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ScienceDirect

Polymer 49 (2008) 1527–1537

polymer

www.elsevier.com/locate/polymer

Functionalization of conjugated copolymers with phosphorescent iridium complexes and carbazole/1,3,4-oxadiazole dendrons via click chemistry

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Received 5 November 2007; received in revised form 22 December 2007; accepted 14 January 2008
Available online 20 January 2008

Abstract

New types of polyfluorene derivatives containing Ir complexes and carbazole/1,3,4-oxadiazole dendrons on the side chain have been synthesized through ‘‘click chemistry’’ efficiently. By introducing propargyl group into the binaphthyl unit on the polyfluorene backbone, different Ir complex- and functional dendron-containing azides could be quantitatively clicked into the main chain through the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition. The efficiency of the click reaction was confirmed by using ^{1}H NMR and FT-IR spectra. The resulting copolymers exhibited desirable properties, such as excellent solubility, good thermal stability, high molecular weights and narrow molecular weight distribution. The photophysical properties of the copolymers in solutions and solid films were investigated, and the results indicated that the energy transfer from the main chain to the green or red Ir complex was incomplete, and more efficient energy transfer in solid films was observed as compared with that in solution.

Keywords: Polyfluorene; Iridium complex; Click chemistry

1. Introduction

In the past few years, organic phosphorescent transition-metal complexes have attracted increasing attention, since they can harvest both singlet and triplet exicitons, enabling internal quantum efficiencies close to 100% [1]. Among phosphorescent heavy-metal complexes, iridium complexes have been recognized as one of the best phosphorescent material candidates because of their intense phosphorescence at room temperature and significantly shorter phosphor lifetime compared with other heavy-metal complexes [2]. To simplify the device fabrication and improve the performance of the resulting devices, iridium complexes were often doped into host materials, such as carbazole-containing polymers, conjugated poly(9,9-alkylfluorene) and its derivatives [3]. Although this approach has successfully produced highly efficient polymer light-emitting diodes, the obtained devices may undergo phase segregation, and consequently lead to fast reduction of efficiency with increasing current density. A possible solution to this problem is to introduce phosphorescent complexes into the polymer backbone via chemical bonds. Recently, a number of solution-processable phosphorescent polymers have been prepared by attaching iridium complexes to the side chain or main chain through the copolymerization of monomers containing the desired metal complex [4,5]. For example, Chen et al. synthesized phosphorescent conjugated polymers based on a polyfluorene backbone with iridium complex pendants attached to the C-9 position of the fluorene group [4a]. Holmes et al. reported chelating polymers with iridium complexes in the main chains [5a]. Alternatively, phosphorescent polymers can also be synthesized by the modification of polymers with the metal complex in a post polymerization reaction.

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0032-3861/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.01.033

This strategy is modular, with the potential of introducing different metal complexes onto the polymer backbone. However, in sharp contrast to the copolymerization method, so far very few examples of phosphorescent polymers have been synthesized by using the latter approach [4d,6]. This is probably due to the less availability of a high yielding orthogonal covalent functionalization method.

Recently, the copper(I)-catalyzed Huisgen's azide–alkyne $(3+2)$ cycloaddition reaction, the so-called "click" reaction [7], has proven to be an excellent tool towards novel functional materials [8]. This type of reaction is characterized by excellent yields, high tolerance to different functional groups, mild and simple reaction conditions, and simple work-up of products. By using such a cycloaddition "click" reaction, Reek and Bunz independently prepared polyfluorene-based conjugated polymers by the step-growth polymerization of diazido and diethynyl conjugated building blocks [9]. Weck and co-workers synthesized unconjugated polymers with a variety of pendant iridium complexes via click chemistry [4d]. Most recently, we have successfully employed the click approach to prepare new types of dendronized conjugated polymers as potential blue light-emitting materials [10].

As an extension of our previous work on light-emitting dendrimers [10,11], we report here a simple yet highly efficient route for the synthesis of new types of phosphorescent conjugated polymers bearing both different iridium complexes and carbazole- and/or 1,3,4-oxadiazole-based dendrons as pendants via click chemistry. Poly(9,9-dihexylfluorene) was selected as the host because of its high fluorescence, good chemical and thermal stability [12]. The incorporation of twisted non-planar binaphthyl into the polyfluorene backbone, on one hand, can provide hydroxyl groups for postfunctionalization. On the other hand, introduction of the twisted non-planar binaphthyl moiety randomly into the rod-like conjugated polymer backbone could control the conjugation length and alter the packing of the polymer chains in the solid phase [13]. Furthermore, dendrons with peripheral carbazole and/or 1,3,4-oxadiazole groups may play the role of not only site isolation but also hole- and electron-transporting [14].

2. Experimental

2.1. Materials and methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM 300 spectrometer. TMS was used as internal reference for all the compounds. Elemental analysis was performed using a Flash EA 1112 series elemental analyzer (Thermo Quest CE Instruments). Mass spectra were recorded with a Surveyor MSQ Plus (FINNGAN) spectrometer. MALDI-TOF mass spectra were measured by an APEX-II spectrometer (Bruker) at the acceleration voltage of 19 000 V, using α-cyano-4-hydroxycinnamic acid as matrix material. FT-IR spectra were recorded in a transmission mode using a Jasco Fourier Transform Infrared Spectrometer (FT/IR-480 plus). The relative molecular weights of the copolymers were determined by gel permeation chromatography (GPC) in THF using a Waters 515 system with RI detector and applying linear calibration with polystyrene. Differential scanning calorimetry (DSC) was carried out using a DSC 822e (Mettler Toledo) at a heating rate of 10 °C/min under a nitrogen atmosphere (−30–250 °C). Thermogravimetric analysis (TGA) was performed using a Netzsch STA 409 PC at a heating rate of 20 °C/min under a nitrogen atmosphere (30–800 °C). Absorption spectra were taken by a UV-2401 (PC) S UV–vis recording spectrophotometer (Shimadzu) with a 10-mm quartz cell at 20 °C. Photoluminescence (PL) was measured with an F-4500 (Hitachi) fluorescence spectrophotometer with a 10-mm quartz cell at 20 °C. The films were spin-coated from a 10 mg/mL toluene solution at 2000 rpm.

6,6′-Dibromo-2,2′-bis(methoxylmethyl)-1,1′-binaphthol (**6**) [15], 2,7-dibromo-9-fluorene, 2,7-dibromo-9,9-dihexylfluorene (**7**), 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) (**8**) [16], Fréchet-type dendritic azides (**5a** and **5b**) [17] were synthesized according to the published methods. All other starting materials and reagents were of analytic purity without further purification, unless otherwise noted. THF and toluene were distilled over sodium/benzophenone under nitrogen atmosphere. Chloroform and *N*,*N*-dimethylformamide were distilled over calcium hydride. Acetone and acetylacetone were distilled over anhydrous K_2CO_3. Ethoxyethanol was distilled over magnesium turnings.

2.2. Synthesis of functionalized acetylacetone ligand **2**

Acetylacetone (4.0 mL, 38.9 mmol) was added dropwise over 10 min to a stirred suspension of sodium hydride (70% dispersion in mineral oil, 1.47 g, 42.8 mmol) in dry THF (150 mL) at 0 °C. After the mixture was stirred for further 20 min at the same temperature, *n*-butyllithium (2.5 M in hexane, 17.1 mL, 42.8 mmol) was then added dropwise over 10 min to the stirred mixture. Then, 1,6-dibromohexane (9.0 mL, 58.4 mmol) was added quickly to the stirred mixture at 0 °C. The reaction mixture was stirred for 1 h at the same temperature and for a further 1 h at rt. Then, the reaction was quenched with saturated aqueous ammonium chloride, and the solution was acidified by using 2 M hydrochloric acid (4 mL). The aqueous phase was separated, and extracted twice with ethyl acetate (2 × 10 mL). The combined organic phase was washed with saturated aqueous sodium chloride, and dried over anhydrous sodium sulfate. After removal of the organic solvent, the crude product was purified by flash chromatography with ethyl acetate/petroleum ether (1/20, v/v) as eluent to give the intermediate diketone **1** as colorless oil (4.30 g, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32–1.44 (m, 6H), 1.56–1.63 (m, 2H), 1.80–1.90 (m, 2H), 2.05 (s, 2.5H), 2.23–2.29 (m, 2.2H), 2.51 (t, $J=7.2$ Hz, 0.4H), 3.40 (t, $J=6.8$ Hz, 2H), 3.58 (s, 0.4H), 5.50 (s, 0. 8H), 15.51 (s, 0.8H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.2, 24.9, 25.5, 27.3, 27.9, 28.4, 28.7, 28.9, 30.8, 32.7, 33.8, 38.1, 43.6, 57.8, 99.7, 191.3, 194.1, 202.1, 204.0 ppm.

A mixture of diketone **1** (3.16 g, 12.0 mmol), NaN_3 (0.94 g, 14.4 mmol), and KI (0.20 g, 1.2 mmol) in DMSO (28 mL) was stirred at 30 °C for 24 h. Then, the reaction mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic phase was washed with saturated aqueous sodium chloride, and dried over anhydrous sodium sulfate. After removal of the organic solvent, the crude product was purified by flash chromatography on silica with ethyl acetate/petroleum ether (1/20, v/v) as eluent to give azide functionalized diketone **2** (2.51 g, 93%) as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12–1.26 (m, 6H), 1.45 (br, 4H), 1.91 (s, 2.5H), 2.09–2.15 (m, 2.2H), 2.36 (t, $J = 7.3$ Hz, 0.4H), 3.12 (t, $J = 6.9$ Hz, 2H), 3.43 (s, 0.4H), 5.36 (s, 0.8H), 15.38 (s, 0.8H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.1, 24.8, 25.5, 26.5, 28.7, 28.8, 29.0, 29.6, 30.8, 38.1, 43.6, 51.4, 57.8, 99.7, 191.3, 194.1, 202.0, 204.0 ppm. MS (ESI): *m/z* 224.2 $[M]^+$.

2.3. Synthesis of green-emitting iridium complex-containing azide *3a*

A mixture of $[Ir(ppy)_2Cl]_2$ (500 mg, 0.47 mmol), diketone **2** (262 mg, 1.17 mmol), and K_2CO_3 (395 mg, 3.73 mmol) in 2-ethoxyethanol (30 mL) was heated to 70 °C, and stirred for 24 h. After cooling to room temperature, the reaction mixture was poured into a sodium chloride aqueous solution (100 mL). The resulting precipitate was collected by filtration, washed with water, methanol and hexane, and dried under vacuum. The crude product was further purified by column chromatography on neutral alumina with CH_2Cl_2/petroleum ether (2/1, v/v) as eluent to give **3a** as a yellow powder (545 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86–1.27 (m, 8H), 1.38–1.48 (m, 2H), 1.72 (s, 3H), 1.90 (t, $J = 7.2$ Hz, 2H), 3.14 (t, $J = 6.9$ Hz, 2H), 5.11 (s, 1H), 6.17–6.26 (m, 2H), 6.61–6.75 (m, 4H), 7.02–7.05 (m, 2H), 7.47 (t, $J = 7.1$ Hz, 2H), 7.64–7.79 (m, 4H), 8.42 (d, $J = 5.7$ Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.5, 26.6, 28.7, 28.8, 28.9, 29.0, 41.5, 51.5, 100.0, 118.2, 118.4, 120.7, 121.2, 121.3, 123.7, 123.9, 129.0, 129.1, 133.1, 133.3, 136.8, 144.8, 148.1, 148.2, 148.3, 168.7, 184.8, 188.0 ppm. IR (KBr, cm^{-1}): ν 3043, 2928, 2855, 2093, 1576, 1512, 1475, 1417, 1306, 1263, 1159, 1059, 1029, 757, 733. MS (ESI): *m/z* 725.2 $[M]^+$. Anal. Calcd. for $C_{33}H_{34}IrN_5O_2$: C 54.68, H 4.73, N 9.66; found: C 55.07, H 4.83, N 9.92.

2.4. Synthesis of red-emitting iridium complex-containing azide *3b*

This Ir complex was prepared with the similar procedure as above by using $[Ir(btp)_2Cl]_2$ (600 mg, 0.46 mmol) as starting material. The crude product was purified by column chromatography on neutral alumina with CH_2Cl_2/petroleum ether (2/1, v/v) as eluent to give **3b** as a red powder (603 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87–1.00 (m, 2H), 1.03–1.31 (m, 6H), 1.44–1.54 (m, 2H), 1.78 (s, 3H), 1.98 (t, $J = 7.2$ Hz, 2H), 3.20 (t, $J = 6.9$ Hz, 2H), 5.24 (s, 1H), 6.20–6.29 (m, 2H), 6.77–6.83 (m, 2H), 6.93–7.07 (m, 4H), 7.57–7.65 (m, 4H), 7.69–7.75 (m, 2H), 8.41 (t, $J = 5.4$ Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.5, 26.8, 28.5, 28.6, 28.8, 28.9, 41.2, 51.5, 100.2, 118.0, 118.2, 118.4, 118.6, 122.7, 123.6, 124.8, 124.9, 125.7, 125.8, 135.0, 135.1, 137.9, 138.0, 142.2, 142.4, 146.6, 146.6, 146.9, 147.0, 149.1, 149.3, 166.1, 166.2, 184.8, 188.0 ppm. IR (KBr, cm^{-1}): ν 3052, 2927, 2855, 2093, 1600, 1574, 1514, 1473, 1404, 1294, 1263, 1155, 1065, 1024, 909, 763, 729. MS (ESI): *m/z* 837.2 $[M]^+$.

2.5. Synthesis of carbazole peripherally functionalized dendritic azide *5a*

A mixture of the second-generation dendritic bromide CZG_2CH_2Br (**4a**) (680 mg, 0.51 mmol), NaN_3 (332 mg, 5.11 mmol), and KI (17 mg, 0.10 mmol) in DMSO (15 mL) was stirred at 60 °C for 20 h. Then the reaction mixture was poured into CH_3OH (100 mL). The white precipitate was collected and precipitated from methanol again. After drying, **5a** was obtained as a white powder (585 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.71–1.76 (m, 8H), 1.94–2.03 (m, 8H), 3.81 (t, $J = 5.8$ Hz, 8H), 4.17 (s, 2H), 4.28 (t, $J = 6.8$ Hz, 8H), 4.87 (s, 4H), 6.28–6.53 (m, 9H), 7.16–7.21 (m, 8H), 7.27–7.43 (m, 16H), 8.05 (d, $J = 7.7$ Hz, 8H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.9, 27.0, 42.7, 54.9, 67.6, 70.1, 101.0, 102.0, 105.9, 107.3, 108.7, 118.9, 120.5, 123.0, 125.8, 137.8, 139.1, 140.5, 160.3, 160.4 ppm. IR (KBr, cm^{-1}): ν 3050, 2938, 2874, 2098, 1597, 1483, 1456, 1381, 1329, 1237, 1154, 1059, 835, 750, 725. MALDI-TOF mass: *m/z* 1294.5 $[M]^+$, 1317.5 $[M + Na]^+$, 1333.5 $[M + K]^+$. Anal. Calcd. for $C_{85}H_{79}N_7O_6$: C 78.86, H 6.15, N 7.57; found: C 79.15, H 6.52, N 7.20.

2.6. Synthesis of 1,3,4-oxadiazole peripherally functionalized dendritic azide *5b*

This compound was prepared with the similar procedure as above for **5a** by using the second-generation dendritic bromide $OXDG_2CH_2Br$ (**4b**) (870 mg, 0.54 mmol) as starting material. Dendron **5b** was obtained as a white solid (727 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (s, 36H), 4.17 (s, 2H), 4.92 (s, 4H), 5.06 (s, 8H), 6.45–6.62 (m, 9H), 7.48 (t, $J = 8.2$ Hz, 16H), 7.96–8.07 (m, 16H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.1, 35.1, 54.8, 69.4, 69.9, 101.8, 106.5, 107.3, 121.0, 123.6, 126.1, 126.8, 127.1, 127.7, 137.8, 139.5, 140.6, 155.4, 159.9, 160.1, 164.1, 164.7 ppm. IR (KBr, cm^{-1}): ν 3054, 2960, 2870, 2097, 1598, 1551, 1452, 1417, 1370, 1270, 1157, 1063, 1017, 839, 732. MALDI-TOF mass: *m/z* 1570.2 $[M]^+$, 1593.4 $[M + Na]^+$, 1609.4 $[M + K]^+$. Anal. Calcd. for $C_{97}H_{91}N_{11}O_{10}$: C 74.17, H 5.84, N 9.81; found: C 73.96, H 5.76, N 9.64.

2.7. Synthesis of *PFYNE*

Under nitrogen, to a suspension of NaH (700 mg, 20.4 mmol) in dried THF (100 mL) and DMF (20 mL) was slowly added **PFOH** [10] (1.210 g, 0.75 mmol) at 0 °C. After stirring for about 4 h, propargyl bromide (1.40 mL, 16.20 mmol) was slowly added via a syringe. The mixture was stirred in dark at room temperature for 3 days. A small amount of water was then slowly added to quench the reaction. After organic solvent was evaporated under reduced pressure, CH_2Cl_2 (200 mL) and 1 M HCl aqueous solution (50 mL) was added to dissolve the residue. The organic phase was separated and washed with brine (30 mL), and dried over $MgSO_4$. After removal of organic solvent, the resulting solid was redissolved in a small amount of

CH_2Cl_2. The solution was poured into CH_3OH/petroleum ether (v/v, 5/1) to precipitate the final product. Then, the polymer was dried under vacuum at 50 °C to afford **PFYNE** as a gray solid (1.230 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.69–0.71 (br, 40H), 1.05–1.18 (br, 48H), 2.03 (br, 16H), 2.37 (br, 2H), 4.61 (br, 4H), 7.24–7.27 (br, 3H), 7.40–7.75 (br, 27H), 8.02–8.11 (br, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 22.6, 23.9, 29.7, 31.5, 40.4, 55.4, 56.5, 57.4, 75.4, 79.4, 116.6, 119.3, 120.0, 120.6, 121.6, 125.8, 126.2, 127.2, 128.8, 129.8, 130.2, 133.2, 137.4, 140.1, 140.6, 151.0, 151.5, 151.9, 153.4, 155.6 ppm. IR (KBr, cm^{-1}): ν 3309, 3027, 2953, 2927, 2855, 1595, 1483, 1458, 1377, 1338, 1277, 1221, 1092, 1055, 1001, 936, 884, 748, 723.

2.8. General procedure for the preparation of dendronized polymers *P1–P5* via click chemistry

To a solution of **PFYNE** (34.0 mg, 20.1 μmol) and the corresponding azide compounds (**3a**, **3b**, **5a** or **5b**, 40.2 μmol in total) in THF (2 mL) was added $Cu(PPh_3)_3Br$ (5.0 mg, 5.4 μmol), CuI (2.0 mg, 10.5 μmol) and *N*,*N*-diisopropylethylamine (DIPEA, 80.4 μmol) under stirring vigorously. The reaction mixture was heated at 35 °C, and stirred at the same temperature under nitrogen for 3 days. The crude product was evaporated to dryness, and then passed through a neutral alumina column with CH_2Cl_2/CH_3OH (5/1, v/v) as eluent to remove the catalyst. The copolymers (**P1–P5**) were then precipitated into methanol from dichloromethane several times to remove excess azide compounds.

2.8.1. Polymer *P1*

This compound was prepared from **3a** (7.3 mg, 10.1 μmol) and **5a** (39.2 mg, 30.2 μmol) to give **P1** as a yellow powder (54.0 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.64–0.72 (br, 41H), 0.97–1.06 (br, 51H), 1.47 (br, 1H), 1.65 (br, 13.5H), 1.90–2.02 (br, 29H), 3.57 (br, 12H), 4.20 (br, 12H), 4.70–5.22 (br, 12H), 6.02–6.63 (br, 16.5H), 6.94–7.12 (br, 13H), 7.24–7.42 (br, 30H), 7.53–7.78 (br, 27H), 7.96–7.98 (br, 16H), 8.39 (br, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 23.9, 25.8, 26.9, 29.7, 31.5, 40.4, 42.7, 55.4, 67.6, 70.1, 100.9, 106.0, 108.6, 118.9, 120.0, 120.4, 121.6, 122.9, 125.7, 126.2, 130.0, 132.2, 138.8, 140.1, 140.4, 140.6, 151.8, 160.3 ppm. IR (KBr, cm^{-1}): ν 3050, 2926, 2857, 1597, 1457, 1332, 1242, 1160, 1055, 816, 749, 724. Anal. Calcd. for $C_{270}H_{279.5}Ir_{0.5}N_{13}O_{12}$: C 81.18, H 7.05, N 4.56; found: C 80.93, H 7.18, N 4.39.

2.8.2. Polymer *P2*

This compound was prepared from **3b** (8.4 mg, 10.1 μmol) and **5a** (39.2 mg, 30.2 μmol) to give **P2** as a red powder (68.1 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.69–0.71 (br, 41H), 1.05–1.18 (br, 51H), 1.48 (br, 1H), 1.65 (br, 13.5H), 2.00–2.23 (br, 29H), 3.71 (br, 12H), 4.20 (br, 12H), 4.61–5.11 (br, 12H), 6.11–6.83 (br, 15.5H), 7.09–7.11 (br, 14H), 7.26–7.39 (br, 30H), 7.60–7.75 (br, 27H), 7.95–7.98 (br, 16H), 8.31 (br, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 23.9, 25.8, 27.0, 28.5, 29.7, 31.5, 40.4, 42.7, 55.4, 67.6, 70.1, 101.0, 101.9, 106.0, 107.1, 108.7, 118.9, 120.0, 120.4, 121.6, 123.0, 123.6, 124.9, 125.8, 126.2, 128.4, 129.9, 133.2, 136.9, 138.0, 138.8, 140.1, 140.4, 140.6, 145.0, 151.9, 160.3 ppm. IR (KBr, cm^{-1}): ν 3050, 2927, 2857, 1598, 1457, 1378, 1330, 1243, 1160, 1056, 817, 749, 728. Anal. Calcd. for $C_{272}H_{279.5}Ir_{0.5}N_{13}O_{12}S$: C 80.65, H 6.95, N 4.49; found: C 80.44, H 7.22, N 4.21.

2.8.3. Polymer *P3*

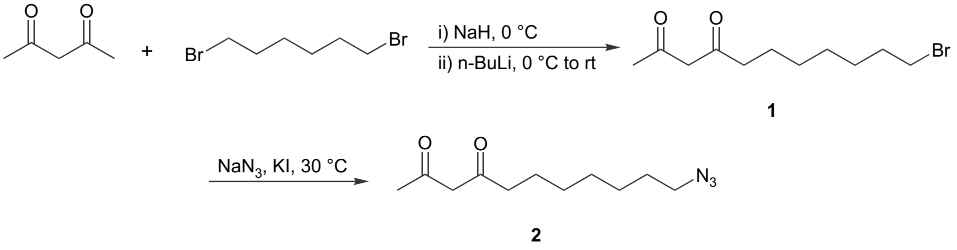
This compound was prepared from **3b** (8.4 mg, 10.1 μmol) and **5b** (47.6 mg, 30.2 μmol) to give **P3** as a red powder (72.0 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.69–0.71 (br, 41H), 1.05 (br, 51H), 1.26 (br, 54H), 1.47 (br, 1H), 1.69 (br, 1.5H), 2.01 (br, 17H), 3.91 (br, 1H), 4.76–5.22 (br, 30H), 6.19–6.86 (br, 17.5H), 7.40–7.75 (br, 57H), 7.91–7.99 (br, 28H), 8.31 (br, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 23.9, 26.7, 28.5, 29.7, 31.1, 31.5, 35.1, 40.4, 53.8, 55.4, 69.4, 69.9, 101.8, 106.5, 107.1, 118.5, 120.0, 121.0, 121.6, 122.7, 123.6, 124.9, 125.7, 126.1, 126.8, 127.1, 127.7, 128.6, 133.2, 137.2, 138.0, 139.2, 140.1, 140.5, 151.9, 155.4, 159.9, 160.2, 164.1, 164.7 ppm. IR (KBr, cm^{-1}): ν 3054, 2927, 2860, 1599, 1494, 1459, 1371, 1268, 1157, 1061, 1018, 960, 819, 732, 724. Anal. Calcd. for $C_{290}H_{297.5}Ir_{0.5}N_{19}O_{18}S$: C 78.00, H 6.72, N 5.96; found: C 77.41, H 6.89, N 5.82.

2.8.4. Polymer *P4*

This compound was prepared from **3a** (4.4 mg, 6.0 μmol), **3b** (5.1 mg, 6.0 μmol) and **5a** (36.5 mg, 28.2 μmol) to give **P4** as a red powder (65.6 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.70–0.72 (br), 1.06–1.18 (br), 1.48 (br), 1.65 (br), 1.90–2.23 (br), 3.71 (br), 4.20 (br), 4.69–5.12 (br), 6.19–6.66 (br), 7.09–7.11 (br), 7.26–7.30 (br), 7.60–7.86 (br), 7.95–7.98 (br), 8.31 (br) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 23.9, 25.8, 27.0, 28.5, 29.7, 31.5, 40.4, 42.7, 55.4, 67.6, 70.1, 101.0, 106.0, 107.1, 108.7, 118.9, 120.0, 120.4, 121.6, 122.9, 123.6, 125.7, 126.2, 127.2, 128.4, 128.8, 130.0, 133.2, 136.9, 138.0, 139.7, 140.1, 140.4, 140.6, 144.8, 151.9, 154.0, 160.3 ppm. IR (KBr, cm^{-1}): ν 3051, 2927, 2856, 1597, 1457, 1377, 1330, 1242, 1159, 1055, 817, 749, 725. Anal. Calcd. for $C_{266}H_{275}Ir_{0.6}N_{12.8}O_{11.6}S_{0.6}$: C 80.44, H 6.98, N 4.51; found: C 80.33, H 7.18, N 4.49.

2.8.5. Polymer *P5*

This compound was prepared from **3a** (4.4 mg, 6.0 μmol), **3b** (5.1 mg, 6.0 μmol), **5a** (18.3 mg, 14.1 μmol) and **5b** (22.2 mg, 14.1 μmol) to give **P5** as an orange powder (67.6 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.69–0.80 (br), 1.05–1.18 (br), 1.26 (br), 1.46 (br), 1.66 (br), 1.91–1.94 (br), 3.75 (br), 4.22 (br), 4.70–5.05 (br), 6.20–6.68 (br), 7.03–7.11 (br), 7.21–7.75 (br), 7.95–7.97 (br), 8.40 (br) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 23.9, 25.8, 26.9, 29.7, 31.1, 31.5, 35.1, 40.4, 42.6, 53.4, 55.4, 67.6, 69.4, 70.0, 101.9, 105.9, 106.6, 107.1, 108.6, 118.8, 120.0, 120.4, 121.0, 121.5, 122.9, 123.6, 125.7, 126.1, 126.8, 127.1, 127.7, 140.0, 140.4, 140.6, 151.8, 155.4, 159.9, 160.3, 164.0, 164.7 ppm. IR (KBr, cm^{-1}): ν 3052,



Scheme 1. Synthesis of functionalized acetylacetone ligand **2**.

2927, 2858, 1598, 1458, 1330, 1267, 1158, 1057, 818, 749, 725. Anal. Calcd. for $C_{274.4}H_{283.4}Ir_{0.6}N_{15.6}O_{14.4}S_{0.6}$: C 79.13, H 6.86, N 5.25; found: C 78.93, H 7.19, N 5.01.

3. Result and discussion

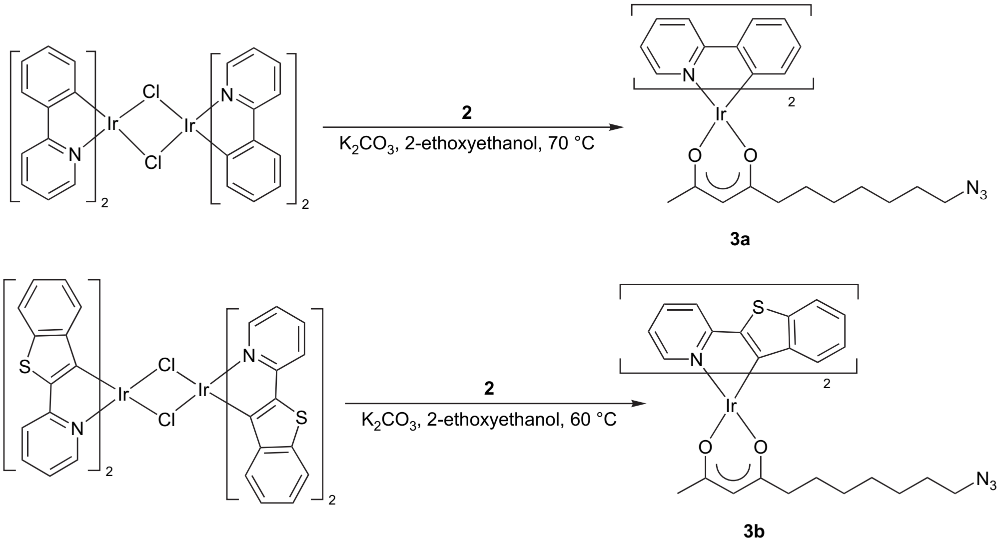
3.1. Synthesis of cyclometalated iridium complex-containing azides

The synthesis of the functionalized acetylacetone ligand **2** carrying the hexylethylene-tethered azide group is shown in Scheme 1. Compound **1** was prepared from acetylacetone and hexyldibromide according to the reported method [18]. Reaction of **1** with NaN_3 in the presence of KI afforded the desired β-diketone ligand **2** in high yield. Its molecular structure was confirmed by ^{1}H NMR and mass spectra.

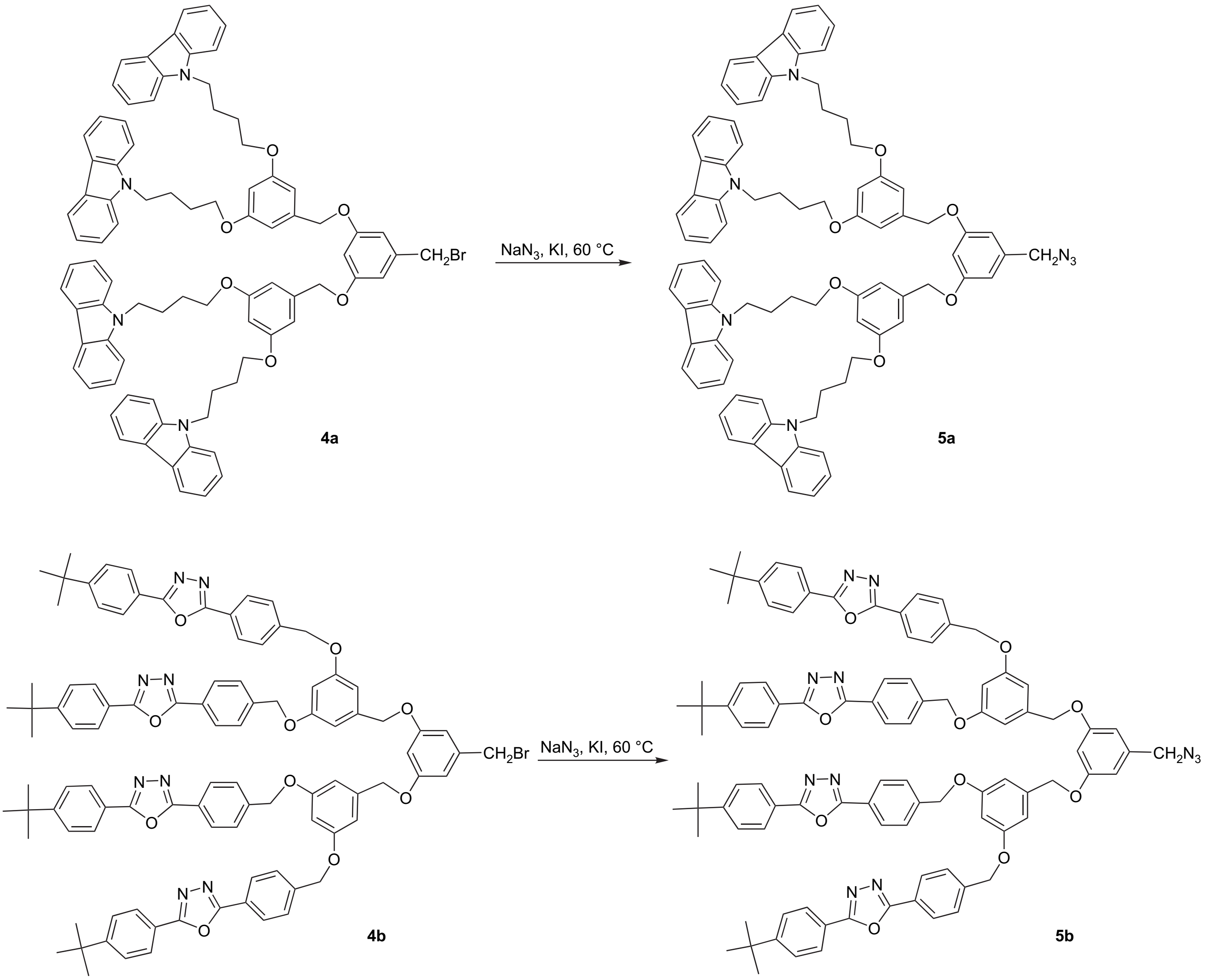
Formation of the iridium complex by reaction of the diketone ligand with the corresponding chloro-bridged iridium dimer is outlined in Scheme 2. Initially, according to the reported procedures [19], a mixture of the diketone ligand **2** and $[Ir(ppy)_2Cl]_2$ was heated at 130 °C in the presence of K_2CO_3 as a base in 2-ethoxyethanol, however, only affording trace product **3a**. After many attempts, it was found that the reaction was highly sensitive to the reaction temperature. When reaction of **2** with $[Ir(ppy)_2Cl]_2$ was carried out at 110, 90 and 70 °C, the reaction yield was found to be 30%, 63% and 81%, respectively. The low yield under high reaction temperature was probably due to the decomposition of the azide group. Similarly, reasonable reaction yield for the red-emitting iridium complex **3b** was achieved under similar conditions. We also noticed that the reaction of **2** with $[Ir(btp)_2Cl]_2$ proceeded smoothly even at room temperature, affording moderate yield when the reaction time was prolonged to 36 h. Both iridium complexes were purified by flash chromatography on neutral alumina, and characterized by ^{1}H and ^{13}C NMR and FT-IR spectra, and elemental analysis. The results obtained are consistent with the desired molecular structures.

3.2. Synthesis of carbazole/1,3,4-oxadiazole peripherally functionalized dendritic azides

The second-generation carbazole-based and 1,3,4-oxadiazole-based dendritic bromides were synthesized by using convergent strategy according to the published procedures [17]. The reactions between sodium azide with the corresponding dendritic bromide (CZG_2CH_2Br **4a** or $OXDG_2CH_2Br$ **4b**) were carried out in the presence of KI at 60 °C for 20 h, affording the desired dendritic azides **5a** and **5b** in 89% and 86% yields, respectively (Scheme 3). Both azido compounds were characterized by ^{1}H and ^{13}C NMR, FT-IR and TOF-MS spectra as well as elemental analysis. All results were consistent with the proposed structures.



Scheme 2. Synthesis of iridium complex-containing azides **3a** and **3b**.



Scheme 3. Synthesis of the second-generation dendritic azides **5a** and **5b**.

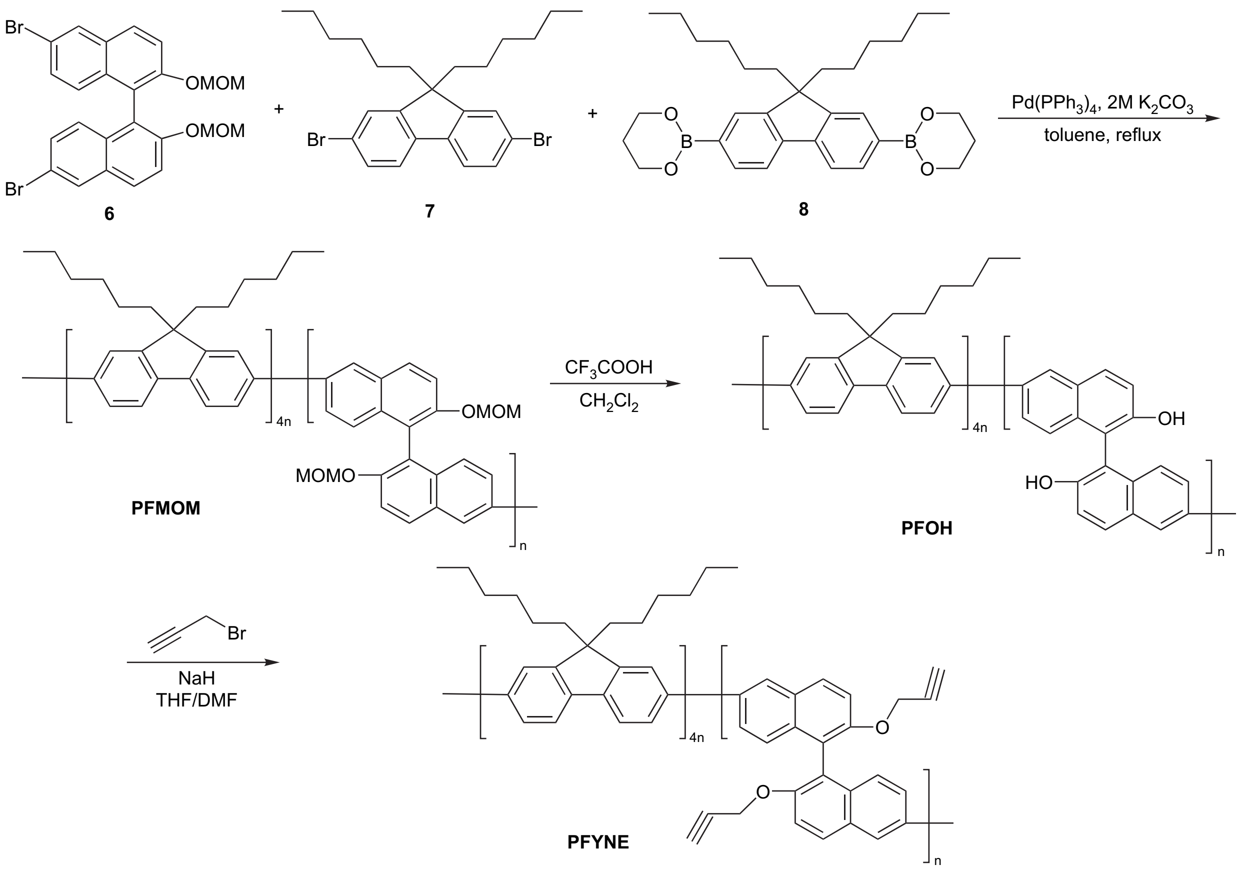
*3.3. Synthesis of polyfluorene derivative bearing alkyne pendants, **PFYNE***

Polyfluorene derivative **PFYNE** bearing alkyne pendants was prepared via three steps according to our previous reported method [10], as shown in Scheme 4. The three monomers (**6**, **7** and **8**) were firstly synthesized according to the reported literature procedures [15,16]. Then, the Suzuki polycondensation of methoxylmethyl (MOM)-protected binaphthyl monomer **6**, 2,7-dibromo-9,9-dihexylfluorene **7** with 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) **8** in the presence of 2 mol% $Pd(PPh_3)_4$ generated the MOM-protected polymer **PFMOM**. Subsequent hydrolysis of the MOM groups by TFA followed by alkylation with propargyl bromide afforded the desired copolymer **PFYNE** in high reaction yields.

The conversion of **PFMOM** to **PFOH** was confirmed by ^{1}H NMR spectra (Fig. 1A and B). The disappearance of the signals corresponding to MOM group and the presence of the signal at 5.07 ppm corresponding to −OH in the ^{1}H NMR spectra were observed. The conversion of **PFOH** to **PFYNE** was also identified not only by the FT-IR spectrum of **PFYNE** which exhibited ≡C−H stretch at 3309 cm^{-1} but also by the presence of the signal at 2.37 ppm corresponding to ≡C−H in the ^{1}H NMR spectrum (Fig. 1C). Based on the results of ^{1}H NMR analysis, high conversion (>95%) in every step was achieved. The molecular structure of **PFYNE** was further characterized by ^{13}C NMR spectrum as well as gel permeation chromatography (GPC).

*3.4. Synthesis and characterization of iridium complex-containing dendronized polyfluorene derivatives **P1−P5***

Polyfluorene derivatives (**P1−P5**) bearing both iridium complexes and carbazole/1,3,4-oxadiazole peripherally functionalized dendrons as pendants were prepared from **PFYNE** and the iridium complex-containing azides (**3a** and **3b**) and dendritic azides (**5a** and **5b**) by click chemistry as shown in Scheme 5.



Scheme 4. Synthesis of polyfluorene derivative **PFYNE** bearing alkyne pendants.

Initially, the Huisgen 1,3-dipolar cycloadditions were carried out in a mixture of water and THF using 5 mol% $CuSO_4 \cdot 5H_2O$/10 mol% sodium ascorbate as the in situ reducing agent to generate the active Cu(I) species. However, the click reaction was found to be sluggish, and complete conversion could not be achieved even at prolonged reaction time. It might be because of the relatively low reactivity of the iridium complex-containing azides. As a result, $Cu(PPh_3)_3Br$/CuI were selected as the catalyst, and DIPEA as the base. To our delight, the click reaction proceeded smoothly in THF or toluene at 35 °C for 3 days. Almost quantitative conversion was observed, as monitored by ^1H NMR spectra. It was found that the reaction was much faster in THF than in toluene. Notably, the reaction was sensitive to the reaction temperature. When the temperature was lower than 25 °C, the cycloaddition was rather slow. In contrast, some brown precipitate was observed when the temperature was higher than 50 °C, which might be the cross-linked byproduct between the alkynes. Therefore, click reactions between **PFYNE** and the dendritic azides and the iridium complex-containing azides were carried out in THF in the presence of 13 mol% of $Cu(PPh_3)_3Br$, 25 mol% of CuI and 2 equiv DIPEA at 35 °C, the desired functionalized polyfluorenes **P1–P5** were obtained in 79–83% yield, respectively. All these resulting iridium complex-containing copolymers are readily soluble in conventional solvents, such as THF, toluene, dichloromethane and chloroform, due to the introduction of dendritic wedges as well as the alkyl chain at 9,9' positions of fluorene units.

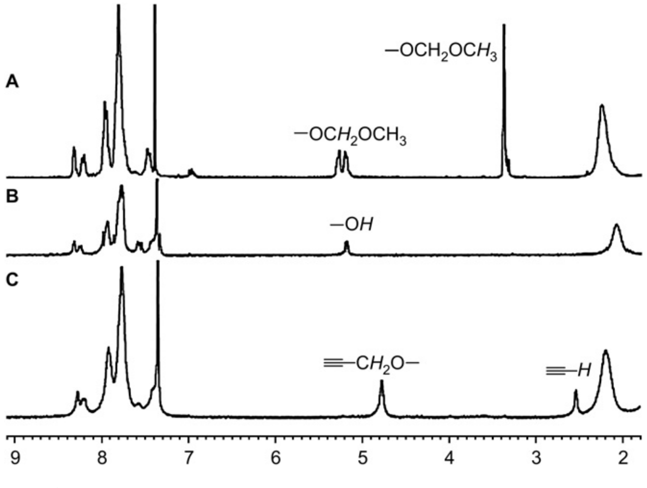
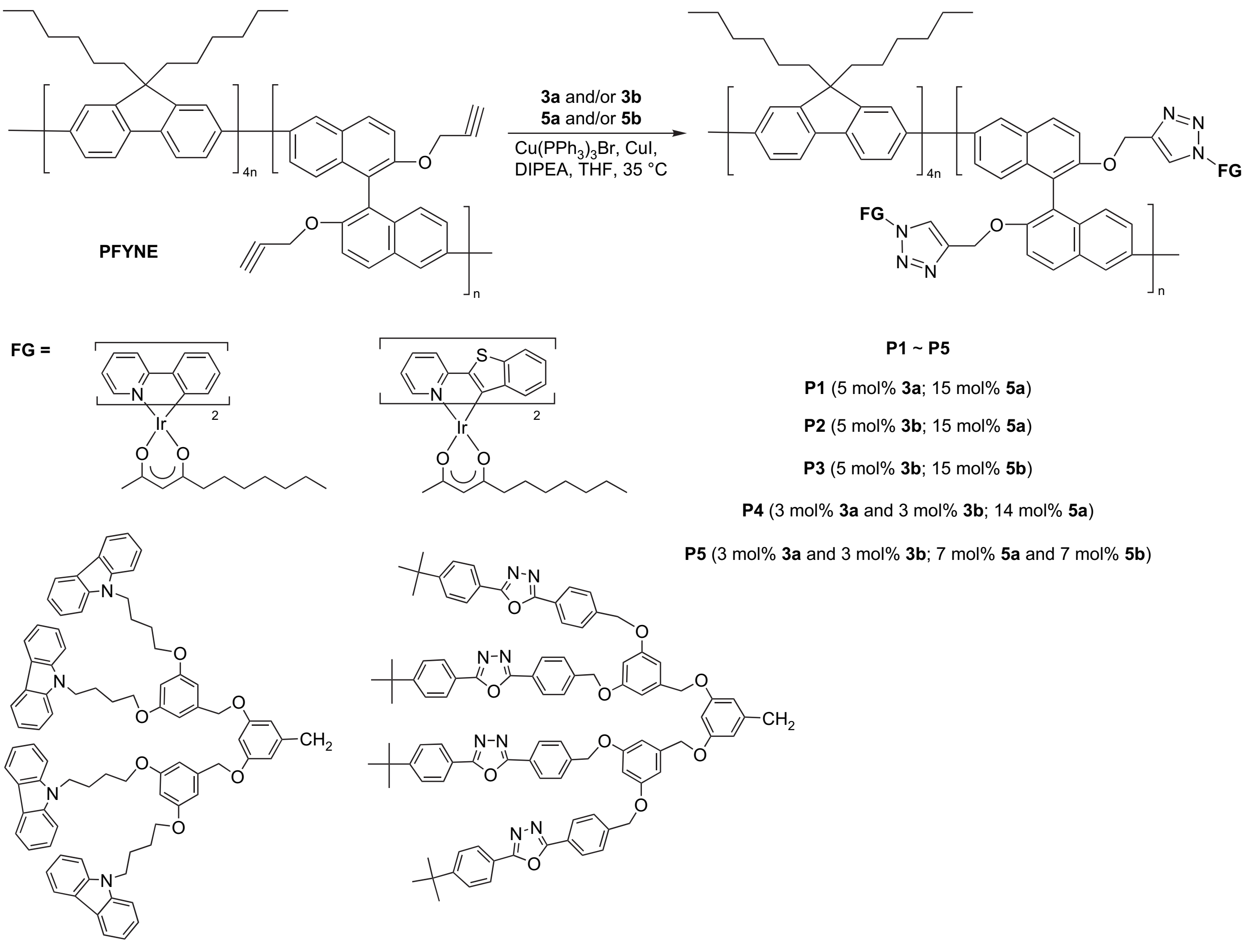


Fig. 1. ^1H NMR spectra of polymers **PFMOM** (A), **PFOH** (B) and **PFYNE** (C).

These copolymers **P1–P5** were well characterized by ^1H and ^{13}C NMR and FT-IR spectra and elemental analysis. As shown in Fig. 2, the disappearance of the signals corresponding to ≡C–H at 2.37 ppm in the ^1H NMR spectra was observed, indicating complete conversion of alkyne groups on **PFYNE**. On the other hand, the characteristic peaks corresponding to the pyridine ring proton on the iridium complex at about 8.4 ppm were observed in all the copolymers **P1–P5**. The attachment of



Scheme 5. Synthesis of iridium complex-containing dendronized polyfluorene derivatives **P1–P5**.

carbazole and/or 1,3,4-oxadiazole dendrons onto the copolymer backbone was confirmed by the presence of the signals at about 1.26 ppm (for 1,3,4-oxadiazole protons) and 3.75 and 4.22 ppm (for carbazole protons). IR data also confirmed that neither propargyl (3309 cm^{-1}) nor azide (2093–2098 cm^{-1}) residues remained in the final copolymers. In addition, the elemental analysis results were consistent well with the calculated ones.

The molecular weights of these copolymers (**P1–P5** and **PFYNE**) were determined by gel permeation chromatography (GPC) with THF as the eluent, calibrated against polystyrene standards. As shown in Table 1, the number-average molecular weights ($\overline{M_n}$) of these dendronized polymers **P1–P5** were found to be more than 9.00×10^4, and quite narrow molecular weight distributions (1.41–1.53) were observed. These number-average molecular weights are lower than that of **PFYNE** than the calculated ones, which partially attributes to the underestimated data for dendronized polymer when determined by GPC method [20,21].

The thermal properties of these dendronized copolymers **P1–P5** were investigated using thermal gravimetric analysis (TGA) under nitrogen atmosphere. As shown in Table 1, all copolymers exhibited excellent thermal stability with onset degradation temperatures (T_d) above 300 °C, indicating that the incorporation of dendritic pendant did not affect the thermal stability. Then, we studied the thermally induced phase transition behavior of these copolymers by differential scanning calorimetry (DSC) in nitrogen atmosphere. The results are summarized in Table 1. The T_gs of these copolymers **P1–P5** were in the range of 89–97 °C, and the DSC curves showed no crystallization and melting peaks but only T_gs although polyfluorenes usually reveal a crystallization temperature due to their crystalline nature in the solid state. This result obviously indicates that the presence of both the twisted binaphthyl units and dendritic wedges suppresses the crystallization and the chain aggregation of the copolymers effectively. In addition, it is worth noticing that all these dendronized copolymers were found to have higher glass transition temperatures (T_gs) as compared with the reported polyfluorenes ($T_g = 51$ °C) [22].

3.5. *Photoluminescent properties of the functionalized copolymers* ***P1–P5***

The emission wavelengths of the copolymers **P1–P5** in solutions and solid films are summarized in Table 1. The UV–vis absorption spectra of copolymers **P1–P5** in toluene

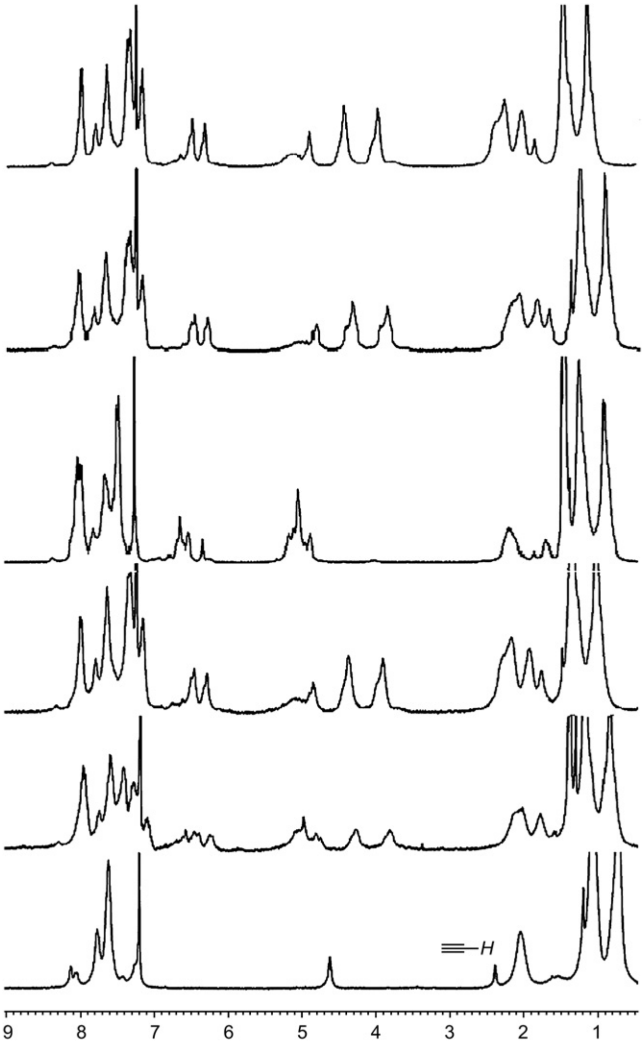


Fig. 2. ^{1}H NMR spectra of the functionalized copolymers **P1–P5** and **PFYNE**.

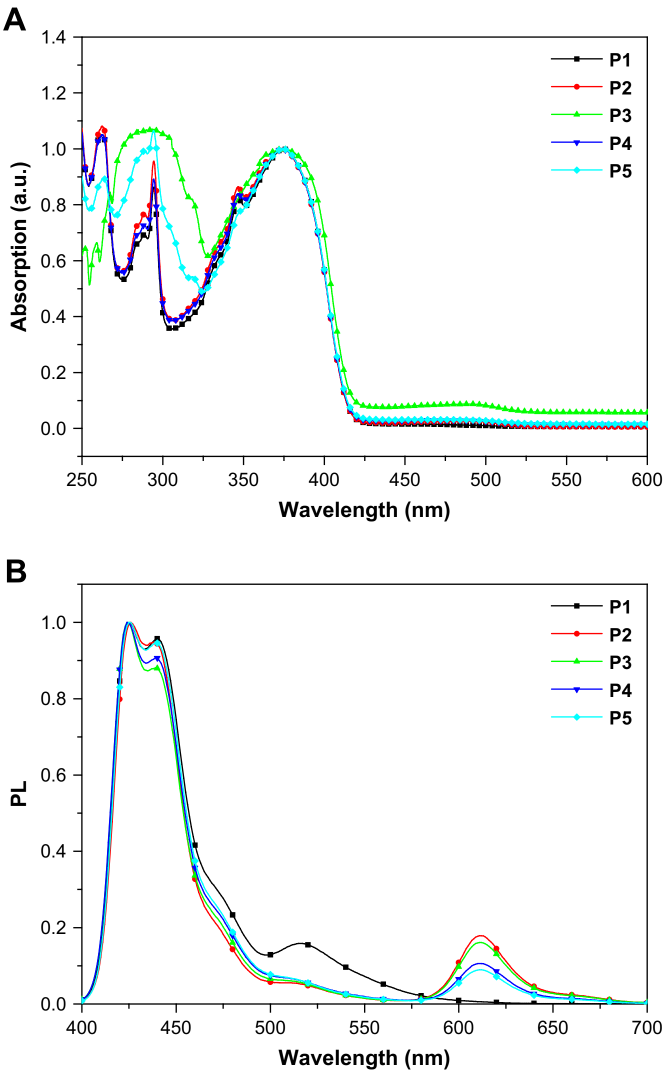


Fig. 3. (A) Normalized UV–vis absorption spectra of the functionalized copolymers **P1–P5** in toluene (1×10^{-5} M). (B) Normalized PL spectra of the functionalized copolymers **P1–P5** in toluene (5×10^{-5} M) excited at 380 nm.

(1×10^{-5} M) are shown in Fig. 3A. In the high energy region, all the copolymers exhibited the absorption peak at 374 nm, and copolymers **P1**, **P2**, **P4** and **P5** exhibited the distinct absorption peak of carbazole at about 346 nm. While in the lower energy region, from 380 nm to 550 nm, all these copolymers exhibited weak and broad absorption of MLCT states of iridium complex. The normalized photoluminescent spectra of the copolymers in toluene (1×10^{-5} M) are shown in Fig. 3B. All copolymers **P1–P5** showed typical strong blue emission from the main chains. Additional green emission at around 520 nm from Ir(ppy)$_2$(acac) for **P1** and red emission at around

Table 1
Physical and photophysical properties of the dendronized copolymers **P1–P5**

Polymers	$\overline{M_n}$[a] ($\times 10^4$)	$\overline{M_n}$[b] ($\times 10^4$)	PDI[a]	T_d (°C)[c]	T_g (°C)	λ_{PL} (nm)	
						Solution[d]	Film[e]
P1	9.80	10.5	1.51	366	93	425, 440, 517	421, 444, 515
P2	9.81	10.6	1.53	352	93	426, 439, 611	420, 439, 616
P3	10.83	11.4	1.41	348	90	425, 439, 613	420, 441, 614
P4	9.03	10.5	1.50	361	97	424, 439, 612	420, 440, 613
P5	9.71	10.8	1.50	316	89	425, 439, 612	421, 439, 615

[a] Molecular weights determined by GPC in THF using polystyrene standards.
[b] Data calculated based on the amount of attached pendants. For **PFYNE**, $\overline{M_n} = 6.27 \times 10^4$ (PDI = 1.73).
[c] Temperature at which 5% weight loss was observed.
[d] Emission in toluene solution (5×10^{-5} M) at $\lambda_{ex} = 380$ nm.
[e] Emission in films on quartz slides at $\lambda_{ex} = 380$ nm.

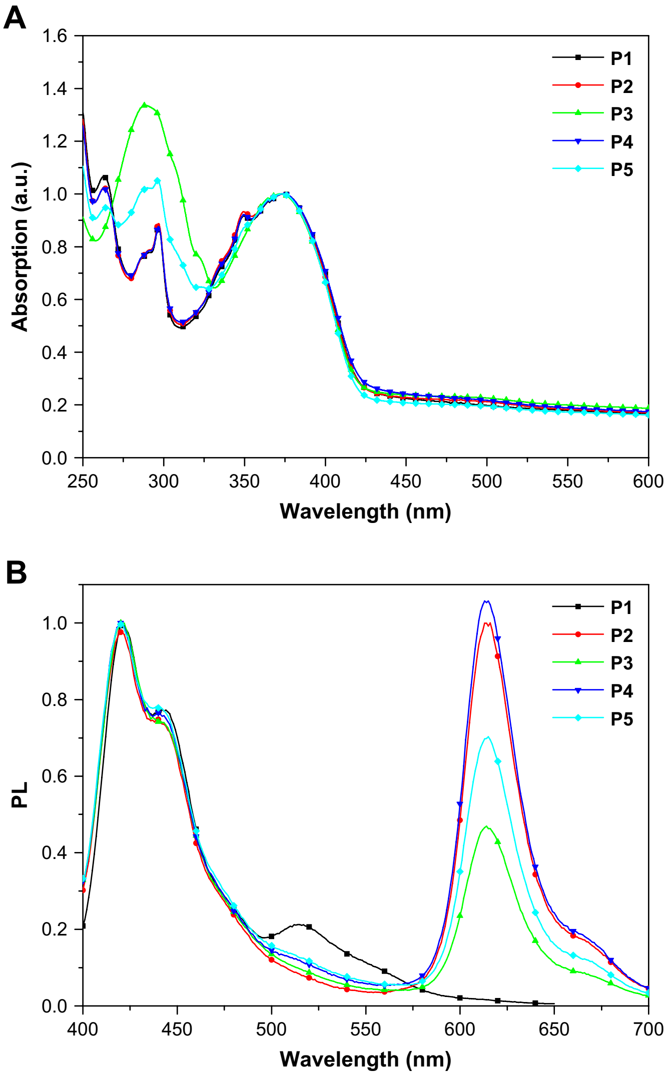


Fig. 4. (A) Normalized UV–vis absorption spectra of the functionalized copolymers **P1**–**P5** in thin films. (B) Normalized PL spectra of the functionalized copolymers **P1**–**P5** in thin films excited at 380 nm.

612 nm from Ir(btp)$_2$(acac) for **P2**–**P5** were also observed. Notably, copolymers modified by both red Ir complex and green Ir complex (**P4** and **P5**) only exhibited red emission. The disappearance of green emission was probably due to the efficient energy transfer from green Ir(ppy)$_2$(acac) to red Ir(btp)$_2$(acac) or the energy back transfer to the main chain [4a,23,24]. Obviously, the weak green or red emissions indicated that the energy transfer from the main chain to the Ir complexes was incomplete even at a high red Ir content of 5 mol% (such as **P2** and **P3**). These results are similar to that of Ir complex-modified polyfluorenes prepared by copolymerization method [4a].

The UV–vis absorption spectra and photoluminescent spectra of copolymers **P1**–**P5** in solid films were also collected (Fig. 4A and B). Very similar absorption spectra as those in toluene solutions were observed. Although strong blue emissions from the main chains for these copolymers in solid films have also been observed, the intensities for the red emission in the solid films were significantly higher than those in solutions. This was partially due to the close packing of polymer backbone which consequently enhanced the energy transfer.

4. Conclusions

A series of polyfluorene derivatives containing both iridium complexes and carbazole/1,3,4-oxadiazole dendrons on the side chain were synthesized through the Cu(I)-catalyzed Huisgen 1,3-dipolar click cycloaddition. This strategy was demonstrated to be simple yet efficient and modular, with the potential to quantitatively introduce different Ir complexes and functional dendrons onto the polyfluorene backbone. These copolymers exhibited excellent solubility, high molecular weight, and good thermal stability, indicating that they are promising candidates for solution-processable phosphorescent materials.

Acknowledgments

Financial support of this work by the Major State Basic Research Development Program of China (Grant no. 2002CB613403) and the National Natural Science Foundation of China are acknowledged with thanks. The authors also thank Professor Yong-Ming Chen for his help on GPC measurements.

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2008.01.033.

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