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Siloles and Acetenyl Aromatics Copolymers: Synthesis, Characterization and Photophysical Properties

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Two copolymers, poly(1,1-dimethyl-3,4-diphenylsilole-alt-*N*-hexyl-3,6-diethynylcarbazole) (PS-DyCz) and poly-(1,1-dimethyl-3,4-diphenylsilole-alt-2,7-diethynyl-9,9'-dihexylfluorene) (PS-DyF), were synthesized by Sonogashira coupling reaction of 2,5-dibromo-1,1-dimethyl-3,4-diphenylsilole and *N*-hexyl-3,6-diethynylcarbazole or 2,7-diethynyl-9,9'-dihexylfluorene, respectively. The chemical structures of the copolymers were characterized by NMR, FT-IR techniques. Their thermal and photophysical properties were evaluated by TGA, DSC, UV-Vis and fluorescence spectroscopy, respectively. The weight-averaged molecular weights (M_w) of PS-DyCz and PS-DyF are 1.20×10^4 and 3.83×10^4 Da, respectively. The degree of polymerization is 8 and 22 units. These π -conjugated polymers exhibited lower band-gap of 2.25 and 2.70 eV due to the presence of silole rings and C=C triple bonds in their backbone, the results were consistent with the density functional (DFT) calculations at the B3LYP/6-31G* level.

Keywords silole, acetylene, carbazole, fluorene, conjugated polymer, density functional theory

Introduction

Silole (silacyclopentadiene) has recently been highlighted as an important building block for polymer light-emitting diodes (PLED),^[1-3] field-effect transistors (FET),^[1,2,4] bulk heterojunction (BHJ) solar cells^[5-7] and explosives detection.^[8-13] Silole possesses low-lying LUMO energy level associated with the σ^* - π^* conjugation arising from the interaction between the σ^* orbital of two exocyclic σ bonds in the silicon atom and the π^* orbital of the butadiene moiety. Silole also exhibits high electron affinity and unique aggregation-induced emission (AIE).^[14-16] Therefore, the conjugated polymers containing silole ring can reduce band-gap value and enhance carrier mobility.

Carbazole-based polymers have high hole-transport ability and wide band-gap energy transfer. Meanwhile, ethynylene group is a key π -spacer for efficient electronic communication of π -chromophores in the constructions of poly(aryleneethynylene)s^[17] or poly(diethynylcarbazole-arylene).^[18,19] On the other hand, fluorenebased polymers such as polyfluorenes (PFs) have emerged as emitting materials suitable for using in PLEDs because of their highly efficient photoluminescence (PL), excellent thermal and oxidative stability, and good solubility.^[20] Fluorene-based polymers containing C=C triple bond facilitate electronic communication because of their structural rigidities, for example, poly(2,7-fluorene ethynylene)s (PFEs) have high quantum efficiency, broad emission range and low band gap.^[21] Silole-acetylene polymeric systems are particularly interesting because they display unusually narrow band gaps and high electron affinities.^[22-25] If siloleacetylene building block could be incorporated into carbazole or fluorene polymeric chain, the new assembly should display improved hole-transport properties, and suppress the aggregation and/or excimers formation of molecules.^[26,27]

Therefore, we synthesized two copolymers consisting of silole and diethynylcarbazole, or diethynylfluorene moieties in the backbone. And the chemical structures of two polymers were characterized by NMR, FT-IR techniques, their thermal and photophysical properties were evaluated by TGA, DSC, UV-Vis and fluorescence spectroscopy, and theoretical calculations were carried out using density functional theory (DFT) method at B3LYP/6-31G*level.^[28]

Experimental

Materials and instruments

Tetrahydrofuran was distilled from sodium and benzophenone under an Ar atmosphere prior to use. Tri-

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ethylamine was refluxed and distilled over calcium hydride prior to use. Phenylacetylene and 3-methyl-1butyn-3-ol were distilled prior to use. Zinc chloride was dried by refluxing in thionyl chloride and stored in Ar atmosphere. All other chemicals were purchased from commercial supplier and used without further purification. Reactions were carried out under dry argon atmosphere when necessary.

¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 400 spectrometer. Chemical shifts (δ) are expressed downfield from tetramethylsilane using the residual protonated solvent as internal standard (chloroform-d, ¹H δ 7.26 and ¹³C δ 77.0). Coupling constants are expressed in hertz. Molecular weights and polydispersity index of polymers were obtained on a Waters 1515 using a calibration of curve of polystyrene standards, with tetrahydrofuran as the eluent. UV-vis absorption spectra were measured on a Varian Cary 100 spectrometer. Fluorescence spectra were recorded on a Varian Cary Eclipse spectrometer. FT-IR spectra were collected from a Nicolet Magna-IR 550 spectrometer. Thermogravimetric analysis (TGA) was carried out using Netzsch STA 409 PC/PG under N2 atmosphere. Differential scanning calorimetry (DSC) analysis was made on a Netzsch STA 409 PC/PG under nitrogen atmosphere.

Synthesis of bis(phenylethynyl)dimethylsilane (1)

Magnesium ribbons were scraped off oxidation layers, cut into small pieces (2.45 g, 0.1 mol) and activated with two grains of free iodine. THF (10 mL) was added via syringe and stirred for 30 min. Bromoethane (10.90 g, 0.1 mol) dissolved in THF (25 mL) was added dropwise over ca. 20 min into the magnesium suspension. Then the mixture was refluxed for 1 h and cooled to room temperature. Phenylacetylene (10.20 g, 0.1 mol) dissolved in THF (20 mL) was added dropwise and refluxed for 2 h. Me₂SiCl₂ (6.45 g, 0.05 mol) dissolved in THF (20 mL) was added dropwise at room temperature and refluxed for 3 h. After the mixture was cooled to room temperature, water (50 mL) and ethyl acetate (50 mL) were added to the flask. The organic phase was separated and extracted with ethyl acetate (50 mL \times 2). The combined extract was dried by anhydrous Na₂SO₄, and then the filtrate was concentrated to dryness under a reduced pressure. The yellow-white solid was dissolved in a minimal amount of boiling hexane, and then cooled in a freezer $(-30 \text{ }^{\circ}\text{C})$ for 1 h to give the product as off-white powder that was collected by vacuum filtration (9.29 g, 71%). ¹H NMR (400 MHz, CDCl₃) δ : 7.53 -7.50 (m, 4H, ArH), 7.36-7.29 (m, 6H, ArH), 0.49 (s, 6H, Si(CH₃)₂); ¹³C NMR (100 MHz, CDCl₃) δ: 132.1, 128.8, 128.2, 122.7, 105.9, 90.6, 0.5.

Synthesis of 2,5-dibromo-1,1-dimethyl-3,4-diphenylsilole (3)

Naphthalene (4.820 g, 37.6 mmol, 4.7 equiv.) was dissolved in THF (24 mL) and degassed *in vacuo*, and

then bubbled with Ar for 30 min. Lithium slice (0.250 g, 36 mmol, 4.5 equiv.) was added to the reaction mixture under a stream of Ar. The solution was stirred for 6 h giving a thick dark green LiNaph solution. Bis(phenylethynyl)dimethylsilane (1, 2.083 g, 8 mmol) was dissolved in THF (40 mL), degassed under reduced pressure, and then bubbled with Ar for 30 min, and added dropwise into LiNaph solution at room temperature over ca. 20 min. The solution was protected from light by wrapping the reaction vessel in aluminium foil and cooled to -10 °C. Anhydrous ZnCl₂ (5.452 g, 40 mmol, 5 equiv.) dissolved in THF (33 mL) was added dropwise into the naphthalenide/silane mixture over ca. 30 min and stirred for 20 min at -10 °C. The suspension was then cooled to -78 °C and *N*-bromosuccinamide (3.560 g, 20 mmol, 2.5 equiv.) dissolved in THF (16 mL) was added quickly via syringe. After stirring for 1 h at -78 °C, the cold reaction mixture was poured into vigorously stirred half-saturated aqueous NH₄Cl (150 mL) and extracted with ethyl acetate (50 mL \times 3). The organic extracts were combined and washed successively with half-saturated Na₂S₂O₃ (50 mL), water (100 mL), brine (50 mL \times 2), then dried by anhydrous Na₂SO₄, and filtered through a thin pad of silica. The naphthalene/dibromosilole mixture was concentrated and subjected to a column chromatograph (silica gel, petroleum ether), providing off-white product (1.442 g, 43%). ¹H NMR (400 MHz, CDCl₃) δ : 7.19–7.15 (m, 6H, ArH), 6.97-6.95 (m, 4H, ArH), 0.46 (s, 6H, Si(CH₃)₂); ¹³C NMR (100 MHz, CDCl₃) δ: 156.0, 136.9, 129.0, 127.5, 127.4, 122.7, -6.3. MS (EI) *m/z*: 419.9 ([M]⁺).

Synthesis of 3,6-diiodocarbazole (4)

Carbazole (6.0 g, 36 mmol), KI (7.8 g, 47 mmol) and KIO₃ (10.0g, 47 mmol) were dissolved in acetic acid (150 mL) at room temperature. The reaction mixture was heated to 80 °C for 6 h. Then the mixture was cooled to room temperature, filtered and washed successively with water, saturated Na₂CO₃, saturated Na₂S₂O₃ and water. The crude product was recrystallized from ethanol to give a white solid (11.0 g, 73%). ¹H NMR (400 MHz, CDCl₃) δ : 8.33 (d, *J*=1.6 Hz, 2H, ArH), 8.07 (s, 1H, NH), 7.68 (dd, *J*=8.5, 1.7 Hz, 2H, ArH), 7.21 (d, *J*=8.5 Hz, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃) δ : 138.5, 134.8, 129.4, 124.6, 112.7, 82.4.

Synthesis of N-hexyl-3,6-diiodocarbazole (5)

A mixture of 3,6-diiodocarbazole (4, 4.2 g, 10 mmol), 1-bromohexane (2.0 g, 12 mmol) and K₂CO₃ (7.0 g, 50 mmol) in DMF (35 mL) was stirred at 80 °C under argon for 4 h. The mixture was then cooled to room temperature and poured into 200 mL of water. The crude product was collected from filtration and washed completely with water. Recrystallization from hexane gave pure product as white solid (4.10 g, 82%). ¹H NMR (400 MHz, CDCl₃) δ : 8.32 (d, *J*=1.6 Hz, 2H, ArH), 7.71 (dd, *J*=8.6, 1.7 Hz, 2H, ArH), 7.16 (d, *J*= 8.6 Hz, 2H, ArH), 4.21 (t, *J*=7.2 Hz, 2H, NCH₂),

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1.85–1.76 (m, 2H, CH₂), 1.37–1.23 (m, 6H, CH₂), 0.85 (t, J=7.0 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ : 139.5, 134.5, 129.3, 124.0, 110.9, 81.6, 43.2, 31.5, 28.8, 26.9, 22.5, 14.0.

Synthesis of *N*-hexyl-3,6-di(3-hydroxy-3-methylbutynyl)carbazole (6)

N-Hexyl-3,6-diiodocarbazole (5, 2.00 g, 4 mmol) and 3-methyl-1-butyn-3-ol (1.01 g, 12 mmol) were dissolved in Et₃N (40 mL), and degassed in vacuo, and then bubbled with Ar for 30 min. Under a stream of Ar, Pd(PPh₃)₂Cl₂ (70 mg, 0.1 mmol), PPh₃ (80 mg, 0.3 mmol) and CuI (153 mg, 0.8 mmol) were added. The reaction mixture was refluxed overnight, and cooled to room temperature. The mixture was filtered and washed with ethyl acetate (3 times). The solvent was then removed under reduced pressure, and the residual was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, V: V=2:5) to afford a white solid (1.60 g, 96%). ¹H NMR (400 MHz, CDCl₃) δ: 8.13 (d, J=1.00 Hz, 2H, ArH), 7.52 (dd, J=8.5, 1.5 Hz, 2H, ArH), 7.30 (d, J=8.5 Hz, 2H, ArH), 4.24 (t, J=7.2 Hz, 2H, NCH₂), 2.12 (s, 2H, OH), 1.88–1.78 (m, 2H, CH₂), 1.67 (s, 12H, (CH₃)₂), 1.38-1.23 (m, 6H, CH₂), 0.85 (t, J = 7.0 Hz, 3H, hexyl-CH₃); ¹³C NMR (100 MHz, $CDCl_3$) δ : 140.4, 129.6, 124.2, 122.3, 113.2, 108.8, 92.0, 83.1, 65.8, 43.3, 31.7, 31.5, 28.9, 26.9, 22.5, 13.9.

Synthesis of N-hexyl-3,6-diethynylcarbazole (7)

With vigorous stirring, a mixture of N-hexyl-3,6di(3-hydroxy-3-methylbutynyl)-carbazole (6, 1.0 g, 2.4 mmol) and potassium hydroxide (404 mg, 7.2 mmol) in 60 mL of isopropanol was heated at reflux for 4 h under Ar atmosphere . Upon cooling, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, CH₂Cl₂/ petroleum ether, V: V=2:5) to afford an off-white solid (570 mg, 79%). ¹H NMR (400 MHz, CDCl₃) δ : 8.22 (d, J=0.9 Hz, 2H, ArH), 7.61 (dd, J=8.5, 1.5 Hz, 2H, ArH), 7.33 (d, J=8.5 Hz, 2H, ArH), 4.27 (t, J=7.2 Hz, 2H, NCH₂), 3.08 (s, 2H, \equiv CH), 1.89–1.80 (m, 2H, CH_2), 1.38–1.23 (m, 6H, CH_2), 0.86 (t, J=7.0 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 140.6, 130.1, 124.7, 122.2, 112.7, 108.9, 84.7, 75.4, 43.3, 31.5, 28.9, 26.9, 22.5, 14.0; HRMS (ESI) calcd for C₂₂H₂₁N 299.1674, found 299.1666.

Synthesis of 2,7-diiodofluorene (8)

Fluorene (4.155 g, 25 mmol) was dissolved in 130 mL of the mixed solvent (CH₃COOH/H₂O/H₂SO₄= 100/20/3) with mechanical stirrer at 80 °C (internal temperature). Then, periodic acid dihydrate (2.849 g, 12.5 mmol) and iodine (6.345 g, 25 mmol) were quickly added. The reaction mixture was stirred for 3 h and the abundant white precipitate was formed. The mixture was cooled, and the pale yellow solid was collected by filtration and washed successively with water, saturated Na₂CO₃ and water. The crude product was recrystallized

from hexane to give a white solid (9.23 g, 88%). ¹H NMR (400 MHz, CDCl₃) δ : 7.87 (s, 2H, ArH), 7.70 (d, J=8.0 Hz, 2H, ArH), 7.49 (d, J=8.1 Hz, 2H, ArH), 3.83 (s, 2H, CH₂).

Synthesis of 2,7-diiodo-9,9'-dihexylfluorene (9)

Into 250 mL three-neck flask, 2,7-diiodofluorene (8, 5.016 g, 12 mmol) and DMSO (20 mL) were added, and heated to 60 °C. Then, tetra-n-butylammonium bromide (0.81 g, 2.5 mmol), 50% aqueous NaOH (8 mL) and 1-bromohexane (5.943 g, 36 mmol) were added. The reaction mixture was stirred at 80 °C under Ar atmosphere for 8 h, and cooled to room temperature. Then, 80 mL of 1 mol \cdot L⁻¹ HCl was added and the mixture was extracted with ethyl acetate. The organic layer was washed by 1 mol \cdot L⁻¹ HCl and water (3 times), and dried over anhydrous MgSO₄. The solvent was then removed under reduced pressure and the yellow oil was purified by column chromatography (silica gel, petroleum ether) to afford a pale yellow solid (5.758 g, 82%). ¹H NMR (400 MHz, CDCl₃) δ: 7.69-7.61 (m, 4H, ArH), 7.40 (d, J=8.5 Hz, 2H, ArH), 1.98–1.81 (m, 4H, ArCCH₂), 1.16 - 1.01 (m, 12H, (CH₂)₃), 0.79 (t, J = 7.1 Hz, 6H, CH_3), 0.60-0.48 (m, 4H, CH_2CH_3).

Synthesis of 2,7-bis(trimethylsilyl)-9,9'-dihexyl-fluorene (10)

2,7-Diiodo-9,9'-dihexylfluorene (9, 2.662 g, 4.5 mmol) was dissolved in 40 mL of Et₃N under argon atmosphere. CuI (35 mg) and Pd(PPh₃)₂Cl₂ (58 mg) were added to the stirred solution. Trimethylsilylacetylene (1.340 g, 13.5 mmol, 3 equiv.) dissolved in Et₃N (25 mL) was added dropwise into the mixture and heated to reflux for 8 h. After the reaction mixture was cooled to room temperature, the formed precipitate triethylammonium hydroiodide was filtered off. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, petroleum ether) to afford a white solid (1.336 g, 57%). ¹H NMR (400 MHz, CDCl₃) δ : 7.59 (d, J=7.8 Hz, 2H, ArH), 7.45 (dd, J=7.9, 1.2 Hz, 2H, ArH), 7.41 (s, 2H, ArH), 1.98–1.89 (m, 4H, ArCCH₂), 1.17–0.96 (m, 12H, (CH₂)₃), 0.77 (t, J=7.2 Hz, 6H, CH₃), 0.61-0.45 (m, 4H, CH₂CH₃), 0.28 (s, 18H, SiCH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 150.9, 140.8, 131.2, 126.2, 121.7, 119.8, 106.1, 94.2, 55.2, 40.4, 31.5, 29.7, 23.6, 22.6, 14.0, 0.05.

Synthesis of 2,7-diethynyl-9,9'-dihexylfluorene (11)

2,7-Bis(trimethylsilyl)-9,9'-dihexylfluorene (10, 527 mg, 1 mmol), CH₂Cl₂ (10 mL), methanol (10 mL) and KOH (1 mol·L⁻¹, 4 mL) were added to 100 mL flask, and stirred at room temperature under argon atmosphere overnight. Water (30 mL) and diethyl ether (30 mL) were added to the reaction mixture, the organic layer was separated and the aqueous layer was extracted with diethyl ether (20 mL×2). The combined extract was washed with brine and dried over anhydrous MgSO₄.

The solvent was removed under reduced pressure to yield the title compound as off-white solid (360 mg, 94%). ¹H NMR (400 MHz, CDCl₃) δ : 7.63 (d, *J*=7.8 Hz, 2H, ArH), 7.50-7.45 (m, 4H, ArH), 3.15 (s, 2H, \equiv CH), 1.97-1.90 (m, 4H, ArCCH₂), 1.15-0.96 (m, 12H, (CH₂)₃), 0.76 (t, *J*=7.2 Hz, 6H, CH₃), 0.64-0.50 (m, 4H, CH₂CH₃); ¹³C NMR (100 MHz, CDCl₃) δ : 151.0, 141.0, 131.2, 126.5, 120.8, 120.0, 84.5, 55.2, 40.2, 31.5, 29.6, 23.6, 22.6, 14.0. HRMS (ESI) cald for C₂₉H₃₄ 382.2661, found 382.2655.

Synthesis of poly(1,1-dimethyl-3,4-diphenylsilole-alt-N-hexyl-3,6-diethynyl-carbazole) (PS-DyCz)

2,5-Dibromo-1,1-dimethyl-3,4-diphenylsilole (3. 420 mg, 1 mmol) and N-hexyl-3,6-diethynylcarbazole (7, 300 mg, 1 mmol) were dissolved in the mixture of toluene (10 mL) and Et₃N (3 mL), and degassed under reduced pressure, and then bubbled with Ar over ca. 30 min. Under a stream of argon was added Pd(PPh₃)₄ (50 mg) and CuI (20 mg). The mixture was heated to 60 °C. stirred for 3 d. The mixture was cooled to room temperature and filtered and evaporated to dryness under a reduced pressure. The residue was dissolved in CHCl₃ (3 mL), and precipitated from methanol (35 mL). The precipitation procedure was repeated three times to remove any unreacted monomer and low molecular weight oligomers. A precipitation was collected by vacuum filtration and dried in vacuum for 1 h at 60 °C. The resultant polymer was obtained as red powder (263 mg, 37%). ¹H NMR (400 MHz, CDCl₃) δ : 8.60–6.80 (m, ArH), 4.22 (br, NCH₂), 1.82 (br, CH₂CH₃), 1.57 (br, (CH₂)₃), 0.84 (br, CH₃), 0.66 (br, Si(CH₃)₂); FT-IR (KBr) v: 3447 (w), 3056 (w), 2957 (s), 2926 (s), 2853 (m), 2139 (w), 1625 (m), 1595 (m), 1482(s), 1381 (m), 1350 (m), 1284 (m), 1259 (s), 1091 (m), 1022 (m), 802 (s), 695 (m) cm⁻¹. GPC (THF) $M_{\rm w}$: 12045, $M_{\rm n}$: 4562, PDI: 2.6.

Synthesis of poly(1,1-dimethyl-3,4-diphenylsilole-alt-2,7-diethynyl-9,9'-dihexyl-fluorene) (PS-DyF)

The polymer was synthesized by the similar method described in the synthesis of PS-DyCz. 2,5-Dibromo-1,1-dimethyl-3,4-diphenylsilole (**3**, 420 mg, 1 mmol), 2,7-diethynyl-9,9'-dihexylfluorene (**11**, 383 mg, 1 mmol), Pd(PPh₃)₄ (53 mg) and CuI (17 mg) were used in this case. The resultant polymer was obtained as yellowish brown solid (324 mg, 40%). ¹H NMR (400 MHz, CDCl₃) δ : 8.10–7.30 (m, ArH), 7.20–6.70 (m, ArH), 3.12 (br, \equiv CH), 2.12–1.78 (m, CH₂), 1.20–0.96 (m, CH₂), 0.79 (t, J = 7.2 Hz, CH₃), 0.70–0.45 (m, Si(CH₃)₂); FT-IR (KBr) *v*: 3435 (m), 2924 (s), 2851 (m), 2136 (w), 1600 (w), 1460(m), 1414 (w), 1257 (w), 1095 (w), 889 (w), 818 (m), 675 (w) cm⁻¹. GPC (THF), M_w : 38266, M_n : 14277, PDI: 2.7.

Results and Discussion

Synthesis and characterization

The 2,5-dibromosilole monomer was synthesized by

Grignard reaction and Tamao's endo-endo intramolecular reductive cyclization (Scheme 1).^[29-31]

Scheme 1 Synthesis of dibromosilole



Reagents and conditions: (a) EtMgBr, diethyl ether, reflux, 2 h; Me_2SiCl₂, 35 $^\circ\!C$, 3 h. (b) LiNaph, THF, 6 h; ZnCl_2/THF, –10 $^\circ\!C$, 20 min. (c) NBS/THF, –78 $^\circ\!C$, 1 h.

The *N*-hexyl-3,6-diethynylcarbazole (7) was synthesized through four steps (Scheme 2). 3,6-Diiodocarbazole (4) was prepared from carbazole by a diiodination reaction,^[19] which was alkylated with 1-bromohexane in the presence of K₂CO₃ to afford *N*-hexyl-3,6-diiodocarbzole (5).^[4] Then, the Pd/Cu-catalyzed cross-coupling reaction of 5 and 3-methyl-1-butyn-3-ol gave compound 6, which was deprotected to afford 7 under KOH/isopropanol condition. The overall yield was 79%.

Scheme 2 Synthesis of *N*-hexyl-3,6-diethynylcarbazole (7) monomer



Reagents and conditions: (a) KI, KIO₃, AcOH, 80 $^{\circ}$ C, 6 h. (b) n-C₆H₁₃Br, K₂CO₃, DMF, 80 $^{\circ}$ C, 4 h. (c) 3-Methyl-1-butyn-3-ol, Pd(PPh₃)₂Cl₂, PPh₃, Cul, Et₃N, reflux, overnight. (d) KOH, isopropanol, reflux, 4 h.

The synthesis of 2,7-diethynyl-9,9'-dihexylfluorene (11) was similar to the synthesis of 7 (Scheme 3), which was prepared by diiodination of fluorene, alkylation with 1-bromohexane in the presence of 50% NaOH aq, Sonogashira cross-coupling reaction using trimethyl-silylacetylene as alkynylation reagent and finally de-

FULL PAPER

protection.^[32] Notably, when 3-methyl-1-butyn-3-ol was used as alkynylation reagent, deprotection of the cross coupling product under KOH/isopropanol condition gave fickle results in our laboratory. In contrast, deprotection of 2,7-bis(trimethylsilyl)-9,9'-dihexylfluorene (10) yielded almost quantitatively diethynylfluorene as white powder. The structures of 7 and 11 were confirmed by ¹H and ¹³C NMR, which were consistent with the literature.^[21]

Scheme 3 Synthesis of 2,7-diethynyl-9,9'-dihexylfluorene (11) monomer



Reagents and conditions: (a) l_2 , H_5IO_6 , AcOH, H_2SO_4 , H_2O , reflux, 80 °C, 3 h. (b) *n*-C₆H₁₃Br, tetrabutylammonium bromide, 50% aqueous NaOH, DMSO, 80 °C, 8 h. (c) Trimethylsilylacetylene, Pd(PPh₃)₂Cl₂, Cul, Et₃N, reflux, 8 h. (d) KOH (1 mol•L⁻¹), CH₂Cl₂, MeOH, room temperature, overnight.

Both copolymers PS-DyCz and PS-DyF were synthesized by Sonogashira coupling between 2,5-dibromosilole and correspondingly equimolar diethynyl compounds in toluene and triethylamine after stirring for 3 d (Scheme 4). Since the palladium catalyst is quite sensitive to oxygen and 2,5-dibromosilole is easily decompose under light, the polymerization reaction was run in the dark using a standard Schlenk technique. The copolymers are both soluble in common solvents such as chloroform, toluene, acetone and tetrahydrofuran, etc. The molecular weight and the polydispersity index (PDI) were measured by GPC using THF as an eluent and polystyrene as the standard, and corresponding data are summarized in Table 1. The weight-averaged molecular weight (M_w) and PDI are 1.20×10^4 Da and 2.6 for PS-DyCz, and 3.83×10^4 Da and 2.7 for PS-DyF, respectively. The number-average molecular weight (M_n) is 4.56×10^3 Da for PS-DyCz and 1.43×10^4 Da for PS-DyF, and corresponding degree of polymerization (n)is 8 and 22 silole-acetenyl aromatics units, respectively. The difference of their *n* values was mainly attributed to the copolymer's innate structure. PS-DyF is closer to linear structure, but PS-DyCz tends to spiral structure,^[33] because 3,6-position substitution of carbazole has about 60° angle to produce larger steric hinderance.

The structures of copolymers were also characterized by ¹H NMR and FT-IR. ¹H NMR indicates the chemical Scheme 4 Synthesis and structures of copolymers PS-DyCz and PS-DyF



Reagents and conditions: (a) $Pd(PPh_3)_4$, Et_3N , toluene, 60 °C, 3 d.

 Table 1 Molecular weight and thermal properties of copolymers

Copolymer	M _n /Da	$M_{\rm w}$ /Da	PDI	n ^a	$T_{\rm d}/°{\rm C}$	$T_{\rm g}/^{\circ} {\rm C}$
PS-DyCz	4562	12045	2.6	8	319	<i>b</i>
PS-DyF	14277	38266	2.7	22	341	<i>b</i>

^{*a*} Degree of polymerization, that is the number of PS-DyCz or PS-DyF repeat units depicted in. ^{*b*} No glass transition signals were observed.

structure of each monomer unit of the alternating copolymer. We can assign some characteristic proton resonance, including one proton resonating at δ 0.60 (br) for Si-CH₃ of silole ring, and one proton resonating at δ 4.22 (br) for N-CH₂ of 7, or at δ 0.79 (t) for hexyl-CH₃ of 11. The NMR results confirmed the chemical structure of the alternating copolymer (see the Experimental Section for details).

The FT-IR spectra of PS-DyCz and PS-DyF copolymer are shown in Figure 1 and Figure 2, respectively. The C \equiv C stretching vibration of PS-DyCz and PS-DyF is observed at 2140 (w) and 2136 (w) cm⁻¹, and Si-C stretching vibration at 802 (s) and 818 (m) cm⁻¹, respectively. The strong stretching vibration of Si-C shows more silole ring incorporated in the chain of copolymer.







Figure 2 FT-IR spectrum of PS-DyF copolymer.

Thermal properties

The thermal behavior of copolymers was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the corresponding data are summarized in Table 1. DSC analysis revealed that no glass transition signals were detected for all the copolymers. This observation may be due to the stiffness of the copolymer's main chain.[34] Thermal stability is an important criterion for evaluating the candidate of polymer for optoelectronic applications due to the involvement of thermal processes in the device fabrications and operations.^[35] The TGA plots (Figure 3) showed that copolymers PS-DyCz and PS-DyF are thermally stable with only about 5% weight loss (T_d) in a N₂ atmosphere at temperatures of 319 °C and 341 °C, respectively, similar to HB-car $(T_d=356 \text{ °C})^{[4]}$ and aryleneethynylene-carbazole hyperbranched polymer $(T_d = 418 \text{ °C})$.^[36] The high decomposition temperatures of these two copolymers are mainly attributed to thermal stability characteristic of silole rings.^[5] Meanwhile, a little higher decomposition temperature of PS-DyCz than that of PS-DvF indicated that PS-DvCz existed branch structure of polymer in some extent. The results indicated that these two copolymers possessed good



Figure 3 TGA curves of copolymers at a heating rate of 10 $^{\circ}C/$ min under N₂ atmosphere.

thermal stability, which is adequate for their applications in polymer solar cells (PSCs)^[37] and other optoelectronic devices.

Absorption and emission spectra

The UV-Vis absorption spectra of the copolymers in THF are shown in Figure 4. The photophysical properties and optical band gap data of the copolymers are summarized in Table 2. The polymer concentration values are calculated based on the molecular weight of a repeating unit.



Figure 4 UV-Vis absorption spectra of copolymer PS-DyCz (a) and PS-DyF (b) in THF solution at two concentration.

The absorption spectra of PS-DyCz (Figure 4) showed that there were four peaks located at 251, 303, 380, and 467 nm. The absorption peaks observed at 251 and 303 nm are due to the π - π * transitions of the carbazole core,^[1] and are red-shifted relative to that of monomer 7 (λ =290 nm).^[38] This phenomenon suggests the extensive conjugation length in the copolymer. The peaks at 380 (shoulder) and 467 nm are attributed to silole ring incorporated in the main chain of copolymer.^[30] With increasing of copolymer contents, the absorptions are gradually intensified.

In contrast to PS-DyCz, the UV-Vis spectra of PS-DyF (Figure 4b) exhibited a larger molar absorption (ε) and narrow absorption range in the solution. The weaker absorption band at around 250–325 nm is most probably the absorption band of fluorene.^[39] Thus, the

Table 2 Optical band gaps and photophysical properties of copolymers

	Tuble 2 Option only Superior properties of experiments							
Copolymer —	Absorption ^{<i>a</i>}			Poind can $\Delta E^b/aV$	Eluo ressones 1 c/nm			
	$\lambda_{\rm max}/{\rm nm}$	$\varepsilon/(L \cdot mol^{-1} \cdot cm^{-1})$	Onset/nm	Band-gap ΔE /ev	Fiuo-rescence λ_{max} /IIII			
PS-DyCz	251, 303, 380, ^d 467	$0.42 \times 10^5, 0.32 \times 10^5, 0.22 \times 10^5, 0.11 \times 10^5$	550	2.25	542, 569			
PS-DyF	$391^{d}, 418$	0.90×10^5 , 1.18×10^5	460	2.70	$429, 460^d$			

^{*a*} In THF. ^{*b*} Estimated by absorption edge, $\Delta E = (1240 \text{ eV} \cdot \text{nm})$ (absorption onset⁻¹). ^{*c*} Excited at 460 nm for PS-DyCz and 391 nm for PS-DyF. ^{*d*} Shoulder peak.

maximum absorptions at 391 (shoulder) and 418 nm in the Figure 4b arised from the absorption of silole ring. The ε_{max} (1.18×10⁵ L•mol⁻¹•cm⁻¹) of PS-DyF is about 3 times larger than that of PS-DyCz (ε_{max} , 0.42×10⁵ L•mol⁻¹•cm⁻¹), which is attributed to the longer effective conjugated chain or larger degree of polymerization.^[40] Moreover, copolymer containing more ethynyl units seemed to have relatively larger molar absorption coefficient compared to the polymer with less ethynyl units (see Figure 2 and Figure 4b).^[33]

The optical band gap of PS-DyCz and PS-DyF is estimated to be 2.25 and 2.70 eV based on its solution onset absorption wavelength. These narrow band gaps are particularly attributed to low-lying LUMO energy level of silole-acetylene polymeric systems,^[2] which were lower than those of V-shaped carbazole-fluorene oligomers (2.95 eV)^[26,33] or poly(2,7-fluorene ethynylene) (PFE, around 2.88 eV).^[21] The characteristic of low band-gap suggested their potential application as photovoltaics cell and other materials.

The fluorescence emission spectra of PS-DyCz and PS-DyF in THF solution at different concentrations at room temperature are shown in Figure 5 and Figure 6, respectively, which showed broad emission bands with PL intensity enhancement by increasing concentration. Figure 5 showed that the broad emission band was over 500-750 nm and maximum emission peaks located at 542 and 569 nm for the THF solution at 6.4×10^{-5} mol·L⁻¹. The PL intensity of copolymer increased with increasing the concentration of copolymer from 8×10^{-7} to 6.4×10^{-5} mol·L⁻¹, which is caused by the aggregate-



Figure 5 PL spectra of copolymer PS-DyCz in THF solution at different concentration. Excitation wavelength: 460 nm.



Figure 6 PL spectra of copolymer PS-DyF in THF solution at different concentration. Excitation wavelength: 391 nm.

enhanced emission (AEE) effect and spiral structure of copolymer.^[33] But the decrease from 6.4×10^{-5} to 8×10^{-4} mol·L⁻¹ is mainly due to aggregation-caused quenching (ACQ) effect. Therefore, this change of PL intensity is the comprehensive result of AEE and ACQ effect. Then, the fluorescence intensity of PS-DyF was also not monotone increasing relation with concentration, and maximum intensity is 428 and 455 nm at 1.1×10^{-5} mol·L⁻¹. The intensity increased from 2.2×10^{-7} to 1.1×10^{-5} mol·L⁻¹ and decreased from 1.1×10^{-5} to 1.76×10^{-4} mol·L⁻¹. This phenomenon is the competitive result of AEE and ACQ effect, which is identical with PL of copolymer PS-DyCz. As same as UV-Vis spectra of PS-DyF, there is not the fluorescence of fluorene observed at 300-350 nm.^[41]

Density functional theoretical calculations

Density functional theory (DFT) calculations were performed at B3LYP/6-31G* level using copolymers' trimer models, 2,5-bis(2,7-diethynylfluorene)silole and 2,5-bis(3,6-diethynylcarbazole)silole (Figure 7). The orbital plots suggested that the HOMOs were distributed over both acetenyl aromatics (diethynylcarbazole and diethynyl-fluorene) and silole rings, but the LUMOs were mainly localized in the silole ring and ethynyl spacer. These characters of silole ring and ethynyl spacer lowered the band gap between HOMO and LUMO energy level. The frontier orbital energy of -5.4eV for PS-DyCz calculated by DFT is 0.3 eV less than that of PS-DyF (-5.1 eV), but the LUMOs are equivalent. And the calculated bandgaps are obviously greater than those estimated by absorption onset values. This result was mainly caused by the difference of trimer models used in the DFT calculations and the realistic polymers,^[42] the trimer models are small molecules, while PS-DyCz or PS-DyF has a degree of polymerization of 8 or 22, respectively.



Figure 7 Pictorial representations of HOMO and LUMO eigenfunctions and eigenvalues for copolymers' model trimers. (a) HOMO PS-DyCz trimer, -5.4 eV; (b) LUMO PS-DyCz trimer, -1.9 eV; (c) HOMO PS-DyF trimer, -5.1 eV; (d) LUMO PS-DyF trimer, -1.9 eV.

Conclusions

We have successfully synthesized and characterized two novel conjugated copolymers poly(silole-ethynyl carbazole)s (PS-DyCz) and poly(silole-ethynylfluorene)s (PS-DyF) by Sonogashira coupling reaction. To investigate their thermal behavior, we carried out the TGA and DSC measurements, and demonstrated that they had good thermal stability with decomposition temperature at 391 °C for PS-DyCz and 341 °C for PS-DyF. The absorption peaks of PS-DyCz and PS-DyF copolymer in THF solution demonstrated at 380, 467 nm and 391, 418 nm, respectively, and the absorption intensities were enhanced with the increase of their concentration. But PS-DyF displayed larger molar absorption coefficient due to more ethynyl units in the polymer backbone. The maximum emission peaks of PS-DyCz and PS-DyF located at 542, 569 nm and 428, 455 nm, and fluorescence spectrum showed broad emission bands. Owing to silole and acetylene incorporated into the main chain of copolymers, the band gap of PS-DyCz and PS-DyF fell to 2.25 and 2.70 eV, respectively.

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