

Multicomponent Tandem Polymerization of Aromatic Alkynes, Carbonyl Chloride, and Fischer's Base toward Poly(diene merocyanine)s[†]

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Cite this paper: *Chin. J. Chem.* 2019, 37, 1264–1270. DOI: 10.1002/cjoc.201900256

Summary of main observation and conclusion Multicomponent polymerization (MCP) is a popular tool to construct polymers with diverse structure, simple operation, and high efficiency, which faces the challenges of limited product structures. Multicomponent tandem polymerization (MCTP), combining two or multiple reactions in a one-pot fashion, could expand the scope of MCP and enrich the polymer structures. Herein, a one-pot three-component tandem polymerization of diynes, carbonyl chloride, and Fischer's base has been developed to afford conjugated poly(diene merocyanine)s with mild condition, satisfactory molecular weights (M_w up to 10 900 g/mol) and yields (up to 81%). The polymers enjoy good solubility and high thermal stability. The unique emission behavior of the model compound and polymer show that they are aggregation-induced emission (AIE)-active, suggesting that the diene merocyanine moiety is a potential AIEgen. This MCTP shows great potential in the preparation of functional polymer materials, which could build new AIE functional units directly from the polymerization, demonstrating its synthetic simplicity and elegance.

Background and Originality Content

In the past decade, inspired by the advantages of multicomponent reactions (MCRs) such as high efficiency, mild condition, atom economy, simple reactants, and structural diversity,^[1–4] they were introduced to polymer chemistry and a large number of multicomponent polymerizations (MCPs) were developed which bring new functional polymer structures and materials.^[5–7] Typical MCPs include Ugi four-component polymerizations,^[8–10] Passerini three-component polymerizations,^[11–13] A³-polycouplings of alkynes, aldehydes, and amines,^[14] MCPs based on alkynes and sulfonyl azides,^[15–16] catalyst-free MCPs of elemental sulfur, amine, and alkynes/isocyanides,^[17–18] and many other MCPs.^[19–25] Compared with traditional one-component or two-component polymerizations, MCPs enjoy a series of unique advantages such as great structural diversity of polymer products, and high efficiency of chemical conversion, in situ construction of multiple types of covalent bonds from a single polymerization, and so on.

The preparation of optoelectronic polymers with conjugated structures from MCPs remains quite challenging due to the limited solubility of conjugated polymers, possible defects from the products, and narrow range of applicable monomers.^[26–29] The reported MCPs generally produce non-conjugated products such as polyamides, polyamines, and poly(ester-amide)s.^[30–32] To explore the general applicability of MCPs and their polymerization product structures, a popular tandem strategy in organic synthesis has been introduced to MCPs.^[33–37] The multicomponent tandem polymerizations (MCTPs) were developed to synthesize heteroatom or heterocycles-containing conjugated polymers or sequence-controlled polymers with well-defined structures in one pot.^[38–41] For example, sulfur-rich conjugated polymers with good stereoselectivity was prepared through the MCTP of alkynes, carbonyl chlorides, and thiols;^[38] conjugated polypyrazoles were prepared from the MCTP of alkyne, carbonyl chlorides, and benzohydrazines;^[39] polypyrimidines could be obtained from the coupling-addition-cyclization-oxidation four-step MCTP of alkyne,

guanidine hydrochloride, DMSO, and O₂,^[42] most recently, poly(indolone)s with acid-triggered fluorescence response property were synthesized through MCTP.^[43] These works have proved the great potential of MCTPs for the facile construction of conjugated polymers with complex structures and advanced functionalities.

The rapid access to a series of luminescent merocyanines were reported by Müller *et al.* through a MCR of alkynes, aryl chlorides, and Fischer's base.^[44] In this reaction, alkyne **A** and acid chloride **B** were first reacted to form ynone **C** through Sonogashira coupling (Scheme S1). Fischer's base **D** then attacked ynone **C** as a β -site enamine nucleophilic reagent to produce zwitterionic intermediate **E**, which then underwent proton transfer and 1,4-dipolar cyclization in the presence of ethanol to generate cyclobutene intermediate **F**, which was sterically and electronically sensitive. After electrocyclic ring opening, the diene-merocyanine product **G** was furnished.

In this work, through proper design of the monomer structures, and optimization of the polymerization conditions in each step, this MCR was developed to a one-pot three-component tandem polymerization of aromatic alkynes, aryl chloride, and Fischer's base for the efficient and convenient synthesis of poly(diene merocyanine)s with cross conjugation in satisfactory yields. Meanwhile, the small molecular model compound was found to be a new type of aggregation-induced emission (AIE) structure. In other word, the MCTP could build new AIE functional units directly and efficiently in the polymer backbone, which has reflected great synthetic elegance.

Results and Discussion

Polymerization

To develop this one-pot two-step three-component tandem polymerization of diynes, carbonyl chloride, and Fischer's base for the synthesis of conjugated poly(diene merocyanine)s with

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[†] Dedicated to Professor Qing-Yun Chen on the occasion of his 90th birthday.

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cross-conjugated alkene moieties and carbonyl groups, modified Sonogashira coupling reaction and the following addition-cyclization-ring opening reactions were combined in a sequential manner in a one-pot procedure. Compound **1a** with *cis*- and *trans*-tetraphenylethene moieties was designed as the diyne monomer to polymerize with the commercially available terephthaloyl dichloride **2** and Fischer's base **3**. The highly distorted structure of **1a** brings strong steric hindrance, which can efficiently enlarge the intermolecular distance and reduce the intermolecular interaction, resulting in good solubility of the resultant polymer product even without any solubilizing groups.^[45-47]

The multicomponent tandem polymerization of **1a**, **2**, and **3** was conducted under the following condition: **1a** and **2** were first reacted at room temperature in the presence of Pd(PPh₃)₂Cl₂, CuI, and Et₃N under nitrogen, generating alkynone-containing polymer intermediate **P1** in situ, which was then directly reacted with the freshly added excess amount of **3** at 80 °C for 16 h without isolation and purification to afford poly(diene merocyanine) **P2a** from this one-pot procedure (Scheme 1). The MCTP was carried out in different solvents such as toluene, dioxane, THF, and DMF (Table S1). Insoluble precipitates formed rapidly in toluene or dioxane and only trace amount of precipitate was formed in DMF. THF was found to be the proper solvent which provided polymer product with a *M_w* of 10100 g/mol in 88% yield.

Ethanol was reported to be beneficial to the enamine addition,^[44] the amount of ethanol added in the second step was hence investigated (Table S2). In the absence of ethanol or with less than 1.9 mol/L of ethanol, polymer can be obtained with satisfactory yield, however, the chemical structure analysis of the product suggests that the conversion is incomplete. When 3.4 mol/L of ethanol was added, polymer with clean expected structure and high *M_w* can be obtained.

The reaction time of the second step of the MCTP after the addition of **3** was then optimized (Table 1). Before 16 h, the pol-

ymers intermediate formed from the first step gradually converted to the poly(diene merocyanine) structure, but was incomplete, which will be discussed below. During the conversion process, there is a slight decrease of the *M_w* observed, probably due to the different polymer segment configuration of **P1** and **P2a**. After 16 h, complete conversion could be achieved in the polymer product with a *M_w* of 10900 g/mol in 81% yield. No obvious change could be observed for both yield and *M_w* of the product afterwards.

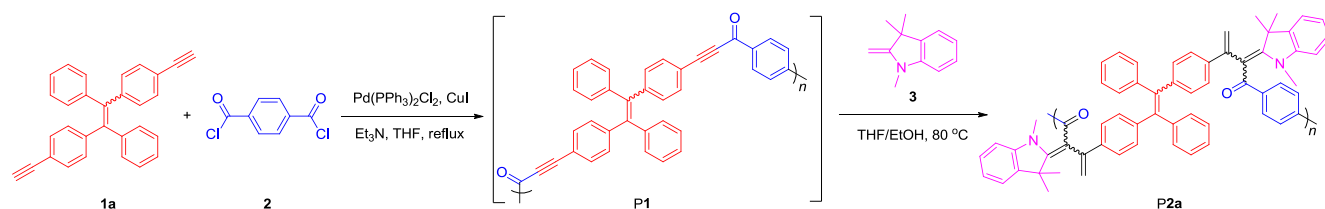
Table 1 Time course of the second step of the polymerization^a

Entry	Time/h	Yield/%	<i>M_w</i> ^b /(g/mol)	<i>M_w</i> / <i>M_n</i> ^b	C ^c
1 ^d	0	88	9200	1.21	
2	1	37	14500	1.98	○
3	3	71	13900	1.89	○
4	5	87	13400	1.99	○
5	12	85	11400	1.87	○
6	16	81	10900	1.83	✓
7	18	82	10500	1.78	✓
8 ^e	24	88	10100	1.75	✓

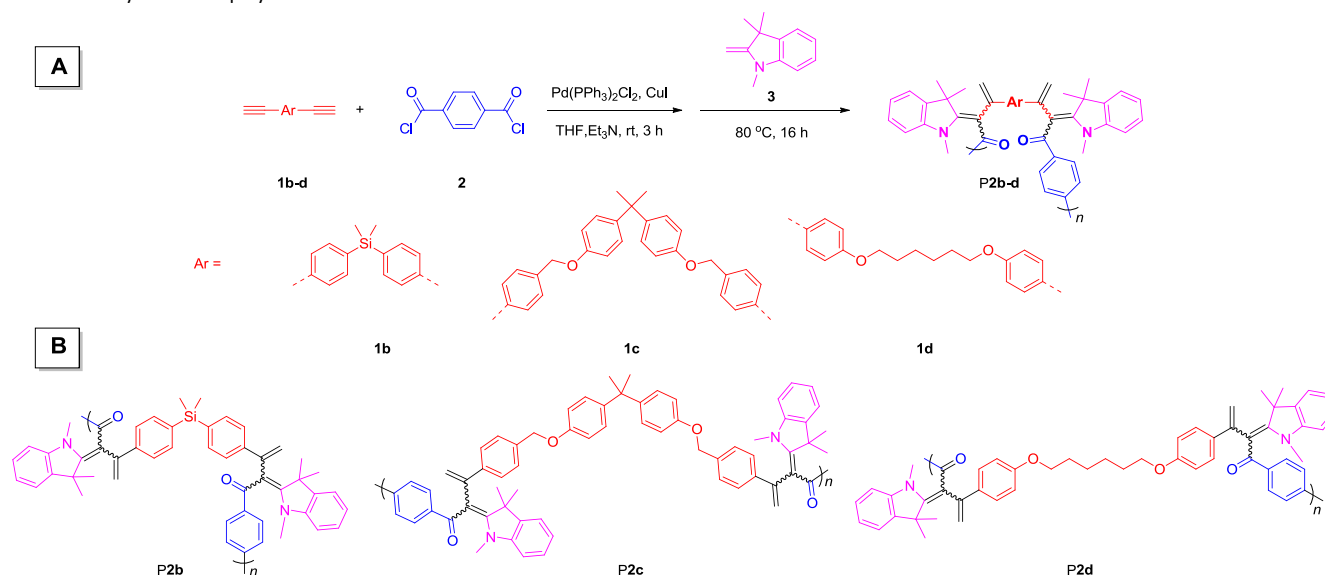
^aMonomers **1a** and **2** were reacted at room temperature in THF under nitrogen in the presence of Pd(PPh₃)₂Cl₂, CuI, and Et₃N for 3 h. Afterwards, 1 mL of ethanol and **3** were injected into the polymerization solution which then reacted at 80 °C. [**1a**] = [**2**] = 0.05 mol/L, [Et₃N] = 0.1 mol/L, [Pd(PPh₃)₂Cl₂] = 0.002 mol/L, [CuI] = 0.008 mol/L, and [**3**] = 3[**1a**]. ^bEstimated by GPC in DMF on the basis of a linear polymethylmethacrylate calibration. ^cConversion: ✓ = complete conversion, ○ = partial conversion. ^dPolymerization data of **P1**. ^eData taken from Table S1, entry 3.

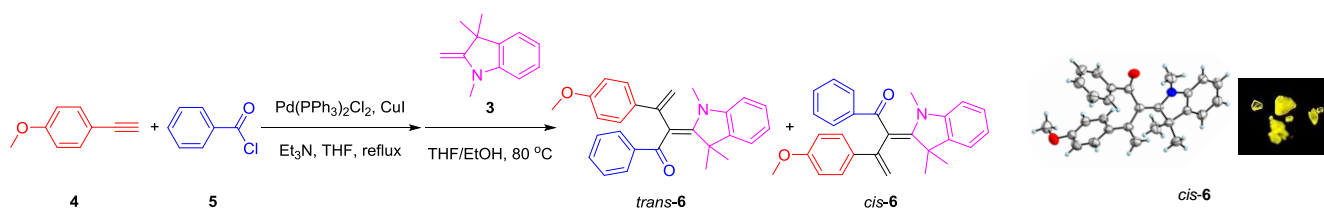
Last but not least, three other aromatic diyne monomers **1b–d** were designed and synthesized for the MCTP. Poly(diene merocyanine)s **P2b–d** with moderate yields and *M_w*s were obtained, suggesting the general applicability of this MCTP (Scheme 2 and Table S3).

Scheme 1 MCTP of diyne **1a**, carbonyl chloride **2**, and Fischer's base **3**



Scheme 2 Syntheses of polymers **P2b–d**



Scheme 3 Syntheses and single crystal structure of model compound **6****Structural characterization**

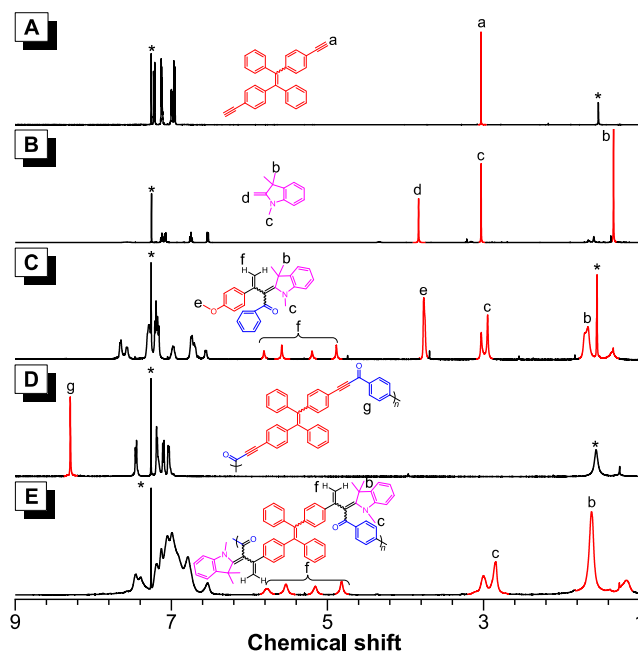
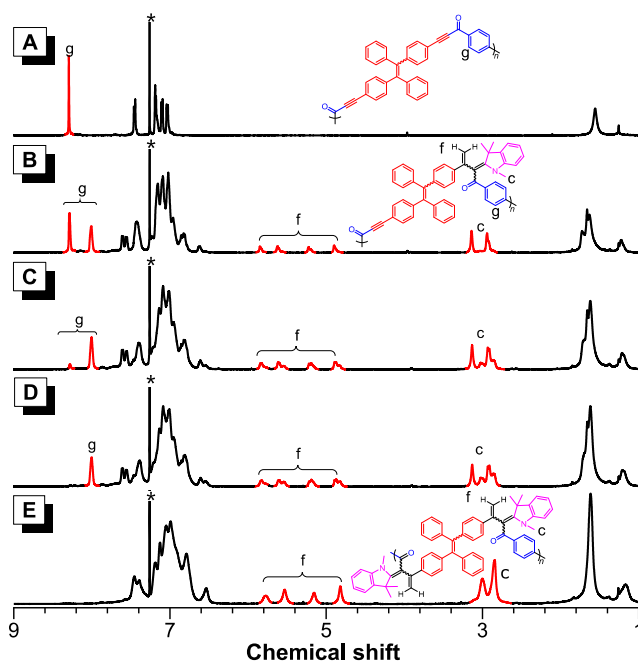
To characterize the chemical structures of the poly(diene merocyanine)s **P2a–d**, model compound **6** with similar chemical structures as the repeating unit of the polymers was designed and synthesized in 93% yield as the mixture of *cis*- and *trans*-isomers through the corresponding one-pot two-step tandem reaction (Scheme 3). The single crystal structure of *cis*-**6** was gained from the mixed solvents of dichloromethane and hexane, proving the expected diene merocyanine structure (Table S4). The standard spectroscopies such as IR, ^1H and ^{13}C NMR spectra of polymers were then compared with those of **6** as well as monomers to confirm the polymer structures.

For example, in the IR spectrum of **P2a** as shown in Figure S1, the $\equiv\text{C-H}$ and $\text{C}\equiv\text{C}$ stretching vibrations of monomer **1a** at 3276 and 2109 cm^{-1} , respectively, have all disappeared, revealing the total consumption of acetylene bonds. Furthermore, the $\text{C}\equiv\text{C}$ and C=O stretching vibrations of polyalkynone intermediate **P1** at 2191 and 1646 cm^{-1} , respectively, have also disappeared in the spectrum of **P2a**, suggesting complete conversion of the alkynone moieties from the intermediate. Meanwhile, a new C=O peak emerged at 1599 cm^{-1} in the spectrum of **P2a**, which is in accordance with the spectrum of **6**, proving the newly formed carbonyl groups in the polymer product.

The ^1H NMR spectrum of **P2a** reveals more structure details through the comparison with those of monomers **1a** and **3**, model compound **6**, and polymer intermediate **P1** (Figure 1). In the spectrum of **P2a**, the resonance peak of $\equiv\text{C-H}$ of monomer **1a** at δ 3.03, the resonance peak of $=\text{CH}_2$ of monomer **3** at δ 3.83, and the characteristic resonance peak of the neighboring aromatic protons of carbonyl groups from polymer intermediate **P1** at δ 8.29 are all absent, proving that the monomers and intermediates are totally consumed. Most importantly, like the spectrum of model compound **6**, there are two sets of vinyl proton peaks emerged at δ 5.53/4.82, and δ 5.77/5.15 in the spectrum of **P2a**, and the methyl peaks are emerged at δ 2.84 and 3.00, which is in agreement with the diene merocyanine structure.

The above-mentioned time-dependent conversion from polymer intermediate **P1** to **P2a** can also be proved by ^1H NMR spectra (Figure 2). The products of the MCTP were isolated after 1 h, 6 h, 9 h, and 16 h of the addition of monomer **3**, and the ^1H NMR spectra were measured to compare with that of the polymer intermediate **P1** formed before the addition of **3**. With the prolonged reaction time, the characteristic aromatic peak of **P1** at δ 8.29 gradually decreased. Meanwhile, three new groups of peaks emerged at δ 8.00, δ 5.85/5.23, 5.62/4.90, and δ 3.14/2.94 after the addition of **3** until the completion of the transformation, indicating the neighboring aromatic protons of the carbonyl group, the olefin protons, and the methyl protons, respectively, from the half-converted structures shown in Figure 2. These peaks eventually disappeared and the characteristic olefin peaks of **P2a** at δ 5.77/5.15, and δ 5.53/4.82, and methyl peaks at δ 3.00 and 2.84 gradually increased, revealing the gradual transformation from **P1** to **P2a** in 16 h.

Similarly, in the ^{13}C NMR spectra of **P2a** (Figure 3), both the resonances of the terminal acetylene carbons of **1a** at δ 77.56 and 83.84, and peaks of the internal acetylene carbons of **P1** at δ

**Figure 1** ^1H NMR spectra of (A) **1a**, (B) **3**, (C) **6**, (D) **P1**, and (E) **P2a** in CDCl_3 . The solvent peaks were marked with asterisks.**Figure 2** ^1H NMR spectra of (A) **P1**, and products obtained after (B) 1 h, (C) 6 h, (D) 9 h and (E) 16 h of the addition of **3** in CDCl_3 . The solvent peaks were marked with asterisks.

87.50 and 94.86 were absent. Meanwhile, the carbonyl peak of **P1**

at δ 177 had shifted to δ 196 in the spectra of P2a, again proving the monomers **1a**, **3**, and intermediate **P1** were converted to P2a.

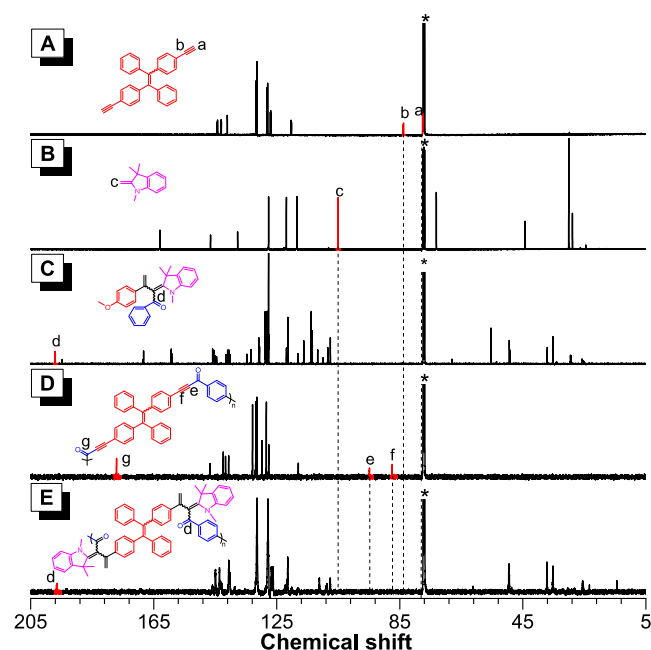


Figure 3 ^{13}C NMR spectra of (A) **1a**, (B) **3**, (C) **6**, (D) **P1**, and (E) **P2a** in CDCl_3 . The solvent peaks were marked with asterisks.

In addition, the chemical structures of other poly(diene merocyanine)s **P2b–d** were also characterized by IR and ^1H NMR spectra (Figures S2 and S3), providing similar evidences to prove their structures, although incomplete conversion was observed in P2d according to its IR spectrum.

Solubility and thermal stability

P1 and **P2a** could dissolve well in common organic solvents such as THF, chloroform, and DMF, despite of their rigid main chain and multiple aromatic rings. These polymers also enjoy high thermal stability (Figure 4). The decomposition temperatures of **P1** and **P2a** at 5 wt% weight loss are 454 and 383 $^\circ\text{C}$, respectively. Moreover, these polymers enjoy high thermal resistance even at 800 $^\circ\text{C}$, and the char yields are as high as 84% (**P1**) and 68% (**P2a**), probably owing to the heat-assisted crosslinking of the acetylene or olefin bonds within the polymer structures.

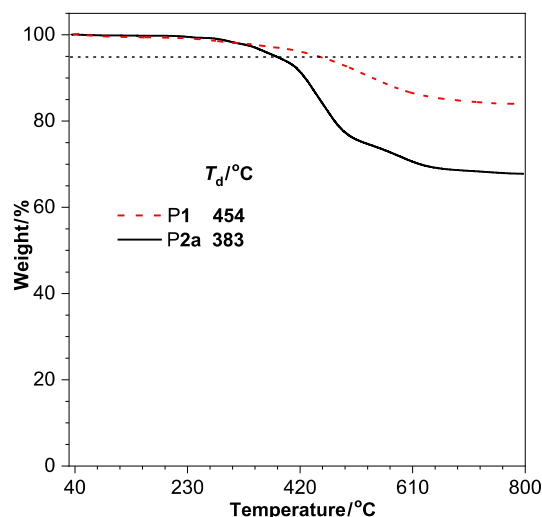


Figure 4 TGA thermograms under N_2 with a heating rate of 20 $^\circ\text{C}/\text{min}$.

Photophysical properties

With the unique diene merocyanine chromophore, luminescence behavior of model compound **6** and **P2a** were investigated as examples (Figure 5). The THF solutions of **6** and **P2a** shared similar UV absorption maxima at 394 (**6**) and 400 nm (**P2a**), however, they were both non-emissive. The crystal of **6**, on the other hand, possessed strong emission at 557 nm with a fluorescence quantum efficiency of 37%, suggesting its typical aggregation-induced emission property. The PL spectra of **6** in THF/water mixtures suggested that it was non-emissive in most of the aqueous mixtures except in 99 vol% aqueous mixture where a strong emission peak emerged at 533 nm (Figure S4). The solid thin film of **P2a** showed emission at 566 nm, which was also AIE-active.

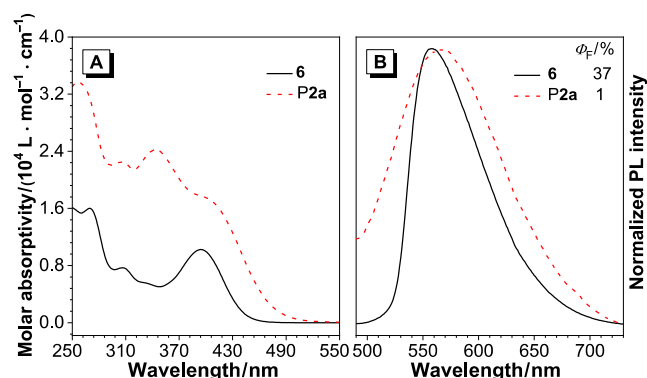


Figure 5 (A) Absorption spectra of **6** and **P2a** in THF solution. (B) Normalized PL spectra of crystal of **6** and thin film of **P2a**. Concentration: 10 $\mu\text{mol}/\text{L}$. Absolute fluorescence quantum yields (Φ_{F} s) were measured by a calibrated integrating sphere. λ_{ex} : 470 (**6**) and 420 nm (**P2a**).

Conclusions

In this work, a one-pot two-step three-component tandem polymerization was reported for the synthesis of conjugated polymers. Through the Sonogashira coupling reaction of alkyne and aryl chloride under the catalysis of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and CuI , the active polyalkynone was generated *in situ* to directly react with the freshly added Fischer's base to undergo further addition-cyclization-ring opening reactions to afford poly(diene merocyanine)s. Through careful characterization of the polymer structure by comparing their spectra with that of the single crystal of small molecular model compound **6**, the expected diene merocyanine structures were confirmed with the existence of the *cis/trans*-isomerized structures of the middle olefin moieties. The time-dependent gradual transformation from the polyalkynone intermediate to the final polymer product was also studied to reveal the polymerization process. Furthermore, the model compound **6** was found to be a new type of aggregation-induced emission structure and from the polymerization, these AIE functional units were built directly on the polymer backbone. It is anticipated that such MCTP with simple procedure and high efficiency could provide an ideal tool for the diversity-oriented synthesis of polymer materials with conjugated structures and advanced functionalities.

Experimental

Materials

Alkynes **1a–d** were synthesized according to the reported literatures.^[48–51] $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and Fischer's base **3** were purchased from TCI; terephthaloyl dichloride **2** was purchased from Alfa Aesar; CuI and 4-ethynylanisole **4** were purchased from Energy Chemical; benzoyl chloride **5** was purchased from Sigma-Aldrich; tetrahydrofuran, triethylamine and ethanol were purchased from

Guangzhou Chemical Reagent Co., Ltd. THF was dried and distilled under nitrogen atmosphere with sodium benzophenone ketyl before utilization. The triethylamine was dried over 4 Å molecular sieves and stored under nitrogen. All the organic solvents were dried and distilled before use. All these commercially available reactants were used as obtained without further purification.

Instruments

^1H and ^{13}C NMR spectra were measured on a Bruker Avance 500 MHz NMR spectrometer using deuterated chloroform as solvent and tetramethylsilane as internal reference. FT-IR spectra were recorded on a Bruker Vector 33 FT-IR spectrometer. High resolution mass spectrometry measurements were tested on a GCT premier CAB 048 mass spectrometer. The number (M_n) and weight-average (M_w) molecular weights and polydispersity indices ($\text{PDI} = M_w/M_n$) of polymers were estimated by a Waters Associates 515 gel permeation chromatography (GPC) system. THF was utilized as eluent at a flow rate of 1 mL/min. A set of monodispersed linear polymethylmethacrylate covering the M_w range of 10^3 – 10^7 g/mol were utilized as standards for molecular weight calibration. Thermogravimetric analysis was performed on a NETZSCH TG 209 F1 under nitrogen with a heating rate of 20 °C/min. UV-vis absorption spectra and fluorescence spectra were recorded on a SHIMADZU UV-2600 spectrophotometer and a Horiba Fluoromax-4 fluorescence spectrophotometer, respectively. The absolute fluorescence quantum yields were recorded on a Hamamatsu C11347-11 Quantaaurus-QY.

Synthetic procedures

All the reactions and polymerizations were conducted under nitrogen according to the standard Schlenk procedures.

3-(4-Methoxyphenyl)-1-phenyl-2-(1,3,3-trimethylindolin-2-ylidene)but-3-en-1-one (**6**): $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (56 mg, 0.08 mmol) and CuI (30 mg, 0.04 mmol) were added into a 50 mL two-neck round-bottom flask equipped with a magnetic stir bar under nitrogen. 20 mL of distilled THF was injected into the reaction system, followed by the addition of **4** (260 μL , 2 mmol), **5** (230 μL , 2 mmol), and triethylamine (290 μL , 2.1 mmol). The reaction system was stirred at room temperature for 3 h. Afterwards, 5 mL of ethanol and **3** (530 μL , 3 mmol) was injected into the reaction system and further reacted at 80 °C for 16 h. The reaction was terminated by adding 30 mL of water into the solution and extracted by 30 mL of dichloromethane three times. The organic phases were then combined and the solvent was evaporated to furnish the crude product, which was purified through silica-gel chromatography using petroleum/ethyl acetate ($V/V = 20/1$) as the eluent. An orange solid was obtained in 93 % yield. ^1H NMR (CDCl_3 , 500 MHz) δ : 7.66–7.57 (m, 2H), 7.29 (m, 3H), 7.24–7.16 (m, 4H), 6.97 (d, $J = 5.1$ Hz, 1H), 6.75–6.71 (m, 2H), 6.56 (d, $J = 7.0$ Hz, 1H), 5.81 (s, 1/2H), 5.58 (s, 1/2H), 5.20 (s, 1/2H), 4.88 (s, 1/2H), 3.76 (s, 3H), 3.03 (s, 1.3H), 2.95 (s, 1.7H), 1.68 (s, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 197.14, 168.30, 159.32, 159.10, 145.86, 145.32, 145.10, 144.56, 141.53, 140.97, 140.57, 140.22, 134.68, 133.34, 128.79, 128.65, 128.55, 128.10, 127.79, 127.68, 127.62, 121.87, 121.44, 121.38, 116.22, 113.82, 113.47, 111.70, 108.40, 107.57, 55.35, 49.39, 49.22, 37.07, 35.23; IR (KBr) ν : 3090, 3043, 2966, 2929, 1600, 1570, 1507, 1444, 1413, 1360, 1283, 1236, 1176, 1123, 1070, 1030, 924, 824, 768, 724, 696, 616, 560 cm^{-1} .

P1: **1a** (76 mg, 0.20 mmol), **2** (41 mg, 0.20 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (6 mg, 0.008 mmol), and CuI (6 mg, 0.032 mmol) were added into a 10 mL Schlenk tube equipped with a magnetic stir bar under nitrogen. 4 mL of THF and triethylamine (56 μL , 0.40 mmol) were then injected into the reaction mixture and stirred at room temperature for 3 h. The reaction mixture was dropped into 200 mL of methanol by a cotton filter to terminate the polymerization and form precipitate, which was allowed to stand overnight. After filtration, the crude product was washed with CH_3OH and dried

under vacuum overnight to produce **P1** as a yellow solid in 81% yield. $M_w = 20\,300$ g/mol, $M_w/M_n = 2.51$. ^1H NMR (CDCl_3 , 500 MHz) δ : 8.29, 7.45, 7.18, 7.10, 7.03; ^{13}C NMR (CDCl_3 , 125 MHz) δ : 177.09, 146.68, 142.41, 141.64, 140.64, 132.88, 131.81, 131.45, 129.75, 128.39, 127.61, 118.00, 94.86, 87.50; IR (KBr) ν : 2191, 1644, 1500, 1402, 1284, 1205, 1026, 1005, 703 cm^{-1} .

The typical procedure for the multicomponent tandem polymerizations was given below using the polymerization of **1a**, **2**, and **3** for example. **P2a**: **1a** (76 mg, 0.20 mmol), **2** (41 mg, 0.20 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (6 mg, 0.008 mmol), and CuI (6 mg, 0.032 mmol) were added into a 10 mL Schlenk tube equipped with a magnetic stir bar under nitrogen. 4 mL of THF and triethylamine (56 μL , 0.40 mmol) were then injected into the reaction mixture and stirred at room temperature for 3 h. Afterwards, 1 mL of ethanol and **3** (120 μL , 0.60 mmol) were injected into the mixture, which was further reacted at 80 °C for 16 h. The polymerization was terminated by dropping the mixture into 200 mL of CH_3OH through a cotton filter to form precipitate. The polymer product was allowed to stand overnight. After filtration, the crude product was washed with CH_3OH and dried under vacuum overnight.

P2a was obtained as a brownish yellow solid in 81 % yield. $M_w = 10900$ g/mol, $M_w/M_n = 1.83$. ^1H NMR (CDCl_3 , 500 MHz) δ : 8.08–7.30, 7.24–6.65, 6.53, 5.76, 5.53, 5.15, 4.82, 3.35–2.56, 1.61, 1.17; ^{13}C NMR (CDCl_3 , 125 MHz) δ : 196.54, 144.91, 143.62, 140.61, 140.21, 131.41, 127.83, 126.77, 126.20, 121.42, 111.16, 107.61, 49.47, 37.17, 35.20, 25.52, 14.45; IR (KBr) ν : 2960, 1724, 1628, 1599, 1488, 1364, 1297, 1219, 1129, 1072, 1020, 914, 876, 745, 700 cm^{-1} .

P2b was obtained as a yellow solid in 61 % yield. $M_w = 8400$ g/mol, $M_w/M_n = 2.01$. ^1H NMR (CDCl_3 , 500 MHz) δ : 8.01–7.08, 6.95, 6.71, 6.48, 5.90, 5.62, 5.20, 4.89, 2.91, 1.61, 1.25, 0.46; IR (KBr) ν : 2962, 1718, 1627, 1594, 1488, 1382, 1303, 1222, 1130, 1072, 1020, 914, 812, 777, 742 cm^{-1} .

P2c was obtained as a light yellow solid in 57 % yield. $M_w = 4800$ g/mol, $M_w/M_n = 1.21$. ^1H NMR (CDCl_3 , 500 MHz) δ : 7.98–7.28, 7.12, 6.96, 6.81, 6.51, 5.90, 5.64, 5.24, 4.93, 3.0, 1.45; IR (KBr) ν : 2963, 1720, 1633, 1605, 1509, 1366, 1297, 1224, 1130, 1072, 1013, 914, 880, 830, 744 cm^{-1} .

P2d was obtained as a brownish yellow solid in 73 % yield. $M_w = 7400$ g/mol, $M_w/M_n = 1.52$. ^1H NMR (CDCl_3 , 500 MHz) δ : 8.37–7.34, 7.21, 6.75, 5.78, 5.57, 5.16, 4.81, 4.33, 3.92, 3.32–2.69, 2.11–0.73; IR (KBr) ν : 2935, 1719, 1635, 1600, 1506, 1385, 1249, 1172, 1112, 1019, 918, 832, 745 cm^{-1} .

Supporting Information

The supporting information for this article, including the reported reaction mechanism for the MCR of aromatic alkynes, aryl chlorides and Fischer's base synthesis; effect of solvent, ethanol's concentration and monomer structures on the polymerization; single crystal data of *cis*-**6**; FT-IR spectra of **1a**, **3**, **6**, **P1**, and **P2a–d**; ^1H NMR spectra of **P2b–d** and PL spectra of **6** in THF/water mixtures, is available on the WWW under <https://doi.org/10.1002/cjoc.201900256>.

Acknowledgement

This work was partially supported by the National Natural Science Foundation of China (21490573, 21822102, 21774034, 21490574, and 21788102), the Natural Science Foundation of Guangdong Province (2016A030306045 and 2016A030312002), and the Innovation and Technology Commission of Hong Kong (ITC-CNERC14SC01).

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Manuscript received: June 12, 2019

Manuscript revised: September 25, 2019

Manuscript accepted: September 29, 2019

Accepted manuscript online: October 4, 2019

Version of record online: November 12, 2019