

SYNTHESIS OF POLYFLUORENES BEARING LATERAL PYRENE-TERMINATED ALKYL CHAINS FOR DISPERSION OF SINGLE-WALLED CARBON NANOTUBES*

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Abstract Two kinds of polyfluorenes bearing two lateral pyrene terminated alkyl chains and two alkyl chains per repeating unit were synthesized by Suzuki polycondensation and used to disperse single-walled carbon nanotubes (SWCNT) in organic solvents. Stable polymer-SWCNT complex can be formed *via* the multivalent π - π stacking interaction of the lateral pyrene functional groups and the polyfluorene backbone with the outer surface of carbon nanotubes; meanwhile the lateral alkyl chains can impart good solubility to the complex. As expected, polyfluorenes bearing lateral pyrene functional groups and octyl chains exhibited much higher carbon nanotube solubility in common organic solvents than the corresponding polyfluorenes bearing only octyl chains. Photophysical studies indicated that the formation of polymer-SWCNT complex can effectively quench the fluorescence of polyfluorenes.

Keywords: Carbon Nanotubes; Polyfluorenes; π - π stacking; Suzuki polycondensation.

INTRODUCTION

Carbon nanotube has great advantages and potential applications because of its excellent electric and mechanical properties^[1]. Single-walled carbon nanotube (SWCNT) is an excellent electron acceptor due to its delocalized π conjugated systems, and an ideal for transporting electron due to its one-dimensional nanostructure^[2–4]. However, its poor solubility in any solvent becomes an obstacle in the way of its applications^[5, 6]. The supramolecular functionalization of single-walled carbon nanotubes by aromatic molecules with planar structures, such as pyrene^[5] and porphyrin^[7], has attracted significant attentions in the past few years. Such kind of noncovalent functionalization provides a way of avoiding the surface defect and keeping the electron conformation of the SWCNT, so that the excellent and unique photoelectric properties of the SWCNT could be retained^[8–11]. Recent research works have revealed that the interaction between the surface of carbon nanotubes and conjugated polymers is much stronger than that in the π -conjugated small molecule systems^[12–14]. Thus, a stable complex of polymers and carbon nanotube is able to be formed. Being functionalized properly, these complexes of conjugated polymers and carbon nanotubes will show a rather high solubility in solvents and a remarkably good electric-conducting property. Hence, the great potential of carbon nanotubes in the application fields of molecular devices, biological sensors, photovoltaic cells and many other areas will be explored and developed^[15].

Among all of the known conjugated polymers, polyfluorene, as a blue light-emitting material, has received

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a great deal of interest because of its excellent photonic and electronic properties, as well as its thermal stability. This kind of material has been widely used as an effective component in the construction of thin film transistors^[16–19], organic light-emitting diodes^[20], organic solar cells^[21] and biosensors^[22, 23]. Especially, polyfluorene derivatives have been used for the dispersion of SWCNTs^[24–29].

Multivalency is frequently used by nature to achieve higher binding affinities when the monovalent binding is weak. This idea has been used by Tang *et al.* to prepare polyacetylene/SWCNT hybrids^[30, 31]. Here we report the use of two kinds of polyfluorenes carrying lateral pyrene functional groups for the modification of SWCNTs via “multivalent” supramolecular interactions to enhance the SWCNT solubility in common organic solvents. We demonstrated that the conjugated polymers with “multivalent” binding sites have much better performance, as we expected, in the dispersion of SWCNTs.

EXPERIMENTAL

Materials

The catalyst precursor Pd(PPh₃)₄ was prepared according to the literature^[32] and stored in a Schlenk tube under nitrogen. Pyrene boronic ester (**1**)^[33], 1-(6-bromohexyloxy)-4-bromobenzene (**2**)^[34], 2,7-dibromo-9,9-di(4'-hydroxy)phenylfluorene (**3**)^[35] and 9,9-dioctylfluorene-2,7-diboronic ester (**7**)^[36] were prepared according to the literature. SWCNT was purchased from Shenzhen Nanotechnologies Co. Ltd. All other chemicals were purchased from Aldrich or Acros and used without further purification. Dichloromethane (CH₂Cl₂) and *N,N*-dimethylformamide (DMF) were distilled over CaH₂. Tetrahydrofuran (THF) was distilled over sodium and benzophenone. Acetone was distilled over K₂CO₃. All reactions were performed under an atmosphere of nitrogen and monitored by TLC with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200–300 mesh).

Characterization

¹H- and ¹³C-NMR spectra were recorded on a Bruker AV400 spectrometer in CDCl₃. UV-Vis absorption spectra were obtained on a Shimadzu UV-Vis spectrophotometer model UV-1601 PC. Fluorescence spectra were recorded on a Hitachi F-4500 spectrometer. Combustion analyses were performed on a Flash EA 1112 analyzer. The SEM images were recorded with a field emission scanning electron microscope (S-4800, Hitachi) operating at an accelerating voltage of 5 kV. The TEM images were recorded with a transmission electron microscope (JEOL JEM-1011) operating at an accelerating voltage of 100 kV. The GPC measurements were performed on a Waters 410 system against polystyrene standards with THF as an eluent. The TGA measurements were performed on a Thermal Analyst 2100.

Compound S1

A mixture of compound **1** (2.4 g, 7.3 mmol), **2** (2.7 g, 8.1 mmol), NaHCO₃ (0.6 g, 7.2 mmol), THF (40 mL) and water (15 mL) was carefully degassed under nitrogen before and after Pd(PPh₃)₄ (105 mg, 0.091 mol) was added. The mixture was heated to reflux and stirred under nitrogen overnight. Brine (50 mL) and CH₂Cl₂ (100 mL) were added; the organic layer was separated; the aqueous layer was extracted with CH₂Cl₂ (100 mL); the combined organic layers were dried over anhydrous Na₂SO₄ and evaporated to dryness. The residue was purified by chromatography on silica gel eluting with *n*-hexane/CH₂Cl₂ (3:1) to afford compound **S1** as a colorless solid (2.8 g, 84%). ¹H-NMR (400 MHz, CDCl₃, δ): 8.23–8.16 (m, 4H), 8.09 (s, 2H), 8.04–7.97 (m, 3H), 7.56 (d, 2H), 7.10 (d, 2H), 4.08 (t, 2H), 3.46 (t, 2H), 1.96–1.87 (m, 4H), 1.60–1.55 (br, 4H). ¹³C-NMR (100 MHz, CDCl₃, δ): 158.67, 137.71, 133.60, 131.76, 131.20, 130.52, 128.75, 127.87, 127.49, 126.14, 125.58, 125.19, 124.89, 124.83, 114.58, 68.03, 34.03, 32.91, 29.36, 28.16, 25.57. Anal Calcd for C₂₈H₂₅BrO: C, 73.20; H, 5.92. Found: C, 73.47; H, 5.92.

Monomer 4

A mixture of **3** (300 mg, 0.590 mmol), **S1** (600 mg, 1.31 mmol), butanone (250 mL) and K₂CO₃ (450 mg, 3.26 mmol) was heated to reflux and stirred under N₂ for 36 h. Butanone was removed under reduced pressure,

the residue was partitioned between CH_2Cl_2 (100 mL) and aqueous NaOH solution (100 mL); the organic layer was separated; the aqueous layer was extracted with CH_2Cl_2 (50 mL); and the combined organic layers were dried over anhydrous Na_2SO_4 . After the removal of the solvent, the residue was purified by chromatography on a silica gel column with *n*-hexane/ CH_2Cl_2 (3:2) as the eluent to afford compound **4** as a colorless solid (610 mg, 82%). ^1H -NMR (400 MHz, CDCl_3 , δ): 8.22–8.18 (m, 8H), 8.09 (s, 4H), 8.02–7.95 (m, 6H), 7.54–7.47 (m, 10H), 7.09–7.05 (m, 8H), 6.79 (d, 4H), 4.08 (t, 4H), 3.95 (t, 4H), 1.92–1.81 (m, 8H), 1.59–1.57 (br, 8H). ^{13}C -NMR (100 MHz, CDCl_3 , δ): 158.69, 158.37, 153.90, 138.02, 136.52, 133.53, 131.78, 131.69, 131.19, 130.49, 129.21, 127.89, 127.62, 127.46, 127.40, 126.13, 125.18, 125.14, 124.88, 124.82, 121.97, 114.57, 68.02, 64.55, 29.42, 26.08, 22.85. Anal Calcd for $\text{C}_{81}\text{H}_{64}\text{Br}_2\text{O}_4$: C, 77.07; H, 5.08. Found: C, 76.76; H, 5.22.

Compound S2

To a stirred solution of **5** (5.0 g, 17.8 mmol) in THF (100 mL) was added dropwise a solution of *n*-BuLi (10 mL, 25 mmol, 2.5 mol/L in *n*-hexane) at -78°C under nitrogen. The mixture was stirred for 1 h at this temperature. 1,10-Dibromodecane (7.5 mL, 33.5 mmol) was then added, and the mixture was stirred overnight and allowed to warm to room temperature. The mixture was poured into water; the organic layer was separated; the aqueous layer was extracted with diethyl ether (3×50 mL); and the combined organic layers were dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by chromatography on a silica gel column eluting with petroleum ether to afford **S2** as a colorless solid (2.8 g, 37%). ^1H -NMR (400 MHz, CDCl_3 , δ): 8.22–8.18 (m, 8H), 8.09 (s, 4H), 8.02–7.95 (m, 6H), 7.54–7.47 (m, 10H), 7.09–7.05 (m, 8H), 6.79 (d, 4H), 4.08 (t, 4H), 3.95 (t, 4H), 1.92–1.81 (m, 8H), 1.59–1.57 (br, 8H). ^{13}C -NMR (100 MHz, CDCl_3 , δ): 137.33, 131.50, 130.99, 129.74, 128.65, 127.59, 127.27, 127.13, 126.52, 125.80, 125.13, 124.82, 124.66, 123.56, 34.13, 33.65, 32.88, 31.97, 29.84, 29.60, 29.55, 29.48, 28.81, 28.21. Anal Calcd for $\text{C}_{26}\text{H}_{29}\text{Br}$: C, 74.10; H, 6.94. Found: C, 74.12; H, 7.00.

Monomer 6

A mixture of **S2** (0.49 g, 1.16 mmol), 2,7-dibromo-9H-fluorene (0.17 g, 0.52 mmol), $\text{PhCH}_2\text{NEt}_3\text{Cl}$ (0.04 g, 0.15 mmol) and DMSO (100 mL) was carefully degassed and charged with nitrogen. To the mixture was added dropwise a degassed aqueous NaOH solution (2 mL, 40 wt%). The mixture was stirred at room temperature for 48 h. Water was added, and the mixture was extracted with diethyl ether (200 mL). The organic layer was separated, washed with water (3×50 mL) and dried over anhydrous Na_2SO_4 . After the removal of the solvent, the residue was purified by chromatography on silica gel column eluting with petroleum to afford compound **6** as a colorless solid (0.28 g, 53%). ^1H -NMR (400 MHz, CDCl_3 , δ): 8.27 (d, 2H), 8.17–8.14 (m, 4H), 8.11–8.07 (m, 4H), 8.02–7.96 (m, 6H), 7.85 (d, 2H), 7.48–7.42 (m, 4H), 7.44 (d, 2H), 3.31 (t, 4H), 1.89 (m, 4H), 1.80 (m, 4H), 1.31 (m, 4H), 1.28 (m, 4H), 1.18–0.91 (m, 16H), 0.58 (m, 4H). ^{13}C -NMR (100 MHz, CDCl_3 , δ): 152.67, 139.19, 137.50, 131.59, 131.08, 130.27, 129.79, 128.72, 127.67, 127.36, 127.18, 126.58, 126.29, 125.86, 125.45, 125.21, 124.88, 124.72, 123.67, 121.59, 121.25, 55.80, 53.55, 40.23, 33.73, 32.05, 29.91, 29.62, 29.59, 29.25, 23.72. Anal Calcd for $\text{C}_{65}\text{H}_{64}\text{Br}_2$: C, 77.68; H, 6.42. Found: C, 77.44; H, 6.49.

P1

A mixture of compound **4** (107 mg, 0.084 mmol), compound **7** (55 mg, 0.085 mmol), NaHCO_3 (0.30 g, 3.6 mmol), THF (10 mL) and water (4 mL) was carefully degassed before and after $\text{Pd}(\text{PPh}_3)_4$ (1.0 mg, 0.87 μmol) was added. The mixture was heated to reflux and stirred under nitrogen for 96 h. Brine (50 mL) and CH_2Cl_2 (100 mL) were added, and the organic layer was separated and dried over anhydrous Na_2SO_4 . After the removal of the solvent, the residue was precipitated in methanol. The resulted precipitate was collected by filtration and dried under vacuum to give **P1** as a grayish solid (112 mg, 88%). ^1H -NMR (400 MHz, CDCl_3 , δ): 8.19–7.91 (br, 18H), 7.84–7.83 (br, 2H), 7.71 (br, 6H), 7.54–7.51 (br, 8H), 7.31–7.28 (br, 4H), 7.05–7.02 (br, 4H), 6.84–6.82 (br, 4H), 4.03 (m, 4H), 3.94 (br, 4H), 2.03 (br, 4H), 1.83 (br, 8H), 1.55 (br, 8H), 1.08 (br, 20H), 0.81–0.79 (br, 10H). ^{13}C -NMR (100 MHz, CDCl_3 , δ): 158.64, 158.10, 151.67, 141.77, 138.13, 137.69, 135.91, 133.47, 131.72, 131.14, 130.44, 129.47, 128.70, 128.40, 127.82, 127.57, 127.41, 126.07, 125.67, 125.54, 125.10, 124.77, 68.13, 55.41, 34.83, 34.37, 31.89, 30.47, 29.40, 26.07, 25.76, 22.72, 21.33, 14.23. Anal Calcd for $[\text{C}_{110}\text{H}_{104}\text{O}_4]_n$: C, 88.53; H, 7.06. Found: C, 84.28; H, 6.71.

P2

A mixture of compound **6** (120 mg, 0.119 mmol), compound **7** (77 mg, 0.120 mmol), NaHCO_3 (0.36 g, 4.3 mmol), THF (10 mL), toluene (10 mL) and water (6 mL) was carefully degassed before and after $\text{Pd}(\text{PPh}_3)_4$ (2.0 mg, 1.72 μmol) was added. The mixture was heated to reflux and stirred under nitrogen for 96 h. Brine (30 mL) and CHCl_3 (50 mL) were added, and the organic layer was separated and dried over anhydrous Na_2SO_4 . After the removal of the solvent, the residue was precipitated into methanol. The resulted precipitates were collected by filtration and dried under vacuum to give **P2** as a grayish solid (86 mg, yield 58%). ^1H -NMR (400 MHz, CDCl_3 , δ): 8.22–8.20 (br, 2H), 8.12–8.09 (br, 4H), 8.06–8.01 (br, 4H), 7.97–7.91 (br, 6H), 7.81–7.76 (br, 6H), 7.68 (br, 8H), 3.26 (m, 4H), 2.11 (br, 6H), 1.76 (br, 4H), 1.40 (br, 4H), 1.26 (br, 4H), 1.13–1.07 (br, 38H), 0.77 (br, 14H). ^{13}C -NMR (100 MHz, CDCl_3 , δ): 152.03, 140.70, 140.25, 137.53, 131.65, 131.15, 129.87, 128.79, 127.74, 127.40, 127.26, 126.64, 126.38, 125.92, 125.28, 124.95, 124.79, 123.71, 121.70, 120.21, 55.56, 40.60, 33.80, 32.12, 31.99, 30.22, 30.02, 29.76, 29.41, 24.12, 22.81, 14.30. Anal Calcd for $[\text{C}_{94}\text{H}_{110}]_n$: C, 91.06; H, 8.94. Found: C, 87.34; H, 68.61.

RESTULTS AND DISCUSSION**Molecular Design**

The chemical structures of pyrene derivatives (**S1** and **S2**) and pyrene functionalized polyfluorenes (**P1** and **P2**) used to disperse single-walled carbon nanotubes (SWCNT) in organic solvents by noncovalent interactions are shown in Chart 1. It is well known that pyrene molecules can form non-covalent interaction with the curvature out surface of carbon nanotubes. Compounds **S1** and **S2** are pyrene derivatives, their pyrene functional groups can have monovalent interaction with SWCNT and their alkyl chains can improve their solubility in organic solvents. Polymers **P1** and **P2** are composed of three parts: the conjugated polymer main chain, which would provide unique optoelectronic properties and π - π interactions with SWCNTs; the flexible alkyl chains, which would endow the polymer with good solubility; and the large number of pyrene function groups, which would provide multivalent interaction sites for the single-walled carbon nanotubes. Compared with pyrene small molecules **S1** and **S2**, the larger number of pyrene functional groups in polymers **P1** and **P2** would endow conjugated polyfluorenes with a higher binding affinity to SWCNT *via* multivalent interactions. For control experiments, poly(9,9-dioctylfluorene) (**PF**) and pyrene containing small molecules **S1** and **S2** were also designed and synthesized.

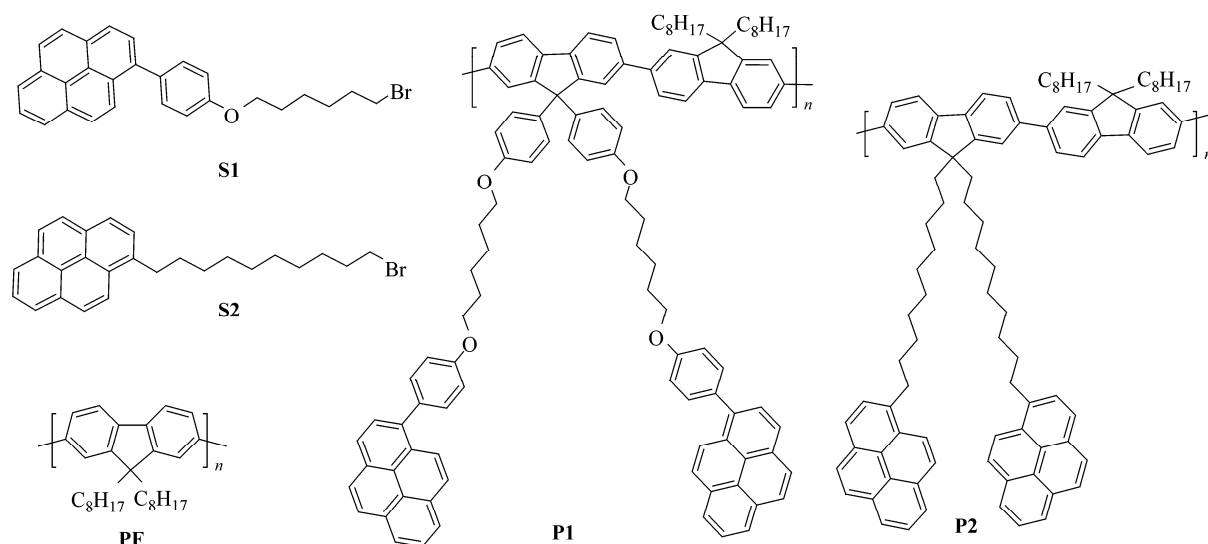
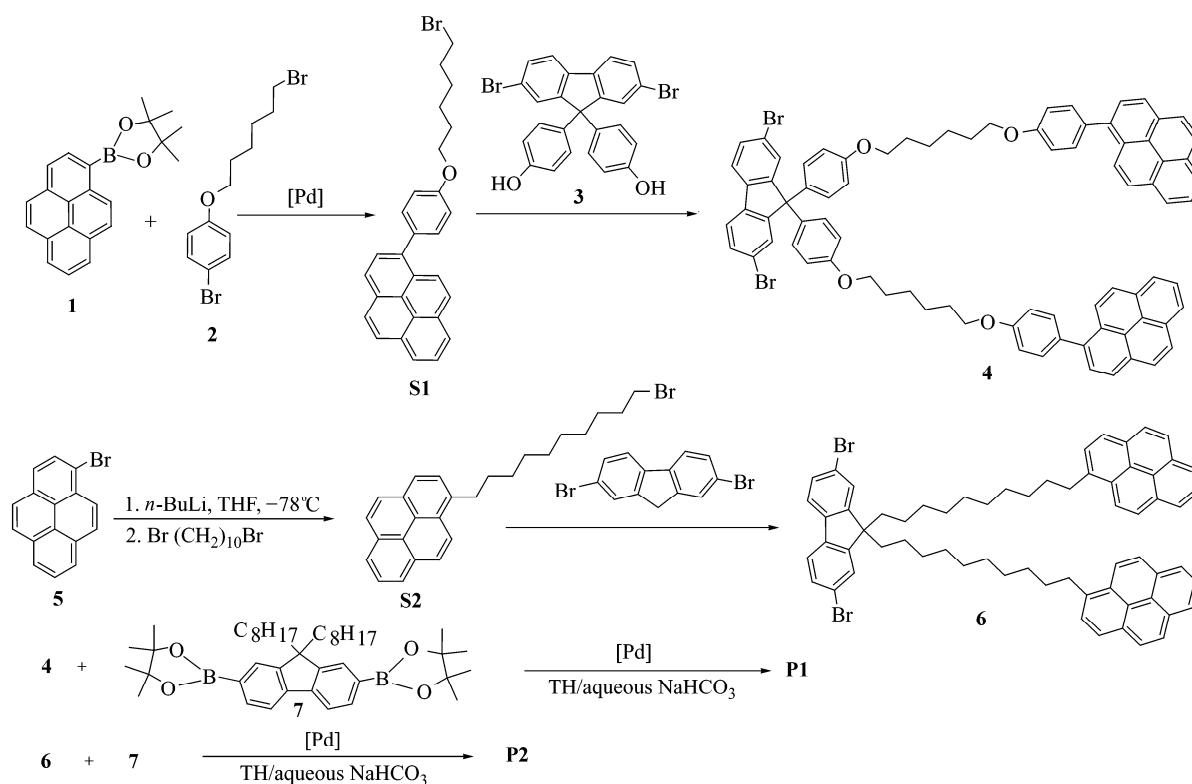


Chart 1 Pyrene derivatives and pyrene functionalized polyfluorenes used for dispersion of SWCNTs by noncovalent interactions

Synthesis of Pyrene Derivatives and Pyrene Functionalized Polyfluorenes

The synthetic routes of pyrene derivatives **S1** and **S2** and pyrene containing 2,7-dibromofluorene monomers **4** and **6** are shown in Scheme 1. Suzuki-Miyaura cross-coupling of 4,4,5,5-tetramethyl-2-(pyren-1-yl)-1,3,2-dioxaborolane **1** and 1-(6-bromohexyloxy)-4-bromobenzene **2** afforded pyrene derivative **S1** in a yield of 84%. Reaction of 2,7-dibromo-9,9-bis(4-hydroxyphenyl)-9H-fluorene **3** and compound **S1** under K_2CO_3 /butanone conditions gave the desired monomer **4** in a yield of 82%. The preparation of monomer **6** is started from commercially available 1-bromopyrene. The treatment of 1-bromopyrene in a THF solution at -78°C with *n*-BuLi generated pyrene anion by halo-lithium exchange reaction, then the formed pyrene anion further reacted with 1,10-dibromodecane to afford compound **S2** in a yield of 37%. Monomer **6** was accomplished in a yield of 53% by the reaction of 2,7-dibromofluorene and compound **S2** in DMSO with aqueous NaOH as a base and triethylbenzylammonium chloride as the phase transfer catalyst. The purity of these new compounds was confirmed by ^1H - and ^{13}C -NMR spectroscopy and elemental analysis. Suzuki-Miyaura-Schlüter polycondensation of dibromo monomers **4** and 4,4,5,5-tetramethyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctyl-9H-fluoren-7-yl)-1,3,2-dioxaborolane **7** was carried out in a biphasic mixture of aqueous NaHCO_3 and THF with freshly prepared $\text{Pd}(\text{PPh}_3)_4$ as the catalyst precursor to afford **P1** in a yield of 88%. Under similar conditions, the polymerization of **6** and **7** proceeded very rapidly. A large amount of grayish precipitates, which would not redissolve in THF, were formed during the polymerization. The polymerization of **6** and **7** was therefore carried out under slightly modified conditions. There was no precipitation when a biphasic mixture of aqueous NaHCO_3 and THF/toluene was used as the media for polymerization. **P2** was obtained as a grayish solid in a yield of 58%. Both **P1** and **P2** are readily soluble in common organic solvents, such as THF, toluene and chloroform. The number average molecular weights of **P1** and **P2** were determined to be 66×10^3 and 70×10^3 , respectively, by gel permeation chromatography (GPC) eluting with THF and calibrated with polystyrene standards.



Scheme 1 Synthesis of pyrene derivatives **S1** and **S2**, monomers **4** and **6**, and polymers **P1** and **P2**

Noncovalent Functionalization of SWCNTs

As shown in Chart 1, pyrene containing small molecules **S1** and **S2** and pyrene containing polyfluorenes **P1** and **P2** were used to disperse SWCNT in organic solvents *via* noncovalent interactions. The solubility of noncovalently functionalized SWCNTs in organic solvents was carefully measured by using a method reported in the literature^[21]. First, 10 mg of modifier (**S1**, **S2**, **PF**, **P1**, and **P2**) were dissolved in 1 mL of THF. Then, 2 mg of pristine SWCNT were added into each solution. The mixture was subject to ultrasound for 1 h. The resulting dispersion was centrifuged for 10 min at a speed of 3000 r/min, and then kept undisturbed overnight. The upper dark clear solution was carefully decanted and collected. The dark solution was filtrated with membrane filter with a pore diameter of 450 nm, and the collected dark solids were washed adequately with a large amount of THF (4×50 mL) to remove the excess modifiers. The membrane filter with dark solids sticking on it was dried under high vacuum. The dark residue was carefully peeled away from the membrane filter and weighed. Polymer-SWCNT complex was again added into 1 mL of THF, and the above mentioned procedure was repeated to measure the solubility in THF with non-excess modifier. Solubilities of the polymer-SWCNT complexes in THF with excess and non-excess modifiers are listed in Table 1.

Table 1. Solubilities of SWCNT complexes in THF with excess and non-excess of modifiers (**S1**, **S2**, **P1**, **P2** and **PF**)

Modifiers	Excess	Non-excess
S1	Not stable	Not stable
S2	Not stable	Not stable
P1	1.1 mg/mL	0.6 mg/mL
P2	1.6 mg/mL	0.7 mg/mL
PF	0.5 mg/mL	0.2 mg/mL

In the experiment, we noticed that when pyrene containing small molecules **S1** and **S2** was used to functionalize SWCNTs, no stable dispersion could be formed even with large amount of excess modifiers existed. With polymers **PF**, **P1** and **P2** as modifiers, the SWCNT/polymer complex had a better solubility when there were excess polymers existed than that in the absence of free polymers. This suggested a polymer-SWCNT bound-unbound equilibrium existed in the solution^[24]. The formed dispersions have been stable for months without visible precipitation. And for polymers **P1** and **P2**, they had notably better modification effect on nanotubes, owing to the multivalent interactions of conjugated main chains and pyrene groups with the outer surface of SWCNTs.

Microscopy

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the microscopic structures of the polymer-SWCNT complexes. Samples used here were prepared by dip-coating the solutions of the complexes onto silicon wafers or copper grids. As shown in Fig. 1, the SEM and TEM images illustrated that the polymer-SWCNT complexes were mixtures of polymer functionalized individual and aggregated bundles nanotubes, and the polymers were unevenly bounded onto the nanotubes. The **P1**-SWCNT and **P2**-SWCNT complexes showed much narrower nano-bundles in comparison with **PF**-SWCNT complex. As the curvature and the surface energy of a single SWCNT is rather high, pristine SWCNTs are all entangled together. And obviously, a relatively thicker bundle is easier for a π conjugated modifier stacking onto its surface. It is obvious that polymer **PF** has less interacting sites with the SWCNT than polymers **P1** and **P2**. The **PF**-SWCNT complex will be less stable than **P1**-SWCNT and **P2**-SWCNT complexes. Hence, the **PF**'s ability of separation and dispersion of carbon nano-bundles will be weaker than that of **P1** and **P2**. Therefore, polymers pyrene-functionalized polyfluorenes **P1** and **P2**, especially **P2**, are probably able to disperse SWCNTs into thinner bundles or individual nanotubes.

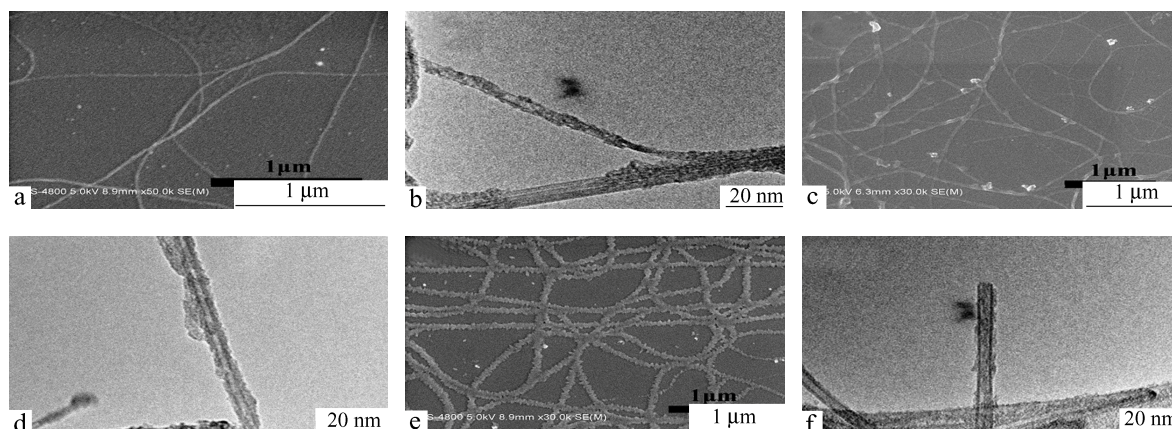


Fig. 1 SEM images of polymer-SWCNT complexes (a) **P1**-SWCNT, (c) **P2**-SWCNT and (e) **PF**-SWCNT; TEM images of polymer-SWCNT complexes (b) **P1**-SWCNT, (d) **P2**-SWCNT and (f) **PF**-SWCNT

TGA Measurements

Polymer-SWCNT complex samples used for thermal gravimetric analysis (TGA) measurements were prepared by washing with a large amount of THF to remove the excess of free polymer. TGA curves of pure polymers were also measured for the control experiment. The polymer content in the polymer-SWCNT complex was determined by the method reported by Adronov *et al.*^[24]. As shown in Fig. 2, **P1**, **P2**, and **PF** exhibit a high

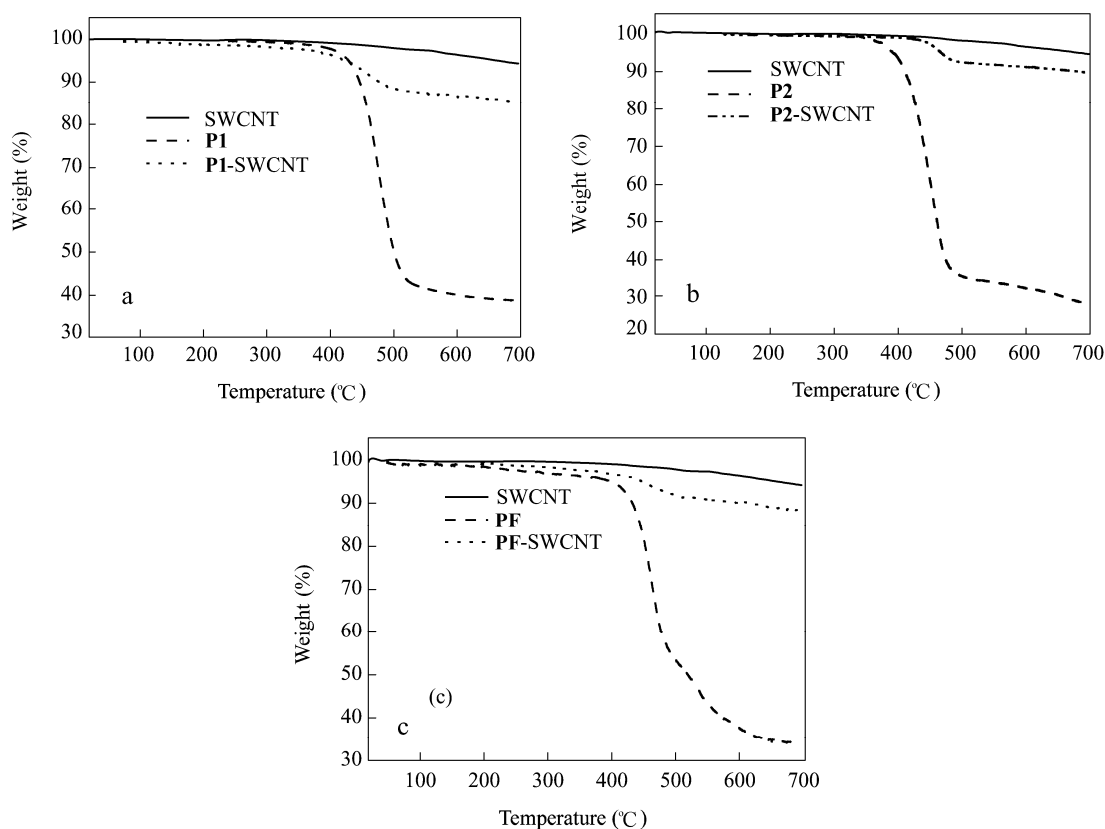


Fig. 2 TGA traces of (a) SWCNT, **P1** and **P1**-SWCNT; (b) SWCNT, **P2** and **P2**-SWCNT and (c) SWCNT, **PF** and **PF**-SWCNT

thermal stability, showing 5% weight loss at 428°C, 388°C and 400°C, respectively. The major mass loss for the polymer occurs at *ca.* 450°C, corresponding to the loss of alkyl side chains within these polymers^[21]. The observed weight loss ratios of **P1**, **P2** and **PF** at 700°C are 61%, 72% and 66%, respectively, which are roughly in agreement with calculated weight percentages for the side chains (two octyl side chains and two pyrene-terminated decylene chains) of 64% for **P1**, 72% for **P2** and 58% for **PF**. Under the same condition, the **P1**-SWCNT, **P2**-SWCNT and **PF**-SWCNT complexes lost 15%, 11% and 12% of their weights, respectively, in the range of the weight loss temperature of pure polymers. Based on these results, we could roughly calculate the weight percent of SWCNT in the complexes to be 75% for **P1**-SWCNT complex, 85% for **P2**-SWCNT complex and 82% for **PF**-SWCNT complex. And the actual solubility of SWCNT (excluding the contribution of the polymers) in THF was then calculated to be 0.45 mg/mL for **P1**, 0.60 mg/mL for **P2** and 0.16 mg/mL for **PF**.

Optical Properties

Optical properties of polymer-SWCNT complexes free of excess polymers were studied with UV-Visible absorption and fluorescence spectroscopy. Figure 3 shows UV-Visible absorption and fluorescence emission spectra of **P1**, **P1**-SWCNT, **P2**, **P2**-SWCNT, **PF** and **PF**-SWCNT in THF solutions. In solution, **P1** exhibited two absorption bands in the ultraviolet region. The band peaked at 352 nm is due to the absorption of lateral pyrenylphenyl moieties in the polymer; whereas the absorption band peaked at 383 nm is attributed to the absorption of the polyfluorene main chain. The **P1**-SWCNT complex exhibited similar absorption spectrum, and no marked spectral shift was observed. **P2** displayed three absorption peaks located at 314, 327 and 344 nm and one absorption band located at 382 nm. The three absorption peaks were attributed to the absorption of alkyl

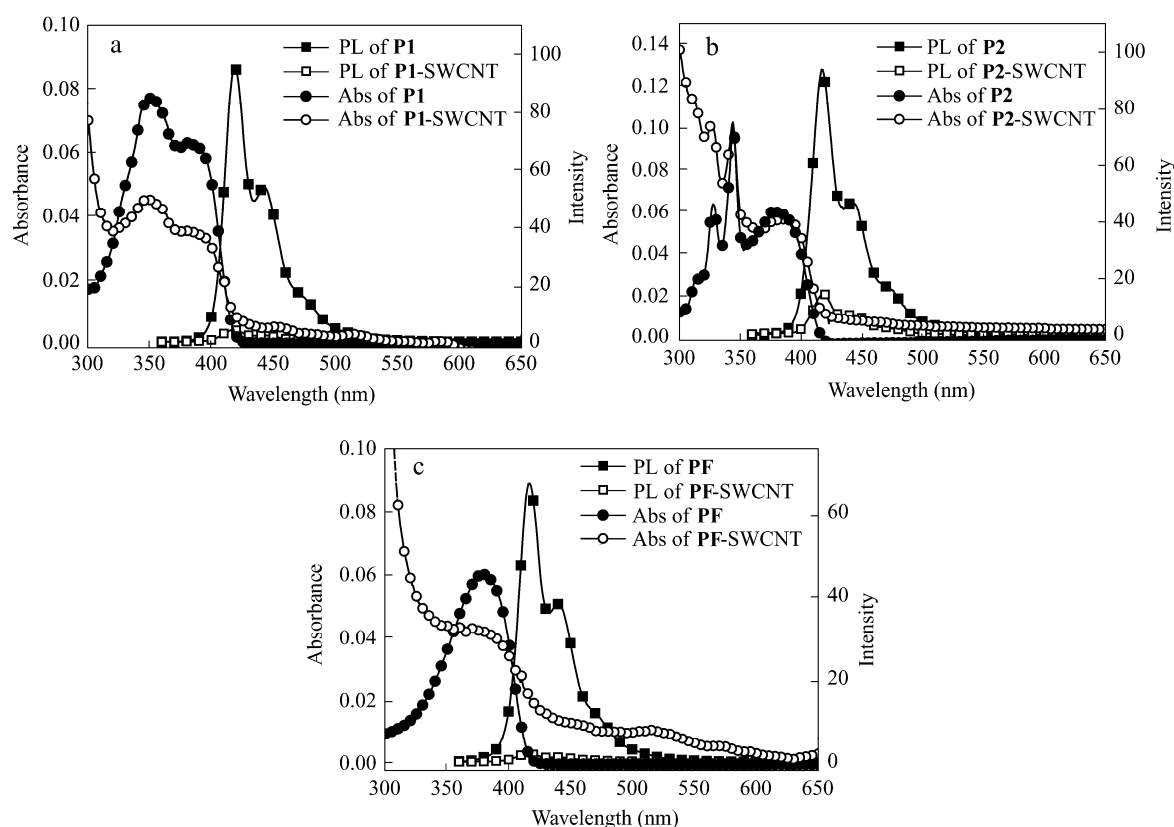


Fig. 3 UV-Vis absorption and fluorescence emission spectra of (a) **P1** and **P1**-SWCNT, (b) **P2** and **P2**-SWCNT, (c) **PF** and **PF**-SWCNT

substituted pyrenes; whereas the absorption band located at 382 nm is attributed to the absorption of polyfluorene main chain. **P2**-SWCNT complex showed three absorption peaks located at 314, 327 and 344 nm and one absorption band located at 387 nm, which was bathochromically shifted for about 5 nm in comparison with that of **P2**. The bathochromic shift may arise from the complexation of polymer main chain with carbon nanotubes, which could make the polymer backbone become more planar^[14, 24]. In solution, the photoluminescent emission spectra of **P1** and **P2** are similar to that of **PF** with two peaks located at 416 and 440 nm, indicating the Förster energy transfer from pyrene units to polyfluorene backbone is very efficient. Upon the formation of polymer-SWCNT complexes, the photoluminescence of the polymers was all markedly quenched by the nanotubes. It is noteworthy that the polymer-SWCNT complexes and the polymers have coincident emission spectra with the same peak position and the band shape. The photoluminescence quantum efficiencies (PLQEs) of the polymer-SWCNT complexes were measured using the corresponding pure polymers as the standard (assuming the PLQE of pure polymer is 100%) to be 9% for the **P1**-SWCNT complex, 11% for **P2**-SWCNT complex and 4% for **PF**-SWCNT, indicating that the SWCNTs quenched most of the fluorescence of the polymers bounded to them.

CONCLUSIONS

We have designed and synthesized two kinds of polyfluorenes bearing two lateral alkyl chains and two pyrene-terminated alkyl chains per repeating unit. The lateral alkyl chains endow polymers and the polymer-SWCNT hybrids with good solubility in organic solvent, and the polyfluorene backbone and the lateral pyrene groups can interact with the aromatic surface of the single-walled carbon nanotube non-covalently *via* π - π interactions. Compared with the compound or the polymer only bearing either pyrene groups or conjugated fluorene chain, the as-synthesized “multivalent” conjugated polymers have shown significantly higher solubility for single-walled carbon nanotubes in common organic solvents.

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