Canadian Journal of Chemistry
Revue canadienne de chimie

π -Conjugated Polymers with Pendant Coumarins: Design, Synthesis, Characterization, and Interactions with Carbon Nanotubes

Journal:	<i>Canadian Journal of Chemistry</i>
Manuscript ID	cjc-2016-0205.R1
Manuscript Type:	Article
Date Submitted by the Author:	08-Jun-2016
Complete List of Authors:	Adronov, Alex; McMaster University, Chemistry and Chemical Biology Imit, Mokhtar; McMaster University, Chemistry and Chemical Biology Imin, Patigul; McMaster University, Chemistry and Chemical Biology
Keyword:	conjugated polymer, carbon nanotubes, light harvesting, energy transfer

**π -Conjugated Polymers with Pendant Coumarins: Design,
Synthesis, Characterization, and Interactions with Carbon
Nanotubes**

Mokhtar Imit, Patigul Imin, and Alex Adronov*

Department of Chemistry and Chemical Biology, the Brockhouse Institute for Materials
Research, McMaster University, Hamilton, Ontario, Canada

Email: adronov@mcmaster.ca

[*] Department of Chemistry and Chemical Biology

McMaster University

1280 Main St. W.

Hamilton, ON

L8S 4M1

Tel: (905) 525-9140 x 23514

Fax: (905) 521-2773

Abstract

A series of new fluorene-based π -conjugated polymers having coumarin derivatives as part of dendritic side chains were designed and prepared using Suzuki-Miyaura cross-coupling reaction. A new coumarin derivative, bearing a heptyl side-chain for solubility was utilized to ensure solubility of the final polymers. It was found that fluorescence resonance energy transfer (FRET) from the coumarins to the polyfluorene backbone was efficient, especially for the polymers decorated with lower-generation dendrons. Each of the polymers was found to interact strongly with the surface of single-walled carbon nanotubes (SWNTs) in THF, and their ability to selectively disperse specific SWNT chiralities was investigated. Photoluminescence studies revealed that the strong polymer emission is efficiently quenched in the corresponding supramolecular complexes with SWNTs. This high quenching efficiency indicates that the coumarin-polymer FRET system can be supramolecularly bound to the surface of single-walled carbon nanotubes (SWNTs) to produce an energy transfer system in which the energy absorbed by the donor coumarin chromophores is channeled to the SWNTs.

Keywords: conjugated polymer, carbon nanotubes, energy transfer, light harvesting

Introduction

Since their discovery,¹ single-walled carbon nanotubes (SWNT) have attracted a great deal of interest as a result of their unique properties, including remarkable mechanical strength,² thermal and electronic conductivity,^{3–6} and photophysical characteristics.^{7–9} These properties have spawned investigation of SWNTs in a variety of applications, including field-effect transistors (FETs),^{10,11} sensors,^{12–16} photovoltaics,^{17–19} flexible printed circuits,²⁰ touch screens,²¹ microelectronic interconnects,²² and numerous other devices.²³ However, application of these novel nanostructures is often hampered by the heterogeneous character of as-produced SWNT samples. All the generally used methods of nanotube production, including high-pressure carbon monoxide disproportionation (HiPco),²⁴ carbon vapour deposition (CVD),²⁵ arc-discharge,²⁶ laser ablation,²⁷ and plasma torch growth,²⁸ result in mixtures composed of both metallic and semiconducting SWNTs that also vary in length, diameter, and roll-up angles. Moreover, unmodified carbon nanotubes exhibit extremely low solubility and poor dispersability within almost all common organic and aqueous solvents. Several methods aimed at dispersing and purifying SWNTs have recently been developed, including density-gradient ultracentrifugation (DGU),²⁹ agarose gel filtration,³⁰ electrophoresis,³¹ and selective supramolecular functionalization with conjugated polymers.^{32–35} Of these techniques, the selective interaction of conjugated polymers with specific carbon nanotubes is becoming increasingly important as it is an inexpensive and easily scalable process. In addition, the structural diversity of conjugated polymers allows the preparation of a multitude of structures with specific properties and functions.

Recent studies have shown that many conjugated polymer backbones, including polyfluorenes,³² polythiophenes,^{36,37} poly(phenylene vinylene)s,³⁸ poly(phenyl acetylene)s,^{39,40}

and polycarbazoles,^{33,34,41} can interact strongly with the surface of carbon nanotubes in a non-covalent fashion. It has also been found that the fluorescence of conjugated polymers that are bound to the nanotube surface is efficiently quenched through energy or electron transfer to the nanotube.^{42–44} This suggests that decoration of SWNTs with conjugated polymers can result in a light-harvesting assembly, where the polymer absorbs photons and transfers their energy to the nanotube. However, individual conjugated polymers exhibit relatively narrow absorption bands, limiting their capacity to harvest light. To increase the light absorption capacity, a cascade energy transfer system can be envisioned, involving light-harvesting chromophores decorating the conjugated polymer that is adsorbed to the nanotube surface. Coumarins are an attractive family of chromophores due to their structural variability and corresponding differences in absorption and emission ranges, high emission quantum yields, and photostability.^{45–47} Moreover coumarin derivatives are frequently used as signaling units in sensors and in sophisticated photophysical systems involving fluorescence resonance energy transfer (FRET).^{48–50} The efficiency of FRET depends on the magnitude and orientation of the transition dipole moments of the two chromophores, the spectral overlap of the donor emission and acceptor absorption, and the average interchromophoric distance (R), where efficiency is inversely proportional to R^6 .^{51–53}

The significant spectral overlap between the emission of 7-hydroxycoumarin and the absorption of polyfluorene makes it possible to use these components as a FRET pair. Furthermore, polyfluorene derivatives are known to interact strongly with the surface of SWNTs, allowing the coumarin-polyfluorene-SWNT combination to form a supramolecular assembly that will behave as light-harvesting antenna and energy transfer cascade. Such a system is capable of converting high energy UV radiation into heat (NIR radiation). In this work, we report the

preparation of polyfluorene polymers that are decorated with dendritic coumarin-functionalized side-chains, which exhibit efficient FRET. These polymers form supramolecular interactions with SWNTs, which quench direct and sensitized polyfluorene emission through either energy or electron transfer.

Experimental

Materials and Characterization: Single-walled carbon nanotubes (HiPco SWNTs) were purchased from NanoIntegris (batch number: R1-901) and used without any further treatment. Reagent grade chemicals and solvents were purchased from Aldrich, ACROS Chemical Co., and other chemical suppliers and used as received. ^1H and ^{13}C NMR spectra were obtained on Bruker Avance 700 MHz, 600 MHz or 200 MHz instruments, and the non-deuterated solvent signal was used as the internal standard for ^1H -NMR spectra. Polymer molecular weight and polydispersity index (PDI) were estimated by gel permeation chromatography (GPC) analysis using a Waters 2695 Separations Module equipped with a Waters 2996 photodiode array detector, a Waters 2414 refractive-index detector, and two Jordi Labs Jordi Gel DVB columns. Polystyrene standards were used for calibration, and THF was used as the eluent at a flow rate of 1.0 mL/min. Raman spectra were collected with a Renishaw InVia Laser Raman spectrometer equipped with a 300 mW Renishaw laser (785 nm, 1200 L/mm grating). The Raman system was also equipped with a Leica microscope having 5 $\times$, 20 $\times$, and 50 $\times$ objectives as well as a USB camera for sample viewing. The 785 nm laser was operated at 1% intensity to avoid damage to the sample. Samples were prepared by drop-casting the polymer (or SDBS) and SWNT dispersions onto a clean silicon substrate. Ultrasonication was carried out in a Branson Ultrasonics B2510 bath sonicator. Filtration carried out through a 200 nm-pore Teflon membrane (Millipore). UV/vis-NIR absorption spectra were measured using a Varian Cary 5000

spectrophotometer. Fluorescence spectra were measured using a Jobin-Yvon SPEX Fluorolog 3.22 equipped with 450 W Xe lamp and an InGaAs detector, also using a 10 mm quartz cuvette. Slit widths for both excitation and emission were set to 8 nm band-pass, and correction factor files were applied to account to instrument variations. Photoluminescence maps were obtained at 25 °C, with 5 nm intervals for both the excitation and emission. Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q50 thermogravimetric analyzer under Argon with a temperature range from 20 to 800 °C and the temperature gradient of 5 °C /min. All measurements were done under Ar, with sample masses ranging from 1 to 2 mg.

Synthesis of monomers and polymers

9,9'-Didodecyfluorene-2,7-diboronic acid bis(1,3-propanediol)ester: A 100 mL round bottom flask equipped with a magnetic stir bar was charged with a solution of 9,9'-didodecyfluorene-2,7-diboronic acid (0.542 g, 1 mmol), 1,3-propanediol (0.61 g, 8 mmol) and 25 mL diethyl ether, and stirred at room temperature for overnight. Then the reaction was quenched by adding 25 mL of water, and extracted with diethyl ether (3×30 mL). The organic layer was washed with water (25 mL), brine (25 mL) and dried over anhydrous MgSO₄. The solvent was removed via rotary evaporation, and the resulting product was dried under vacuum at 40 °C. A colorless gel was isolated with a yield of 93% (0.62 g). ¹H NMR (200 MHz, CDCl₃), δ_H [ppm]: 7.77~7.60 (m, 6H), 4.20(t, *J* = 5.4 Hz, 8H), 2.08 (t, *J* = 4.8 Hz, 4H), 1.95 (m, 4H), 1.48~0.84 (m, 40H), 0.60 (s, 6H). HR-MS (EI⁺): *m/z* [M+H]⁺ = 670.5304, found = 670.5324.

Ethyl 3-oxodecanoate (1):^{50, 51} A 100 mL round bottom flask equipped with a magnetic stir bar was charged with a mixture of octylaldehyde (1.28 g, 10 mmol), ethyl diazoacetate (1.36 g, 12

mmol), MoO₂Cl₂ (~0.10 g, 0.5 mmol), dry CH₂Cl₂ (10 mL). The resulting mixture was stirred at 30 °C under Ar. The conversion of starting material was monitored by TLC (Hexane:EtOAc, 90:10/v:v). After complete disappearance of starting material (about 10 hours), CH₂Cl₂ was evaporated and the crude mixture was diluted with 20 mL of H₂O. After extracting with ethyl acetate (3×30 mL) the organic layer was dried over anhydrous Na₂SO₄. Ethyl acetate was evaporated and the residue was purified by column chromatography (silica gel, hexane:EtOAc = 90:10/volume) to give the pure β-keto ester as a colourless liquid with a yield of 80% (1.70 g). ¹H NMR (CDCl₃, 200 MHz, δ/ppm): 4.18 (q, *J* = 7.2 Hz, *J* = 7.0 Hz, 2H), 3.40(s, 1H), 2.51 (t, *J* = 7.3 Hz, 2H), 1.58~0.84 (m, 16H).

4-Heptyl-7-hydroxycoumarin (2):^{50, 51} To a 100 mL round bottom flask equipped with a magnetic stirrer, ethyl 3-oxodecanoate (1.07g, 5 mmol), resorcinol (0.55g, 5 mmol), small amount of *p*-toluenesulfonic acid (~10 mol %) and 10 mL mixture of H₂SO₄ and methanol (70:30/v:v) were added. The mixture was stirred at room temperature, and the reaction was monitored by TLC. When no starting material was observed by TLC (silica gel, hexane:EtOAc, 9:1/v:v), the reaction mixture was diluted with 20 mL of water and extracted with CH₂Cl₂ (3×25 mL). The organic layer was washed with water (25 mL), brine (25 mL) and dried over anhydrous MgSO₄. Then the solvent was removed by rotary evaporation, and the crude product was purified by recrystallization from ethanol. After drying under vacuum for 24 h, the product was obtained as an off-white solid with yield of 83% (1.17 g). ¹H NMR (200 MHz, CDCl₃), δ_H [ppm]: 7.52 (d, 1H), 7.03(s, 1 H), 6.86 (d, 1 H), 3.75 (b, 1H), 2.73 (t, 2 H), 1.67(t, 2H), 1.29 (m, 8H), 0.86 (t, 3H). ¹³C NMR (150 MHz, CDCl₃), δ_C [ppm]: 162.9, 160.0, 158.1, 155.2, 125.8, 113.5, 112.7, 110.0, 103.6, 32.0, 31.7, 29.4, 29.0, 28.4, 22.6, 14.0. HRMS-ESI: *m/z* [M+H]⁺ = 261.1491,

found = 261.1484.

2,7-Dibromo-9,9-bis(6'-bromohexyl)fluorene (3):⁵² 2,7-dibromofluorene (2.30 g, 10 mmol) was added in one portion to a mixture of 1,6-dibromodecane (10 mL, 65 mmol), tetrabutylammonium bromide (0.2 g) and 10 mL of sodium hydroxide aqueous solution (~50 % w/w) in a 100 mL round bottom flask equipped with a magnetic stir bar. The mixture was stirred for 2 h at 75 °C under nitrogen atmosphere. After diluting the reaction mixture with 80 mL of dichloromethane and 30 mL of water, the organic phase was separated, and it was washed with water (30 mL) and brine (30 mL), respectively. The organic layer was then dried over anhydrous MgSO₄, and dichloromethane was evaporated by rotary evaporation. Unreacted 1,6-dibromodecane was collected by vacuum distillation, and the crude product was purified by silica gel column chromatography using hexanes and chloroform (9:1/v:v) as the eluent. The product was obtained as white crystals in 85% yield (6.1 g). ¹H NMR (CDCl₃, 200 MHz, δ/ppm): 7.43 (m, 2H), 7.51(d, *J* = 7.0 Hz, 4H), 3.29 (t, *J* = 6.6 Hz, 4H), 1.92 (t, *J* = 8.1 Hz, 4H), 1.67(t, *J* = 6.9 Hz, 4H), 1.58~0.58 (m, 16 H).

2,7-Dibromo-9,9'-bis(10''-(4-heptyl-7-coumarinoxy)hexyl)fluorene (4): A 100 mL round bottom flask equipped with a magnetic stir bar was charged with a solution of 2,7-dibromo-9,9'-bis(6-bromohexyl)fluorene (0.65 g, 10 mmol), 4-heptyl-7-hydroxycoumarin (0.78 g, 30 mmol), K₂CO₃ (2 g, 14.5 mmol), and KI (0.1 g, 0.6 mmol) in 30 mL of acetone. Then the mixture was stirred at reflux for 24 h under argon. The reaction mixture was then cooled to room temperature, and solid was removed by filtration. The solvent was removed by vacuum rotatory evaporation, and the crude product was purified by column chromatography using silica (hexane: ethyl acetate, 9:1/v:v). A viscous oil was obtained after removal of the solvent by vacuum rotatory

184 evaporation. The product was dried under vacuum overnight at 45 °C (0.97 g, 87 % yield). ¹H
185 NMR (200 MHz, CDCl₃), δ_H [ppm]: 7.44 (m, 8H), 6.80(d, *J* = 2.6 Hz, 1H), 6.74(s, 4H), 6.10 (s,
186 2H), 3.88 (t, *J* = 6.4 Hz, 4H), 2.69(t, *J* = 7.0 Hz, 4H), 1.92 (t, *J* = 7.6 Hz, 4H), 1.58~0.84 (m, 16
187 H), 0.60 (s, 6H). ¹³C NMR (150 MHz, CDCl₃), δ_C [ppm]: 162.1, 161.7, 156.7, 155.6, 152.5,
188 139.1, 130.2, 126.2, 125.2, 121.5, 121.2, 112.8, 112.7, 110.8, 101.5, 68.6, 65.7, 40.2, 31.9, 31.7,
189 29.8, 29.5, 29.4, 29.2, 29.3, 29.2, 28.9, 28.3, 25.9, 23.6, 22.6, 14.1. HRMS-ESI: *m/z* [M+H]⁺ =
190 1007.3470, found [M+H]⁺ = 1007.3476.

191
192 **7-(3-Bromopropoxy)-4-heptylcoumarin (5):** A 100 mL round bottom flask equipped with a
193 magnetic stir bar was charged with 4-heptyl-7-hydroxycoumarin (1.3 g, 5 mmol), 1, 3-
194 dibromopropane (4.04 g, 20 mmol), K₂CO₃ (2 g, 14.5 mmol), KI (0.1 g, 0.6 mmol) and 50 mL
195 acetone. Then the mixture was stirred under reflux for 24 h under argon. The reaction mixture
196 was cooled to room temperature, solid was removed by filtration, and then the solvent was
197 removed by vacuum evaporation. The crude product was purified by column chromatography
198 using silica (hexane:ethyl acetate = 9:1 v/v). A viscous oil was obtained after removal of the
199 solvent by vacuum rotatory evaporation with a yield of 80% (1.52 g). ¹H NMR (600 MHz,
200 CDCl₃), δ_H [ppm]: 7.52 (d, *J* = 8.6 Hz, 1H), 6.87(d, *J* = 2.6 Hz, 1H), 6.83(s, 1H), 6.12 (s, 1H),
201 4.17 (t, *J* = 6.0 Hz, 2H), 3.58(t, *J* = 6.5 Hz, 2H), 2.71(t, *J* = 7.4 Hz, 2H), 1.65 (t, *J* = 7.4 Hz, 2H),
202 1.45~1.10 (m, 8H), 0.85(t, *J* = 6.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃), δ_C [ppm]: 162.3,
203 161.3, 156.0, 143.4, 128.7, 113.0, 101.4, 68.4, 33.7, 32.6, 28.8, 27.9, 25.2. HRMS-CI: *m/z* [M]⁺
204 =380.0987, found = 380.0987.

205
206 **7-(3-Azidopropoxy)-4-heptylcoumarin (6):** A 100 mL round bottom flask equipped with a

magnetic stir bar was charged with a mixture of 7-(3-bromopropoxy)-4-heptylcoumarin (1.4 g, 5 mmol), NaN₃ (0.65 g, 10 mmol) and 10 mL of DMF. The reaction mixture was heated at 100°C overnight. After cooling to room temperature, the mixture was poured into water and extracted with CH₂Cl₂ (3×30 mL), washed with water (30 mL) and brine (30 mL), separately. The organic layer was dried over anhydrous MgSO₄, and the solvent was removed by vacuum rotatory evaporation to give pure azide **6** as a white solid with a yield of 96% (1.65 g). ¹H NMR (600 MHz, CDCl₃), δ_H [ppm]: 7.52 (d, *J* = 8.8 Hz, 1H), 6.87(d, *J* = 2.2 Hz, 1H), 6.83(s, 1H), 6.12 (s, 1H), 4.17 (t, *J* = 5.7 Hz, 2H), 3.52(t, *J* = 6.3 Hz, 2H), 2.71(t, *J* = 7.0 Hz, 2H), 2.38 (t, *J* = 5.9 Hz, 2H), 1.65 (t, *J* = 5.6 Hz, 2H), 1.45~1.10 (m, 8H), 0.85(t, *J* = 6.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃), δ_C [ppm]: 161.5, 156.6, 155.5, 125.4, 113.2, 112.5, 110.9, 101.6, 65.1, 48.1, 31.9, 29.4, 29.0, 22.6, 14.1. HRMS-ESI: *m/z* [M+H]⁺ = 344.1971, found = 344.1974.

1-Bromomethyl-3,5-bis(prop-2-ynyloxy)benzene (7):²⁹ To a 100 mL round bottom flask equipped with a magnetic stirrer, propargyl bromide in toluene (1.8 g, 15 mmol), 3,5-dihydroxybenzyl alcohol (1.4 g, 10 mmol), K₂CO₃ (4.2 g, 30 mmol), KI (0.2 g, 1.2 mmol), 18-crown-6 (0.05 g, 0.2 mmol) and 50 mL of acetone were added. The mixture was stirred under reflux overnight and then cooled down to room temperature. After removing inorganic salts by filtration, the solvent was concentrated. The crude product was purified by flash silica gel chromatography by eluting the product in hexanes and ethyl acetate (hexanes:EtOAc, 9:1/v:v) to give the 3,5-bis(2-propynyloxy)benzenemethanol as a pale yellow liquid (2.0 g, 93% yield). ¹H NMR (CDCl₃, 200 MHz, δ/ppm): 6.60(s, 2H), 6.51(s, 1H), 4.65 (s, 4H), 4.63(s, 2H), 2.50(s, 2H), 1.71(s, 1H).

A 100 mL round bottom flask equipped with a magnetic stir bar was charged with a

230 solution 1.08 g of the above product 3,5-bis(prop-2-ynyloxy)benzenemethanol (5 mmol)
231 dissolved in 30 mL of THF, and CBr₄ (2.65 g, 8 mmol) and PPh₃ (2.1 g, 8 mmol) were added
232 portionwise under vigorous stirring. After stirring at room temperature overnight, the mixture
233 was filtered and THF was removed by vacuum rotatory evaporation. The crude product was
234 purified by flash silica gel chromatography eluting with hexanes and ethyl acetate
235 (hexanes:EtOAc, 9:1/v:v) to give product **7** as off-white powder with a yield of 52% (0.72 g). ¹H
236 NMR (CDCl₃, 200 MHz, δ /ppm): 6.65(s, 2H), 6.56(s, 1H), 4.67 (s, 4H), 4.42 (s, 2H), 2.54(s,
237 2H). MS: m/z (M) = 804.31, found (M+H⁺) = 805.32.

238
239 **9,9'-Bis(3,5-bis(prop-2-ynyloxy)benzyl)-2,7-dibromo-9H-fluorene (8):** A 100 mL round
240 bottom flask equipped with a magnetic stir bar was charged with a mixture of 2,7-
241 dibromofluorene (0.324 g, 1 mmol), tetrabutylammonium bromide (~6 mg, 0.02 mmol), and 20
242 mL of DMSO, and then the mixture was degassed for 15 min by bubbling with nitrogen. 5 mL of
243 aqueous NaOH solution (~50%, w/w) was added and stirred vigorously for 10 min under
244 nitrogen. The solution of **8** (0.84 g, 3 mmol) in 10 mL of degassed DMSO was added to the
245 above mixture, and the mixture was stirred under nitrogen for 8 h. The reaction was quenched by
246 adding 30 mL of water, and the aqueous layer was extracted with CH₂Cl₂ (3×50 mL), washed
247 with water (30 mL) and brine (30 mL), separately. The organic phase was dried over MgSO₄,
248 and the solvent was removed by vacuum rotatory evaporation. The residue was purified by
249 column chromatography with hexanes and CHCl₃ (hexanes:CHCl₃, from 4:1 to 1:1/v:v). The
250 final product was further purified via recrystallization from CHCl₃ and ethanol, and a white
251 powder was obtained with a yield of 76% (0.55 g). ¹H NMR (600 MHz, CDCl₃), δ_H [ppm]:
252 7.56(s, 2H), 7.38(d, J = 6.0, 2H), 7.28(s, 2H), 6.30 (s, 2H), 5.95 (s, 4H), 4.40 (s, 8H), 3.30 (s,

4H), 2.48(s, 4H). ^{13}C NMR (150 MHz, CDCl_3), δ_{C} [ppm]: 161.5, 156.6, 155.5, 125.4, 113.2, 112.5, 110.9, 101.6, 65.1, 48.1, 31.9, 29.4, 29.0, 22.6, 14.1. HRMS-ESI: m/z $[\text{M}+\text{H}]^+ = 720.0433$, found = 721.0411.

Compound 9: A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **8** (0.14 g, 0.2 mmol), compound **6** (0.42 g, 1.2 mmol), sodium ascorbate (0.08 g, 0.4 mmol) and 8 mL inhibitor free THF. The flask was sealed with a rubber septum and purged with argon for 10 min. CuSO_4 (0.03 g, 0.12 mmol) was dissolved in 2.5 mL of H_2O and added to the reaction mixture. The resulting mixture was vigorously stirred at room temperature for 12 h under Ar (or sonicated 2-3 hours under the same conditions). The organic layer was diluted with 25 mL of CH_2Cl_2 , washed with water (20 mL) and brine (20 mL), separately. The organic layer was dried over MgSO_4 and concentrated by vacuum rotatory evaporation. The final product was purified by silica gel column chromatography using ethyl acetate and CH_2Cl_2 (CH_2Cl_2 : EtOAc, from 4:1 to 1:1/ v:v). After drying under vacuum overnight, the target product was obtained as a white powder with a yield of 91% (0.38 g). ^1H NMR (600 MHz, CDCl_3), δ_{H} [ppm]: 7.48 (m, 10H), 7.22(s, 4H), 6.85(d, $J = 6.4$ Hz, 4H), 6.82(s, 4H), 6.20 (s, 2H), 6.08 (s, 4H), 5.50 (s, 4H), 4.81 (s, 8H), 4.55 (t, $J = 6.8$ Hz, 8H), 3.99 (t, $J = 5.6$ Hz, 8H), 3.17(s, 4H), 2.73(t, $J = 7.6$ Hz, 8H), 2.46 (t, $J = 6.2$ Hz, 8H), 1.62(t, 8H), 1.50~1.10(m, 32H), 0.86(t, $J = 7.0$ Hz, 12H). ^{13}C NMR (150 MHz, CDCl_3), δ_{C} [ppm]: 161.4, 161.2, 158.4, 156.6, 155.4, 143.9, 138.8, 130.6, 129.1, 128.0, 125.5, 123.1, 120.6, 113.3, 112.3, 110.9, 109.5, 101.8, 64.8, 61.8, 47.1, 31.9, 31.7, 29.4, 29.0, 28.3, 22.6, 14.1. MALDI-TOF-MS: $m/z = 2095$, found $[\text{M}+\text{Na}]^+ = 2118$.

Compound 10: A 100 mL round bottom flask equipped with a magnetic stir bar was charged

with 3,5-dihydroxybenzyl alcohol (0.14 g, 1 mmol), compound **5** (0.84 g, 2.2 mmol), K₂CO₃ (2 g, 14.5 mmol), KI (0.1 g, 0.6 mmol), a catalytic amount 18-crown-6 (0.026 g, 0.1 mmol), and 50 mL of acetone. The mixture was stirred under reflux overnight and then cooled down to room temperature. After filtration, the solvent was concentrated by rotatory evaporation and purified by flash silica gel chromatography, eluting the product with hexanes and ethyl acetate (hexanes:EtOAc, from 9:1 to 1:1/v:v). The product was obtained as a white solid with yield of 70 % (0.52 g). ¹H NMR (600 MHz, CDCl₃), δ_H [ppm]: 7.49 (d, *J* = 8.4 Hz, 4H), 6.85(d, 2H), 6.82(s, 2H), 6.55(s, 2H), 6.39(s, 1H), 6.10 (s, 2H), 4.63(s, 2H), 4.17(m, 8H), 2.66 (t, *J* = 7.1 Hz, 4H), 2.26 (t, *J* = 5.8 Hz, 4H), 1.93(s, 1H), 1.66(m, 4H), 1.55~1.05 (b, 16H), 0.86 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃), δ_C [ppm]: 160.1, 156.7, 155.5, 143.7, 125.3, 112.7, 110.8, 105.4, 101.6, 100.5, 65.2, 64.9, 64.1, 31.9, 31.7, 29.4, 29.0, 28.3, 22.6, 14.1. HRMS-ESI: *m/z* [M+H]⁺ = 741.4003, found = 741.4003.

Compound 11: A 100 mL round bottom flask equipped with a magnetic stir bar was charged with compound **10** (0.74g, 1 mmol) in 30 mL of THF. Then CBr₄ (2.65 g, 8 mmol) and PPh₃ (2.1 g, 8 mmol) were separately added portionwise. After stirring at room temperature overnight, the mixture was filtered and THF was removed via rotatory evaporation. The crude product was purified by flash silica gel chromatography eluting with a mixture of hexanes, ethyl acetate, and CH₂Cl₂ (hexane:EtOAc:CH₂Cl₂, 1:1:1/v:v:v). The obtained yield was 73 % (0.59 g), and the resulting product was used for the next step without further purification. ¹H NMR (600 MHz, CDCl₃), δ_H [ppm]: 7.49 (d, *J* = 8.4 Hz, 4H), 6.85(d, *J* = 8.4 Hz, 1H), 6.82(s, 1H), 6.40(s, 3H), 6.09 (s, 2H), 4.372(s, 2H), 4.12(m, 8H), 2.68(t, *J* = 7.2 Hz, 4H), 2.26 (t, *J* = 5.8 Hz, 4H), 1.65(t, *J* = 6.8 Hz, 4H), 1.50~1.10(b, 16H), 0.86(t, *J* = 6.8 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃), δ_C

[ppm]: 161.6, 160.1, 156.6, 155.5, 125.4, 113.0, 112.6, 110.8, 107.7, 101.7, 64.9, 64.2, 31.8, 31.7, 29.4, 29.0, 28.3, 22.6, 14.1. HRMS-ESI: m/z $[M+H]^+ = 805.3159$, found = 805.3168.

0.4 g of the above product (0.5 mmol) and NaN_3 (0.65 g, 10 mmol) in 10 mL DMF were placed into a 100 mL round bottom flask, equipped with a magnetic stir bar, and stirred at 100 °C overnight. The mixture was poured into water and extracted with CH_2Cl_2 (3×30 mL). After drying the organic layer over anhydrous MgSO_4 , and removal of solvent by vacuum rotatory evaporation, the pure azide was obtained as a white solid with a yield of 94% (0.36 g). ^1H NMR (600 MHz, CDCl_3), δ_{H} [ppm]: 7.49 (d, $J = 8.7$ Hz, 4H), 6.85 (d, $J = 7.7$ Hz, 2H), 6.82 (s, 2H), 6.44 (s, 3H), 6.09 (s, 2H), 4.22 (s, 2H), 4.16 (m, 8H), 2.66 (t, $J = 6.8$ Hz, 4H), 2.26 (t, $J = 6.0$ Hz, 4H), 1.61 (t, $J = 6.0$ Hz, 4H), 1.50~1.10 (b, 16H), 0.86 (t, $J = 6.9$ Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3), δ_{C} [ppm]: 161.7, 160.3, 156.6, 155.5, 137.9, 125.4, 113.0, 112.6, 110.8, 106.7, 101.7, 101.2, 64.9, 64.2, 54.8, 31.9, 29.4, 29.0, 28.3, 22.6, 14.1. HRMS-ESI: m/z $[M+H]^+ = 766.4067$, found = 766.4064.

Compound 12: This monomer was synthesized according to a procedure similar to that for compound **9** using compound **8** and compound **11**. The product was obtained as an off-white powder with a yield of 90%. ^1H NMR (600 MHz, CDCl_3), δ_{H} [ppm]: 7.97 (s, 2H), 7.45 (m, 12H), 7.22 (s, 8H), 6.85 (d, $J = 6.4$ Hz, 8H), 6.82 (s, 8H), 6.40 (s, 8H), 6.18 (s, 2H), 6.05 (s, 8H), 5.86 (s, 4H), 5.35 (s, 8H), 4.78 (s, 8H), 4.16 (t, $J = 5.9$ Hz, 8H), 4.09 (t, $J = 5.8$ Hz, 8H), 3.16 (s, 4H), 2.63 (t, $J = 7.6$ Hz, 16H), 2.20 (t, $J = 5.9$ Hz, 16H), 1.61 (t, $J = 7.4$ Hz, 16H), 1.50~1.10 (m, 64H), 0.86 (t, 24H). ^{13}C NMR (150 MHz, CDCl_3), δ_{C} [ppm]: 161.7, 160.4, 158.4, 156.6, 155.5, 150.3, 138.8, 138.5, 136.8, 130.5, 128.0, 125.4, 122.8, 121.5, 120.5, 113.0, 112.6, 110.7, 109.5, 106.8,

101.6, 101.4, 101.0, 64.9, 64.4, 61.9, 54.2, 31.8, 29.4, 29.0, 28.2, 22.6, 14.1. MALDI-TOF-MS:
 $m/z = 3784$, found $[M+Na]^+ = 3807$.

General Procedure for Suzuki-Miyaura Cross-Coupling Polymerization:^{10,31} A 100 mL Schlenk tube equipped with a magnetic stir bar was charged with a mixture 7 mL toluene, 3 mL aqueous 2 M K_2CO_3 (aq.), 1-2 drops of Aliquat 336, new fluorene monomer decorated with coumarin units (compound **4**, **9** and **12**, respectively) (0.3 mmol), and 9,9'-didodecyfluorene-2,7-diboronic acid bis(1,3-propanediol)ester (0.201 g, 0.3 mmol). Then the mixture was degassed via sonication under continuous bubbling with Ar for 30 min. $Pd(PPh_3)_4$ (~ 1.0 mol %) was added, and the resulting mixture was stirred at 90 °C under Ar for 48 h. After cooling to room temperature, the mixture was poured into 300 mL of methanol. The precipitated material was recovered by filtration, and washed for 24 h using methanol (150 mL) and acetone (150 mL) separately, to remove oligomers and catalyst residues.

Polymer 1 (PFF): grey-beige powder, yield: 84%. 1H NMR (200 MHz, $CDCl_3$), δ_H [ppm]: 7.85 (br, 8 H), 7.65 (br, 4 H), 2.09 (br, 8 H), 1.13 (br, 56 H), 0.73 (br, 20 H). UV-vis (THF): $\lambda_{max} = 382$ nm, GPC: $M_n=6636$ g/ mol, $M_w=8693$, $M_w/M_n=1.31$.

Polymer 2: beige powder, yield: 75%, 1H NMR (600 MHz, $CDCl_3$), δ_H [ppm]: 7.80~7.40 (b, 12 H), 7.32~7.25 (b, overlapped with $CHCl_3$), 6.75 (m, 4H), 6.21 (b, 2 H), 5.21 (b, 2H), 3.92 (b, 4H), 2.06 (b, 8H), 1.26~1.55 (m, 72 H), 0.84 (b, 6 H). UV-vis (THF): $\lambda_{max}= 381$ nm, $M_n=8377$, $M_w=15956$, PDI=1.9.

Polymer 3: grey-beige powder, yield: 70%. ^1H NMR (600 MHz, CDCl_3), δ_{H} [ppm]: 7.70~7.30 (b, 23 H), 7.20~6.60(b & m, 8 H), 6.50~6.00(b, 12 H), 5.10~4.70 (b, 6 H), 4.60~4.40 (b, 8 H), 4.10~3.80 (b, 8 H), 3.40~3.20 (b, 4 H), 2.80~2.5 (b, 8 H), 2.45~2.20 (b, 8 H), 2.20~1.9 (b, 8 H), 1.70~1.55 (b, 8H), 1.18~1.09 (b, 60 H), 0.78 (t, 20 H). UV-vis (THF): λ_{max} = 328-370 nm (broad with two distinctive peaks), M_{n} =8403, M_{w} =12917, PDI=1.5.

Polymer 4: grey-beige powder, yield: 65%. ^1H NMR (600 MHz, CDCl_3), δ_{H} [ppm]: 7.70~7.30 (b, 19 H), 7.20(b, 4H), 7.00~6.60(b, 16 H), 6.50~6.20 (b, 14 H), 6.15~5.90 (b, 6 H), 5.4(b, 8 H), 4.7(b, 8 H), 4.30~3.80 (b, 32 H), 3.30~3.1 (b, 4 H), 2.80~2.5 (b, 12 H), 2.30~1.9 (b, 20 H), 1.70~1.5 (b, 14 H), 1.18~1.09 (b, 120 H), 0.78 (t, 30 H). UV-vis (THF): λ_{max} = 328-370 nm (broad with two distinctive peaks), M_{n} =7217, M_{w} =10300, PDI=1.4.

Preparation of the polymer and SWNT supramolecular complexes:^{10,23} A mixture of SWNTs (2.5 mg) and polymer (7.5 mg) in 10 ml THF was sonicated for 60 min. Undissolved SWNTs bundles and other impurities were removed by centrifugation at 8,300 g for 30 min. Then the homogeneous solution was filtered through a 200 nm-pore-diameter Teflon membrane and the residue was repeatedly washed with THF in order to remove excess free polymer (this is determined by disappearance of fluorescence in the filtrate). Then the polymer-SWNT complex was dissolved in 10 mL of THF again by sonicating for another 30 min, and undissolved parts were removed using centrifugation at 5,000 g for 35 min. The dark, clear supernatant solution was found to remain stable, without visible precipitation of nanotubes, for more than one year.

Dispersion of SWNTs in SDBS/D₂O:^{63,64} A SWNT sample (5 mg) was added to a solution of

sodium dodecylbenzene sulfonate (SDBS) (350 mg) in 35 mL D₂O. The resulting mixture was sonicated for 60 min using a bath sonicator, and centrifugation was done with an ultracentrifuge at 65,000 g for 4 h. The supernatant was carefully pipetted out of the centrifuge tube and used for subsequent studies.

Results and Discussion

Considering the lack of solubilizing side-chains on coumarin chromophores, introduction of 7-hydroxycoumarins as side chains on a fluorene monomer was expected to produce a poorly soluble structure that would lead to an insoluble polymer. It was therefore necessary to first produce a highly soluble coumarin derivative, which could then be incorporated as a monomer side chain. This was accomplished by initial molybdenum (VI) dichloride dioxide (MoO₂Cl₂) catalyzed condensation of octanal with ethyl diazoacetate to produce β -keto ester **1** (Scheme 1).⁵⁴ Subsequent reaction of **1** with resorcinol under acidic conditions resulted in the desired 4-heptyl-7-hydroxycoumarin **2**.⁵⁵ Reaction of 2,7-dibromo-9,9'-bis(6'-bromohexyl)fluorene (**3**), prepared according to literature procedures,⁵⁶ with **2** under standard Williamson ether synthesis conditions resulted in fluorene monomer **4**, decorated with two coumarin units (Scheme 1).

Scheme 1. Synthesis of fluorene monomer bearing two coumarins.

To increase the number of coumarins per fluorene monomer from 2 to 4 and 8, separate synthetic approaches were undertaken. First, coumarin **2** was treated with 1,3-dibromopropane, followed by reaction with NaN₃ to produce 7-(3-azidopropoxy)-4-heptylcoumarin (**6**) (see Scheme 2). Separately, 1-bromomethyl-3,5-bis(prop-2-ynoxy)benzene (**7**), which was prepared according to literature procedures,⁵⁷ was reacted with 2,7-dibromofluorene to produce the tetra-alkyne-decorated fluorene derivative **8**. Copper-catalyzed “click” coupling of coumarin azide **6** with tetra-alkyne **8** resulted in monomer **9**, bearing 4 coumarins (Scheme 2).

Scheme 2. Synthesis of fluorene monomer bearing 4 coumarins.

The corresponding monomer decorated with 8 coumarins was similarly prepared by a copper-catalyzed “click” coupling procedure (Scheme 3). First, 3,5-dihydroxy benzyl alcohol

399 was treated with coumarin bromide **5** to form an alcohol **10**, which was brominated and azidified
 400 to produce the bis-coumarin azide **11**. Standard “click” coupling of **11** with **8** resulted in the
 401 desired monomer **12**, bearing 8 coumarins (Scheme 3).

Scheme 3. Synthesis of fluorene monomer bearing 8 coumarins.

404 With coumarin-decorated monomers **4**, **9**, and **12** in hand, polymerizations using
 405 Suzuki-Miyaura cross-coupling chemistry with 9,9'-didodecylfluorene-2,7-diboronic acid
 406 bis(1,3-propanediol) as the co-monomer and tetrakis(triphenylphosphine)palladium ($\text{Pd}(\text{PPh}_3)_4$)
 407 were carried out as depicted in Scheme 4.^{42,58} In addition to polymerization of the three
 408 coumarin-decorated monomers, a model polymer (**P1**) with no coumarin decoration was also
 409 prepared using the commercially-available 9,9'-dioctyl-2,7-dibromofluorene as a model

monomer. Each of the coumarin-decorated copolymers, **P2-P4**, exhibited moderate solubility in common organic solvents, such as THF, CHCl_3 , and toluene. Although it was possible to determine the molecular weight by gel permeation chromatography (GPC) for **P1-P4** (Table 1), this data likely underestimates the actual molecular weight as solubility of the polymers (especially **P3** and **P4**) was limited. This prevented high molecular weight fractions from properly dissolving, thus biasing sample composition toward low molecular weights.

Scheme 4. Synthesis of polymers **P1-P4**.

Table 1. Properties of polymers **P1-P4**.

Polymer	λ_{max}	λ_{em}	M_n^a	M_w^a	PDI^a
P1	382	416	6,600	8,700	1.3
P2	381	416	8,400	16,000	1.9
P3	328-370 ^b	411	8,400	12,900	1.5
P4	328-370 ^b	409	7,200	10,300	1.4

^a Values determined by GPC; ^b Broad peak.

UV–Vis and photoluminescence (PL) spectroscopy were used to characterize the optical

properties of the four polymers in dilute THF solution at room temperature. UV-visible absorption spectra of polymers **P1-P4** are depicted in Figure 1a, and clearly show the effect of coumarin incorporation in the polymer side chains. Polymers **P1** and **P2** have almost identical absorption spectra as a result of their similarity in structure and molecular weight (Table 1), except for the absorption shoulder centered around 320 nm for polymer **P2**, caused by the coumarins. This coumarin absorption steadily increased, relative to the polyfluorene backbone absorption, in polymers **P3** and **P4**, which contain exponentially increasing numbers of coumarins. Interestingly, the steric hindrance and molecular distortion caused by the bulky side chains in **P3** and **P4** resulted in significant blue-shifts for the absorption of the polymer backbone, from ca. 380 nm to ca. 360 nm (Figure 1a). In addition, the applicability of the coumarin and polyfluorene backbone for FRET was investigated by comparing the emission spectrum of the coumarin with the absorption spectrum of the model polymer **P1**. As shown in Figure 1b, the emission spectrum of the coumarin almost entirely overlaps with the absorption spectrum of the polyfluorene backbone of **P1**. This spectral overlap indicates that efficient FRET should be possible between the coumarin energy donor and the polyfluorene energy acceptor.

Figure 1. (a) Normalized UV-Vis absorption spectra of **P1-P4** in THF; (b) Normalized UV-Vis absorption and PL spectra of compound **2** and model polymer **P1** in THF.

A comparison between the emission of coumarin **2** and that of the coumarin-decorated

polymer **P2** is given in Figure 2a. The high efficiency of FRET between the coumarin and the polyfluorene is clearly demonstrated by the nearly complete quenching of coumarin emission upon excitation at 320 nm. In this experiment, only emission from the polymer backbone, with a maximum at 420 nm, is observed. Interestingly, excitation of the polyfluorene backbone of **P2** at 382 nm resulted in significantly less emission intensity (Figure 2a, dotted curve), indicating that the coumarins provide a light-harvesting antenna effect in this polymer. However, when **P3** and **P4** are similarly excited at 320 nm, the emission intensity is much lower than that of **P2** (Figure 2b). This indicates that the steric hindrance of the dendritic side-chains in **P3** and **P4** changes the polymer backbone conformation, and dramatically affects its photophysical properties. In the spectrum of **P4**, a small shoulder at shorter wavelengths, corresponding to coumarin emission, also indicates that energy transfer efficiency is diminished in this polymer, likely as a result of the increased distance between donor coumarins and the polymer backbone acceptor. In addition, the fine structure of the emission spectra for **P3** and **P4** is significantly altered relative to **P1** and **P2**, with broader and less well-defined characteristics, along with a slight blue-shift of emission maxima. Again, this indicates that the polymer backbone adopts a different, likely more twisted conformation as a result of dendronization, which decreases the conjugation length in these polymer backbones.

Figure 2. (a) PL spectra of coumarin (**2**), $\lambda_{\text{ex}} = 320$ nm, and polymer **P2**, with $\lambda_{\text{ex}} = 320$ and 382 nm in THF. Vertical arrow denotes fluorescence quenching of the coumarin donors in **P2**. (b) Comparison of emission spectra of equimolar solutions of polymers **P2**, **P3**, and **P4**, with $\lambda_{\text{ex}} = 320$ nm.

The study of the supramolecular complex formation of these polymers with SWNTs was conducted according to previously reported procedures, and as described in the experimental section.^{41,42,59} Initial characterization of the polymer-SWNT complexes was carried out by UV-Vis-NIR absorption spectroscopy (Figure 3). The absorption spectra for SWNT complexes with each polymer, **P2-P4**, exhibit features corresponding to both the polymer absorption (below 450 nm) and SWNT absorption (van Hove singularities above 600 nm), as expected. A control sample, dispersed by the surfactant SDBS, shows the presence of similar SWNT absorption bands, but lacks the absorption corresponding to the polymers. This provides an indication that SWNTs were indeed dispersed by polymers **P2-P4** in THF.

Figure 3. UV-Vis-NIR spectra of SWNT complexes with **P2-P4** in THF. Spectra are vertically offset for clarity.

Raman spectroscopy also provided evidence for the presence of SWNTs in the polymer-SWNT dispersions. Sample preparation involved drop-casting the polymer-SWNT dispersions

onto glass slides and allowing them to air-dry prior to measurement. For all the spectra, excited at 785 nm, signals corresponding to the graphitic (G) and radial breathing mode (RBM) stretches were clearly observed (Figure 4). When compared to the spectrum corresponding to pristine SWNTs, it is clear that the RBM region (Figure 4b) exhibits a significantly decreased band at $\sim 265\text{ cm}^{-1}$. This band arises from bundled (10,2) SWNTs that come into resonance with 785 nm excitation, and is known as the “bundling” peak.⁶⁰ The significant decrease in intensity corresponding to this peak, relative to the spectrum of pristine SWNTs, indicates that SWNTs are well dispersed and exfoliated by the polymers **P2-P4** in solution, and remain exfoliated even upon sample drying.

Figure 4. Raman spectra of the polymer-SWNT complexes using an excitation wavelength of 785 nm, showing the entire spectral range (a), and the magnified RBM region (b). All spectra were normalized to the G-band at $\sim 1590\text{ cm}^{-1}$.

It was found that, upon adsorption of polymers **P2-P4** onto the surface of SWNTs, polymer fluorescence was quenched with near-quantitative efficiency by the nanotubes. Figure 5 compares the polymer emission upon excitation at either the λ_{max} of the coumarin donor chromophores (320 nm), or at the λ_{max} of the polymer backbone (380 nm for **P2** and 370 nm for **P3-P4**), with and without SWNT adsorption. As already discussed, the polymer emission is

499 more intense for **P2** and **P3** upon excitation of the donors, while in **P4** the increased distance
500 between coumarins and the polymer backbone, as well as the change in polymer conformation,
501 cause the sensitized emission to be less intense than the emission from direct excitation.
502 However, regardless of the polymer or excitation wavelength, emission was nearly completely
503 quenched for the polymer-SWNT complexes. This indicates that efficient energy or electron
504 transfer is occurring from both the polymer backbone and the coumarin donors to the nanotube
505 surface. In the case of **P2** and **P3**, it is expected that rapid energy transfer from the coumarins to
506 the polymer backbone is followed by a second transfer to the nanotube on which the polymers
507 are adsorbed. In the case of **P4**, the low-wavelength shoulder in the stimulated emission
508 spectrum ($\lambda_{\text{ex}} = 320 \text{ nm}$) is indicative of a decreased energy transfer efficiency between the
509 coumarins and the polymer (Figure 5c). However, upon adsorption to the nanotube surface, both
510 coumarin and polymer emission is again efficiently quenched. In this case, it is possible that
511 direct energy transfer to the nanotube competes with energy transfer to the polyfluorene
512 backbone. The overall quenching efficiencies for each of the polymer-SWNT complexes upon
513 excitation of either the coumarins or the polyfluorene backbone are given in Table 2.

Figure 5. PL spectra of copolymers and copolymer-SWNT complexes in THF (a) **P2** and **P2-SWNT** excited at 320 and 370 nm; (b) **P3** and **P3-SWNT** excited at 320 and 370 nm; (c) **P4** and **P4-SWNT** excited at 320 and 370 nm.

Table 2. Quenching efficiencies for each of the polymer-SWNT complexes.

Polymer-SWNT Complex	Excitation Wavelength (nm)	Quenching Efficiency (%)
P2-SWNT	320	95
	380	96
P3-SWNT	320	90
	380	93
P4-SWNT	320	94
	380	97

To identify the composition of the SWNTs dispersed by the polymers, photoluminescence excitation maps (PLE) of the polymer-SWNT complexes were also measured. Figure 6 depicts the PLE maps of SWNTs dispersed in THF using **P1-P4**. For reference, the PLE map of just the nanotubes dispersed in D₂O using SDBS is also shown. In these maps, areas of high intensity are depicted in red and areas of low intensity are depicted in blue. The chiral indices (*n*, *m*) for the identified species are labeled on the maps, where the assignments are based on previously reported results.⁸ The PLE map of the pristine SWNT sample dispersed in D₂O using SDBS (Figure 6e) shows the presence of more than 17 different semiconducting nanotubes, a distribution that is similar to what has previously been reported.⁶¹ When the same commercial sample of nanotubes was mixed with polymers **P1-P4** in THF, fluorescence signals from different subsets of dispersed SWNTs were obtained. It should be noted that both excitation and emission wavelengths of the polymer-SWNT complexes were red-shifted by 10-30 nm relative to the signals observed with SDBS in aqueous solution, which is consistent with previously reported comparable systems.^{33,41,61,62} Interestingly, the SWNT composition within dispersions produced with **P1** and **P2** are very similar, dominated by the emission from (6, 5), (7, 5), and (7, 6) chiralities. The increasing steric bulk around the polymer backbone in **P3** and **P4** seems to decrease the selectivity of these polymers for specific

chiralities, as many more fluorescent spots are observed in the PLE maps of dispersions produced with these polymers. It is likely that a helical conformation cannot be achieved with the more bulky side-chains of **P3** and **P4**, and thus these polymers adsorb in a non-specific manner on the nanotube surface. The less bulky **P1** and **P2** can more effectively form helical assemblies, and will preferentially interact with certain nanotube diameters.

Figure 6. PL contour maps of HiPco SWNTs dispersed with P1 in THF (a), P2 in THF (b), P3 in THF (c), P4 in THF (d), and with SDBS in D₂O (e).

Conclusions

A series of coumarin containing new dendron type fluorene monomers were successfully synthesized and their copolymers with 2,7-dibromo-9,9'-didodecylfluorene were obtained using Suzuki-Miyaura cross-coupling reaction. These coumarin containing polymers showed moderate solubility in various common organic solvents such as THF, toluene, CHCl_3 , and can solubilize SWNTs in these solvents to different levels. All of the precursors, monomers, and polymers were characterized by ^1H NMR, ^{13}C NMR and MS. Physical chemistry properties of the polymers were characterized utilizing UV-Vis, TGA and fluorescence spectroscopy. Besides excellent photoluminescence, all of the polymer-SWNT complexes exhibited good photoluminescence quenching as a sign of highly efficient energy transfer between the coumarins and the polymer backbone, and polymer with SWNTs in THF. These characteristics are very important for their potential application as light harvesting and energy conversion complexes.

Acknowledgements. Financial support for this work was provided by the Natural Science and Engineering Research Council of Canada (NSERC), the NSERC Photovoltaic Innovation Network, the Canada Foundation for Innovation (CFI), and the Ontario Innovation Trust (OIT).

References

- (1) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603–605.
- (2) Yu, M.-F.; Files, B.; Arepalli, S.; Ruoff, R. *Phys. Rev. Lett.* **2000**, *84*, 5552–5555.
- (3) Han, Z.; Fina, A. *Prog. Polym. Sci.* **2011**, *36*, 914–944.
- (4) Avouris, P.; Chen, Z.; Perebeinos, V. *Nat. Nanotechnol.* **2007**, *2*, 605–615.

- 575 (5) Avouris, P. *Acc. Chem. Res.* **2002**, 35, 1026–1034.
- 576 (6) Collins, P. G.; Avouris, P. *Sci. Am.* **2000**, 283, 62–69.
- 577 (7) O’Connell, M. J.; Bachilo, S. M.; Huffman, C. B.; Moore, V. C.; Strano, M. S.; Haroz, E.
578 H.; Rialon, K. L.; Boul, P. J.; Noon, W. H.; Kittrell, C.; Ma, J.; Hauge, R. H.; Weisman,
579 R. B.; Smalley, R. E. *Science* **2002**, 297, 593–596.
- 580 (8) Weisman, R. B.; Bachilo, S. M. *Nano Lett.* **2003**, 3, 1235–1238.
- 581 (9) Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Umez, I.; Suzuki, S.; Ohtsuka, Y.; Achiba, Y.
582 *Synth. Met.* **1999**, 103, 2555–2558.
- 583 (10) Terrones, M. *Annu. Rev. Mater. Res.* **2003**, 33, 419–501.
- 584 (11) Dürkop, T.; Getty, S. A.; Cobas, E.; Fuhrer, M. S. *Nano Lett.* **2004**, 4, 35–39.
- 585 (12) Qi, P.; Vermesh, O.; Grecu, M.; Javey, A.; Wang, Q.; Dai, H.; Peng, S.; Cho, K. J. *Nano*
586 *Lett.* **2003**, 3, 347–351.
- 587 (13) Dionisio, M.; Schnorr, J. M.; Michaelis, V. K.; Griffin, R. G.; Swager, T. M.; Dalcanele,
588 E. *J. Am. Chem. Soc.* **2012**, 134, 6540–6543.
- 589 (14) Rivas, G. a.; Rubianes, M. D.; Rodríguez, M. C.; Ferreyra, N. F.; Luque, G. L.; Pedano,
590 M. L.; Miscoria, S. a.; Parrado, C. *Talanta* **2007**, 74, 291–307.
- 591 (15) Pang, X.; Imin, P.; Zhitomirsky, I.; Adronov, A. *Macromolecules* **2010**, 43, 10376–10381.
- 592 (16) Pang, X.; Imin, P.; Zhitomirsky, I.; Adronov, A. *J. Mater. Chem.* **2012**, 22, 9147.
- 593 (17) Rowell, M. W.; Topinka, M. a.; McGehee, M. D.; Prall, H. J.; Dennler, G.; Sariciftci, N.
594 S.; Hu, L.; Gruner, G. *Appl. Phys. Lett.* **2006**, 88, 233506.

- 595 (18) Bindl, D. J.; Safron, N. S.; Arnold, M. S. *ACS Nano* **2010**, *4*, 5657–5664.
- 596 (19) Keru, G.; Ndungu, P. G.; Nyamori, V. O. *Int. J. Energy Res.* **2014**, *38*, 1635–1653.
- 597 (20) Sun, D. M.; Liu, C.; Ren, W. C.; Cheng, H. M. *Small* **2013**, *9*, 1188–1205.
- 598 (21) Hecht, D. S.; Ladous, C.; Drzaic, P.; Fellow, S. I. D. *J. SID* **2009**, *17*, 941–946.
- 599 (22) De Volder, M. F. L.; Tawfick, S. H.; Baughman, R. H.; Hart, J. A. *Science* **2013**, *339*,
600 535–539.
- 601 (23) Jariwala, D.; Sangwan, V. K.; Lauhon, L. J.; Marks, T. J.; Hersam, M. C. *Chem. Soc. Rev.*
602 **2013**, *42*, 2824–2860.
- 603 (24) Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, F.; Colbert, D. T.; Smith, K.
604 a; Smalley, R. E. *Chem. Phys. Lett.* **1999**, *313*, 91–97.
- 605 (25) Kong, J.; Cassell, A. M. *Chem. Phys. Lett.* **1998**, *292*, 567–574.
- 606 (26) Journet, C.; Maser, W. K.; Bernier, P.; Loiseau, a. *Nature* **1997**, *388*, 20–22.
- 607 (27) Guo, T.; Nikolaev, P.; Thess, A.; Colbert, D. T.; Smalley, R. E. *Chem. Phys. Lett* **1995**,
608 *243*, 49–54.
- 609 (28) Kim, K. S.; Cota-Sanchez, G.; Kingston, C. T.; Imris, M.; Simard, B.; Soucy, G. *J. Phys.*
610 *D. Appl. Phys.* **2007**, *40*, 2375–2387.
- 611 (29) Arnold, M. S.; Green, A. A.; Hulvat, J. F.; Stupp, S. I.; Hersam, M. C. *Nat. Nanotechnol.*
612 **2006**, *1*, 60–65.
- 613 (30) Liu, H.; Tanaka, T.; Kataura, H. *J. Phys. Chem. C* **2010**, *114*, 9270–9276.
- 614 (31) Tanaka, T.; Jin, H.; Miyata, Y.; Kataura, H. *Appl. Phys. Express* **2008**, *1*, 114001.1–

- 615 114001.3.
- 616 (32) Nish, A.; Hwang, J. Y.; Doig, J.; Nicholas, R. J. *Nat. Nanotechnol.* **2007**, *2*, 640–646.
- 617 (33) Lemasson, F. A.; Strunk, T.; Gerstel, P.; Hennrich, F.; Lebedkin, S.; Barner-Kowollik, C.;
618 Wenzel, W.; Kappes, M. M.; Mayor, M. *J. Am. Chem. Soc.* **2011**, *133*, 652–655.
- 619 (34) Rice, N. A.; Adronov, A. *J. Polym. Sci. Part A-Polymer Chem.* **2014**, *52*, 2738–2747.
- 620 (35) Ding, J.; Li, Z.; Lefebvre, J.; Cheng, F.; Dubey, G.; Zou, S.; Finnie, P.; Hrdina, A.; Scoles,
621 L.; Lopinski, G. P.; Kingston, C. T.; Simard, B.; Malenfant, P. R. L. *Nanoscale* **2014**, *6*,
622 2328–2339.
- 623 (36) Lee, H. W.; Yoon, Y.; Park, S.; Oh, J. H.; Hong, S.; Liyanage, L. S.; Wang, H. L.;
624 Morishita, S.; Patil, N.; Park, Y. J.; Park, J. J.; Spakowitz, A.; Galli, G.; Gygi, F.; Wong,
625 P. H.-S.; Tok, J. B.-H.; Kim, J. M.; Bao, Z. A. *Nat. Commun.* **2011**, *2*, 541.
- 626 (37) Imin, P.; Cheng, F. Y.; Adronov, A. *Polym. Chem.* **2011**, *2*, 1404–1408.
- 627 (38) Keogh, S. M.; Hedderman, T. G.; Gregan, E.; Farrell, G.; Chambers, G.; Byrne, H. J. *J.*
628 *Phys. Chem. B* **2004**, *108*, 6233–6241.
- 629 (39) Rice, N. A.; Soper, K.; Zhou, N.; Merschrod, E.; Zhao, Y. *Chem. Commun.* **2006**, *4*,
630 4937–4939.
- 631 (40) Liang, S.; Chen, G.; Peddle, J.; Zhao, Y. *Chem. Commun.* **2012**, *48*, 3100.
- 632 (41) Rice, N. A.; Adronov, A. *Macromolecules* **2013**, *46*, 3850–3860.
- 633 (42) Cheng, F.; Imin, P.; Maunders, C.; Botton, G.; Adronov, A. *Macromolecules* **2008**, *41*,
634 2304–2308.

- 635 (43) Chen, J.; Liu, H.; Weimer, W. a.; Halls, M. D.; Waldeck, D. H.; Walker, G. C. *J. Am.*
636 *Chem. Soc.* **2002**, *124*, 9034–9035.
- 637 (44) Cioffi, C.; Campidelli, S.; Sooambar, C.; Marcaccio, M.; Marcolongo, G.; Meneghetti,
638 M.; Paolucci, D.; Paolucci, F.; Ehli, C.; Rahman, G. M. A.; Sgobba, V.; Guidi, D. M.;
639 Prato, M. *J. Am. Chem. Soc.* **2007**, *129*, 3938–3945.
- 640 (45) Murray, R. D. H. *The Natural Coumarins, Occurrence, Chemistry, and Biochemistry*;
641 Wiley: New York, 1982.
- 642 (46) Reynolds, G. A.; Drexhage, K. H. *Opt. Commun.* **1975**, *13*, 222–225.
- 643 (47) Jones, G.; Jackson, W. R.; Choi, C.; Bergmark, W. R. *J. Phys. Chem.* **1985**, *89*, 294–300.
- 644 (48) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701–1710.
- 645 (49) Vasylevska, A. S.; Karasyov, A. A.; Borisov, S. M.; Krause, C. *Anal. Bioanal. Chem.*
646 **2007**, *387*, 2131–2141.
- 647 (50) Briñas, R. P.; Troxler, T.; Hochstrasser, R. M.; Vinogradov, S. A. *J. Am. Chem. Soc.*
648 **2005**, *127*, 11851–11862.
- 649 (51) Van Der Meer, B. W.; Coker, G.; Simon Chen, S. Y. *Resonance Energy Transfer, Theory*
650 *and Data*; Wiley-VCH: Weinheim, 1994.
- 651 (52) Förster, T. *Ann Phys* **1948**, *2*, 55.
- 652 (53) Förster, T. *Z. Naturforsch.* **1949**, *4*, 321.
- 653 (54) Jeyakumar, K.; Chand, D. K. *Synthesis* **2008**, *11*, 1685–1687.
- 654 (55) Afri, M.; Gottlieb, H. E.; Frimer, A. A. *Free Radic. Biol. Med.* **2002**, *32*, 605–618.

- 655 (56) Liu, B.; Bazan, G. C. *Nat. Protoc.* **2006**, *1*, 1698–1702.
- 656 (57) Antoni, P.; Nyström, D.; Hawker, C. J.; Hult, A.; Malkoch, M. *Chem. Commun.* **2007**,
657 2249–2251.
- 658 (58) Chadwick, R. C.; Kardelis, V.; Liogier, S.; Adronov, A. *Macromolecules* **2013**, *46*, 9593–
659 9598.
- 660 (59) Imin, P.; Imit, M.; Adronov, A. *Macromolecules* **2011**, *44*, 9138–9145.
- 661 (60) Heller, D. A.; Barone, P. W.; Swanson, J. P.; Mayrhofer, R. M.; Strano, M. S. *J. Phys.*
662 *Chem. B* **2004**, *108*, 6905–6909.
- 663 (61) Hwang, J.-Y.; Nish, A.; Doig, J.; Douven, S.; Chen, C.-W.; Chen, L.-C.; Nicholas, R. J. *J.*
664 *Am. Chem. Soc.* **2008**, *130*, 3543–3553.
- 665 (62) Rice, N. A.; Subrahmanyam, A. V.; Coleman, B. R.; Adronov, A. *Macromolecules* **2015**,
666 *48*, 5155–5161.
- 667 (63) Cheng, F. Y.; Imin, P.; Lazar, S.; Botton, G. A.; de Silveira, G.; Marinov, O.; Deen, J.;
668 Adronov, A. *Macromolecules* **2008**, *41*, 9869–9874.
- 669 (64) Imin, P.; Imit, M.; Adronov, A. *Macromolecules* **2011**, *44*, 9138–9145.
- 670
- 671

672 TOC Graphic

673

Draft