NJC

PAPER



Cite this: DOI: 10.1039/c5nj03722k

Synthesis and fluorescence study of conjugated polymers based on 2,4,6-triphenylpyridine moieties*

Qianping Ran,^a Jianfeng Ma,^a Tao Wang,^a Shimin Fan,^a Yong Yang,^a Shuai Qi,^a Yixiang Cheng*^b and Fengyan Song*^a

Three novel conjugated polymers based on 2,4,6-triphenylpyridine moieties were synthesized by a Pd-catalyzed Sonogashira coupling reaction. The three polymers P-1, P-2 and P-3 showed strong fluorescence emission with Received (in Montpellier, France) large Stokes' shifts and high quantum yields. We also performed a theoretical calculation analysis to predict the Accepted 28th April 2016 electrochemical and optical properties of the conjugated polymers. The results indicated that although the calculated energy levels were higher than those determined by experiments, the trends of P-1, P-2 and P-3 in DOI: 10.1039/c5nj03722k the band gaps were in good agreement with the ones obtained by UV-vis and CV measurements of the

www.rsc.org/njc

29th December 2015,

Introduction

Conjugated polymers (CPs) have received much attention due to their remarkable optical and electrochemical applications including chemical sensors,¹ electroluminescent devices,² fieldeffect transistors,³ solar cells,⁴ and so on. In comparison with the inorganic counterparts, the main advantages of the organic conjugated polymers are their light weight, flexible nature, solution processability and tunable properties.⁵ Additionally, these delocalizable π -electronic conjugated "molecular wire" polymers can greatly amplify the fluorescence response signal due to facile energy migration along the polymer backbone upon light excitation.^{1,6} Moreover, the conjugated polymers can be systematically modified by the incorporation of rational donor and acceptor moieties into the polymer backbone in an alternating fashion.7

polymers.

2,4,6-Triphenylpyridine, as a well-known electron-deficient heterocyclic unit, has been widely used as the conjugated molecular bridge linker to the polymer main chain.⁸ Pyridine and aromatic heterocyclic derivatives have been widely used as electron transporting/hole blocking materials in LED devices and LED blends because these units have many excellent properties of being a better chromophore, with high electron affinity, high thermal and oxidative stability, and ability for good charge injection and transporting building blocks.9 In addition, introduction of the pyridinyl moiety into the polymer backbone

not only increases the electron affinity of the polymer,^{8a,b} which makes the polymer more resistant to oxidation and also gives the polymer better electron-transporting properties, but also avoids fluorescence quenching due to the intersystem crossing (ISC) effect of the heavy atom.¹⁰ Some of them have been introduced into the polymer backbones to realize the desirable optoelectronic materials.^{8,9} So far, however, there have been few reports on 2,4,6-triphenylpyridine-based conjugated polymers with tunable band gaps.

In this paper, we designed and synthesized three novel conjugated polymers based on 2,4,6-trisphenylpyridine moieties via Sonogashira polymerization. The three polymers P-1, P-2 and P-3 showed strong fluorescence emission with large Stokes' shifts and high quantum yields. The large Stokes' shifts and relatively high quantum yields not only provide the feasibility for biological imaging and biosensing applications,¹¹ but also can achieve high solid state emission intensity or serve as promising electron transporting materials in OLEDs.¹² We also performed a theoretical calculation analysis to predict the electrochemical and optical properties of the conjugated polymers. The results indicated that although the calculated energy levels were higher than those determined by experiments, the trends of P-1, P-2 and P-3 in the band gaps were in good agreement with the ones obtained by UV-vis and CV measurements of the polymers.

Experimental section

Materials and measurements

All solvents and reagents were commercially available and were of analytical reagent grade. THF and Et₃N were distilled from sodium in the presence of benzophenone. NMR spectra were



View Article Online

^a State Key Laboratory of High Performance Civil Engineering Materials (HPCEM), Jiangsu Research Institute of Building Science, Nanjing 210008, Jiangsu, China. E-mail: songfengyan@cnjsjk.cn

^b Key Lab of Mesoscopic Chemistry of MOE and Collaborative Innovation Center of Chemistry for Life Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China. E-mail: yxcheng@nju.edu.cn

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c5nj03722k

obtained using a Bruker Avance 300 spectrometer with 300 MHz for ¹H NMR and 75 MHz for ¹³C NMR, and reported as parts per million (ppm) referenced to TMS as the internal standard. Electrospray ionization mass spectra (ESI-MS) were measured on a Thermo Finnigan LCQ Fleet system. UV-vis spectra were obtained on a Perkin-Elmer Lambda 25 spectrometer. Fluorescence spectra were obtained from a RF-5301PC spectrometer. FT-IR spectra were measured on a Nexus 870 FT-IR spectrometer. Elemental analyses were performed on an Elementar Vario MICRO analyzer. Thermogravimetric analyses (TGA) were performed on a PerkinElmer Pyris-1 instrument under a N₂ atmosphere. Molecular weight was determined by gel permeation chromatography (GPC) using a Waters 244 HPLC pump, and THF was used a solvent relative to polystyrene standards.

The electrochemical measurements were carried out in anhydrous DCM with 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as the supporting electrolyte at a scan rate of 0.05 V s⁻¹ at room temperature under the protection of nitrogen. A gold disk was used as a working electrode, platinum wire was used as a counter electrode and Ag/AgCl (3.0 mol L⁻¹ KCl solution) was used as a reference electrode. The fluorescence quantum yields were determined by the equation: $\Phi_{\rm F}({\rm sample}) = (F_{\rm sample}/F_{\rm ref})(A_{\rm ref}/A_{\rm sample})(n_{\rm sample}^{2}/n_{\rm ref}^{2})\Phi_{\rm F}({\rm ref}),^{13}$ where *F*, *A* and *n* are the measured fluorescence (area under the emission peak), the absorbance at the excitation position, and the refractive index of the solvent, respectively. Rhodamine B (ϕ) = 0.65¹⁴ in EtOH and ZnPc (ϕ) = 0.28¹⁵ in DMF were used as the reference.

Density functional theory (DFT) calculations were performed on polymer repeat units and the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were estimated from the optimized geometry using the B3LYP functional and the 6-31G(d,p) basis set.¹⁶

Syntheses

Compound a. A mixture of benzaldehyde (2.12 g, 20 mmol), acetophenone (4.81 g, 40 mmol), ammonium acetate (24.0 g, 312 mmol) and acetic acid (100 mL) was heated and reacted at 115 °C for 24 h. After cooling to 0 °C, the precipitates were filtered. The obtained crude product was recrystallized by methanol to furnish the desired product a (colorless crystal, yield: 56.5%, 3.47 g). ¹H NMR (300 MHz, CDCl₃): δ 8.05 (d, *J* = 8.1 Hz, 4H), 7.84 (s, 2H), 7.77 (s, 2H), 7.72 (d, *J* = 6.0 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 4H), 7.46–7.57 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 160.4, 156.4, 150.6, 138.4, 137.9, 132.5, 129.1, 128.7, 127.3, 123.6, 117.2. FT-IR (KBr, cm⁻¹): 1632, 1573, 1264, 1135, 735, 587. Anal. calcd for C₂₃H₁₇N: C, 89.87; H, 5.57; N, 4.56. Found: C, 89.80; H, 3.37; N, 3.01.

Compound b. A mixture of 4-butoxybenzaldehyde (3.56 g, 20 mmol), acetophenone (4.81 g, 40 mmol), ammonium acetate (24.0 g, 312 mmol) and acetic acid (100 mL) was heated and reacted at 115 °C for 24 h. After cooling to 0 °C, the precipitates were filtered. The obtained crude product was recrystallized by methanol to furnish the desired product b (colorless crystal, yield: 50.8%, 3.86 g). ¹H NMR (300 MHz, CDCl₃): δ 8.03 (d, *J* = 8.1 Hz, 4H), 7.83 (s, 2H), 7.75 (s, 2H), 7.54–7.66 (m, 6H),

6.99 (dd, J_1 = 6.9 Hz, J_2 = 3.0 Hz, 2H), 4.02 (t, J = 5.7 Hz, 2H), 1.82 (dd, J_1 = 7.5 Hz, J_2 = 3.6 Hz, 2H), 1.55 (dd, J_1 = 8.1 Hz, J_2 = 3.6 Hz, 2H), 0.99 (t, J = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 160.5, 156.3, 149.8, 138.6, 132.3, 129.6, 127.9, 127.7, 123.6, 116.5, 115.2, 67.7, 31.4, 19.3, 13.8. FT-IR (KBr, cm⁻¹): 3021, 2954, 2873, 1543, 1364, 1210, 752, 633. Anal. calcd for C₂₇H₂₅NO: C, 85.45; H, 6.64; N, 3.69. Found: C, 85.53; H, 6.72; N, 3.52.

Compound c. A mixture of 4-(diethylamino)benzaldehyde (3.54 g, 20 mmol), acetophenone (4.81 g, 40 mmol), ammonium acetate (24.0 g, 312 mmol) and acetic acid (100 mL) was heated and reacted at 115 °C for 24 h. After cooling to 0 °C, the precipitates were filtered. The obtained crude product was recrystallized by methanol to afford the residue. The residue was purified by silica gel chromatography (petroleum ether/ ethyl acetate, v/v, 8/1) to afford 4-(2,6-diphenylpyridin-4-yl)-N,Ndiethylaniline (3.32 g, 43.9%) as a deep yellow solid. ¹H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, J = 7.8 Hz, 4H), 7.79 (s, 2H), 7.73 (s, 2H), 7.58–7.67 (m, 6H), 6.78 (d, J = 6.3 Hz, 4H), 3.43 (dd, J₁ = 8.7 Hz, $J_2 = 3.9$ Hz, 4H), 1.23 (t, J = 6.9 Hz, 6H); ¹³C NMR (75 MHz, CDCl_3): δ 160.7, 156.2, 150.4, 138.3, 131.8, 128.1, 127.9, 123.3, 115.7, 111.9, 44.9, 12.4. FT-IR (KBr, cm⁻¹): 3294, 3058, 2975, 2137, 1630, 1486, 1281, 787, 632. Anal. calcd for C27H26N2: C, 85.68; H, 6.92; N, 7.40. Found: C, 85.81; H, 7.03; N, 7.13.

M-2. A mixture of benzaldehyde (2.12 g, 20 mmol), 1-(4bromophenyl)ethanone (7.96 g, 40 mmol), ammonium acetate (24.0 g, 312 mmol) and acetic acid (100 mL) was heated and reacted at 115 °C for 24 h. After cooling to 0 °C, the precipitates were filtered. The obtained crude product was recrystallized by methanol to furnish the desired product (yellowish needle product, yield: 45.7%, 4.24 g). ¹H NMR (300 MHz, CDCl₃): *δ* 8.05 (d, *J* = 8.1 Hz, 4H), 7.85 (s, 2H), 7.71 (d, *J* = 5.7 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 4H), 7.48–7.57 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): *δ* 160.5, 156.4, 150.6, 138.6, 138.2, 132.5, 129.2, 128.7, 127.2, 123.7, 117.2. FT-IR (KBr, cm⁻¹): 1596, 1533, 1240, 1113, 1054, 869, 735, 587. Anal. calcd for C₂₃H₁₅Br₂N: C, 59.38; H, 3.25; N, 3.01. Found: C, 59.13; H, 3.32; N, 3.10. MS (ESI, *m/z*): 465.0.

M-3. A mixture of 4-(diethylamino)benzaldehyde (3.56 g, 20 mmol), 1-(4-bromophenyl)ethanone (7.96 g, 40 mmol), ammonium acetate (24.0 g, 312 mmol) and acetic acid (100 mL) was heated and reacted at 115 °C for 24 h. After cooling to 0 °C, the precipitates were filtered. The obtained crude product was recrystallized by methanol to afford the residue. The residue was purified by silica gel chromatography (petroleum ether/ ethyl acetate, v/v, 10/1) to afford 2,6-bis(4-bromophenyl)-4-(4butoxyphenyl)pyridine (4.75 g, 44.2%) as a colorless crystal. ¹H NMR (300 MHz, CDCl₃): δ 8.02 (d, J = 8.4 Hz, 4H), 7.78 (s, 2H), 7.58–7.67 (m, 6H), 7.02 (dd, $J_1 = 6.6$ Hz, $J_2 = 2.7$ Hz, 2H), 4.02 (t, J = 5.4 Hz, 2H), 1.81 (dd, $J_1 = 7.2$ Hz, $J_2 = 3.3$ Hz, 2H), 1.53 (dd, J_1 = 8.7 Hz, J_2 = 3.9 Hz, 2H), 1.00 (t, J = 6.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 160.3, 156.3, 150.1, 138.3, 132.7, 129.6, 128.3, 128.1, 123.6, 116.5, 115.1, 67.9, 31.3, 19.3, 13.9. FT-IR (KBr, cm⁻¹): 3021, 2931, 2854, 2837, 1599, 1375, 1137, 1086, 823, 752, 633. Anal. calcd for C₂₇H₂₃Br₂NO: C, 60.36; H, 4.31; N, 2.61. Found: C, 60.57; H, 4.48; N, 2.65. MS (ESI, m/z): 537.0.

NJC

M-4. A mixture of 4-(diethylamino)benzaldehyde (3.54 g, 20 mmol), 1-(4-bromophenyl)ethanone (7.96 g, 40 mmol), ammonium acetate (24.0 g, 312 mmol) and acetic acid (100 mL) was heated and reacted at 115 °C for 24 h. After cooling to 0 °C, the precipitates were filtered. The obtained crude product was recrystallized by methanol to furnish the desired product **M-4** (yellow solid, yield: 49.5%, 5.31 g). 1H NMR (300 MHz, CDCl₃): δ 8.05 (d, *J* = 8.1 Hz, 4H), 7.77 (s, 2H), 7.60–7.66 (m, 6H), 6.79 (d, *J* = 5.7 Hz, 4H), 3.43 (dd, *J*₁ = 9.3 Hz, *J*₂ = 4.2 Hz, 4H), 1.22 (t, *J* = 6.6 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 156.2, 150.3, 138.7, 131.8, 128.1, 127.9, 123.3, 115.8, 112.3, 44.7, 12.6. FT-IR (KBr, cm⁻¹): 3342, 3187, 2935, 2200, 1566, 1486, 1367, 1217, 1030, 787, 632. Anal. calcd for C₂₇H₂₄Br₂N₂: C, 60.47; H, 4.51; N, 5.22. Found: C, 60.72; H, 4.68; N, 5.09. MS (ESI, *m*/z): 536.0.

P-1. A mixture of M-1 (46.7 mg, 0.1 mmol), M-2 (46.5 mg, 0.1 mmol), Pd(PPh₃)₄ (5.8 mg, 5% mmol), and CuI (1.0 mg, 5% mmol) was added to THF (6 mL) and Et₃N (6 mL) under a N₂ atmosphere. The reaction mixture was stirred at 75 °C for 48 h. Then the mixture was cooled to room temperature and filtered through a short silica gel column. Then the polymer was precipitated in methanol (80 mL). The polymer was filtered and washed with methanol several times. Further purification could be conducted by dissolving the polymer in THF to precipitate in methanol again. The polymer was dried in vacuum to afford P-1 (43.7 mg, 56.8%) as a deep yellow solid. GPC results: $M_{\rm w} = 12410$, $M_{\rm n}$ = 7020, PDI = 1.77. ¹H NMR (300 MHz, CDCl₃): δ 8.13–8.34 (m, 2H), 8.06 (d, J = 6.0 Hz, 4H), 7.86 (s, 2H), 7.72 (d, J = 6.6 Hz, 3H), 7.64 (d, I = 6.6 Hz, 4H), 7.41-7.57 (m, 4H), 4.27(s, 2H), 1.84 (s, 2H), 0.82–1.47 (m, 38H), 0.86 (s, 4H). FT-IR (KBr, cm⁻¹): 2237, 1839, 1716, 1596, 1533, 1358, 1240, 1113, 1054, 869, 735, 587. Anal. calcd for (C₅₇H₅₈N₂)_n: C, 88.79; H, 7.58; N, 3.63. Found: C, 88.73; H, 7.41; N, 3.54.

P-2. A mixture of M-1 (46.7 mg, 0.1 mmol), M-3 (53.7 mg, 0.1 mmol), Pd(PPh₃)₄ (5.8 mg, 5% mmol), and CuI (1.0 mg, 5% mmol) was dissolved in THF (6 mL) and Et₃N (5 mL) under a N2 atmosphere. The reaction mixture was stirred for 48 h at 75 $^{\circ}$ C. Then the mixture was cooled to room temperature and filtered through a short silica gel column. Then the polymer was precipitated in methanol (80 mL). The polymer was filtered and washed with methanol several times. Further purification could be conducted by dissolving the polymer in THF to precipitate in methanol again. The polymer was dried in vacuum to afford P-2 (51.8 mg, 61.5%) as a pale blue solid. GPC results: $M_{\rm w} = 11\,020$, $M_{\rm n} = 5970$, PDI = 1.85. ¹H NMR (300 MHz, CDCl₃): δ 8.04–8.33 (m, 3H), 7.98 (d, J = 8.7 Hz, 3H), 7.78 (s, 2H), 7,47-7.70 (m, 7H), 7.32-7.40 (m, 2H), 6.96 (d, J = 8.1 Hz, 2H), 4.12-4.27 (m, 2H), 3.94-4.01 (m, 2H), 1.68-1.87 (m, 4H), 1.47-1.52 (m, 3H), 1.00-1.37 (m, 37H), 0.82-1.00 (m, 4H), 0.74-0.82 (m, 5H). FT-IR (KBr, cm⁻¹): 3021, 2931, 2854, 2837, 2237, 1937, 1756, 1599, 1375, 1259, 1137, 1086, 823, 752, 633. Anal. calcd for (C₆₁H₆₆N₂O)_n: C, 86.89; H, 7.89; N, 3.32. Found: C, 86.67; H, 7.73; N, 3.28.

P-3. A mixture of **M-1** (46.7 mg, 0.1 mmol), **M-4** (53.6 mg, 0.1 mmol), Pd(PPh₃)₄ (5.8 mg, 5% mmol), and CuI (1.0 mg, 5% mmol) was dissolved in THF (6 mL) and Et₃N (6 mL) under a N₂ atmosphere. The reaction mixture was stirred for 48 h at 75 °C.

Then the mixture was cooled to room temperature and filtered through a short silica gel column. Then the polymer was precipitated in methanol (80 mL). The polymer was filtered and washed with methanol several times. Further purification could be conducted by dissolving the polymer in THF to precipitate in methanol again. The polymer was dried in vacuum to afford **P-3** (48.9 mg, 58.1%) as a deep red solid. GPC results: $M_w = 9470$, $M_n = 6330$, PDI = 1.49. ¹H NMR (300 MHz, CDCl₃): δ 8.13–8.42 (m, 3H), 8.04 (d, J = 6.0 Hz, 4H), 7.86 (s, 2H), 7.52–7.71 (m, 8H), 7.30–7.48 (m, 3H), 6.78 (d, J = 6.6 Hz, 2H), 4.23–4.31 (m, 3H), 3.44 (dd, $J_1 = 8.7$ Hz, $J_2 = 3.6$ Hz, 2H), 1.69–1.88 (m, 3H), 1.51–1.62 (m, 2H), 1.01–1.47 (m, 38H), 0.87 (s, 6H). FT-IR (KBr, cm⁻¹): 3342, 3187, 2935, 2854, 2837, 2200, 1933, 1748, 1566, 1486, 1367, 1157, 1049, 775, 632. Anal. calcd for (C₆₁H₆₇N₃)_n: C, 86.99; H, 8.02; N, 4.99. Found: C, 86.57; H,7.94; N, 4.85.

Results and discussion

Synthesis and structural features of the monomers and the polymers

The synthetic routes to the monomers and polymers are shown in Scheme 1. 3,6-Diethynyl-9-octadecyl-9H-carbazole (M-1)17 was prepared according to reported literature methods. M-2 was synthesized by the reaction of benzaldehyde, 1-(4-bromophenyl)ethanone, and ammonium acetate in HAc in 45.7% yield. M-3 and M-4 were synthesized according to the synthetic method of M-2. P-1, P-2 and P-3 were synthesized by a Pd-catalyzed Sonogashira coupling reaction from M-1 and M-2/M-3/M-4 in yields of 56.8, 61.5 and 58.1%, respectively (Scheme 2). The chemical structures of the polymers could be verified by ¹H NMR and IR spectroscopy. The complete disappearance of the alkyne proton signals at $\delta \sim 3.3$ confirms the efficient coupling reaction of the alkyne. Meanwhile, the IR spectrum of P-1/P-2/P-3 also shows no absorption bands at about \sim 3300 cm⁻¹ which are assignable to the stretching vibrations of \equiv CH. This demonstrates the successful preparation of the target polymers. As expected, the resonance peaks in the ¹H NMR spectra of polymers are broader than those of monomers due to part to their longer rotational correlation times. The resulting polymers show excellent solubility in common organic solvents including THF, CHCl₃ and CH₂Cl₂. Table 1 summarizes the polymerization results and thermal properties of the polymers. The number average molecular weight and the polydispersity index (PDI) of the polymers measured by GPC were M_n = 7420 and PDI = 1.77 for P-1, M_n = 5970 and PDI = 1.85 for P-2, and M_n = 6330 and PDI = 1.49 for P-3. As shown in Fig. 1, the TGA curves reveal that the degradation temperature (T_d) of 5% weight loss of P-1, P-2 and P-3 is 254, 226 °C and 279 °C, respectively, which indicates the excellent thermal stability of the polymers.

Optical properties

The UV-vis absorption and fluorescence spectra of the polymers, **a**, **b** and **c** are shown in Fig. 2, and the corresponding optical data are listed in Table 2. As shown in UV-vis absorption spectra (Fig. 2a) measured in solutions $(1.0 \times 10^{-5} \text{ mol L}^{-1} \text{ in CH}_2\text{Cl}_2)$, **a**, **b** and **c** displayed one peak centered at 265 nm,



Scheme 2 Chemical structures of the polymers.

Table 1 Molecular weight and thermal properties of point	olymers
--	---------

Polymer	$T_{\rm d}^{\ a} \left(^{\circ} {\rm C}\right)$	$M_{\rm w}^{\ \ b}$ (g mol ⁻¹)	M_n^b (g mol ⁻¹)	PDI
P-1	254	12 410	7020	1.77
P-2	226	11 020	5970	1.85
P-3	279	9470	6330	1.49

^{*a*} Temperature of 5% weight loss measured by TGA in nitrogen. ^{*b*} Molar mass (M_n, M_w) and polydispersity index (PDI) were determined by GPC in THF against polystyrene standards with UV detection set to absorption maxima.

274 nm and 255 nm, respectively. **P-1**, **P-2** and **P-3** show two distinct bands in the absorption spectra. One band at the shorter wavelength region at around 250–295 nm is assigned to their localized π - π * transition, and the other band at a longer wavelength at around 350–375 nm is attributed to the intra-molecular charge transfer (ICT)¹⁸ between electron-rich donors and electron-deficient acceptors. As shown in the emission spectra of Fig. 2b, the model compounds **a**, **b** and **c** can emit fluorescence concerted at 359 nm, 354 nm and 415 nm. While the 2,4,6-trisphenylpyridine unit is introduced into the main chain backbone of the conjugated polymer, the maximum

Published on 29 April 2016. Downloaded by UNIVERSITY OF NEBRASKA on 20/05/2016 09:56:39.



	λ_{abs} (nm)	$\lambda_{\mathrm{ex}} \left(\mathrm{nm} \right)$	$\lambda_{\max}^{a}(nm)$	Stokes shift (cm^{-1})	${\Phi_{\mathrm{F}}}^b$
a	265, 318	263	359	$9.88 imes 10^3$	_
b	274	264	354	8.24×10^3	_
с	255, 292, 353	295	415	$1.39 imes10^4$	_
P-1	260, 319, 355	355	439	1.57×10^4	0.37
P-2	295, 352	361	430	1.06×10^4	0.43
P-3	252, 318, 353	365	470	$1.84 imes10^4$	0.26

 a The emission wavelength $\lambda_{\rm max}$ of the conjugated polymers P-1, P-2 and P-3. ^b Quantum yields were determined with ZnPc as fluorescence reference in DMF ($\phi = 0.28$).



650



Fig. 1 TGA curves of the conjugated polymers P-1, P-2 and P-3



Fig. 2 (a) Normalized UV-vis absorption spectra in CH₂Cl₂ solutions and (b) normalized emission spectra in CH₂Cl₂ solutions of **a**, **b**, **c**, **P-1**, **P-2**, and **P-3**.

emission peaks of P-1 (439 nm), P-2 (430 nm) and P-3 (470 nm) appear red-shifted by 80, 76 and 65 nm, respectively, indicating an efficient extension of π -conjugation along the linkers. Such an obvious result suggests that the 2,4,6-trisphenylpyridine based polymer shows large Stokes' shifts and obvious fluorescence emission, which is expected to be used as potential fluorescent materials.

Electrochemical properties

The redox behaviors of the three polymers were measured by cyclic voltammetry (CV) in a deoxygenated CH₂Cl₂ solution at a Fig. 3 Cyclic voltammograms of the polymers P-1, P-2 and P-3.

NJC

 Table 3
 Electrochemical data for P-1, P-2 and P-3, and the calculated HOMO and LUMO energy values

	From CV^a				From calculation			
	$ \frac{E_{\text{ox}}^{\text{onset } b}}{(\text{V})} $	HOMO ^c (eV)	$E_{\mathrm{red}}^{\mathrm{onset}b}$ (V)	LUMO ^c (eV)	E_{g}^{c} (eV)	$\frac{\text{HOMO}^d}{(\text{eV})}$	LUMO ^d (eV)	E_{g}^{d} (eV)
P-1	0.87	-5.67	-0.72	-4.08	1.59	-5.15	-2.64	2.51
Р-2 Р-3	0.90 0.85	$-5.70 \\ -5.65$	$-0.87 \\ -0.68$	$-3.93 \\ -4.12$	1.77 1.53	$-5.21 \\ -5.24$	$-2.47 \\ -2.92$	2.74 2.32

^{*a*} The ferroncene–ferrocenium couple (Fc/Fc⁺) was used as the internal reference and under our experimental conditions, $E(Fc^+/Fc) = 0.42 \text{ V} \nu s$. Ag/AgCl. ^{*b*} E_{ox} and E_{red} determined from the onset potentials of the oxidation and reduction waves. ^{*c*} $E_{\text{g}} = \text{LUMO} - \text{HOMO}$. ^{*d*} DFT quantum mechanical calculations (B3LYP/6-31G*).

scan rate of 50 mV s⁻¹. All measurements were performed in N₂-saturated solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as the supporting electrolyte, and redox potentials were calibrated using a ferrocene–ferrocenium (Fc–Fc⁺) redox couple as an external standard. Platinum wire was used as a counter electrode and a Ag/AgCl electrode was used as a reference electrode. The polymers were deposited onto the working electrode from CH_2Cl_2 solution. The CV curves of **P-1**, **P-2** and **P-3**

are shown in Fig. 3, and the electrochemical data are summarized in Table 3. The three conjugated polymers underwent irreversible or quasi-reversible oxidation and reduction waves. In their oxidation traces, the onset potentials of P-1, P-2 and P-3 occurred at +0.87 eV, +0.9 eV and +0.85 eV, respectively, essentially arising from the oxidation of electron-donating carbazole units. In their reduction traces, P-1, P-2 and P-3 exhibited similar onset potentials at -0.72 eV, -0.87 eV and -0.68 eV, which can be assigned to the reduction of the electron-accepting 2,4,6-tris(4-phenoxy)-pyridine moiety. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the polymers can be calculated according to the equations HOMO = $-e(E_{ox}^{onset} + 4.8)$ (eV) and LUMO = $-e(E_{red}^{onset} + 4.8)$ (eV).¹⁹ On the basis of these onset potentials, the HOMO/LUMO energy levels of P-1, P-2 and P-3 were determined to be -5.67/-4.08 eV, -5.70/-3.93 eV and -5.65/-3.93 eV with the corresponding electrochemical band gaps of 1.59, 1.77 eV and 1.53 eV, respectively. This demonstrated that the energy levels of conjugated polymers can be effectively tuned by changing the donor and acceptor moieties in the polymer main-chain backbone.



Fig. 4 The LUMO and HOMO energy levels of the repeating unit from DFT calculations.

Molecular orbital calculations

According to Höger's report and Huang's report, there is a nearly proportional relationship between the experimentally determined (CV) and the theoretically calculated energy levels for the HOMOs and LUMOs of these polymers.^{5b,20} The result indicates that the frontier molecular orbital energy levels of polymers could be predictably tuned through theoretical calculations of model molecules. To gain a better insight into the geometric and electronic structures, we performed a theoretical calculation analysis on the model molecules 1, 2 and 3 constituting the corresponding repeat units (Fig. 4). All calculations were performed using the Gaussian 09 program suite by using the B3LYP method and the 6-31G* basis set.¹⁶ Moreover, all the alkyl chains were replaced by methyl and methoxy groups in the calculation for simplicity. Fig. 4 displays the LUMO and the HOMO of model 1-3. The calculated HOMO, LUMO and energy gaps (E_{α}) of the three models are listed in Table 3. As shown in Fig. 4, the LUMO of the three model compounds is mainly localized at the central core of 2,4,6tris(4-phenoxy)-pyridine with a strong contribution to the nitrogen atom, whereas the HOMO localization is not only centered on the core of the tris(4-phenoxy)-pyridine unit with small coefficients, but also partially at the donor carbazole moiety in the polymer backbone. The calculated data show that the model molecules of P-1, P-2 and P-3 have the LUMO and HOMO energy levels in the range of -2.47 to -2.92 eV and -5.15 to -5.24 eV, respectively. The band gaps were determined to be 2.51 eV, 2.74 eV and 2.32 eV for P-1, P-2 and P-3. The LUMO energy level of model 2 is higher than that of models 1 and 3 indicating that the electron accepting ability of M-2 is stronger than that of M-1 and M-3. It can also be found that the order of band gap (E_{g}) was model 2 > model 1 > model 3, which is almost consistent with the UV-vis absorption maxima of the polymers in the order P-3 < P-1 < P-2. Although the calculated energy levels were higher than those determined by experiments, the trends of P-1, P-2 and P-3 in the band gaps were in good agreement with the ones obtained by UV-vis and CV measurements of the polymers.

Conclusions

In summary, we have successfully synthesized three novel polymers **P-1**, **P-2** and **P-3** containing carbazole units and 2,4,6-trisphenylpyridine moieties in the main chain by a Pd-catalyzed Sonogashira coupling reaction. The UV-vis absorption and fluorescence spectra indicate that the introduction of 2,4,6-trisphenylpyridine moieties into the conjugated polymer could significantly affect the optical properties of the polymers. Also, the CV and calculated data further demonstrate that although the calculated energy levels were higher than those determined by experiments, the trends of **P-1**, **P-2** and **P-3** in the band gaps were in good agreement with the ones obtained by UV-vis and CV measurements of the polymers. These photophysical and electrochemical properties indicate that the polymers might have potential device-based applications.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51278232, 51408274 and 51508242) and Natural Science Foundation of Jiangsu Province of China (BK20130048, BK20131011 and BK20151012).

Notes and references

- (a) F. Song, G. Wei, L. Wang, J. Jiao, Y. Cheng and C. Zhu, J. Org. Chem., 2012, 77, 4759–4764; (b) J. Hou, F. Song, L. Wang, G. Wei, Y. Cheng and C. Zhu, Macromolecules, 2012, 45, 7835–7842; (c) F. Song, N. Fei, F. Li, S. Zhang, Y. Cheng and C. Zhu, Chem. Commun., 2013, 49, 2891–2893; (d) G. Wei, S. Zhang, C. Dai, Y. Quan, Y. Cheng and C. Zhu, Chem. – Eur. J., 2013, 19, 16066–16071; (e) G. Wei, Y. Jiang, F. Li, Y. Quan, Y. Cheng and C. Zhu, Polym. Chem., 2014, 5, 5218–5222; (f) F. Li, G. Wei, Y. Sheng, Y. Quan, Y. Cheng and C. Zhu, Polymer, 2014, 55, 5689–5694; (g) F. Song, G. Wei, X. Jiang, F. Li, Y. Cheng and C. Zhu, Chem. Commun., 2013, 49, 5772–5774.
- 2 (a) B. G. Kang, H. Kang, N. G. Kang, C. L. Lee, K. Lee and J. S. Lee, *Polym. Chem.*, 2013, 4, 969–977; (b) L. P. Lu, D. Kabra and R. H. Friend, *Adv. Funct. Mater.*, 2012, 22, 4165–4171; (c) J. J. Intemann, E. S. Hellerich, B. C. Tlach, M. D. Ewan, C. A. Barnes, A. Bhuwalka, M. Cai, J. Shinar, R. Shinar and M. Jeffries-EL, *Macromolecules*, 2012, 45, 6888–6897; (d) P. Zalar, Z. B. Henson, G. C. Welch, G. C. Bazan and T. Q. Nguyen, *Angew. Chem., Int. Ed.*, 2012, 51, 7459–7498; (e) C. C. Cheng, Y. L. Chu, P. H. Huang, Y. C. Yen, C. W. Chu, A. C. M. Yang, F. H. Ko, J. K. Chen and F. C. Chang, *J. Mater. Chem.*, 2012, 22, 18127–18131.
- 3 (a) C. Cheng, C. Yu, Y. Guo, H. Chen, Y. Fang, G. Yu and Y. Liu, *Chem. Commun.*, 2013, 49, 1998–2000; (b) J. Kim, S. H. Kim, T. K. An, S. Park and C. E. Park, *J. Mater. Chem.*, 2013, 1, 1272–1278; (c) W. Zhou, Y. Wen, L. Ma, Y. Liu and X. Zhan, *Macromolecules*, 2012, 45, 4115–4121.
- 4 (a) Z. Li, S. W. Tsang, X. Du, L. Scoles, G. Robertson, Y. Zhang, F. Toll, Y. Tao, J. Lu and J. Ding, Adv. Funct. Mater., 2011, 21, 3331–3336; (b) Y. Wu, Y. Jing, X. Guo, S. Zhang, M. Zhang, L. Huo and J. Hou, Polym. Chem., 2013, 4, 536–541; (c) Y. J. Cheng, S. H. Yang and C. S. Hsu, Chem. Rev., 2009, 109, 5868–5923; (d) 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; (e) A. Balan, D. Baran and L. Toppare, Polym. Chem., 2011, 2, 1029–1043; (f) J.-T. Chen and C.-S. Hsu, Polym. Chem., 2011, 2, 2702–2722.
- 5 (a) X. Ma, X. Mao, S. Zhang, X. Huang, Y. Cheng and C. Zhu, Polym. Chem., 2013, 4, 520–527; (b) X. Ma, X. Jiang, S. Zhang, X. Huang, Y. Cheng and C. Zhu, Polym. Chem., 2013, 4, 4396–4404; (c) X. Jiang, X. Liu, Y. Jiang, Y. Quan, Y. Cheng and C. Zhu, Macromol. Chem. Phys., 2014, 215, 358–364; (d) X. Ma, E. A. Azeem, X. Liu, Y. Cheng and C. Zhu, J. Mater. Chem. C, 2014, 2, 1076–1084; (e) S. Zhang, Y. Sheng, G. Wei, Y. Quan, Y. Cheng and C. Zhu, J. Polym. Sci., Part A: Polym. Chem., 2014, 52, 1686–1692.

- 6 (a) S. W. Thomas III, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339–1386; (b) S. Rochat and T. M. Swager, *ACS Appl. Mater. Interfaces*, 2013, **5**, 4488–4502.
- 7 (a) B. S. Harrison, M. B. Ramey, J. R. Reynolds and K. S. Schanze, J. Am. Chem. Soc., 2000, 122, 8561–8562; (b) D. L. Wang, J. Wang, D. Moses, G. C. Bazan and A. J. Heeger, Langmuir, 2001, 17, 1262–1266; (c) N. DiCesare, M. R. Pinto, K. S. Schanze and J. R. Lakowicz, Langmuir, 2002, 18, 7785–7787; (d) M. R. Pinto, B. M. Kristal and K. S. Schanze, Langmuir, 2003, 19, 6523–6533.
- 8 (a) J. A. Mikroyannidis, P. A. Damouras, V. G. Maragos, L. R. Tsai and Y. Chen, *Eur. Polym. J.*, 2009, 45, 284-294;
 (b) A. Kraft, A. C. Gromsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, 37, 402-444; (c) T. Kanbara, N. Saito, T. Yamamoto and K. Kubota, *Macromolecules*, 1991, 24, 5883-5885; (d) T. Kanbara, T. Kushida, N. Saito, I. Kuwajima, K. Kubota and T. Yamamoto, *Chem. Lett.*, 1992, 583-586; (e) Y. W. Wang, D. D. Gebler, D. K. Fu, T. M. Swager, A. G. MacDiarmid and A. J. Epstein, *Synth. Met.*, 1997, 85, 1179-1182.
- 9 (a) K. J. Fallon, N. Wijeyasinghe, N. Yaacobi-Gross, R. S. Ashraf, D. M. E. Freeman, R. G. Palgrave, M. Al-Hashimi, T. J. Marks, I. McCulloch, T. D. Anthopoulos and H. Bronstein, *Macromolecules*, 2015, 48, 5148–5154; (b) D. Liu, W. Zhao, S. Zhang, L. Ye, Z. Zheng, Y. Cui, Y. Chen and J. Hou, *Macromolecules*, 2015, 48, 5172–5178; (c) Y. Kim, D. X. Long, J. Lee, G. Kim, T. J. Shin, K. W. Nam, Y. Y. Noh and C. Yang, *Macromolecules*, 2015, 48, 5179–5187; (d) J. H. Wu and G. S. Liou, *Polym. Chem.*, 2015, 6, 5225–5232.
- 10 N. J. Turro, *Modern molecular Photochemistry*, Benjamin/ Cummings Publ. Co., New York, 1978, p. 48.
- 11 (a) X. Zhang, J. Yu, Y. Rong, F. Ye, D. T. Chiu and K. Uvdal, *Chem. Sci.*, 2013, 4, 2143–2151; (b) I. Wu, J. Yu, F. Ye, Y. Rong, M. E. Gallina, B. S. Fujimoto, Y. Zhang, Y.-H. Chan, W. Sun, X.-H. Zhou, C. Wu and D. T. Chiu, *J. Am. Chem. Soc.*, 2015, 137, 173–178; (c) S.-Y. Liou, C.-S. Ke, J.-H. Chen, Y.-W. Luo, S.-Y. Kuo, Y.-H. Chen, C.-C. Fang and C.-Y. Wu, ACS Macro Lett., 2016, 5, 154–157; (d) B. Song,

Y. Zhong, S. Wu, B. Chu, Y. Su and Y. He, *J. Am. Chem. Soc.*, 2016, **138**, 4824–4831.

- 12 (a) Y. Zhou, J. W. Kim, R. Nandhakumar, M. J. Kim, E. Cho,
 Y. S. Kim, Y. H. Jang, C. Lee, S. Han, K. M. Kim, J.-J. Kim and
 J. Yoon, *Chem. Commun.*, 2010, 46, 6512–6514; (b) X. Ma,
 J. Jiao, J. Yang, X. Huang, Y. Cheng and C. Zhu, *Polymer*,
 2012, 53, 3894–3899; (c) D. Frath, J. Massue, G. Ulrich and
 R. Ziessel, *Angew. Chem., Int. Ed.*, 2014, 53, 2290–2310.
- 13 D. F. Eaton, Pure Appl. Chem., 1988, 60, 1107-1114.
- 14 G. E. Crosby and J. N. Denmas, J. Phys. Chem., 1971, 75, 991–1024.
- 15 X. J. Jiang, S. L. Yeung, P. C. Lo, W. P. Fong and D. K. P. Ng, J. Med. Chem., 2011, 54, 320–330.
- 16 (a) R. Yoshii, A. Nagai and Y. Chujo, J. Polym. Sci., Part A: Polym. Chem., 2010, 48, 5348–5356; (b) R. Gresser, H. Hartmann, M. Wrackmeyer, K. Leo and M. Riede, Tetrahedron, 2011, 67, 7148–7155; (c) M.-J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M.-A. Robb, J. R. Cheeseman, J. A. Montgomery and J.-A. Pople, et al., Gaussian 03, Revision C. 02, Gaussian, Inc., Wallingford CT, 2004.
- 17 T. Kanbara, N. Saito, T. Yamamoto and K. Kubota, *Macromolecules*, 1991, 24, 5883–5885.
- (a) X. Peng, F. Song, E. Lu, Y. Wang, W. Zhou, J. Fan and Y. Gao, *J. Am. Chem. Soc.*, 2005, 127, 4170–4171; (b) G. Qian, Z. Zhong, M. Luo, D. Yu, Z. Zhang, D. Ma and Z. Y. Wang, *J. Phys. Chem. C*, 2009, 113, 1589–1595; (c) F. Song, X. Ma, J. Hou, X. Huang, Y. Xiang and C. Zhu, *Polymer*, 2011, 52, 6029–6036.
- (a) C.-C. Ho, Y.-C. Liu, S.-H. Lin and W.-F. Su, *Macromolecules*, 2012, 45, 813–820; (b) X. Ma, J. Jiao, J. Yang, X. Huang, Y. Cheng and C. Zhu, *Polymer*, 2012, 53, 3894–3899; (c) Y. Ie, J. Huang, Y. Uetani, M. Karakawa and Y. Aso, *Macromolecules*, 2012, 45, 4564–4571.
- 20 (a) F. M. Pasker, S. M. Le Blanc, G. Schnakenburg and S. Höger, Org. Lett., 2011, 13, 2338–2341; (b) T. Tao, Y. X. Peng, W. Huang and X. Z. You, J. Org. Chem., 2013, 78, 2472–2481.