range from 0.87 to 1.29 dL/g at 30 °C (Table 1). The thermal stability of the resulting polymers was investigated with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA analysis reveals that the onset temperatures T_d of **PCzTPY**, **PSiTPY** and **PNTPY** are 408, 414 and 432 $^{\circ}$ C, respectively, and the T_g of the resulting polymers are at about 170 °C (Table 1), which indicate that the metallo-polymers are stable enough for applications in optoelectronic devices.



Fig. 1. ¹H NMR spectra of the monomeric building blocks **CzTPY**, **SiTPY** and **NTPY** in chloroform-*d* and the supramolecular polymers **PCzTPY**, **PSiTPY** and **PNTPY** in DMSO- d_6 at 298 K.

Table 1

The physical properties of the metallo-supramolecular	ar polymers.
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Polymer	$\eta_{inh}{}^a \left(dL/g\right)$	Yield (%)	T _g (°C)	$T_d(^{\circ}C)$
PCzTPY	1.29	94	169.7	408
PSiTPY	0.92	88	167.4	414
PNTPY	0.87	83	170.3	432

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

3.2. Optical properties

Fig. 2 shows the absorption spectra of CzTPY, SiTPY and NTPY in a dilute dichloromethane solution and the solid PL spectra. The corresponding data are summarized in Table 2. In solution, all three building blocks display $\pi - \pi^*$ transitions within a similar short wavelength range with maxima centered at 284, 280 and 278 nm for CzTPY, SiTPY and NTPY, respectively. Additionally, all of the building blocks exhibit broad absorption bands at long wavelengths, which appears to originate from strong intramolecular charge transfer (ICT) transitions from the electron-acceptor to electron-donor moieties [34,35]. In contrast to the absorption at short wavelengths, the absorption at long wavelengths of the building blocks exhibit strong differences, and the maxima are centered at 351, 368 and 430 nm for CzTPY, SiTPY and NTPY, respectively. Compared to **CzTPY**, the large red shifts of the absorption maxima of NTPY (~79 nm) and SiTPY (~17 nm) arise from the stronger electron-donating ability of the DTP and DTS units in NTPY and SiTPY than the electron-donating ability of the carbazole



Fig. 2. UV–vis absorption spectra of **CzTPY**, **SiTPY** and **NTPY** in a dilute dichloromethane $(10^{-5} \text{ mol } L^{-1})$ solution (a) and solid-state photoluminescence spectra and photographic images of the fluorescence (b).

	$\lambda_{abs,max}^{a}$ [nm]	$\lambda_{em,max}^{b}$ [nm]	Ø ^c	$\lambda_{em,max}^{d}$ [nm]	HOMO [eV]	LUMO [eV]	Egelece [eV]
CzTPY	284, 351	415	0.32	427	-5.55	-2.76	2.79
SiTPY	280, 368	478	0.25	481	-5.47	-2.76	2.71
NTPY	278, 430	497	0.13	506	-5.06	-2.74	2.32

Table 2 Photophysical and electrochemical properties for the monomeric building blocks CzTPY, SiTPY and NTPY.

 a,b In a dilute dichloromethane (10⁻⁵ mol L⁻¹) solution.

^b The excitation wavelength is 330 nm.

 c Determined against quinine sulfate in 0.05 M aqueous H_2SO_4 ($\Phi=0.546$) as a standard.

^d In the solid-state, and the excitation wavelength is 330 nm.

^e E_{g}^{elec} = electrochemical band gap (LUMO-HOMO).

unit in **CzTPY**. As shown in Fig. 2 (b), the building blocks **CzTPY**, **SiTPY** and **NTPY** exhibit blue, yellow green and orange photoluminescence, respectively. The PL maxima of **CzTPY**, **SiTPY** and **NTPY** in solid state are 427, 481 and 506 nm, respectively, exhibiting slight red-shift compared with that in chloroform solution, which are 415, 478, and 497 nm for **CzTPY**, **SiTPY** and **NTPY**, respectively (Table 2). With the increase of electron-donating ability, the obvious red shift of PL is consistent with the results from UV–vis spectroscopy. In addition, broad emission peaks and long tails extending to ~700 nm were observed, suggesting that there is a high probability that these building blocks will aggregate in the solid state.

The absorption spectra and PL spectra of the target metallosupramolecular polymers in thin films are shown in Fig. 3, and their corresponding data are summarized in Table 3. All three metallo-polymers exhibit similar absorption bands related to $\pi - \pi^*$ transitions of the conjugated backbones at short wavelengths, and the absorption maxima in film are 340, 336 and 338 nm for PCzTPY, **PSiTPY** and **PNTPY**, respectively. Distinct intramolecular charge transfer (ICT) transition absorptions at long wavelengths are observed. In contrast to the $\pi - \pi^*$ transitions, the absorption bands resulting from ICT transitions depend heavily on the electrondonating ability of the donor and electron-withdrawing ability of the acceptor moiety in the main chain of the resulting metallopolymers. The electron-donating properties of the donors have a strong effect on the absorption bands of the target metallosupramolecular polymers. The introduction of a strong electrondonor unit into the polymer backbone containing Zn-terpyridine moieties causes a red-shifted absorption band. As shown in Fig. 3, PCzTPY, PSiTPY and PNTPY possess ICT transition absorption maxima at 394, 431 and 509 nm, respectively, which demonstrates an increasing red shift as the electron-donating ability of the electron-donor units increases in the order carbazole. DTS and DTP. respectively. In moving from the monomeric building blocks to the corresponding zinc ion-directed supramolecular polymers, the absorption maxima from the ICT transition red shift 43, 63 and 79 nm for PCzTPY, PSiTPY and PNTPY, respectively. The sharp red shifts arise from the incorporation of the transition metal ions into the backbones of the resulting metallo-polymers, which enhances the electron-deficiency ability of the terpyridine moieties compared to the free terpyridine moieties in the monomeric molecules CzTPY, SiTPY and NTPY. Consequently, in sharp contrast to the monomeric building blocks, the colors of the resulting metallopolymers PCzTPY, PSiTPY and PNTPY are yellow, orange and purple black, respectively (Fig. 3(c)). Moreover, the corresponding photoluminescence colors of PCzTPY, PSiTPY and PNTPY are yellow, orange-yellow and wine, respectively, and the PL maxima in film are 443, 553, and 586 nm. Clearly, designing the D-A structures via the introduction of electron-donating units and the interaction of the transition metal ions with the terpyridine moieties enables greater control of their photophysical properties. Further, the photoluminescence quantum efficiencies of the polymers PCzTPY,

PSiTPY were 0.36 and 0.17, respectively, whereas the photoluminescence intensity of the polymer **PNTPY** was very weak (0.06).

3.3. Electrochemical properties

Cyclic voltammetry (CV) was employed to examine the electrochemical properties of the monomeric building blocks and their corresponding zinc ion-directed metallo-supramolecular polymers and to determine their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies (Fig. 4). All of the polymers exhibit both oxidation and reduction waves, which reflects the presence of both electron-donating and electron-accepting units in the conjugated backbone of the polymers. All of the building blocks and the three polymers displayed reversible reduction processes under scanning at negative potential, whereas the oxidation processes for CzTPY and SiTPY were irreversible/quasi-reversible. However, the oxidation processes of NTPY and PNTPY exhibit good reversibility at positive scanning. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the building blocks and polymers are estimated from the onset of the oxidation and reduction curves, respectively [36], and the data are listed in Tables 2 and 3. The LUMO energy levels of the building blocks CzTPY, SiTPY and NTPY are determined to be -2.76, -2.76 and -2.74 eV, respectively. Clearly, the identical terpyridine electron-withdrawing units within the building blocks cause the similar LUMO energy levels. The LUMO energy levels of the corresponding metallo-polymers are -3.43, -3.47 and -3.51 eV for PCzTPY, PSiTPY and PNTPY, respectively, and it is clear that there are no obvious differences among them. The LUMO energy levels of the polymers are lower than that of the corresponding building blocks because of the introduction of electron-withdrawing metal ions into the main chains of the polymers. Therefore, the ICT is favorable and becomes enhanced, which is consistent with the results from UV-vis spectroscopy. Additionally, the HOMO energy levels of the monomeric building blocks and the corresponding polymers are similar because the monomeric molecules and the backbones of the polymers contain identical electron-donating moieties. As seen in Tables 2 and 3, the HOMO energy levels of the building blocks are -5.55, -5.47 and -5.06 eV for CzTPY, SiTPY and NTPY, respectively, and the HOMO energy levels of the polymers are -5.55, -5.44 and -5.07 eV for PCzTPY, PSiTPY and **PNTPY**, respectively, which are consistent with the order of the electron-donating abilities of the donor moieties in the monomeric building blocks and the metallo-polymers: carbazole < DTS < DTP. It should be noted that, compared with the energy gaps of the monomeric molecules, the reduced energy gaps of the polymers (i.e., 2.07, 1.97 and 1.56 eV for PCzTPY, PSiTPY and PNTPY, respectively) result from reducing the energy of the corresponding LUMOs (Tables 2 and 3 and Fig. 5). Furthermore, the polymer PNTPY exhibits the lowest energy gap (1.56 eV), which arises from





Fig. 3. UV-vis absorption spectra (a) and photoluminescence spectra(b) of the polymers PCzTPY, PSiTPY and PNTPY in film, and the appearances and photographic images of the fluorescence of the polymers (c).

Table 3

Optical and electrochemical properties of the metallo-supramolecular polymers PCzTPY, PSiTPY and PNTPY.

Polymer	In CHCl ₃			Film			HOMO [eV]	LUMO [eV]	Egelec e [eV]
	$\lambda_{abs,max}$ [nm]	$\lambda^a_{em,max}$ [nm]	Ø ^b	λ _{max} [nm]	$\lambda_{em,max} c [nm]$	$E_g^{opt d} [eV]$			
PCzTPY	348	478	0.36	340, 394	443	2.38	-5.50	-3.43	2.07
PSiTPY	296, 406	517	0.17	336, 431	553	2.21	-5.44	-3.47	1.97
PNTPY	284, 461	567	0.06	338, 509	583	1.90	-5.07	-3.51	1.56

^{a,c}The excitation wavelength is 330 nm.

^bDetermined against quinine sulfate in 0.05 M aqueous H₂SO₄ ($\Phi = 0.546$) as a standard.

^dOptical bandgap E_{α}^{opt} was determined from the onset of the absorption spectra of the thin films.

 ${}^{e}E_{g}^{elec} =$ electrochemical band gap (LUMO-HOMO).

two sources: one is the introduction of a strong electron-donating fused planar DTP donor unit, which is capable of increasing the HOMO energy level of the resulting polymer, and the second is the introduction of the transition metal zinc ion into the backbone of the resulting polymer, which lowers its LUMO energy level.

4. Conclusions

In conclusion, three new donor-acceptor monomeric building blocks based on the fused electron-donating units carbazole, DTS

and DTP, namely **CzTPY**, **SiTPY** and **NTPY**, respectively, were synthesized by the Pd-catalyzed Suzuki coupling reaction and well characterized using a variety of techniques. Under moderate conditions, the donor–acceptor metallo-supramolecular polymers **PCzTPY**, **PSiTPY** and **PNTPY** were obtained *via* a zinc ion-directed self-assembly polymerization. With the increase of the electrondonating abilities of the donors incorporated into the backbones of the target metallo-polymers, the absorption maxima arising from ICT transitions clearly red shift to 394, 431 and 509 nm for **PCzTPY**, **PSiTPY** and **PNTPY**, respectively. Further, the reduced





Voltage / V

Fig. 4. Cyclic voltammograms of the building blocks **CZTPY**, **SiTPY** and **NTPY** and their corresponding metallo-supramolecular polymers **PCZTPY**, **PSiTPY** and **PNTPY** on a Pt electrode measured in 0.1 mol L^{-1} Bu₄NPF₆ acetonitrile solutions with an Ag/AgCl electrode (saturated KCl) as the reference electrode at a scan rate of 100 mV s⁻¹.



Fig. 5. Energy level diagram for the building blocks CZTPY, SiTPY and NTPY and their corresponding metallo-supramolecular polymers PCZTPY, PSiTPY and PNTPY.

energy gaps of the metallo-supramolecular polymers are 2.07, 1.97 and 1.56 eV, respectively. These results demonstrate that the dual combination of introducing a strong electron-donating fused moiety to the polymers plus the coordination of the 2,2':6',2"-terpyridine electron-withdrawing unit with a transition metal ion is an effective approach to tune the photophysical properties of metallosupramolecular polymers, including absorption properties, luminescence color, energy gap, LUMO and HOMO. Moreover, the resulting polymers possess highly pure and narrow energy gaps and are thus promising materials for use as high carrier mobility materials and novel polymer solar cells. Further modifications to the building blocks of the metallo-supramolecular polymers and an investigation of their performance are currently underway.

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References

- Patra A, Pan M, Friend CS, Lin T-C, Cartwright AN, Prasad PN, et al. Electroluminescence properties of systematically derivatized organic chromophores containing electron donor and acceptor groups. Chem Mater 2002;14:4044–8.
- [2] Tang Z-M, Lei T, Wang J-L, Ma Y, Pei J. Star-shaped donor-π-acceptor conjugated molecules: synthesis, properties, and modification of their absorptions features. J Org Chem 2010;75:3644–55.
- [3] Hudson Z, Liu X-Y, Wang S. Switchable three-state fluorescence of a nonconjugated donor-acceptor triarylborane. Org Lett 2011;13:300-3.
- [4] Chochos CL, Tagmatarchis N, Gregoriou VG. Rational design on n-type organic materials for high performance organic photovoltaics. RSC Adv 2013;3: 7160–81.
- [5] Beverina L, Sanguineti A, Battagliarin G, Ruffo R, Roberto D, Righetto S, et al. UV absorbing zwitterionic pyridinium-tetrazolate: exceptional transparency/ optical nonlinearity trade-off. Chem Commun 2011;47:292–4.
- [6] Ko Y-G, Kwon W, Yen H-J, Chang C-W, Kim DM, Kim K, et al. Various digital memory behaviors of functional aromatic polyimides based on electron donor and acceptor substituted triphenylamines. Macromolecules 2012;45: 3749–58.
- [7] Du C, Li W, Duan Y, Li C, Dong H, Zhu J, et al. Conjugated polymers with 2,7linked 3,6-difluorocarbazole as donor unit for high efficiency polymer solar cells. Polym Chem 2013;4:2773–82.
- [8] Braunecker WA, Owczarczyk ZR, Garcia A, Kopidakis N, Larsen RE, Hammond SR, et al. Benzodithiophene and imide-based copolymers for photovoltaic applications. Chem Mater 2012;24:1346–56.
- [9] Beaujuge PM, Pisula W, Tsao HN, Ellinger S, Müllen K, Reynolds JR. Tailoring structure–property relationships in dithienosilole–benzothiadiazole donor–acceptor copolymers. J Am Chem Soc 2009;131:7514–5.
- [10] Chen C-H, Hsieh C-H, Dubosc M, Cheng Y-J, Hsu C-S. Synthesis and characterization of bridged bithiophene-based conjugated polymers for photovoltaic applications: acceptor strength and ternary blends. Macromolecules 2010;43: 697–708.
- [11] Stalder R, Grand C, Subbiah J, So F, Reynolds JR. An isoindigo and dithieno[3,2b:2',3'-d]silole copolymer for polymer solar cells. Polym Chem 2012;3:89–92.
- [12] Chu T-Y, Lu J, Beaupre S, Zhang Y, Pouliot J-R, Wakim S, et al. Bulk heterojunction solar cells using thieno[3,4-c]pyrrole-4,6-dione and dithieno[3,2-b: 2',3'-d]silole copolymer with a power conversion efficiency of 7.3%. J Am Chem Soc 2011;133:4250–3.
- [13] Liao L, Dai L, Smith A, Durstock M, Lu J, Ding J, et al. Photovoltaic-active dithienosilole-containing polymers. Macromolecules 2007;40:9406–12.
- [14] Mercier LG, Mishra A, Ishigaki Y, Henne F, Schulz G, Bäuerle P. Acceptor-donor-acceptor oligomers containing dithieno[3,2-b:2',3'-d]pyrrole and thieno[2,3-c]pyrrole-4,6-dione units for solution-processed organic solar cells. Org Lett 2014;16:2642-5.
- [15] Yue W, Larsen-Olsen TT, Hu X, Shi M, Chen H, Hinge M, et al. Synthesis and photovoltaic properties from inverted geometry cells and roll-to-roll coated large area cells from dithienopyrrole-based donor—acceptor polymers. J Mater Chem A 2013;1:1785–93.
- [16] Bujak P, Kulszewicz-Bajer I, Zagorska M, Maurel V, Wielgus I, Pron A. Polymers for electronics and spintronics. Chem Soc Rev 2013;42:8895–999.
- [17] He X, Baumgartner T. Conjugated main-group polymers for optoelectronics. RSC Adv 2013;3:11334–50.
- [18] Zhan X, Zhu D. Conjugated polymers for high-efficiency organic photovoltaics. Polym Chem 2010;1:409–19.
- [19] Hwang SH, Moorefield CN, Dai L, Newkome GR. Functional nanohybrids constructed via complexation of multiwalled carbon nanotubes with novel hexameric metallomacrocyles. Chem Mater 2006;18:4019–24.
- [20] Islam A, Chowdhury FA, Chiba Y, Komiya R, Fuke N, Ikeda N, et al. Synthesis and characterization of new efficient tricarboxyterpyridyl (β-diketonato) ruthenium(ii) sensitizers and their applications in dye-sensitized solar cells. Chem Mater 2006;18:5178–85.
- [21] Newkome GR, He E, Godínez LA, Baker GR. Neutral highly branched metallomacromolecules: incorporation of a (2,2':6',2'-terpyridine)ruthenium(II) complex without external counterions. Chem Commun 1999:27–8.
- [22] Gohy J-F, Lohmeijer BGG, Varshney SK, Décamps B, Leroy E, Boileau S, et al.

Stimuli-responsive aqueous micelles from an abc metallo-supramolecular triblock copolymer. Macromolecules 2002;35:9748–55.

- [23] Maier A, Tieke B. Coordinative layer-by-layer assembly of electrochromic thin films based on metal ion complexes of terpyridine-substituted polyaniline derivatives. J Phys Chem B 2012;116:925–34.
- [24] Liu Y, Wang Z, Zhang X. Characterization of supramolecular polymers. Chem Soc Rev 2012;41:5922–32.
- [25] Wild A, Winter A, Schlütter F, Schubert US. Advances in the field of π -conjugated 2,2':6',2'-terpyridines. Chem Soc Rev 2011;40:1459–511.
- [26] Zhang K, Zha Y, Peng B, Chen Y, Tew GN. Metallo-supramolecular cyclic polymers. J Am Chem Soc 2013;135:15994–7.
 [27] Chen X, Ma L, Cheng Y, Xie Z, Wang L. Luminescent supramolecular polymers:
- [27] Chen X, Ma L, Cheng Y, Xie Z, Wang L. Luminescent supramolecular polymers: Cd²⁺ directed polymerization and properties. Polym Int 2007;56:648–54.
- [28] Guillet P, Fustin CA, Wouters D, Hoeppener S, Schubert US, Gohy JF. Amphiphilic brushes from metallo-supramolecular block copolymers. Soft Matter 2009;5:1460–5.
- [29] Aspley CJ, Williams JAG. Palladium-catalysed cross-coupling reactions of ruthenium bis-terpyridyl complexes: strategies for the incorporation and exploitation of boronic acid functionality. New J Chem 2001;25:1136–47.
- [30] Miyaura N, Suzuki A. Palladium-catalyzed cross-coupling reactions of

organoboron compounds. Chem Rev 1995;95:2457-83.

- [31] Karl M, John AS. Alkylboranes in the suzuki-miyaura coupling: stereochemical and mechanistic studies. J Org Chem 1998;63:461-70.
 [32] Storrier GD, Colbran SB, Craig DC. Transition-metal complexes of terpyridine
- [32] Storrier GD, Colbran SB, Craig DC. Transition-metal complexes of terpyridine ligands with hydroquinone or quinone substituents. J Chem Soc Dalton Trans 1998:1351–63.
- [33] Dobrawa R, Würthner F. Photoluminescent supramolecular polymers: metalion directed polymerization of terpyridine-functionalized perylene bisimide dyes. Chem Commun 2002:1878–9.
- [34] Roberto D, Tessore F, Ugo R, Bruni S, Manfredi A, Quici S. Terpyridine Zn(II), Ru(III) and Ir(III) complexes as new asymmetric chromophores for nonlinear optics: first evidence for a shift from positive to negative value of the quadratic hyperpolarizability of a ligand carrying an electron donor substituent upon coordination to different metal centres. Chem Commun 2002: 846-7.
- [35] Wang X-Y, Guerzo AD, Schmehl RH. Preferential solvation of an ILCT excited state in bis(terpyridine-phenylene-vinylene) Zn(II) complexes. Chem Commun 2002:2344–5.
- [36] Pommerehne J, Vestweber H, Guss W, Mahrt RF, Bässler H, Porsch M, et al. Efficient two layer leds on a polymer blend basis. Adv Mater 1995;7:551–4.