

Microwave-assisted One-pot Three-component Polymerization of Alkynes, Aldehydes and Amines toward Amino-functionalized Optoelectronic Polymers*

Tao Jia, Nan-nan Zheng, Wan-qing Cai, Jie Zhang, Lei Ying, Fei Huang** and Yong Cao
*Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices,
South China University of Technology, Guangzhou 510640, China*

Abstract We present a microwave-assisted one-pot polymerization with three-components of alkynes, aldehydes and amines for the synthesis of new amino-functionalized optoelectronic polymers. The polymerization of diynes (**1a–1c**), dialdehydes (**2a** and **2b**) and dibenzylamine catalyzed by InCl_3 was carried out smoothly within 1 h under microwave radiation, yielding four soluble polymers with high molecular weights. The resulting polymers **P1** and **P2** could be easily dissolved in alcohol and thus utilized as the cathode interlayer for polymer solar cells (PSCs). Compared with the control device, the PSCs with **P1** and **P2** as the cathode interlayer and PTB7-Th:PC₇₁BM as the photoactive layer exhibited significantly higher power conversion efficiencies (PCEs) of 9.49% and 9.16%, respectively. These results suggest that this polycoupling reaction is an efficient approach to construct three-component polymers for the practical applications.

Keywords One-pot three-component polymerization; Polymer solar cells; Cathode interlayer

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-017-1890-0>.

INTRODUCTION

The direct conversion of simple chemical building blocks into organic compounds with unique property is one of the most critical goals in chemistry science. Among numerous synthetic strategies, multicomponent reactions (MCRs) fascinate chemists because of their ability to generate complex molecules in an economic approach. In MCRs, multiple reactions are combined into one step without isolating intermediates, thereby increasing the molecular diversity and complexity in a fast and efficient fashion^[1–3]. Hence this strategy has received tremendous attention of organic chemists. Nowadays, the integration of MCRs into combinatorial syntheses for the preparation of a library of compounds is found to be very powerful for the generation of diverse organic molecules, leading to the rapid development of synthetic chemistry^[4–13]. Meanwhile, the development of multicomponent polymerizations (MCPs) has become a growing demand for the synthesis of functional polymers that possess well-defined structures, ordered sequences of monomer units and multifunctionalities. Despite of a variety of challenges, such as the narrow monomer scope, low molecular weight and solubility of polymer products and structural defects caused by unanticipated side reactions, a series of MCPs have been successfully developed and employed for the preparation of functional polymers^[14–22]. For instance, Meier and

* This work was financially supported by the National Natural Science Foundation of China (No. 21490573).

** Corresponding author: Fei Huang (黄飞), E-mail: msfhuang@scut.edu.cn

Invited paper for special issue of “Opto-electronic Functional Polymer”

Received September 30, 2016; Revised November 2, 2016; Accepted November 3, 2016

doi: 10.1007/s10118-017-1890-0

co-workers introduced the Passerini MCR for the synthesis of sequence-defined substituted polyamides^[23]. Choi *et al.* reported a versatile Cu-catalyzed MCP technique that enabled the synthesis of high-molecular-weight, defect-free poly(*N*-sulfonylamidines) from diynes, sulfonylazides, and diamines^[24]. Tang *et al.* developed an efficient multicomponent tandem polymerization of aromatic diyne, diaroyle chloride and ethyl 2-mercaptoacetate under the mild conditions^[25].

Among the employed MCRs, a representative example with great scientific importance is the one-pot three-component coupling of alkyne, aldehyde, and amine (A3-coupling) discovered by Li and co-workers^[26]. Later, Wang and co-workers augmented the reaction scope and reported the indium-catalyzed A3-coupling *via* C–H bond activation^[9]. This reaction could be applied to both aromatic and aliphatic aldehydes and alkynes, producing the products in nearly quantitative yields in most cases with only water as a byproduct. In 2013, Tang reported a new programmable polymerization route, which stemmed from the aforementioned A3-coupling reaction. This polymerization is carried out *via* a one-pot three-component polycoupling reaction of terephthalaldehyde and dibenzylamine with multifold diynes, affording soluble polymers with well-defined structures, high molecular weight (with weight average molecular weight, M_w , up to 51200), and high yields^[27].

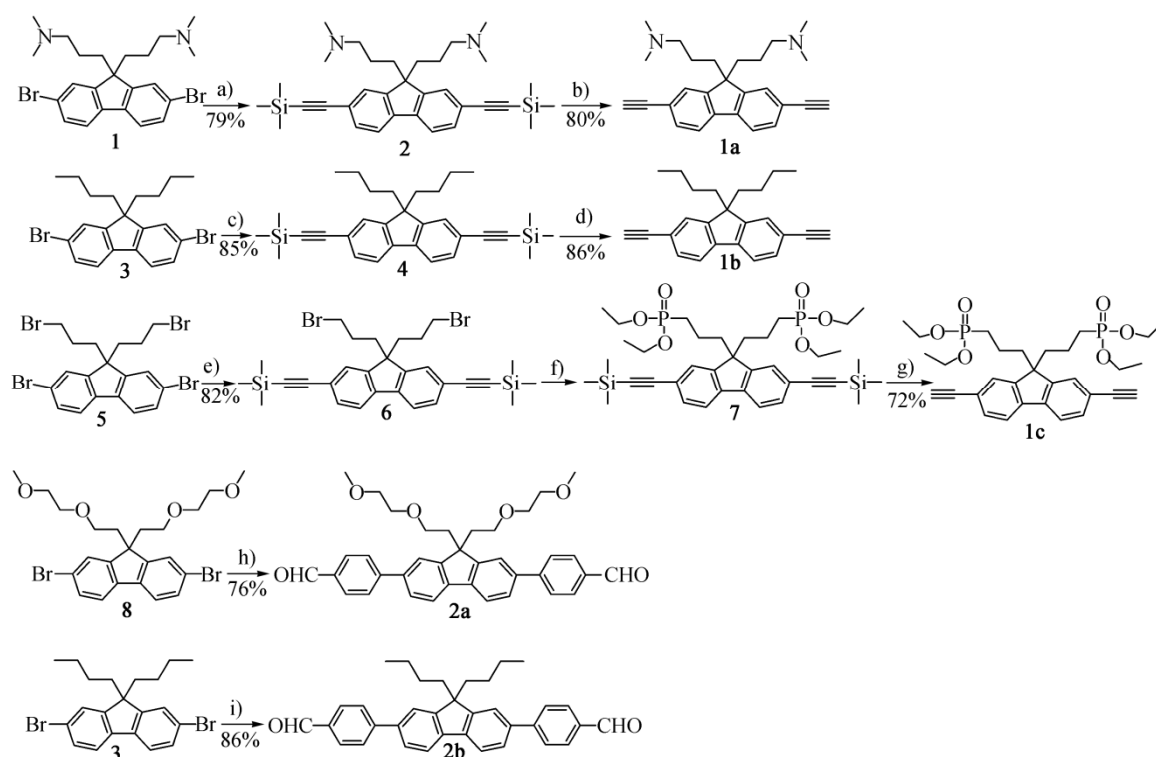
In the past decade, organic electronic devices, such as polymer light-emitting diodes (PLEDs) and solar cells (PSCs), have attracted considerable attention because of their low-cost, high throughput fabrication, light weight, and attractive possibility of direct integration into the flexible devices. Recent progress highlighted that the modification of electrode interfacial layer was an effective strategy to simultaneously improve the efficiency and stability of device. For instance, the utilization of water/alcohol soluble poly[(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN) and its derivatives simultaneously improve the individual photovoltaic parameters of PSCs. The specific advantage of such water/alcohol soluble polymers with amino side groups is that they can be processed from environmentally friendly solvents without damaging the prefabricated light-harvesting layer, and effectively improves the electron extraction. However, such water/alcohol soluble polymers are typically constructed based on two components through palladium-catalyzed Suzuki or Stille cross-coupling polymerization, which limits the versatile choices of monomeric units. Thus, it is of particular interest to prepare such copolymers based on MCP, where three or more independently variable components are involved, and each component plays a specific role to achieve multifunctional polymers. In this context, we devote to exploring the indium-catalyzed three-component polymerization (TCP) by employing multiple monomers of alkyne and aldehyde with functional pendant. The resulting polymers were used as the cathode interlayer for PSCs. TCP was initially conducted according to the previously reported optimal conditions^[27], however, only low molecular weight polymer was afforded. Given the success of microwave-assisted MCRs^[28, 29], we thus attempted to conduct this TCP under microwave irradiation. After deliberately optimizing reaction conditions, all the monomers employing TCP were proceed smoothly, giving targeted polymers with high molecular weight. The obtained polymers exhibited good solubility and satisfactory thermal stability. The resulting polymers of poly[3,3'-(2-(3-(dibenzylamino)-3-(4-(7-(4-(1-(dibenzylamino)ethyl)phenyl)-9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluoren-2-yl)phenyl)prop-1-yn-1-yl)-7-(*pr*-op-1-yn-1-yl)-9*H*-fluorene-9,9-diyl)bis(*N,N*-dimethylpropan-1-amine)] (**P1**) and poly[3,3'-(2-(3-(dibenzylamino)-3-(4-(9,9-dibutyl-7-(4-(1-(dibenzylamino)ethyl)phenyl)-9*H*-fluoren-2-yl)phenyl)prop-1-yn-1-yl)-7-(prop-1-yn-1-yl)-9*H*-fluorene-9,9-diyl)bis(*N,N*-dimethylpropan-1-amine)] (**P2**) with pendant amino groups can be easily dissolved in alcohol in the presence of a trace amount of acetic acid, suggesting their potential applications as cathode interlayer as the previously developed PFN^[30–32]. Based on a conventional device structure of ITO/PEDOT:PSS/PTB7-Th:PC₇₁BM/ETL/Al, PSCs with **P1** and **P2** inter layers exhibit remarkable photovoltaic performances with power conversion efficiencies (PCEs) of 9.49% and 9.16%, which are much higher than that of control devices. These findings suggest that the developed TCP is an efficient approach to synthesize functional polymers for organic electronic devices.

EXPERIMENTAL

Materials and Instruments

All reagents, unless otherwise specified, were obtained from Alfa Aesar or Sigma-Aldrich and used without

further purification. Toluene and THF were dried over Na/diphenyl ketone and freshly distilled prior to use. The TCP was conducted on Discover SP microwave synthesizer. The ^1H - and ^{13}C -NMR spectra were collected on a Bruker AVANCE 500 MHz spectrometer in deuterated chloroform solution at 298 K with tetramethylsilane (TMS) as a reference. Weight-average molecular weights (M_w) and polydispersities (M_w/M_n) of the polymers were estimated on a Waters gel permeation chromatography (GPC) system using THF as the eluent, which was calibrated by polystyrene standards. Thermogravimetric analyses (TGA) were conducted on a NETZSCH TG 209 under a heating rate of $10\text{ K}\cdot\text{min}^{-1}$ in a N_2 flow rate of $20\text{ mL}\cdot\text{min}^{-1}$. UV-Vis spectra were recorded on an HP 8453 spectrophotometer. 3,3'-(2,7-Dibromo-9H-fluorene-9,9-diyl)bis(*N,N*-dimethylpropan-1-amine)^[30] (**1**), 2,7-dibromo-9,9-dibutyl-9H-fluorene^[33] (**3**), 2,7-dibromo-9,9-bis(3-bromopropyl)-9H-fluorene^[34] (**5**), 2,7-dibromo-9,9-bis(2-(2-methoxyethoxy)ethyl)-9H-fluorene^[35] (**8**), 9,9-dibutyl-2-ethynyl-9H-fluorene^[33] (**9**), 4-(9,9-dibutyl-9H-fluoren-2-yl)benzaldehyde^[36] (**10**) were prepared according to the reported methods. Details about the experiments are shown in Schemes 1 and 2.



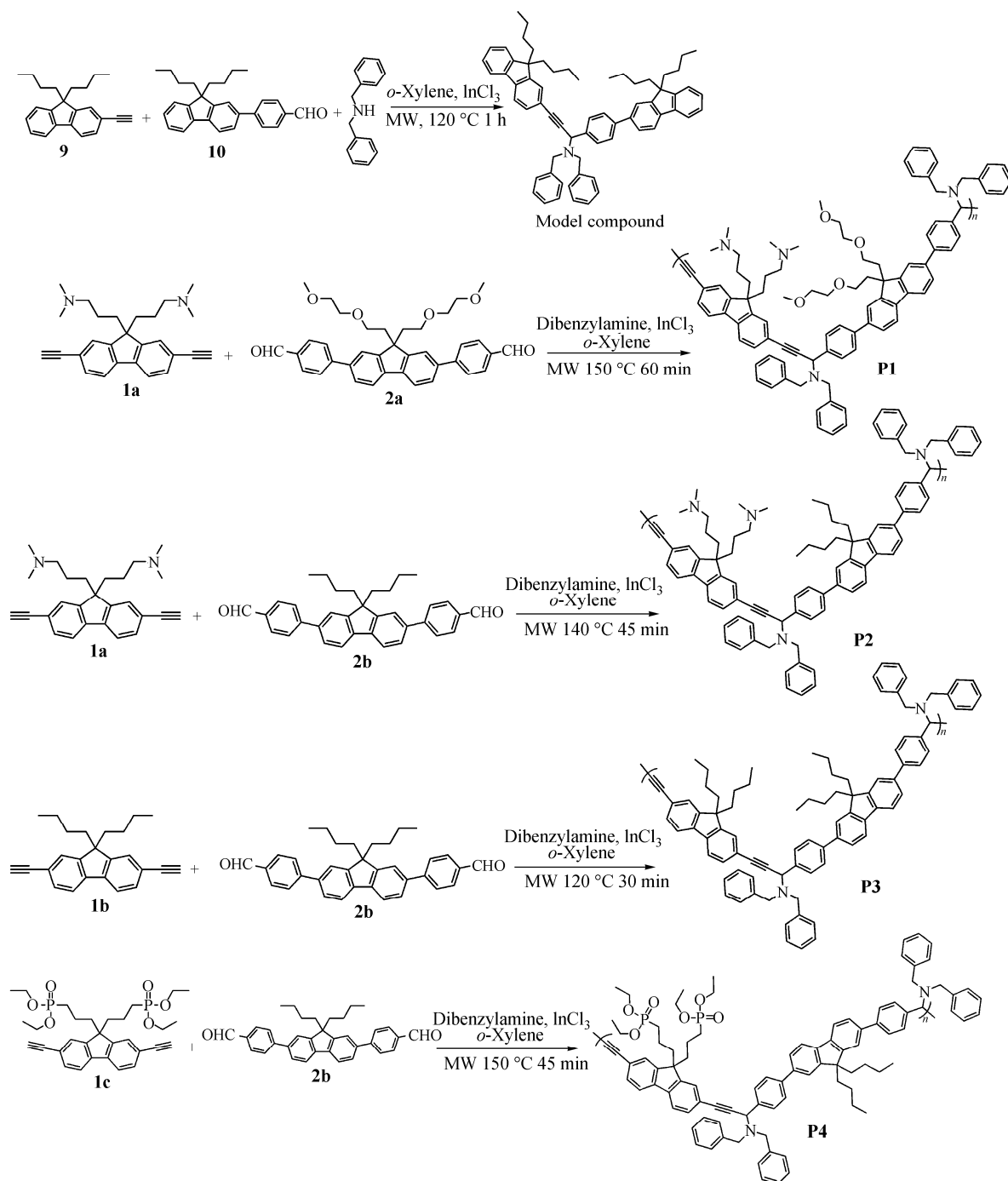
Scheme 1 The synthetic route to the monomers

Reagents and conditions: (a, c, e) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, diisopropylamine, toluene, trimethylsilyl acetylene, 6 h; (b, d, g) MeOH, THF, H_2O , KOH, 1 h; (f) triethylphosphite, reflux, 24 h; (h, i) 4-formylphenylboronic acid, $\text{Pd}(\text{PPh}_3)_4$, toluene, Na_2CO_3 , H_2O , EtOH, 12 h

Device Fabrication and Characterization

Patterned ITO-glass substrates were used as the anode in the PSCs. The ITO coated glass substrates were cleaned by sonication in detergent, deionized water, acetone, and isopropyl alcohol and dried in a nitrogen stream, followed by an oxygen plasma treatment. Subsequently, PEDOT:PSS (40 nm) was spin-coated on a cleaned ITO substrate and heated at $120\text{ }^\circ\text{C}$ for 15 min under vacuum. Then, the predissolved PTB7-Th:PC₇₁BM in chlorobenzene solution was spin-coated onto the top of PEDOT:PSS layer. The thickness of the active layers was about 100 nm. A thin layer ($\sim 5\text{ nm}$) of the water/alcohol soluble polymer **P1** and **P2** was spin-coated from their methanol solution with a concentration of $1\text{ mg}\cdot\text{mL}^{-1}$ on the top of the bulk-heterojunction (BHJ) layer. Finally, the film was transferred into a thermal evaporator and 100 nm of Al were deposited through a shadow

mask (defined active area of 0.04 cm^2) onto the photoactive layer by thermoevaporation in a vacuum chamber with base pressure of $2 \times 10^{-10} \text{ MPa}$. PCEs were measured under an AM1.5G solar simulator (Japan, SAN-EI, XES-40S1). The power of the sun simulation was calibrated before the test by using a standard silicon solar cell, giving a value of $100 \text{ mW}\cdot\text{cm}^{-2}$ in the test. The current density-voltage (J - V) characteristics were recorded with a Keithley 2400 source meter. All the device fabrication processes were carried out in a N_2 -filled glovebox (Braun GmbH).



Scheme 2 The synthetic routes to the model compound and polymers

Preparation of Monomers

3,3'-(2,7-Bis(trimethylsilyl)ethynyl)-9H-fluorene-9,9-diyl)bis(N,N-dimethylpropan-1-amine) (2)

Compound **1** (9.88 g, 20.00 mmol), CuI (0.052 g, 0.28 mmol), Pd(PPh₃)₂Cl₂ (0.475 g, 0.68 mmol) were dissolved in the mixture of toluene (200 mL) and diisopropylamine (60 mL) to yield a yellow solution under argon atmosphere. A solution of trimethylsilyl acetylene (7.06 mL, 50 mmol) in diisopropylamine (30.0 mL) was slowly added into the reaction mixture at room temperature. The reaction mixture was then stirred at 70 °C for 6 h to give a reddish brown suspension. The reaction mixture was cooled to room temperature and extracted with dichloromethane (DCM). The organic layers were combined and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the resulting crude product was purified on a silica gel column chromatography using petroleum ether (PE)/DCM/triethylamine (TEA) (5/1/0.1, *V/V/V*) as the eluent to give **2** as a white solid (8.34 g, 79%). ¹H-NMR (500 MHz, CDCl₃, δ): 7.58–7.56 (d, 2H), 7.44–7.42 (m, 4H), 1.99–1.96 (m, 20H), 0.76–0.69 (m, 4H), 0.28 (s, 18H). ¹³C-NMR (125 MHz, CDCl₃, δ): 150.3, 140.7, 131.3, 126.3, 122.0, 119.9, 105.9, 94.4, 59.7, 54.7, 45.3, 37.6, 22.0.

3,3'-(2,7-Diethynyl-9H-fluorene-9,9-diyl)bis(N,N-dimethylpropan-1-amine) (1a)

A KOH aqueous solution (20 mL, 20%) diluted with methanol (67 mL) was added to a stirred solution of **3** (5.28 g, 10 mmol) in THF (133 mL) under argon atmosphere. The mixture was stirred at room temperature for 1 h and extracted with DCM for three times. The organic fraction was washed with water and dried over anhydrous magnesium sulphate. After filtration and solvent evaporation, the crude product was purified on a silica gel column chromatography using PE/DCM/TEA (3/1/0.15, *V/V/V*) as the eluent to afford **1a** as a white powder (3.26 g, 80%). ¹H-NMR (500 MHz, CDCl₃, δ): 7.62–7.60 (d, 2H), 7.47–7.45 (m, 4H), 3.12 (s, 2H), 2.00–1.96 (m, 20H), 0.76–0.70 (m, 4H). ¹³C-NMR (125 MHz, CDCl₃, δ): 150.5, 141.0, 131.5, 126.5, 121.1, 120.1, 84.4, 77.46, 59.7, 54.8, 45.3, 37.6, 22.0.

((9,9-Dibutyl-9H-fluorene-2,7-diyl)bis(ethyne-2,1-diyl))bis(trimethylsilane) (4)

Compound **3** (8.72 g, 20.00 mmol), CuI (0.052 g, 0.28 mmol), Pd(PPh₃)₂Cl₂ (0.475 g, 0.68 mmol) were combined in toluene (200 mL) and diisopropylamine (60 mL) to yield a yellow solution under argon atmosphere. A solution of trimethylsilyl acetylene (7.06 mL, 50 mmol) in diisopropylamine (30.0 mL) was slowly added into the reaction mixture at room temperature. The reaction mixture was then stirred at 70 °C for 6 h to give a reddish brown suspension. The reaction mixture was cooled to room temperature and extracted with DCM. The organic layers were combined and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the resulting crude product was purified on a silica gel column chromatography using PE/DCM (10/1, *V/V*) as the eluent to give **4** as a light yellow solid (8.0 g, 85%). ¹H-NMR (500 MHz, CDCl₃, δ): 7.60–7.59 (d, 2H), 7.47–7.43 (m, 4H), 1.96–1.93 (m, 4H), 1.09–1.05 (m, 4H), 0.68–0.65 (t, 6H), 0.53–0.51 (m, 4H), 0.29 (s, 18H). ¹³C-NMR (125 MHz, CDCl₃, δ): 150.9, 140.8, 131.2, 126.2, 121.7, 119.8, 106.0, 94.2, 55.1, 40.2, 25.7, 23.0, 13.8.

9,9-Dibutyl-2,7-diethynyl-9H-fluorene (1b)

A KOH aqueous solution (20 mL, 20%) diluted with methanol (67 mL) was added into a stirred solution of **4** (4.70 g, 10 mmol) in THF (133 mL) under argon atmosphere. The mixture was stirred at room temperature for 1 h and extracted with DCM for three times. The organic fraction was washed with water and dried over anhydrous magnesium sulphate. After filtration and solvent evaporation, the crude product was purified on a silica gel column chromatography using PE/DCM (10/1, *V/V*) as the eluent to afford **1b** (2.80 g, 86%) as a white crystal. ¹H-NMR (500 MHz, CDCl₃, δ): 7.64–7.63 (d, 2H), 7.50–7.47 (m, 4H), 3.16 (s, 2H), 1.97–1.94 (m, 4H), 1.10–1.05 (dd, 4H), 0.69–0.66 (t, 6H), 0.57–0.56 (m, 4H). ¹³C-NMR (125 MHz, CDCl₃, δ): 151.0, 141.0, 131.3, 126.5, 120.9, 120.0, 84.5, 77.4, 55.1, 40.0, 25.8, 23.0, 13.8.

((9,9-Bis(3-bromopropyl)-9H-fluorene-2,7-diyl)bis(ethyne-2,1-diyl))bis(trimethylsilane) (6)

Compound **5** (5.65 g, 20.00 mmol), CuI (0.026 g, 0.28 mmol), Pd(PPh₃)₂Cl₂ (0.238 g, 0.34 mmol) were combined in toluene (100 mL) and diisopropylamine (30 mL) to yield a yellow solution under argon atmosphere. A solution of trimethylsilyl acetylene (3.56 mL, 25 mmol) in diisopropylamine (15.0 mL) was slowly injected

into the reaction mixture at room temperature. The reaction mixture was then stirred at 70 °C for 6 h to give a reddish brown suspension. The reaction mixture was cooled and extracted with DCM. The organic layers were combined and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the resulting crude product was purified on a silica gel column chromatography using PE/DCM (10/1, *V/V*) as the eluent to give **6** as a light yellow solid (5.4 g, 90%). ¹H-NMR (500 MHz, CDCl₃, δ): 7.61–7.59 (d, 2H), 7.49–7.44 (m, 4H), 3.12–3.10 (t, 4H), 2.14–2.11 (m, 4H), 1.13–1.07 (m, 4H), 0.29 (s, 18H). ¹³C-NMR (125 MHz, CDCl₃, δ): 149.1, 140.6, 131.9, 126.1, 122.4, 120.2, 105.5, 95.1, 54.0, 38.7, 33.7, 27.0.

Tetraethyl((2,7-diethynyl-9H-fluorene-9,9-diyl)bis(propane-3,1-diyl))bis(phosphonate) (1c)

To a 50 mL two-necked round-bottom flask, compound **6** (5.4 g, 9 mmol) and the excess triethylphosphite (20 mL) were added under argon atmosphere. The reaction mixture was heated to 140 °C for 24 h. After cooling to room temperature, the mixture was subjected to a silica gel column and eluted with DCM/ethylacetate (EA) (1/2, *V/V*). The product **7** was immediately dissolved in the mixture of MeOH (50 mL) and THF (50 mL). NaOH (0.100 g) was added to the stirred solution and the mixture was stirred at room temperature for 0.5 h under argon atmosphere. Then the mixture was extracted with DCM for three times. After the solvent vaporation, the crude product was purified on a silica gel column chromatography using EA as the eluent and recrystallized from *n*-hexane to give **1c** as a white powder (3.70 g, 72% for two steps). ¹H-NMR (500 MHz, CDCl₃, δ): 7.61–7.59 (m, 2H), 7.46–7.44 (m, 4H), 3.93–3.87 (m, 8H), 3.12 (s, 2H), 2.09–2.06 (m, 4H), 1.48–1.41 (m, 4H), 1.17–1.14 (t, 12H), 0.87–0.84 (m, 4H). ¹³C-NMR (125 MHz, CDCl₃, δ): 149.5, 140.9, 131.7, 126.5, 121.4, 120.3, 84.1, 77.8, 61.4, 54.9, 40.7, 40.5, 26.1, 25.0, 16.9, 16.3.

4,4'-(9,9-Bis(2-(2-methoxyethoxy)ethyl)-9H-fluorene-2,7-diyl)dibenzaldehyde (2a)

Compound **8** (5.28 g, 10 mmol), 4-formylphenylboronic acid (3.60 g, 24 mmol), Pd(PPh₃)₄ (0.577 g, 0.5 mmol), Na₂CO₃ (10 mL, 2 mol·L⁻¹ in H₂O) and toluene (100 mL) were added into a two-necked round-bottom flask. The reaction was stirred at 100 °C for 12 h under argon atmosphere. Then the reaction mixture was cooled and extracted with DCM for three times. After solvent evaporation, the crude product was purified on a silica gel column chromatography using PE/EA (2/1, *V/V*) as the eluent to give **2a** as a white crystal (4.39 g, 76%). ¹H-NMR (500 MHz, CDCl₃, δ): 10.08 (s, 2H), 8.01–7.99 (d, 4H), 7.86–7.83 (t, 6H), 7.74–7.73 (d, 2H), 7.70–7.68 (dd, 2H), 3.28–3.26 (dd, 4H), 3.23 (s, 6H), 3.21–3.19 (dd, 4H), 2.90–2.87 (t, 4H), 2.55–2.52 (t, 4H). ¹³C-NMR (125 MHz, CDCl₃, δ): 191.9, 150.3, 147.1, 140.2, 139.2, 135.2, 130.3, 127.7, 127.0, 122.2, 120.7, 71.7, 69.9, 67.1, 59.0, 51.7, 39.8.

4,4'-(9,9-Dibutyl-9H-fluorene-2,7-diyl)dibenzaldehyde (2b)

Compound **3** (4.36 g, 10 mmol), 4-formylphenylboronic acid (3.60 g, 24 mmol), Pd(PPh₃)₄ (0.577 g, 0.5 mmol), Na₂CO₃ (10 mL, 2 mol·L⁻¹ in H₂O) and toluene (100 mL) were added into a two-necked round-bottom flask. The reaction was stirred at 100 °C for 12 h under argon atmosphere. Then the reaction mixture was cooled and extracted with DCM for three times. After solvent evaporation, the crude product was purified on a silica gel column chromatography using PE/DCM (1/1, *V/V*) as the eluent to give **2b** as a white crystal (4.18 g, 86%). ¹H-NMR (500 MHz, CDCl₃, δ): 10.08 (s, 2H), 8.00–7.98 (d, 4H), 7.86–7.83 (t, 6H), 7.67–7.66 (d, 4H), 2.11–2.09 (m, 4H), 1.14–1.10 (dd, 4H), 0.73–0.68 (m, 10H). ¹³C-NMR (125 MHz, CDCl₃, δ): 191.8, 152.0, 147.5, 140.9, 138.9, 135.1, 130.3, 127.7, 126.6, 121.7, 120.5, 55.4, 40.2, 26.0, 23.0, 13.8.

Preparation of the Polymers and Model Compound

Synthesis of P1

Into a 35 mL microwave tube equipped with a magnetic stirrer were placed **1a** (0.115 g, 0.3 mmol), **2a** (0.173 g, 0.3 mmol), dibenzylamine (0.130 g, 0.66 mmol). The oxygen remained in the microwave tube was degassed in an inert atmosphere glovebox. InCl₃ (0.013 g, 0.06 mmol), 4 Å molecular sieve (0.100 g) and degassed *o*-xylene (2.4 mL) were then added into the microwave tube in the glovebox. The reaction apparatus was moved out and irradiated with microwave at 150 °C for 60 min. Afterward, the reaction mixture was cooled, through the 40 μ m filter to remove the catalyst and added into methanol (150 mL) dropwise. The product was then dissolved in *o*-xylene, precipitated in methanol for another two times and dried in vacuum overnight at 40 °C to a constant

weight. **P1** was afforded as a yellow solid (0.292 g, yield 72%), $M_w = 10300$; $M_w/M_n = 1.38$ (GPC, polystyrene calibration). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ): 7.88–7.86 (m, 4H), 7.85–7.80 (m, 6H), 7.67–7.59 (m, 14H), 7.52–7.47 (m, 10H), 7.36–7.34 (m, 10H), 5.05 (s, 2H), 3.91–3.89 (d, 4H), 3.67–3.65 (d, 4H), 2.11–1.97 (m, 24H), 1.10 (m, 4H), 0.70–0.67 (m, 14H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ): 150.5, 149.9, 140.7, 140.4, 140.1, 139.6, 139.4, 138.4, 131.6, 130.3, 129.0, 128.9, 128.4, 128.2, 127.6, 127.1, 126.9, 126.5, 126.2, 122.3, 121.7, 120.2, 89.4, 85.3, 71.7, 69.8, 71.7, 69.8, 67.1, 59.6, 58.9, 56.0, 55.0, 54.7, 51.4, 45.2, 39.8, 37.7, 21.9.

Synthesis of **P2**

P2 was prepared from **1a** (0.115 g, 0.3 mmol), **2b** (0.146 g, 0.3 mmol), dibenzylamine (0.130 g, 0.66 mmol), InCl_3 (0.013 g, 0.06 mmol), 4Å molecular sieve (0.100 g) and degassed *o*-xylene (2.4 mL) using the same method at 140 °C for 45 min. **P2** was obtained as a yellow solid (0.261 g, yield 69%), $M_w = 16400$; $M_w/M_n = 1.40$ (GPC, polystyrene calibration). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ): 7.89–7.85 (m, 4H), 7.81–7.76 (m, 6H), 7.72–7.60 (m, 14H), 7.53–7.45 (m, 10H), 7.39–7.32 (m, 10H), 5.05 (s, 2H), 3.90–3.87 (d, 4H), 3.67–3.65 (d, 4H), 2.13–2.05 (m, 8H), 1.10 (m, 8H), 0.72–0.68 (m, 20H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ): 151.7, 150.5, 140.9, 140.7, 140.1, 139.7, 139.6, 138.2, 131.6, 130.3, 129.9, 128.9, 128.8, 128.4, 127.7, 127.1, 126.9, 126.2, 126.0, 122.3, 121.5, 120.1, 89.3, 85.3, 59.6, 56.0, 55.0, 54.7, 45.2, 40.3, 37.7, 29.3, 26.0, 23.1, 13.8.

Synthesis of **P3**

P3 was prepared from **1b** (0.098 g, 0.3 mmol), **2b** (0.146 g, 0.3 mmol), dibenzylamine (0.130 g, 0.66 mmol), InCl_3 (0.013 g, 0.06 mmol), 4Å molecular sieve (0.100 g) and degassed *o*-xylene (2.4 mL) by using the same method at 120 °C for 30 min. **P3** was obtained as a yellow solid (0.224 g, yield 62%). $M_w = 19700$, $M_w/M_n = 1.72$ (GPC, polystyrene calibration). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ): 7.89–7.85 (m, 4H), 7.81–7.76 (m, 6H), 7.72–7.60 (m, 14H), 7.53–7.45 (m, 10H), 7.39–7.32 (m, 10H), 5.05 (s, 2H), 3.90–3.87 (d, 4H), 3.67–3.65 (d, 4H), 2.13–2.05 (m, 8H), 1.10 (m, 8H), 0.72–0.68 (m, 20H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ): 151.6, 151.2, 140.8, 140.6, 140.0, 139.5, 138.2, 136.4, 131.2, 130.2, 129.5, 128.8, 128.7, 128.3, 127.6, 127.0, 126.9, 126.1, 125.9, 125.7, 121.9, 121.4, 120.6, 119.9, 89.4, 85.1, 56.0, 55.1, 54.7, 40.2, 26.0, 23.1, 13.8.

Synthesis of **P4**

P4 was prepared from **1c** (0.171 g, 0.3 mmol), **2b** (0.146 g, 0.3 mmol), dibenzylamine (0.130 g, 0.66 mmol), InCl_3 (0.013 g, 0.06 mmol), 4Å molecular sieve (0.100 g) and degassed *o*-xylene (2.4 mL) using the same method at 150 °C for 45 min. **P4** was obtained as a yellow solid (0.326 g, yield 75%), $M_w = 15800$; $M_w/M_n = 1.30$ (GPC, polystyrene calibration). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ): 7.89–7.85 (m, 4H), 7.81–7.76 (m, 6H), 7.72–7.60 (m, 14H), 7.53–7.45 (m, 10H), 7.39–7.32 (m, 10H), 5.05 (s, 2H), 3.90–3.87 (d, 4H), 3.67–3.65 (d, 4H), 2.13–2.05 (m, 8H), 1.10 (m, 8H), 0.72–0.68 (m, 20H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ): 151.7, 149.6, 140.7, 140.1, 139.7, 139.6, 138.2, 131.9, 130.3, 128.9, 128.4, 127.7, 127.1, 127.0, 125.9, 122.5, 121.5, 120.4, 120.0, 89.2, 85.3, 61.5, 61.4, 56.0, 55.2, 54.7, 40.3, 26.0, 23.1, 16.4, 13.8.

Synthesis of model compound

9,9-Dibutyl-2-ethynyl-9H-fluorene and 4-(9,9-dibutyl-9H-fluoren-2-yl)benzaldehyde were prepared with the same procedure as the synthesis of compound **1b** and **2b**. Then they were reacted in *o*-xylene with commercially available dibenzylamine in the presence of InCl_3 at 120 °C using a microwave synthesizer to afford *N,N*-dibenzyl-3-(9,9-dibutyl-9H-fluoren-2-yl)-1-(4-(9,9-dibutyl-9H-fluoren-2-yl)phenyl)prop-2-yn-1-amine (model compound). The model compound was characterized by the standard spectroscopic techniques corresponding to its expected molecular structure. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ): 7.88–7.86 (d, 2H), 7.75–7.68 (m, 6H), 7.64–7.63 (t, 1H), 7.59–7.56 (m, 3H), 7.51–7.50 (d, 4H), 7.38–7.29 (m, 11H), 7.25–7.24 (m, 3H), 5.05 (s, 1H), 3.90–3.88 (d, 2H), 3.68–3.65 (d, 2H), 2.05–1.98 (s, 8H), 1.19–1.04 (m, 8H), 0.73–0.60 (m, 20H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ): 151.0, 150.9, 141.4, 140.8, 140.4, 139.7, 139.6, 138.3, 131.1, 128.9, 128.8, 128.3, 127.5, 127.1, 127.0, 126.9, 126.8, 126.1, 125.9, 123.0, 122.9, 121.5, 121.4, 120.0, 119.9, 119.7, 119.6, 89.6, 84.7, 56.0, 55.0, 54.7, 40.2, 26.0, 23.1, 13.8.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymers

The syntheses of a series of functional diynes (**1a–1c**), dialdehydes (**2a** and **2b**) are shown in Scheme 1. To explore the preparation of sequentially well-defined polymers by using the one-pot A3-coupling of diyne, dialdehyde and dibenzylamine, we initially conducted the polycoupling reaction using **1b**, **2b** and dibenzylamine as the model monomers based on the traditional conditions. However, the polycoupling reaction resulted in the target product with relatively low molecular weight (number average molecular weight, $M_n = 2400$). Taking into account the success in microwave-assisted MCRs, we thus attempted to conduct the polycoupling reaction under microwave irradiation. By applying the polycoupling reaction, different monomers proceeded smoothly at the optimized reaction temperature and time, and provided soluble targeted polymers with high molecular weights.

Figure 1 depicts the ^1H -NMR spectra of the monomers **1b**, **2b** and dibenzylamine, polymer **P3**, and the model compound. The characteristic proton signals at $\delta = 3.12$, 10.08, and 3.81 were corresponding to the protons of acetylene, aldehyde, and methylene groups of **1b**, **2b**, and dibenzylamine, respectively, but not presented in the spectrum of **P3**. In the meantime, three new peaks with chemical shift at $\delta = 5.05$, 3.90, and 3.65 emerged. These peaks could be attributed to the methylene protons that connected with nitrogen atom. The ^{13}C -NMR spectrum of **P3** did not exhibit resonance peak of carbonyl carbon of **2b** at chemical shift of $\delta = 191.9$. After polymerization, the resonances of the acetylenic carbon atoms of **1b**, however, shifted from $\delta = 84.5$ and 74.4 to $\delta = 89.4$ and 85.1 , respectively. New peaks corresponding to the resonances of the methylene carbons next to the nitrogen atom of dibenzylamine emerged at the chemical shift of $\delta = 56.0$ and 55.1 . These observations confirmed the structure of the polymers, and were well consistent with the previously reported results^[27].

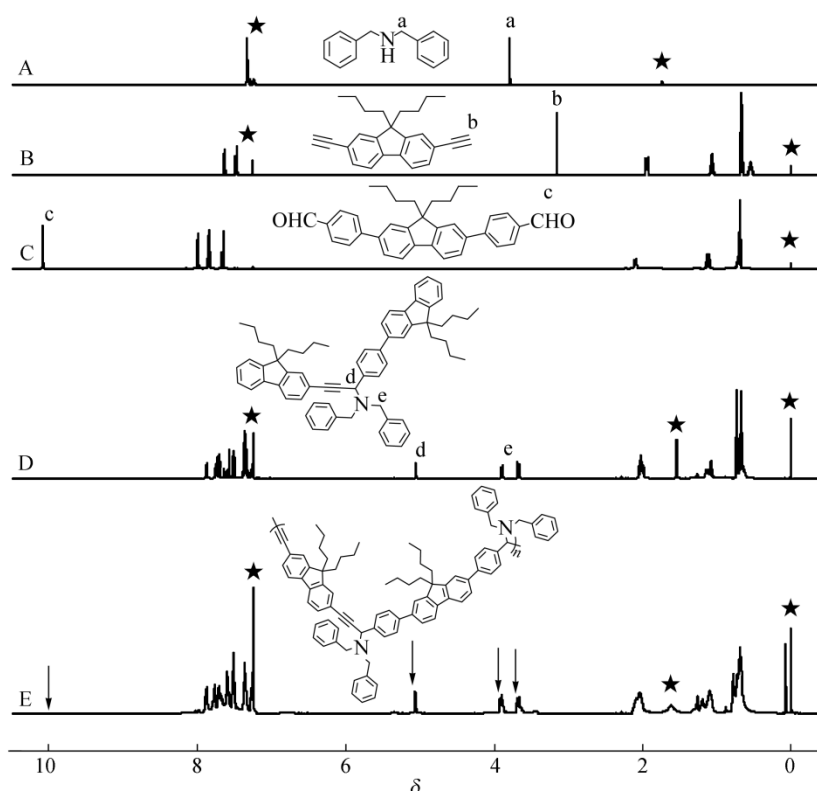


Fig. 1 ^1H -NMR spectra of (A) dibenzylamine, (B) **1b**, (C) **2b**, (D) model compound, and (E) polymer **P3** in deuteratedchloroform (The solvent peaks are marked with asterisks.)

Solubility and Thermal Stability

All the polymers can be easily dissolved in common organic solvents, such as chloroform, THF, toluene, *o*-xylene and chlorobenzene. They also possess good film-forming ability and can be readily fabricated into solid films by spin-coating. Among the targeted polymers, **P1** and **P2** are alcohol soluble and hence are used for the construction of multilayer device by using orthogonal solvents. The thermal properties of the polymers are also evaluated by TGA analysis. As shown in Fig. 2, all the polymers exhibit high thermal stability, exhibiting 5% weight loss at temperature (T_d) higher than 250 °C, which is in accordance with the reported results^[27].

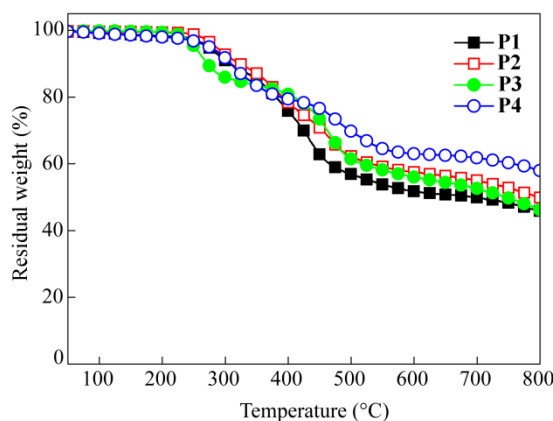


Fig. 2 TGA curves of the polymers with a heating rate of 10 K·min⁻¹

Optical Properties

Figure 3 shows the UV-Vis spectra of the resulting polymers in dilute toluene solutions (a) and solid-state films (b). The absorption spectra in both dilute solutions and thin films show three absorption peaks with absorption maximum at about 340 nm. The similar absorption spectra can be understood as their identical backbone. The absorption spectra of **1b**, **2b** and the corresponding polymers in the toluene solution are also shown in Fig. S1 (in supporting information, SI) for comparison. Due to the non-conjugated backbone, the absorption spectra of resulting polymers are quite comparable to those obtained from the monomeric units. In addition, the UV-Vis spectra of the thin films show slight red-shift, suggesting the existence of aggregation in solid state. The optical band gaps (E_g^{opt}) as evaluated from the absorption onset are 3.08, 3.13, 3.10 and 3.16 eV for **P1**, **P2**, **P3** and **P4**, respectively.

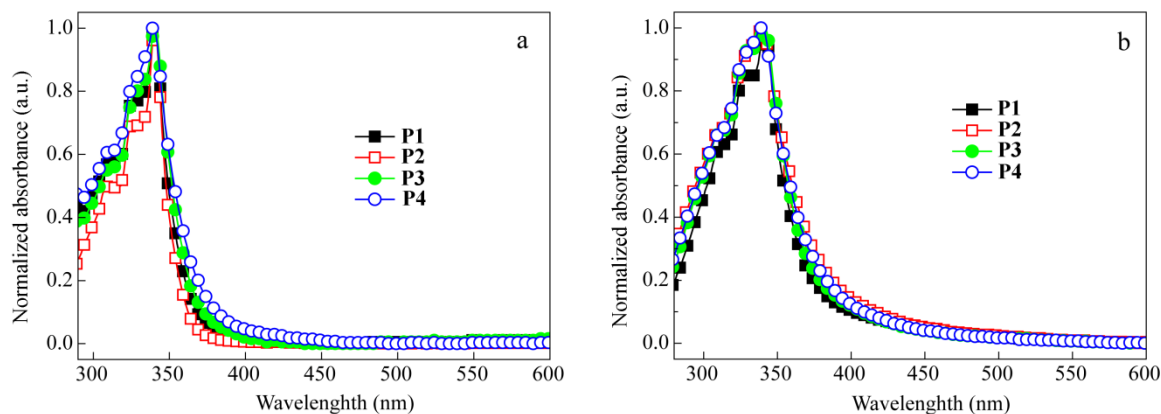


Fig. 3 UV-Vis absorption spectra of the polymers in toluene solution (a) and solid state (b)

Additionally, the photoluminescent (PL) spectra of the copolymers in dilute toluene solution with the concentration of 10^{-4} mol·L $^{-1}$ and as the thin films have been examined, with relevant characteristics shown in Fig. 4. It is noted that the PL spectra both in solution and as thin films exhibit rather broad band, which consists of a relatively weak emissive band located at high-energy region from 380 nm to about 430 nm, and a relatively strong emissive band at low-energy region. The high-energy emission can be attributed to the individual components, while the low-energy band is supposed to be the aggregates. By carefully examining the resulting PL spectra, we note that all the copolymers actually exhibit quite comparable PL spectra both in solution and as thin films, indicating that the side chains have no pronounced effects on the aggregation of polymer backbone. Detail optical property data are summarized in Table 1.

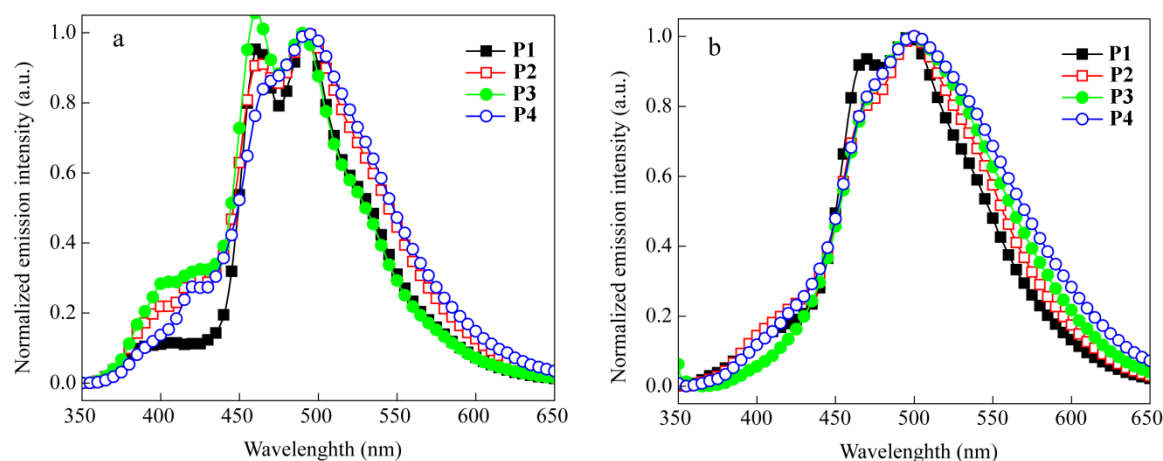


Fig. 4 Normalized photoluminescence spectra of dilute solutions (10^{-4} mol·L $^{-1}$ in toluene) (a) and as thin films (b). The excitation wavelength for the measurement is 340 nm.

Table 1 UV-Vis absorption and electrochemical properties of the polymers

Polymers	λ_{max} (nm)		λ_{onset} (nm)	$E_{\text{g}}^{\text{opt}}$ (eV)	$E_{\text{ox}}^{\text{onset}}$ (V)	E_{HOMO} (eV)	E_{LUMO} (eV)
	Solution	Film	Film				
P1	340	342	392	3.16	0.76	−5.56	−2.40
P2	340	340	402	3.08	0.90	−5.70	−2.62
P3	341	341	396	3.13	0.94	−5.74	−2.61
P4	340	340	400	3.10	0.96	−5.76	−2.66

Electrochemical Properties

Cyclic voltammetry (CV) measurements were used to evaluate the frontier molecular orbital energy levels of the resulting polymers. A Pt electrode, a platinum wire, and a standard calomel electrode (SCE) were respectively used as the working electrode, the counter electrode, and the reference electrode. The potential of the saturated calomel reference electrode is internally calibrated using the ferrocene/ferrocenium redox couple (Fc/Fc^+), which has a known reduction potential of −4.8 eV. As shown in Fig. 5, the onset oxidation potentials for **P1**, **P2**, **P3** and **P4** in the thin films are 0.76, 0.90, 0.94 and 0.96 V (versus Fc/Fc^+), respectively. Thus, the highest occupied molecular orbital (E_{HOMO}) can be estimated according to the empirical formula of $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.8)$ eV. The calculated E_{HOMO} is in the range of −5.56 ~ −5.76 eV for these resulting copolymers, which are analogous to the reported fluorene-based polymers^[37]. It is worth mentioning that **P1** exhibits lower oxidation potential onset and then higher HOMO energy level among the targeted polymers. It is attributed to the oxyethyl (OE) group in the side chain, which is relatively flexible associated with steric hindrance that may potentially facilitate the intermolecular stacking of polymer backbone, thus leading to the slight variation of energy level of **P1** as estimated by CV measurement. Meanwhile, the lowest unoccupied molecular orbital (E_{LUMO}) can be calculated from the E_{HOMO} and $E_{\text{g}}^{\text{opt}}$, by using the equation of $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$, which is in the range of

−2.40 ~ −2.66 eV. The detailed electrochemical data are summarized in Table 1.

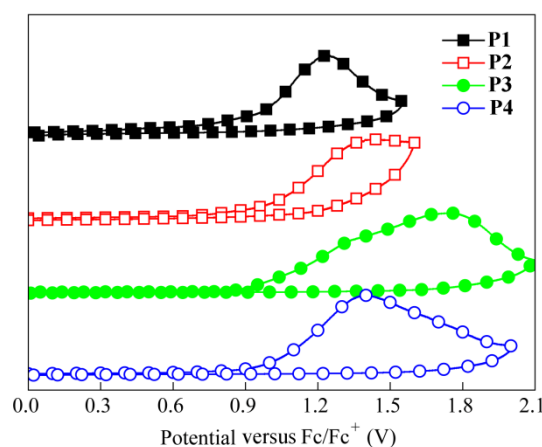


Fig. 5 The CV curves of the polymers films coated on platinum electrodes

Scanning Kelvin Probe Microscopy Study

It is well-established that electron-rich group such as amino group and oxyethyl (OE) group can form interfacial dipoles with metal surfaces and alter the work function (WF)^[38]. Thus, to examine the capability of the targeted polymers and reference material PFN in reducing the WF of the Ag electrode, scanning Kelvin probe measurements were carried out. The WF of the bare Ag was measured to be 4.66 eV, in agreement with the literature^[39]. After coating a thin layer (5 nm) of **P1**, **P2** and PFN on the top of Ag electrode, the WF obviously decreased to −4.17, −4.25 and −4.27 eV, respectively. The more pronounced variation in WF of **P1** treated electrodes suggested that **P1** could form larger interfacial dipoles because of the additional OE group that could lead to better Ohmic contact with the cathode.

P1 and P2 as the Cathode Interlayer

To investigate the interfacial modification effect of the **P1** and **P2** on the PSCs, the devices with configuration of ITO/PEDOT:PSS/PTB7-Th:PC₇₁BM/cathode interlayer/Al were fabricated. Here in the photoactive layer, the narrow band gap conjugated polymer poly[[2,6'-4,8-di(5-ethylhexylthienyl)benzo[1,2-*b*;3,3-*b'*]dithiophene][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-*b'*]thiophenediyl]] (PTB7-Th) was used as the electron-donating material. And [6,6]-phenyl C71-butyric acid methyl ester (PC₇₁BM) was used as the electron-accepting material (Chart 1). A thin layer of **P1** and **P2** (~5 nm) was spin-coated atop the photoactive layer from methanol solution, which acted as the cathode interlayer. For comparison, a control device without cathode interlayer was also fabricated. In addition, to rule out the possible influence caused by the solvents, the devices whose active layers were rinsed with methanol before thermal evaporation of the Al electrode were also fabricated and tested.

Figure 6 shows the current density-voltage (J - V) characteristics of the devices under the 100 mW·cm^{−2} AM1.5G irradiation. Their corresponding short circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and PCE values as extracted from the J - V curves are summarized in Table 2. The control device gave a maximum PCE of 6.75% with a J_{sc} of 15.81 mA·cm^{−2}, a V_{oc} of 0.67 V, and an FF of 64.14%. The reference device with methanol treating the active layer produced the better performance with a maximum PCE of 8.11%. After inserting a thin layer of **P2** (~5 nm), the PCE reached 9.16%, with simultaneously improved parameters of a J_{sc} of 16.14 mA·cm^{−2}, a V_{oc} of 0.78 V, and an FF of 72.85%. In addition, the device with a thin layer of **P1** (~5 nm) as the cathode interlayer exhibited an even higher PCE of 9.49% with an enhanced FF of 74.19%, a V_{oc} of 0.79 V, and a J_{sc} of 16.26 mA·cm^{−2}. With respect to the control device, the V_{oc} and FF of the **P1**- and **P2**-based devices were simultaneously enhanced, leading to the significantly improved device performance. We further investigated the external quantum efficiency (EQE) of devices, with relevant characteristics shown in Fig. 7. The J_{sc} integrated from the integrated value of the EQE spectra were well matched with the device results

(Table S1 in SI). These observations demonstrate that the resulting polymers **P1** and **P2** are effective cathode interlayers for improving the performance of PSCs.

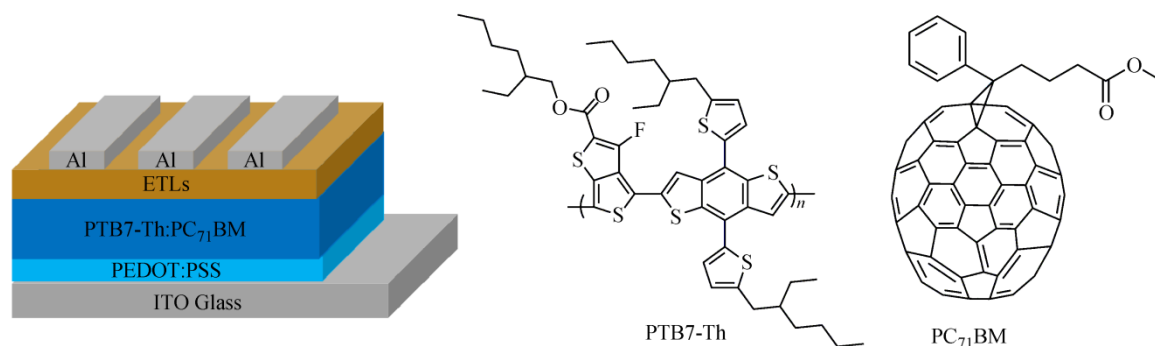


Chart 1 Devices configuration of the PSCs, and the chemical structures of PTB7-Th and PC₇₁BM

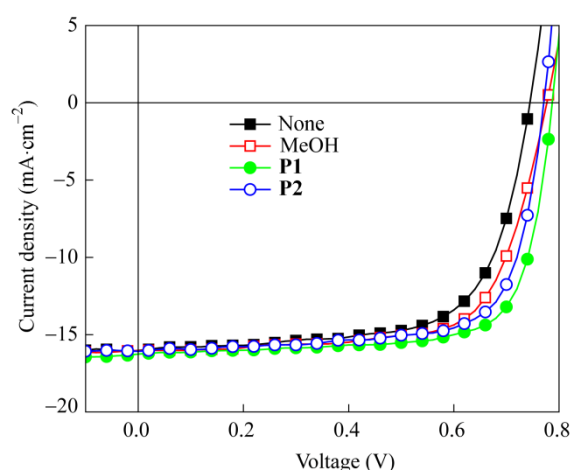


Fig. 6 *J-V* characteristics of the PSCs (device configuration: ITO/PEDOT:PSS/PTB7-Th:PC₇₁BM/cathode interlayer/Al)

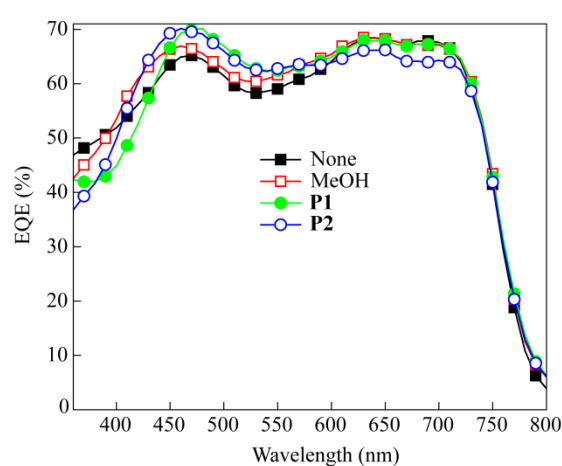


Fig. 7 EQE spectra of the PSCs (device configuration: ITO/PEDOT:PSS/PTB7-Th:PC₇₁BM/cathode interlayer/Al)

Table 2 The photovoltaic parameters of the BHJ devices with a configuration of ITO/PEDOT:PSS/PTB7-Th:PC₇₁BM/ETLs/Al

Cathode interlayer	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF (%)	PCE _{max} (%)
None	15.81	0.67	64.14	6.75
MeOH	15.78	0.75	68.49	8.11
P1	16.26	0.79	74.19	9.49
P2	16.14	0.78	72.85	9.16

CONCLUSIONS

In summary, we have demonstrated a series of functional polymers that are synthesized by multicomponent polymerization. The syntheses are carried out *via* a microwave-assisted one-pot process of diynes, dialdehydes and dibenzylamine based on A3-coupling reaction. The resulting polymers can be easily dissolved in common organic solvents, and exhibit good thermal stability and film forming ability. Thanks to the pendant amine groups, the resulting copolymers **P1** and **P2** can be dissolved in alcohol in the presence of a small amount of acetic acid, which ensures their usage in cathode interlayer to improve the photovoltaic performance of PSCs. The devices utilizing **P1** and **P2** as the cathode interlayer achieve the PCEs of 9.49% and 9.16%, respectively,

which are much higher than that of the control device. These results suggest that the MCP is an effective strategy for the synthesis of functional polymers, and may inspire broad research interests in developing effective polymerization approaches toward multi-functional polymer materials.

REFERENCES

- 1 Ruijter, E., Scheffelaar, R. and Orru, R.V.A., *Angew. Chem., Int. Ed.*, 2011, 50: 6234
- 2 Domling, A. and Ugi, I., *Angew. Chem., Int. Ed.*, 2000, 39: 3168
- 3 Kakuchi, R., *Angew. Chem., Int. Ed.*, 2014, 53: 46
- 4 Rotstein, B.H., Zaretsky, S., Rai, V. and Yudin, A.K., *Chem. Rev.*, 2014, 114: 8323
- 5 D'Souza, D.M. and Mueller, T.J.J., *Chem. Soc. Rev.*, 2007, 36: 1095
- 6 Siamaki, A.R., Sakalauskas, M. and Arndtsen, B.A., *Angew. Chem., Int. Ed.*, 2011, 50: 6552
- 7 Toure, B.B. and Hall, D.G., *Chem. Rev.*, 2009, 109: 4439
- 8 Teiber, M. and Mueller, T.J.J., *Chem. Commun.*, 2012, 48: 2080
- 9 Zhang, Y., Li, P., Wang, M. and Wang, L., *J. Org. Chem.*, 2009, 74: 4364
- 10 Thanh Binh, N., Minh Quan, T., Ermolenko, L. and Al-Mourabit, A., *Org. Lett.*, 2014, 16: 310
- 11 Dhawan, R., Dghaym, R.D. and Arndtsen, B.A., *J. Am. Chem. Soc.*, 2003, 125: 1474
- 12 Rudick, J.G., *J. Polym. Sci., Part A: Polym. Chem.*, 2013, 51: 3985
- 13 Frapper, G., Bachmann, C., Gu, Y., de Sousa, R.C. and Jerome, F., *Phys. Chem. Chem. Phys.*, 2011, 13: 628
- 14 Kakuchi, R. and Theato, P., *ACS Macro Lett.*, 2013, 2: 419
- 15 Kim, H. and Choi, T.L., *ACS Macro Lett.*, 2014, 3: 791
- 16 Ihara, E., Hara, Y., Itoh, T. and Inoue, K., *Macromolecules*, 2011, 44: 5955
- 17 Li, W., Wu, X., Zhao, Z., Qin, A., Hu, R. and Tang, B.Z., *Macromolecules*, 2015, 48: 7747
- 18 Liu, Y., Gao, M., Lam, J.W.Y., Hu, R. and Tang, B.Z., *Macromolecules*, 2014, 47: 4908
- 19 Zhang, Z., You, Y.Z., Wu, D.C. and Hong, C.Y., *Macromolecules*, 2015, 48: 3414
- 20 Zheng, C., Deng, H., Zhao, Z., Qin, A., Hu, R. and Tang, B.Z., *Macromolecules*, 2015, 48: 1941
- 21 Kreye, O., Trefzger, C., Sehlinger, A. and Meier, M.A.R., *Macromol. Chem. Phys.*, 2014, 215: 2207
- 22 Yang, L., Zhang, Z., Cheng, B., You, Y., Wu, D. and Hong, C., *Sci. China Chem.*, 2015, 58: 1734
- 23 Kreye, O., Toth, T. and Meier, M.A.R., *J. Am. Chem. Soc.*, 2011, 133: 1790
- 24 Lee, I.H., Kim, H. and Choi, T.L., *J. Am. Chem. Soc.*, 2013, 135: 3760
- 25 Deng, H., Hu, R., Zhao, E., Chan, C.Y.K., Lam, J.W.Y. and Tang, B.Z., *Macromolecules*, 2014, 47: 4920
- 26 Li, C.J. and Wei, C., *Chem. Commun.*, 2002: 268
- 27 Chan, C.Y.K., Tseng, N.W., Lam, J.W.Y., Liu, J., Kwok, R.T.K. and Tang, B.Z., *Macromolecules*, 2013, 46: 3246
- 28 Chauveau, E., Marestin, C. and Mercier, R., *Polymer*, 2014, 55: 6435
- 29 Hugel, H.M., *Molecules*, 2009, 14: 4936
- 30 Huang, F., Wu, H.B., Wang, D., Yang, W. and Cao, Y., *Chem. Mater.*, 2004, 16: 708
- 31 Wang, J., Lin, K., Zhang, K., Jiang, X.F., Mahmood, K., Ying, L., Huang, F. and Cao, Y., *Adv. Energy Mater.*, 2016, 6
- 32 Lu, J., Cai, W., Zhang, G., Liu, S., Ying, L. and Huang, F., *Acta Chimica Sinica (in Chinese)*, 2015, 73: 1153
- 33 Zhu, Y., Guang, S., Xu, H., Su, X. and Liu, X., *J. Mater. Chem. C*, 2013, 1: 5277
- 34 Xu, Q., An, L., Yu, M. and Wang, S., *Macromol. Rapid Commun.*, 2008, 29: 390
- 35 Bura, T. and Ziessel, R., *Tetrahedron Lett.*, 2010, 51: 2875
- 36 Sommer, J.R., Shelton, A.H., Parthasarathy, A., Ghiviriga, I., Reynolds, J.R. and Schanze, K.S., *Chem. Mater.*, 2011, 23: 5296
- 37 Fang, J., Wallikewitz, B.H., Gao, F., Tu, G., Muller, C., Pace, G., Friend, R.H. and Huck, W.T., *J. Am. Chem. Soc.*, 2011, 133: 683
- 38 Xing, Y., Sun, C., Yip, H.L., Bazan, G.C., Huang, F. and Cao, Y., *Nano Energy*, 2016, 26: 7
- 39 Wu, Z.H., Sun, C., Dong, S., Jiang, X.F., Wu, S.P., Wu, H.B., Yip, H.L., Huang, F. and Cao, Y., *J. Am. Chem. Soc.*, 2016, 138: 2004