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Synthesis of Conjugated Polymers Containing Diketopyrrolopyrrole (DPP) Building Block and the Photophysical Study

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Electronic Supplementary Information

Abstract Sonogashira coupling of two different diketopyrrolopyrrole (DPP)-containing dihaloarenes with the same aromatic bisalkyne resulted in two new conjugated polymers with the same backbone but different pendant groups on the DPP moiety. The polymers were found to have designed chemical structures *via* structural characterizations in comparison with three monomers. The molecular weight measurement further demonstrated the formation of polymers with polydispersity index around 2, consistent with the polycondensation nature of the polymerization based on Sonogashira coupling. Both polymers could dissolve in many organic solvents, and the one with long alkyl side group on DPP moiety had better solubility. Photophysical investigation showed that both polymers had typical absorption/emission of conjugated polymers, and varying the solvent did not have large influence. Compared with other polar solvents, toluene reduced the quantum yield of fluorescence of the polymers, especially for the one with long alkyl pendant group, accompanying with slight red-shift in absorption/emission. The difference in the absorption/emission wavelengths between the polymers was similar to that between the corresponding monomers. Adding water into the THF solution of polymers reduced the emission intensity but no red-shift was observed. Discussion about the structure-property relationships was carried out in detail.

Keywords Conjugated polymer; Diketopyrrolopyrrole; Building block; Sonogashira coupling; Photophysics

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INTRODUCTION

Conjugated polymers (CPs) have aroused great attention in the past several decades because they are very promising to be applied as the key materials in many fields, such as electronic display, photovoltaic device, and fluorescence sensing/imaging.^[1–8] Developing a platform for incorporating building blocks with some specific properties into the conjugated backbone will greatly extend the application of these materials. Diketopyrrolopyrrole (DPP), as a small molecular dye, possesses many distinctive characteristics like planar structure and electron deficiency, strong emission, extremely high thermal stability, and photostability as well as easy structural modifiability.^[9–11] DPP and its derivatives have been widely used as paints/inks, fluorescent probes, and organic photovoltaics.^[9,12–14] Recently, DPP-based CPs were reported for photovoltaic or sensing applications and their semiconducting or fluorescence properties were investigated.^[15–22] Preparing DPP-based CPs with new chemical structures and good solubility may bring more applications of CPs in these fields.

Various methods have been employed to introduce DPP

building blocks into the conjugated backbone, such as Stille coupling, Suzuki coupling, and direct arylation polycondensation.^[23–25] However, to our knowledge, only a few reports employed Sonogashira coupling to synthesize DPP-based conjugated polymers.^[26–30] Polymerization based on Sonogashira coupling between bisalkyne and dihaloarene to form poly(aryleneethynylene) can be used for dedicate tuning of the structure of the conjugated backbone as well as the pendant group.^[6,31–34] Here we report the synthesis of two new DPP-based conjugated polymers that can dissolve in organic solvents. Two dibrominated DPP monomers with different pendant groups were synthesized *via* the reaction between the secondary amine on DPP and alkyl bromide or anhydride. Sonogashira coupling of these two monomers with the same aromatic bisalkyne resulted in two conjugated polymers, **PPE-DPP1** and **PPE-DPP2**, with the same backbone but different pendant groups on the DPP moiety (Scheme 1). The structure and photophysics of the polymers were characterized and compared. The similarity and difference in the photophysical properties were also investigated.

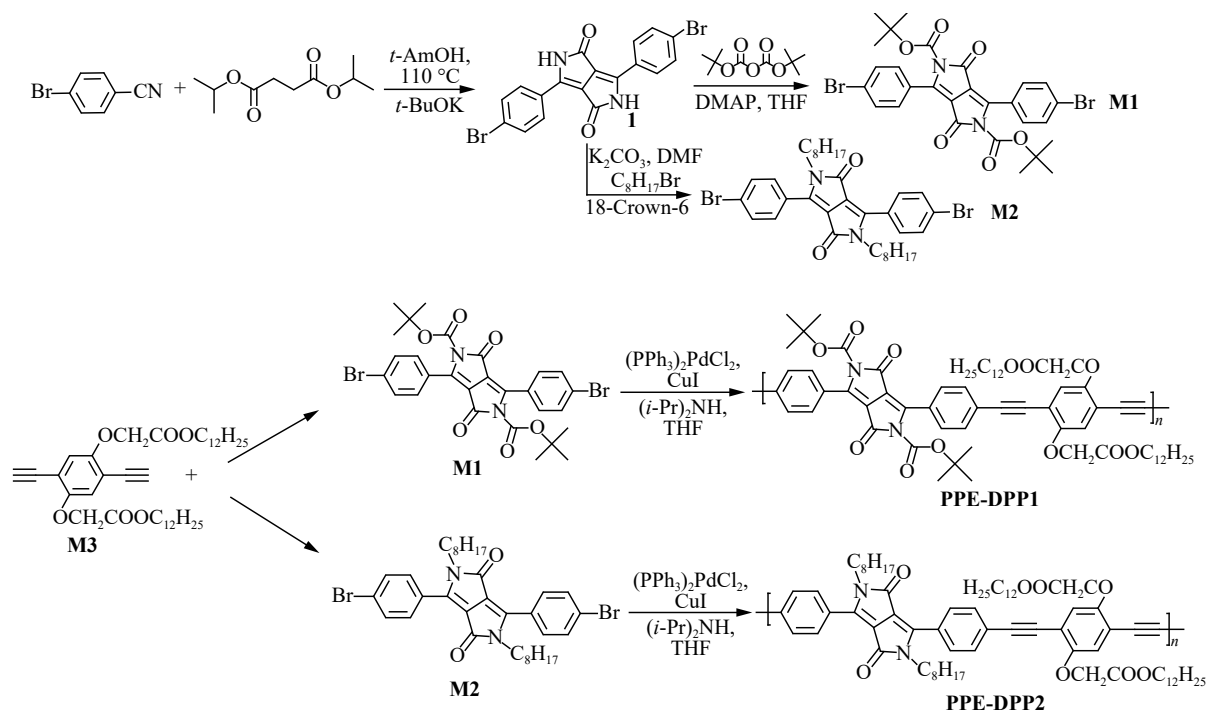
EXPERIMENTAL

Materials

Bis(triphenylphosphine)palladium(II) chloride (PdCl₂-

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Scheme 1 The synthetic strategies for monomers (top) and polymers (bottom)

(PPh₃)₂ and bis(trimethylsilyl)acetylene were obtained from J&K Chemical Ltd. 4-Bromo-benzonitrile and 1-bromooctane were purchased from Energy Chemical Co., Ltd. Diisopropyl succinate, 4-dimethylaminopyridine (DMAP), and 18-crown-6 were purchased from Adamas Reagent Co., Ltd. Other commercially available reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were of analytical purity and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was dried by distillation from sodium metal and kept under argon. Diisopropylamine was distilled over potassium hydroxide before use. 2,5-Bis(dodecyloxycarbonylmethoxy)-1,4-diethynylbenzene (**M3**) was synthesized according to our previous work.^[34]

Instruments and General Methods

¹H-NMR spectra were recorded on an Inova 400 MHz NMR spectrometer with tetramethylsilane as the internal standard. Fourier transform infrared (FTIR) spectra were collected on a Vertex 70 spectrophotometer by attenuated total reflection (ATR). Elemental microanalyses were carried out on a Carlo-Erba Elemental Analyzer EA 1110. Gel permeation chromatography (GPC) measurements were performed on a Waters 1515 system with THF as the mobile phase and polystyrene as the standard. UV-Vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Fluorescence emission spectra were measured on a Shimadzu RF-5301 PC spectrophotometer. The fluorescence quantum yields of the monomers and polymers in solution were measured relative to quinine sulfate in H₂SO₄ solution with a quantum yield of 0.546, excited at 365 nm and Rhodamine 6G in ethanol solution with a quantum yield of 0.950, excited at 480 nm, respectively.^[35,36]

Synthesis

3,6-Bis(4-bromophenyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**1**)

Under an argon atmosphere, potassium *tert*-butoxide (4.487 g, 40 mmol) was dissolved in *tert*-amyl alcohol (35 mL) in a 250 mL Schlenk flask. The solution was heated to 110 °C and held for 5 min. Then 4-bromo-benzonitrile (6.374 g, 35 mmol) was added into the flask. After dissolving diisopropyl succinate (3.242 g, 16 mmol) in *tert*-pentyl alcohol (16 mL), the solution was placed in a dropping funnel and dropwisely added into the Schlenk flask. The mixture was stirred at 110 °C for 14 h, and then cooled down to room temperature. It was then poured into the mixture of ethanol (150 mL) and acetic acid (8 mL). The resultant precipitate was collected by filtration, rinsed with ethanol until the filtrate displayed no color, and then dried under vacuum at 80 °C for 24 h to give the product as a dark-red solid (4.221 g, yield 58.9%).

Di-*tert*-butyl-3,6-bis(4-bromophenyl)-1,4-dioxopyrrolo[3,4-*c*]pyrrole-2,5(1*H*,4*H*)-dicarboxylate (**M1**)

The mixture of compound **1** (1.090 g, 2.44 mmol), 4-dimethylaminopyridine (DMAP, 0.730 g, 5.97 mmol), and dry THF (25 mL) was stirred in 100 mL Schlenk flask, followed by dropwise addition of di-*tert*-butyldicarbonate (2.252 g, 10 mmol) under argon atmosphere. The reaction mixture was stirred at room temperature overnight and poured into 200 mL of deionized water to give a precipitate which was collected after filtration. Then, the resultant crude product was dissolved in dichloromethane again, and the solution was filtered by using a membrane with a pore size of 0.22 μm. The filtrate was washed with deionized water (50 mL) *via* liquid-liquid extraction. The organic phase was collected and dried over anhydrous MgSO₄. After removing

the solvent with rotary evaporation, the solid was recrystallized from CH_2Cl_2 /methanol to give the product as orange powder (0.943 g, yield 59.6%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 7.62 (m, 8H), 1.45 (s, 18H). Elemental analysis Calcd. for $\text{C}_{28}\text{H}_{26}\text{Br}_2\text{N}_2\text{O}_6$ (%): C, 52.03; H, 4.05; N, 4.33; Found: C, 51.36; H, 4.01; N, 4.22.

3,6-Bis(4-bromophenyl)-2,5-dioctyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**M2**)

Under an argon atmosphere, compound **1** (1.620 g, 3.63 mmol) and K_2CO_3 (1.503 g, 10.80 mmol) in 30 mL of dimethylformamide (DMF) were stirred for 1 h at 120 °C in a 100 mL Schlenk flask. Then 18-crown-6 (5.042 mg, 0.02 mmol) was added to the Schlenk flask, followed by slow addition of 1-bromooctane (1.401 g, 7.26 mmol) in 5 mL of DMF. The mixture was stirred for 6 h at 120 °C, cooled to room temperature and poured into 50 mL of water, and extracted with 20 mL of chloroform. The organic phase was collected and washed by 50 mL of water again for 4 more times. The finally collected organic phase was dried over anhydrous MgSO_4 . The crude product was purified *via* column chromatography on silica gel (ethyl acetate: petroleum ether, 1:30, *V/V*). After removing the solvent, an orange powder was obtained (0.756 g, 31.1%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 7.68 (m, 8H), 3.72 (t, 4H), 1.52 (m, 4H), 1.20 (m, 20H), 0.86 (t, 6H). Elemental analysis Calcd. for $\text{C}_{34}\text{H}_{42}\text{Br}_2\text{N}_2\text{O}_2$ (%): C, 60.90; H, 6.31; N, 4.18; Found: C, 61.32; H, 6.57; N, 3.94.

Synthesis of PPE-DPP1

A pre-dried Schlenk flask (100 mL) was charged with **M1** (0.220 g, 0.34 mmol), **M3** (0.208 g, 0.34 mmol), $(\text{PPh}_3)_2\text{-PdCl}_2$ (35 mg, 0.050 mmol), and CuI (5 mg, 0.025 mmol), and dry diisopropylamine (2 mL) and THF (8 mL) were added into the flask under argon. The mixture was refluxed for 24 h at 60 °C under argon and then cooled to room temperature. The mixture was filtered using a membrane with a pore size of 0.22 μm and the filtrate was poured into 200 mL of cold methanol (previously stored in 4 °C refrigerator for 2 h) to precipitate the polymer. After centrifugation (5 min, 3500 r/min), the supernatant was decanted while the precipitate was collected and dried in vacuum for 24 h to give a red-brown solid (0.364 g, 85.7%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 7.77 (m, 4H), 7.66 (m, 4H), 7.02 (m, 2H), 4.74 (s, 4H), 4.24 (d, 4H), 1.68 (m, 4H), 1.44 (m, 4H), 1.24 (m, 36H), 0.87 (d, 6H). Elemental analysis Calcd. for $\text{C}_{68}\text{H}_{88}\text{N}_2\text{O}_{12}$ (%): C, 72.53; H, 7.82; N, 2.48; Found: C, 68.44; H, 7.44; N, 2.13.

Synthesis of PPE-DPP2

A pre-dried Schlenk flask (100 mL) was charged with **M2** (0.268 g, 0.40 mmol), **M3** (0.244 g, 0.40 mmol), $(\text{PPh}_3)_2\text{-PdCl}_2$ (40 mg, 0.057 mmol), and CuI (5 mg, 0.025 mmol), and dry diisopropylamine (2 mL) and THF (8 mL) were added into the flask under argon protection. The mixture was refluxed for 24 h at 60 °C under argon and then cooled to room temperature. The mixture was filtered by using a membrane with a pore size of 0.22 μm and then the filtrate was poured into 200 mL of cold methanol (previously stored in 4 °C refrigerator for 2 h) to precipitate the polymer. After centrifugation (5 min, 3500 r/min), the supernatant was decanted while the precipitate was dried in vacuum for 24 h

to give a red-brown solid (0.392 g, 86.7%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 7.84 (m, 4H), 7.69 (m, 4H), 7.00 (m, 2H), 4.75 (s, 4H), 4.24 (d, 4H), 3.75 (d, 4H), 1.68 (m, 8H), 1.24 (m, 56H), 0.86 (d, 12H). Elemental analysis Calcd. for $\text{C}_{72}\text{H}_{104}\text{N}_2\text{O}_8$ (%): C, 76.83; H, 9.31; N, 2.49; Found: C, 74.19; H, 8.62; N, 2.24.

RESULTS AND DISCUSSION

Synthesis and Characterizations

The monomers and polymers were synthesized according to Scheme 1. The macroscopic images of monomers and polymers in solid under natural light and in solution under natural/UV light are shown in Tables S1 and S2 (in the electronic supplementary information, ESI), respectively. Compound **1** and **M1** were synthesized according to the literature.^[37] **M2** was synthesized with modification following a previous report,^[38] where 18-crown-6 was added together with compound **1** and K_2CO_3 into the flask and the mixture was stirred for 1 h at 120 °C before adding 1-bromooctane. However, the yield of **M2** was very low in our lab according to this procedure. The yield of **M2** was greatly improved by adding 18-crown-6 into the flask after that compound **1** and K_2CO_3 in DMF were stirred for 1 h at 120 °C, and immediately followed by dropwise addition of 1-bromooctane. The sequence of reagent addition was revised based on the following consideration.^[39,40] In this reaction system, the function of basic K_2CO_3 is to remove the proton on nitrogen in compound **1**. However, K_2CO_3 is non-soluble in DMF and 18-crown-6 can chelate K^+ to promote the solubility of K_2CO_3 in DMF. 18-Crown-6 might evaporate during the heating process at 120 °C since its boiling point is 116 °C. Therefore, 18-crown-6 as the phase transfer catalyst might lose its catalytic effect if another reagent (1-bromooctane) was not added before its complete evaporation. Thus adding 18-crown-6 after complete dissolution of compound **1** and right before adding 1-bromooctane is favorable for improving the yield of **M2**. The resultant monomers (**M1** and **M2**) appeared as orange powder under natural light and were highly soluble in most organic solvents, such as toluene, chloroform, THF, dioxane, and methylene chloride.

Two new conjugated polymers (PPE-DPP1 and PPE-DPP2) were synthesized under a regular Sonogashira coupling condition, with $(\text{PPh}_3)_2\text{PdCl}_2$ and CuI as the catalyst and co-catalyst. The polymerization was performed in THF/diisopropylamine mixed solvent under argon atmosphere. Both polymers displayed dark-red color under natural light. Both of them could dissolve in toluene, chloroform, THF, dioxane, and methylene chloride, but they displayed apparent difference in solubility, very likely due to the different side groups hanging on the DPP unit. PPE-DPP2 instantly dissolved in solvents mentioned above but PPE-DPP1 required long-time stirring (such as 48 h) for dissolving about 1 mg in 10 mL solvent (such as toluene, chloroform, THF, dioxane, and methylene chloride). In addition, PPE-DPP2 could dissolve in ethyl acetate, but PPE-DPP1 could not. The short side group on the DPP unit of PPE-DPP1 might reduce the solubility, compared with the long alkyl group on the DPP unit of PPE-DPP2.

The $^1\text{H-NMR}$ spectra of monomers and polymers are shown in Fig. 1, with peaks labelled for corresponding protons on the chemical structures. The proton signal around 3.38 ppm in the spectrum of **M3** (proton of bisalkyne) disappears in the spectra of polymers, suggesting the polymerizations were completed. Other signals in the polymers' spectra are just a supposition of signals from the corresponding bisalkyne and dihaloarene. It is to be noted that the signals for polymers are broader than those for monomers, which is also consistent with the formation of polymers.

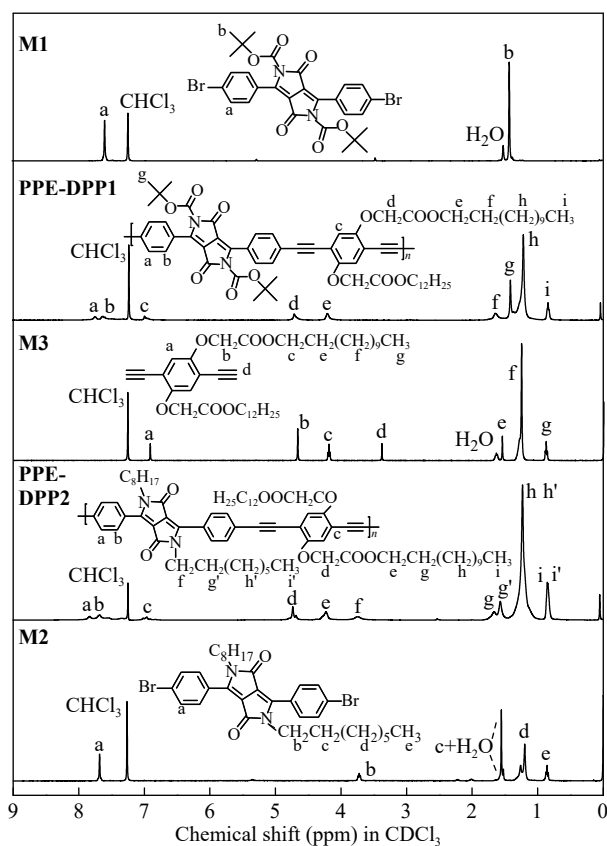


Fig. 1 $^1\text{H-NMR}$ spectra of the monomers and polymers

The FTIR spectra are shown in Fig. 2, and bands in three regions are marked out for comparison. The first region is for C—H stretching vibration around 3000 cm^{-1} , the second region is for C=O stretching vibration between $1650\text{--}1800\text{ cm}^{-1}$, and the third region is for C—N and C—O stretching vibration between $1050\text{--}1250\text{ cm}^{-1}$. In the first region, the bands in all the spectra for aromatic C—H stretching (usually between $3000\text{--}3200\text{ cm}^{-1}$ wavenumber) are very small or illegible, which is reasonable since compared with the aliphatic C—H bonds, much fewer aromatic C—H bonds exist in the monomers and polymers (except **M1**) in

this study. Apparent difference can be seen between **M1** and **M2** for the aliphatic C—H stretching (between $2800\text{--}3000\text{ cm}^{-1}$), as **M1** has much fewer aliphatic C—H bonds than **M2**. However, after polymerization with **M3**, which also has long alkyl chain, such difference in the aliphatic C—H stretching vibration band becomes less obvious between **PPE-DPP1** and **PPE-DPP2**. In the second region, **M1** has two types of C=O stretching vibration from the amides, one in the lactam ring and the other outside. Combined with the C=O vibration from ester in **M3**, typical supposition of these three types of C=O vibration is found in the spectrum of **PPE-DPP1**. Similar supposition of C=O vibration in **M3** (ester) and **M2** (lactam, only one type of C=O bond) can also be found in the spectrum of **PPE-DPP2**. In the third region, **M1** has C—O and C—N stretching vibration, but **M2** only has the C—N vibration. **M3** has two types of C—O vibration. The spectra of **PPE-DPP1** and **PPE-DPP2** in this region exactly combine the bands from corresponding monomers. In brief, the IR spectra are consistent with the expected structures of the two polymers.

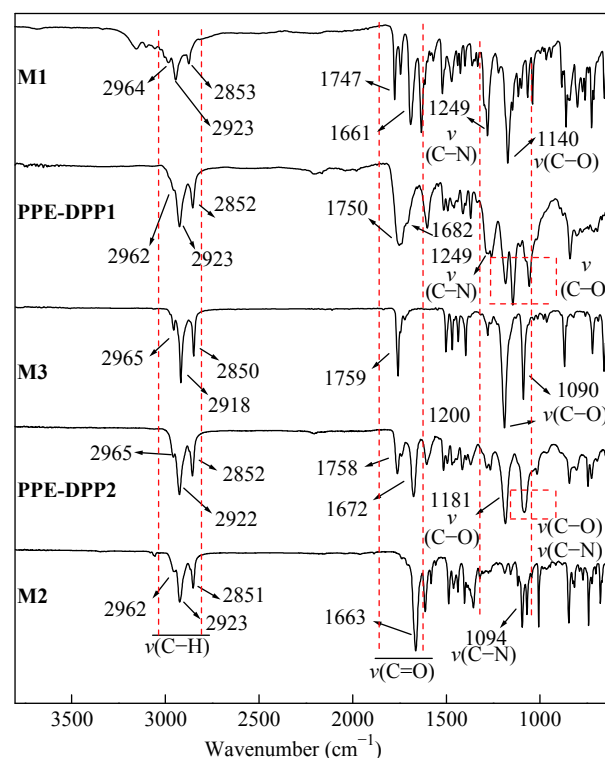


Fig. 2 FTIR spectra of monomers and polymers

The molecular weights were measured by gel permeation chromatography (GPC) using polystyrene as the standard. The data are shown in Table 1. **PPE-DPP1** has a number-average molecular weight (M_n) of $1.62 \times 10^4\text{ g/mol}$ and the cal-

Table 1 The GPC and photophysical data^a for the polymers

Sample	$M_n \times 10^{-4}$ (g/mol)	PDI	X_n	$\lambda_{\text{max,abs}}$ (nm)		$\lambda_{\text{max,em}}$ (nm)		Φ_f	
				THF	Toluene	THF	Toluene	THF	Toluene
PPE-DPP1	1.62	2.11	28	498	512	562	561	0.17	0.10
PPE-DPP2	1.55	1.84	27	516	520	581	588	0.11	0.05

^a Measured in different solvents, such as THF and toluene

culated degree of polymerization (X_n) is about 28. **PPE-DPP2** has a number-average molecular weight (M_n) of 1.55×10^4 g/mol and X_n is about 27. The polydispersity index of both is around 2, a typical value for polycondensation, which is consistent with the nature of polymerization based on Sonogashira coupling. The elemental analysis data for the polymers are shown in the experimental section, which are also very close to the theoretical value calculated based on the repeating unit of polymers.

Photophysical Study

The photophysical characterizations were carried out on **M1**, **M2**, **PPE-DPP1**, and **PPE-DPP2** in different solvents, such as CHCl_3 , CH_2Cl_2 , THF, dioxane, and toluene. It is to be noted that the solvents were selected based on the consideration that they can dissolve all polymers and monomers. The absorption/emission spectra are shown in Figs. S1–S4 (in ESI). The absorption/emission maxima and the quantum yields of fluorescence in different solvents are summarized in Tables S3–S6 (in ESI). For representative, the spectra in THF are shown in Fig. 3, and the photophysical data of **PPE-DPP1** and **PPE-DPP2** in THF and toluene are listed in Table 1. For the monomers, their absorption and emission spectra only display small degree of red-shift, in the typical non-polar solvent toluene, compared with those in other solvents, with no big variation in the quantum yield of fluorescence. As for the polymers, **PPE-DPP1** displays 4 nm

red-shift in the absorption maximum and almost no change in emission maximum with a lower quantum yield when changing the solvent from THF to toluene, while **PPE-DPP2** displays 4 and 7 nm red-shifts in the maxima of absorption and emission, respectively, with a reduced quantum yield almost in half. Usually, intramolecular charge transfer (ICT) can be found in the DPP based-molecules, since DPP moiety is very electron-deficient and can act as a strong acceptor.^[10] The ICT effect can be reinforced or weakened by increasing or reducing the polarity solvent and lead to a red-shift or blue-shift in the emission.^[41] Therefore, we can make a conclusion that ICT is not obvious in the monomers or polymers in this study, very likely due to no strong electron-donating groups to form the donor-acceptor pair with DPP unit. Another characteristic of DPP is that it has a planar aromatic structure, which makes the π - π stacking with neighboring molecules possible.^[10] The observation about slight red-shift and reduced emission quantum yield (more obvious in the case of **PPE-DPP2**), which resulted from changing THF to toluene, can be attributed to that toluene can assist the formation of π - π stacking.

Comparing the absorption/emission spectra of monomers and polymers in THF as shown in Fig. 3, the polymers display absorption peak at a longer wavelength and several shoulders at lower wavelengths, but only one single peak in the emission. These phenomena are typical for conjugated polymers since they usually have several chromophores, including monomeric units and conjugated backbone. However, emission always takes place at the longest wavelength from the conjugated backbone, because excitation energy migrates to the lowest fluorophore. **PPE-DPP2** has about 18 nm red-shift in the absorption and emission, compared with **PPE-DPP1**, which may originate from the monomers since **M1** and **M2** also have similar difference in the absorption and emission wavelength. Such difference is very likely due to the different side groups attached to DPP moiety, a strong electron-withdrawing group in the case of **PPE-DPP1** and a weak electron-donating group in the case of **PPE-DPP2**, which results in different HOMO-LUMO energy gaps.

The emission of **PPE-DPP1** and **PPE-DPP2** was further investigated by adding water into the polymer THF solution. As shown in Fig. 4, the emission intensity keeps decreasing for both polymers when increasing the water content but with negligible shift in the emission wavelength, suggesting the addition of water had no influence on the intramolecular electron distribution of **PPE-DPP1** and **PPE-DPP2**. The reduced emission intensity should be due to the precipitation of polymer out of the THF solution. Upon addition of 10% water, the intensity of **PPE-DPP1** was decreased by about 43% of the initial intensity and the intensity of **PPE-DPP2** was reduced by about 56%. However, the decrease in intensity slowed down afterwards, especially for **PPE-DPP1**. 2.2% of **PPE-DPP1** initial intensity still remained upon the addition of 80% water, but when adding 50% water, only 1.6% of **PPE-DPP2** initial intensity remained. Such different influences on the emission intensity upon water content could be very likely due to the different side groups attached on the

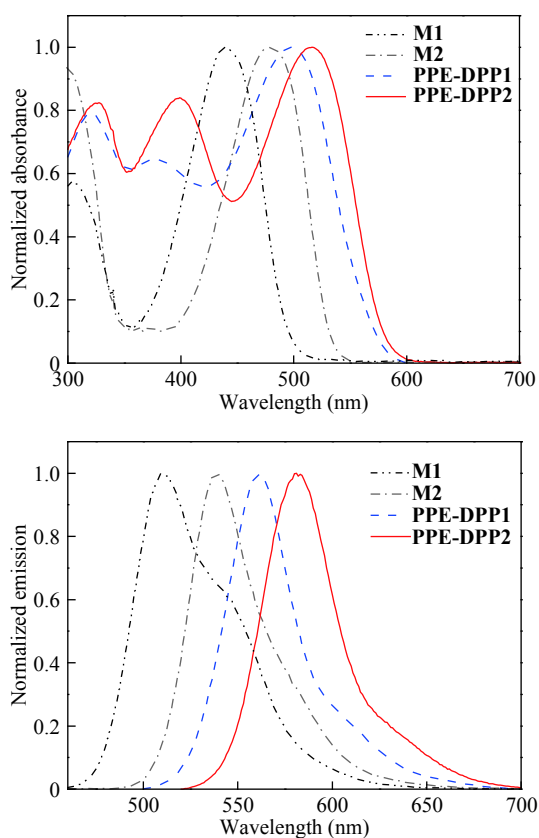


Fig. 3 Absorption (top) and emission (bottom) spectra of monomers and polymers in dilute THF solution. The excitation of monomers was set at 440 nm, the excitation of **PPE-DPP1** was set at 480 nm, and the excitation of **PPE-DPP2** was set at 500 nm.

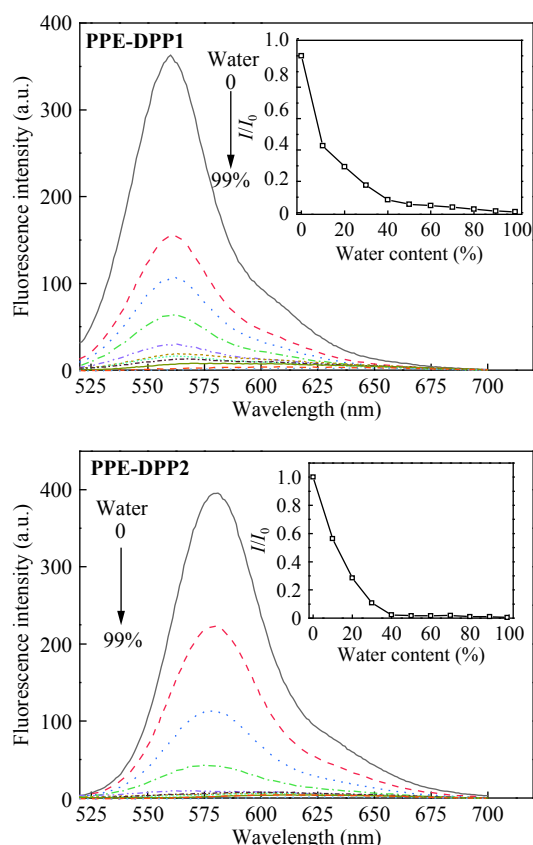


Fig. 4 The emission spectra of **PPE-DPP1** (top) and **PPE-DPP2** (bottom) in THF upon adding water. The concentration of polymers was 5 $\mu\text{mol/L}$ (with respect to the repeating unit). The excitation was 500 nm. The insets show the emission intensity changes at the emission peak.

amide nitrogen. **PPE-DPP2** with longer alkyl group on the nitrogen is easier to precipitate out from water than **PPE-DPP1** with shorter branched carboxylic ester. Therefore, the solubility of the polymers in a solvent plays a more important role than the polarity of the solvent in this study.

CONCLUSIONS

In this study, two new conjugated polymers were successfully synthesized *via* Sonogashira coupling. $^1\text{H-NMR}$ and IR spectra of the polymers were discussed in detail and compared with those of the corresponding monomers, which are consistent with chemical structures of the polymers. GPC data demonstrated the formation of the polymers with a typical polycondensation value for the molecular weight distribution, in accordance with the nature of the Sonogashira coupling polymerization. Photophysical investigation on the polymers was carried out in various aspects, such as changing the solvent polarity, comparing the chemical structure of polymer and monomer, and varying the water content in THF solvent. The results showed that the ICT effect was not obvious for the two DPP-based polymers, but small degree of π - π stack could take place for these polymers in solutions. The differences in the emission/absorption wavelength and the stability of fluorescence in THF upon adding water between two polymers were attributed to the influence on the

electron donating/withdrawing characteristics and the solubility exerted by different side groups on the DPP moiety. Based on the understanding of photophysical properties, these DPP-based polymers can be used as fluorescent chemosensors, taking advantage of the electron-deficiency characteristic combined with the molecular wire feature of the conjugated polymers. Such research is currently on-going in our lab.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2248-6>.

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