

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231700972>

Terthiophene-Jacketed Poly(benzyl ether) Dendrimers: Sonication Synthesis, Electropolymerization, and Polythiophene Film Formation

ARTICLE *in* MACROMOLECULES · DECEMBER 2010

Impact Factor: 5.8 · DOI: 10.1021/ma1017023

CITATIONS

10

READS

46

5 AUTHORS, INCLUDING:



Jin young Park

Kyungpook National University

38 PUBLICATIONS 441 CITATIONS

SEE PROFILE



Rigoberto C. Advincula

Case Western Reserve University

331 PUBLICATIONS 7,169 CITATIONS

SEE PROFILE

Terthiophene-Jacketed Poly(benzyl ether) Dendrimers: Sonication Synthesis, Electropolymerization, and Polythiophene Film Formation

Ramakrishna Ponnappati, Mary Jane Felipe, Jin Young Park, Jonathan Vargas, and Rigoberto Advincula*

Department of Chemistry and Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204-5003, United States

Received July 28, 2010; Revised Manuscript Received November 11, 2010

ABSTRACT: We report the design and synthesis of a series of poly(benzyl ether)-type terthiophene-jacketed dendrimers. These dendrimers were designed as precursor macromolecules, which bear the electroactive terthiophene group that can be cross-linked by electrochemical methods to form a conjugated polymer network (CPN) polythiophene film. Characterization was done by NMR, elemental analysis, MALDI-TOF, and GPC to confirm the chemical structure and macromolecular properties of the dendrimers. Spectroscopic studies of thin films made by electropolymerization of these materials show the role that the dendrimer structure plays in the UV–vis absorption and emission properties of a highly cross-linked conjugated polymer film compared to linear polymers. The distinction is more evident in their emission behavior. Copolymerization studies in particular were made to investigate the formation of more linear π -conjugated sequences and their effect in the spectroscopic properties. The results showed improved intermolecular cross-linking with the formation of more emissive species in the visible region of the spectrum. Spectroelectrochemistry studies of these materials showed a highly reversible electrochromic switching behavior for the films.

Introduction

Dendrimers with electroactive groups at the periphery are of current interest for research in designing efficient organic materials for devices and sensor applications.¹ π -Conjugated polymers such as polythiophene, polypyrrole, polycarbazole, etc., have been studied for their electrical conducting behavior through doping of their linear π systems or by charge carrier generation.² It has been assumed that the efficiency of the charge-carrier transport properties depends on the conjugation length of the “one-dimensional” polymers.³ A wide range of flexible-backbone and rigid-backbone dendrimers such as polyphenylacetylene,⁴ polyphenylenevinylene,⁵ polythiophene,⁶ and polyphenylene⁷ dendrimers have been reported recently. Further studies indicate the importance of persistence length and oligomeric derivatives in determining electro-optical property control and limits.⁸ However, there is no clear understanding of 2D or even 3D charge transport in a networked conjugated polymer structure including energy transfer and emission properties. Recently, our group has focused on electropolymerization approaches using both linear and dendrimeric precursors to form conjugated polymer networks (CPN).⁹ It is expected that dendrimers can provide another insight into the mechanism of electropolymerization owing to their monodispersed, highly branched, and structurally regular macromolecular structures. For example, the synthesis of carbazole-terminated dendrimers to form cross-linked nano-objects has been reported.¹⁰

In order to expand the scope of dendrimer synthesis, recently, we have developed a high yielding and faster poly(benzyl ether) dendrimer synthetic route using sonochemistry, which led to highly comparable yields to the conventional route within hours rather than days.^{9b} Sonication¹¹ and microwave¹² methods have long been employed for enhancing the rate of chemical reactions.

In this case they facilitate high yield and short reaction times for convergent dendrimer synthesis via etherification.

In this work, we report on the convergent synthesis and characterization of a series of terthiophene-jacketed poly(aryl ether) dendrimers. To our knowledge, this is the first attempt to synthesize Fréchet-type poly(aryl ether) dendrons and dendrimers with terthiophene at the periphery. In our design, both the α -positions of the terthiophene are made available for electropolymerization to produce polythiophene-jacketed dendrimers. We have chosen the terthiophene at the periphery of the dendrimers because of the increasing importance of thiophene derivatives in organic electronics research. Thiophene derivatives are one of the most attractive chromophores in photochemistry and have been extensively studied for other electro-optical devices.¹³ Dendrimers with terthiophene at the periphery are also attractive due to their high electroactivity to form a CPN upon electropolymerization or chemical oxidation. There have been a few reports describing the electropolymerization of the peripheral groups on a dendrimer. For example, in one of our studies we have demonstrated the cross-linking of the peripheral carbazole groups of a carbazole-terminated PAMAM dendrimers.¹⁴ Similarly, Crooks et al.¹⁵ have reported the cross-linking of thiophene-terminated PAMAM dendrimers. In our present design, we have chosen the poly(benzyl ether) dendrimer scaffold instead of a linear chain polymer not only to enhance the solubility of the resulting polymer but also to investigate the optoelectronic film properties as a function of dendrimeric generation. Also, the poly(aryl ether) backbone possesses a lower T_g and could undergo conformational changes as a function of generation, which could allow fine-tuning of their electro-optical properties.

Experimental Part

Materials. All the chemicals were purchased from Aldrich Chemical Co. and were used without further purification unless otherwise specified. Solvents were properly distilled to the right purity and used immediately.

*Corresponding author. E-mail: radvincula@uh.edu. Fax: 713-743-1755.

Characterization. NMR spectra were recorded using a General Electric QE 300 spectrometer (^1H 300 MHz). UV-vis spectra were recorded using an Agilent 8453 spectrometer. Fluorescence spectra were obtained on a Perkin-Elmer LS-45 luminescence spectrometer. Elemental analysis was done (samples sent) by Atlantic Analytical Microlabs. The size exclusion chromatography (SEC) or gel permeation chromatography (GPC) analysis was performed using a Viscotek 270 quad detector equipped with a VE3210 UV-vis detector and a VE3580 RI detector. The columns used for finding SEC number-average molecular weight (M_n) type are G3000HHR and GHMHR-M Viscogel. To assess more clearly the identity of the chemical structures, further characterization was performed using MALDI-TOF (matrix-assisted laser desorption ionization time-of-flight) mass spectroscopy (Perseptive Biosystems). The sample was prepared by a method called "thin layer application" using *trans*-3-indoleacrylic acid (IAA) as a matrix. All generations of the dendrimers showed the corresponding ion peak of $M^+ + \text{Na}$.

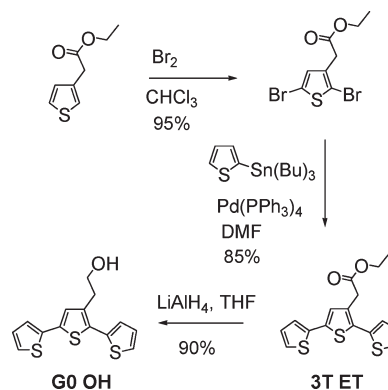
Cyclic voltammetry (CV) was performed on an Amel 2049 potentiostat and power lab/4SP system with a three-electrode cell. In all the measurements the counter electrode was platinum wire and indium tin oxide (ITO) or gold-coated glass as working electrode. The ITO was pretreated with the RCA recipe ($\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NH}_3$; 15.1 g/26.6 g/8.57 g). The gold electrodes were cleaned with a plasma ion cleaner (Plasmod, March). Ag/AgCl was used as a reference electrode.

Synthesis. *Synthesis of Ethyl 2-(2,5-Di(thiophen-2-yl)thiophen-3-yl)acetate (3T ET) (Figure 1).* The synthesis of 3T ET was carried by first synthesizing ethyl 2-(2,5-dibromothiophen-3-yl)acetate as reported in the literature.^{9a} The same literature procedure was modified to synthesize 3T ET. Ethyl 2-(2,5-dibromothiophen-3-yl)acetate (6.4 g, 10 mmol) and 2-(tributylstannyl)thiophene (15 g, 20 mmol) were added to a 30 mL dry DMF solution of dichlorobis(triphenylphosphine)palladium (1.3 g, 1.5 mmol). After three freeze-thaw cycles, the mixture was heated at 100 °C for 48 h. The mixture was cooled to room temperature and poured into a beaker containing 150 mL of water and subsequently extracted with CH_2Cl_2 . The extracted CH_2Cl_2 mixture was dried with Na_2SO_4 . After filtering and evaporation of the solvent, the crude product was purified by chromatography on silica gel using toluene as an eluent. The final product was obtained in 85% yield as pale yellow oil. The characterization of the compound was found in accordance with the literature.^{9a}

Synthesis of 2-(2,5-Di(thiophen-2-yl)thiophen-3-yl)ethanol (G0 OH) (Scheme 1). The compound 3T ET (2 g, 5.9 mmol) in 10 mL of THF was dropwise added under nitrogen to an ice-cooled 100 mL THF suspension of LiAlH_4 (0.32 g, 8.4 mmol). Upon addition, the color of the solution immediately turns red. After complete addition, the ice bath was removed and the reaction was allowed to warm to room temperature and constant stirring was maintained for 12 h. The reaction was quenched by adding water and neutralized by 2 N HCl solution. The red color of the solution immediately turns yellow upon neutralization. The solvent was evaporated, and the resulting mixture was extracted three times using CH_2Cl_2 . The combined CH_2Cl_2 extracts were further washed with water and brine. The organic layer was dried with Na_2SO_4 . After filtering and evaporating CH_2Cl_2 , the reaction mixture was chromatographed using 4:1 CH_2Cl_2 :hexane mixture as eluent. The final product was obtained in 90% yield as oil, which solidifies upon vacuum or even at room temperature if kept for a longer time. ^1H NMR (CDCl_3): (δ ppm) 7.31–7.04 (m, 7H), 3.88 (q, 2H, $J = 6.4$ Hz), 3.01 (t, 2H, $J = 6.4$ Hz). ^{13}C NMR: 136.8, 135.8, 135.7, 135.2, 131.2, 127.8, 127.5, 126.4, 126.3, 125.7, 124.6, 123.8, 62.7, 32.4.

General Method for Etherification Reactions (Method A). The Mitsunobu etherification method was performed using sonication conditions according to a literature procedure reported by our group recently.^{9b} The mixture of alcohol, phenol (or aromatic carboxylic acid), and triphenylphosphine (PPh_3) in minimal THF was cooled to 5 °C with an ice bath and sonicated for

Scheme 1. Synthesis of G0 OH Terthiophene Dendron



5 min. Under sonication, a solution of diisopropyl azodicarboxylate (DIAD) was added dropwise under nitrogen. The water temperature was allowed to warm to room temperature, and precautions were taken to maintain the temperature. (Caution: water in the sonicator turns very hot if sonicated for a long time.) Sonication was performed until the reaction was completed as indicated by TLC. The product was purified using toluene as an eluent by silica gel column chromatography.

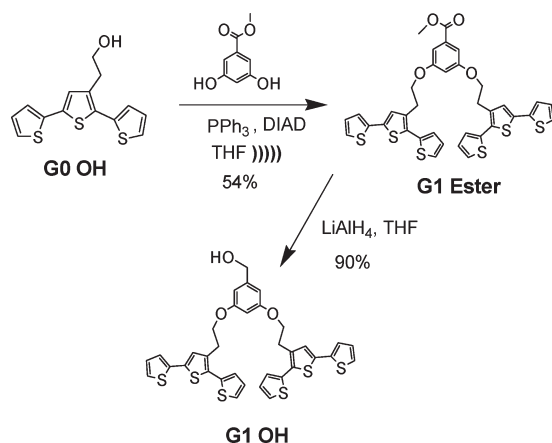
General Method for Lithium Aluminum Hydride (LAH) Reduction of Aromatic Esters to Benzylic Alcohols (Method B). The aromatic ester was added dropwise to a suspension of LAH in THF cooled to 0 °C with an ice bath. The suspension was then allowed to warm to room temperature and stirred until the reaction was completed as indicated by TLC. The reaction was quenched by adding water, and the THF was removed under reduced pressure in a rotary evaporator. The resulting layer was brought to a neutral pH with the addition of 2 N HCl solution and extracted with CH_2Cl_2 . The organic layer were combined, washed with water, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The product was purified by silica gel flash column chromatography using toluene as eluent.

Synthesis of Methyl 3-(2-(2,5-Di(thiophen-2-yl)thiophen-3-yl)ethoxy)-5-(2-(5-(thiophen-2-yl)-2-(thiophen-3-yl)thiophen-3-yl)ethoxy)benzoate (G1 Ester) (Scheme 2). Following the general synthesis method A as described above, a precooled solution of methyl 3,5-dihydroxybenzoate (0.756 g, 4.6 mmol), G0 OH (3 g, 10.2 mmol), and PPh_3 (2.67 g, 10.3 mmol) in THF under sonication was treated with a solution of DIAD (2.06 g, 10.3 mmol) in 3 mL of THF under nitrogen. The solution was sonicated for 3 h to afford a pale yellow solid product in 54% yield after purification. ^1H NMR (CDCl_3): δ (ppm) 7.33–7.02 (m, 16H), 6.64 (t, 1H, $J = 2$ Hz), 4.21 (t, 4H, $J = 7$ Hz), 3.88 (s, 3H), 3.23 (t, 4H, $J = 7$ Hz). Calcd: C, 60.31; H, 3.94; O, 8.93; S, 26.83. Found: C, 60.68; H, 4.19; O, 8.72; S, 26.41.

Synthesis of (3-(2-(2,5-Di(thiophen-2-yl)thiophen-3-yl)ethoxy)-5-(2-(5-(thiophen-2-yl)-2-(thiophen-3-yl)thiophen-3-yl)ethoxy)phenyl)methanol (G1 OH) (Scheme 2). Following the general synthesis method B as described above, the reaction of LAH (0.175 g, 4.7 mmol) in 300 mL of THF with a solution of G1 ester (2 g, 2.7 mmol) in 20 mL of THF afforded white solid in 90% yield. ^1H NMR (CDCl_3): δ (ppm) 7.33–7.00 (m, 14H), 6.52 (d, 2H, $J = 2$ Hz), 6.38 (t, 1H, $J = 2$ Hz), 4.60 (s, 2H), 4.21 (t, 4H, $J = 7$ Hz), 3.23 (t, 4H, $J = 7$ Hz). Calcd: C, 61.01; H, 4.10; O, 6.97; S, 27.92. Found: C, 61.26; H, 4.12; O, 6.78; S, 27.84.

Synthesis of Methyl 3,5-Bis(3-(2-(2,5-di(thiophen-2-yl)thiophen-3-yl)ethoxy)-5-(2-(5-(thiophen-2-yl)-2-(thiophen-3-yl)thiophen-3-yl)ethoxy)benzyloxy)benzoate (G2 Ester) (Scheme 3). Following the general synthesis method A as described above, a precooled solution of methyl 3,5-dihydroxybenzoate (0.221 g, 1.31 mmol), G1 OH (2 g, 2.9 mmol), and PPh_3 (0.786 g, 3 mmol) in THF under sonication was treated with a solution of DIAD (0.606 g, 3 mmol) in 2 mL of THF under nitrogen. The solution was sonicated for 3 h to afford a yellow solid product in 45% yield after

Scheme 2. Synthesis of G1 OH Terthiophene Dendron



purification. ^1H NMR (CDCl_3): δ (ppm) 7.33–7.00 (m, 30H), 6.76 (t, 1H, $J = 2$ Hz), 6.55 (d, 4H, $J = 2$ Hz), 6.40 (t, 2H, $J = 2$ Hz), 4.94 (s, 4H), 4.16 (t, 8H, $J = 7$ Hz), 3.86 (s, 3H), 3.20 (t, 8H, $J = 7$ Hz). Calcd: C, 62.04; H, 4.00; O, 8.48; S, 25.48. Found: C, 61.91; H, 4.12; O, 8.76; S, 25.21.

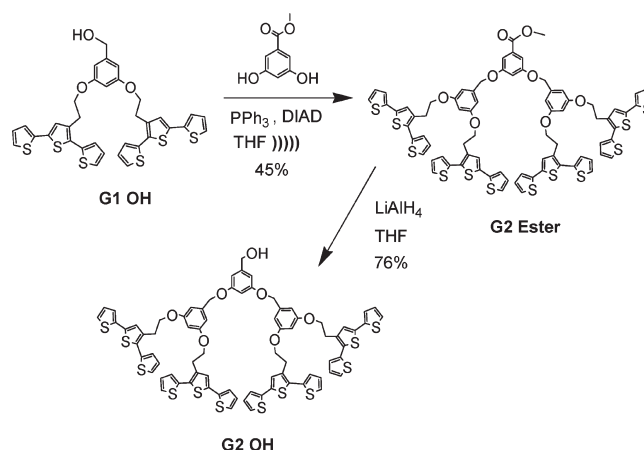
Synthesis of (3,5-Bis(3-(2-(2,5-di(thiophen-2-yl)thiophen-3-yl)ethoxy)-5-(2-(5-(thiophen-2-yl)-2-(thiophen-3-yl)thiophen-3-yl)ethoxy)benzyloxy)phenyl)methanol (G2 OH) (Scheme 3). Following the general synthesis method B as described above, the reaction of LAH (0.085 g, 2.2 mmol) in 300 mL of THF with a solution of G2 ester (2 g, 1.3 mmol) in 15 mL of THF afforded a yellow solid in 76% yield. ^1H NMR (CDCl_3): δ (ppm) 7.33–7.00 (m, 28H), 6.58 (d, 2H, $J = 2$ Hz), 6.55 (d, 4H, $J = 2$ Hz), 6.51 (t, 1H, $J = 2$ Hz), 6.39 (t, 2H, $J = 2$ Hz), 4.92 (s, 4H), 4.60 (s, 2H), 4.16 (t, 8H, $J = 7$ Hz), 3.20 (t, 8H, $J = 7$ Hz). Calcd: C, 62.40; H, 4.08; O, 7.56; S, 25.96. Found: C, 62.45; H, 4.07; O, 7.72; S, 25.76.

Synthesis of Tris(2-(2,5-di(thiophen-2-yl)thiophen-3-yl)ethyl)-benzene-1,3,5-tricarboxylate [G0 D] (Scheme 4). Following the general synthesis method A as described above, a precooled solution of benzene-1,3,5-tricarboxylic acid (63 mg, 0.3 mmol), G0 OH (292 mg, 1 mmol), and PPh_3 (262 mg, 1 mmol) in THF under sonication was treated with a solution of DIAD (202 mg, 1 mmol) in 2 mL of THF under nitrogen. The solution was sonicated for 8 h to afford yellow solid product in 55% yield after purification. ^1H NMR (CDCl_3): δ (ppm) 8.81 (s, 3H), 7.33–7.00 (m, 21H), 4.58 (t, 6H, $J = 8$ Hz), 3.21 (t, 6H, $J = 8$ Hz). Calcd: C, 59.27; H, 3.51; O, 9.29; S, 27.93. Found: C, 59.44; H, 3.60; O, 9.24; S, 27.72. MALDI-TOF of G0 D with $\text{M}^+ = 1032.1$.

Synthesis of Tris(3-(2-(2,5-di(thiophen-2-yl)thiophen-3-yl)ethoxy)-5-(2-(5-(thiophen-2-yl)-2-(thiophen-3-yl)thiophen-3-yl)ethoxy)phenyl)benzene-1,3,5-tricarboxylate [G1 D] (Scheme 4). Following the general synthesis method A as described above, a precooled solution of benzene-1,3,5-tricarboxylic acid (18 mg, 0.085 mmol), G1 OH (200 mg, 0.3 mmol), and PPh_3 (76 mg, 0.3 mmol) in THF under sonication was treated with a solution of DIAD (60 mg, 0.3 mmol) in 2 mL of THF under nitrogen. The solution was sonicated for 12 h to afford yellow solid product in 45% yield after purification. ^1H NMR (CDCl_3): δ (ppm) 8.84 (s, 3H), 7.30–6.95 (m, 42H), 6.54 (s, 6H), 6.38 (s, 3H), 5.24 (s, 6H), 4.14 (t, 12H, $J = 8$ Hz), 3.18 (t, 12H, $J = 8$ Hz). Calcd: C, 61.13; H, 3.60; O, 8.80; S, 26.46. MALDI-TOF of G1 D with $\text{M}^+ = 2222.0$.

Synthesis of Tris(3,5-bis(3,5-bis(2-(2,5-di(thiophen-2-yl)thiophen-3-yl)ethoxy)benzyloxy)phenyl)benzene-1,3,5-tricarboxylate [G2 D] (Scheme 4). Following the general synthesis method A as described above, a precooled solution of benzene-1,3,5-tricarboxylic acid (21 mg, 0.1 mmol), G2 OH (510 mg, 0.35 mmol), and PPh_3 (88 mg, 0.35 mmol) in THF under sonication was treated with a solution of DIAD (72 mg, 0.35 mmol) in 2 mL of THF under nitrogen. The solution was sonicated for 12 h to afford yellow solid product in 40% yield after purification. ^1H NMR (CDCl_3): δ (ppm) 8.84 (s, 3H), 7.30–6.95 (m, 84H), 6.55 (s, 12H), 6.36 (s, 6H), 5.21 (s, 12H)

Scheme 3. Synthesis of G2 OH Terthiophene Dendron



4.14 (t, 24H, $J = 8$ Hz), 3.18 (t, 24H, $J = 8$ Hz). Calcd: C, 62.63; H, 3.94; O, 8.34; S, 25.08. Found: C, 62.54; H, 4.17; O, 8.35; S, 24.95. MALDI-TOF of G2 D with $\text{M}^+ = 4557.7$.

Electrochemical Synthesis of Cross-Linked Dendrimers. The precursor dendrimers were electropolymerized using the CV technique. In a three-electrode cell, 0.1 M tetrabutylammonium perchlorate (TBAP) was taken as a supporting electrolyte along with 5 mM of each dendrimer dissolved in 6 mL of methylene chloride in separate cells. The electropolymerization was performed by sweeping the voltage at a scan rate of 50 mV/s from 0 to 0.8 V against Ag/AgCl as a reference electrode and platinum as a counter electrode. The ITO or gold-coated slides were used as a working electrode and also as a substrate.

Results and Discussion

Synthesis and Characterization. The synthesis was started with ethyl-3-thiophene-3-acetate to produce G0 OH by using a literature procedure.^{9a} The G1 ester was synthesized by a modified Mitsunobu etherification reaction under sonication conditions. The solution was sonicated for 2 h to afford a pale yellow solid product in 54% yield after purification. This is in contrast to several days of refluxing as has been commonly done with this reaction.⁹ The G1 ester was then reduced using LiAlH_4 to produce G1 OH as a pale yellow solid in 90% yield. G2 OH was synthesized in the same way as G1 OH. Scheme 4 shows the route for the synthesis of G0, G1, and G2 dendrimers from their corresponding Gn OH dendrons and the trifunctional acid core. These esterifications were carried out under the same conditions used for the etherification reactions under sonication. All these dendrimers are highly soluble in common organic solvents such as CHCl_3 , CH_2Cl_2 , THF, toluene, ethyl acetate, etc. There is good correspondence between NMR data and elemental analysis for all the synthesis steps, indicating the correct chemical structure and the right purity needed for further physical analysis. Further characterization was performed using GPC and MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight) mass spectroscopy technique. The MALDI-TOF analysis verified the monodispersed masses of all G0, G1, and G2 dendrimers, giving the corresponding ion peak of M^+ as 1032.1, 2222.0, and 4557.7, respectively. This is consistent with the exact calculated MW values for each dendrimer. Figure 1 shows the GPC peak results as a function of retention volume. The polydispersity index was found on the average to be less than 1.02 for all three generations with corresponding MW values not too different from MALDI data with PS calibration: 1201, 2345, and 4611 g/mol for G0, G1, and G2, respectively. More importantly, the elution curves were

Scheme 4. Synthesis of G0 to G2 Terthiophene Dendrimers

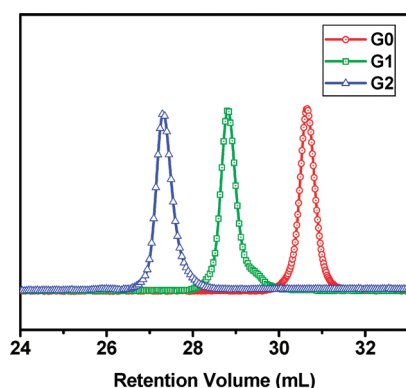
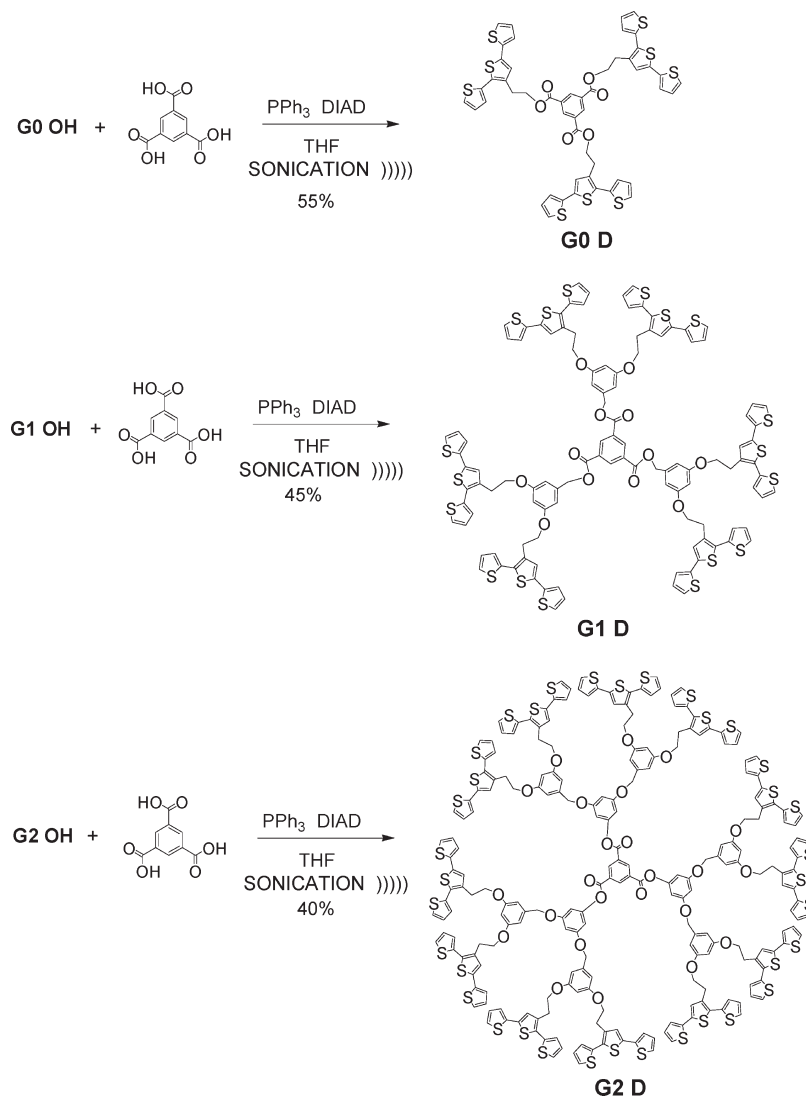


Figure 1. GPC chromatograms of dendrimers showing monomodal distribution.

found to be narrow and monomodal in distribution. A decrease in the retention volume was observed in going from the lowest generation to the highest, which is consistent with an increase in the hydrodynamic volume as the generation increases.

UV Absorption and Emission Studies. Shown in Figure 2a are the optically matched UV–vis absorption spectra of the G0, G1, and G2 dendrimers in methylene chloride. The

broad absorption with λ_{max} 345 nm is attributed primarily to the π – π^* transitions of a terthiophene monomer.¹⁶ The emission spectra of the optically matched samples of the G0, G1, and G2 dendrimers are also shown in Figure 2b. Again, this represents the emission properties of a terthiophene unit (excitation at 345 nm). The fluorescence emission intensities of the G0 and G2 dendrimers seem to be slightly quenched more than that of the G1 dendrimer. This quenching behavior can be attributed to conformational changes due to the dendritic wedges and the restriction that may be imposed on G0 and G2 design.^{17a} This suggests that there may be an optimal conformational freedom required to allow intermolecular interaction between the terthiophene chromophores that may lead to quenching of the emission.^{17b–d} Further studies are underway to understand the influence of the dendrimer generation on the quenching of the emission and fluorescence lifetime measurements, including simulation studies with semi-empirical modeling.

Electropolymerization. Electropolymerization of the dendrimers was carried out by cyclic voltammetry (CV) using indium tin oxide (ITO) as a working electrode, platinum as a counter electrode, and Ag/AgCl as a reference electrode in a three-electrode cell. The dendrimers were electrodeposited (cross-linked) as films using 1.0 mM concentration in methylene chloride containing 0.1 M tetrabutylammonium perchlorate as

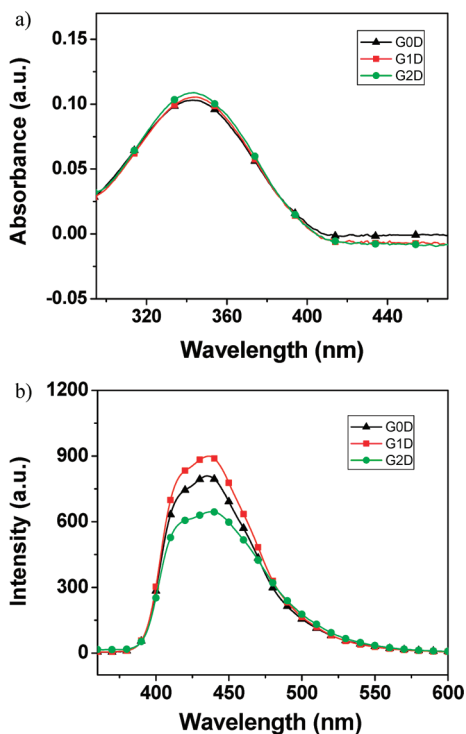


Figure 2. (a) UV-vis absorption spectra and (b) emission spectra excited at 345 nm of G0 D, G1 D, and G2 D in CH_2Cl_2 .

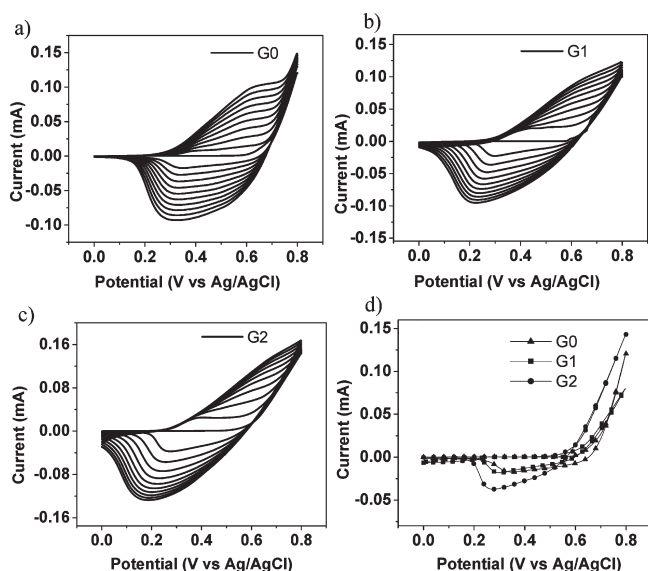


Figure 3. Cyclic voltammograms of 10 cycles for (a) G0, (b) G1, (c) G2, and (d) trace of the first cycles of G0, G1, and G2 for clarity.

Table 1. Dendrimeric Cross-Linked Precursors Showing Peak Anodic and Cathodic Currents/Potentials and Their Corresponding Onsets of Oxidation Potential

dendrimers	onsets	E_{pa} (V)	i_{pa} (mA)	E_{pc} (V)	i_{pc} (mA)	ΔE (V)
G0 D	0.52	0.62	0.10	0.32	−0.09	0.20
G1 D	0.56	0.63	0.12	0.28	−0.10	0.28
G2 D	0.60	0.64	0.15	0.26	−0.14	0.34

a supporting electrolyte. Figure 3 shows different CV traces recorded between 0 and 0.8 V vs Ag/AgCl for all the generations of the dendrimers. Table 1 summarizes the peak anodic and cathodic currents and potentials. A clear decrease in the onset potentials going from G0 to G2 (Figure 3d) is observed.

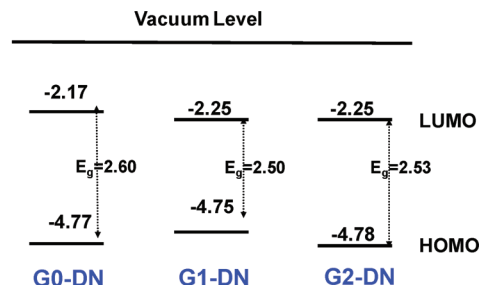


Figure 4. Energy level diagram showing HOMO and LUMO levels for all three dendrimers.

This suggests that there is an optimal conformational freedom required to allow extended conjugation during cross-linking for these dendrimers.^{9b} From the CV traces, the growth of the conducting polymer is reflected by gradually increasing currents in subsequent potential cycles and the simultaneous appearance of the new onset peaks around 0.35 V, which corresponds to the formation of the polythiophene backbone.¹⁸ The slight increase in the peak separation potential reflected the increase in the polymer film resistance as the thickness of the film increased with increasing cycles. These films showed very good stability toward repeated redox cycling. A linear relationship between peak current and scan rate was observed for all these films, suggesting that the redox-active polymer was attached to the electrode with a typical Fickian diffusion behavior as defined by the Cottrell equation.^{9,10} The CV result also suggests that increasing the dendrimer generation increases the amount of cross-linked dendrimer units confirmed by increased peak current. Such an evolution of the polymer structure could be related to the increasing probability of inter- and/or intradendrimer coupling of the terthiophene units as the G_n D increases. But unlike previous studies on carbazole-jacketed poly(benzyl ether) dendrimers, the peak current linearity for the three generations are about the same.^{9b}

In order to determine the band gap of these materials, we performed CV on the cross-linked films using 0.1 mM tetrabutylammonium phosphate (TBAP) as a supporting electrolyte in methylene chloride and a Ag/AgCl reference electrode. All three films showed quasi-reversible oxidative behavior. The ionization potential can be taken as a measure for the energy of the highest occupied molecular orbital (HOMO). The onset oxidation potentials of these materials were determined by the anodic scan. The measured oxidation potentials can be converted into ionization potentials by relating the electrochemical energy scale to the vacuum energy scale.¹⁹ The calculated HOMO energy levels for G0 D, G1 D, and G2 D are −4.77, −4.75, and −4.78 eV, respectively. The LUMO level was estimated from the onset of the UV-vis spectra and was found to be −2.17, −2.25, and −2.25 eV for G0 D, G1 D, and G2 D, respectively.

The AFM images of the cross-linked films are shown in Figure 5. Although it is hard to distinguish any marked differences between the cross-linked films, sharp conical morphological features and uniform surface coverage seemed to be a function of the extent of cross-linking. While G0 D and G2 D form relatively smooth films, G1 D appears to be rougher and forms globular domains, indicating perhaps a greater degree of quasi-particle formation during cross-linking. The root-mean-square roughness (rms) of the dendrimers G0 D, G1 D, and G2 D were found as 5.1, 5.9, and 2.5 nm, respectively. As mentioned earlier, the G1-D is less quenched in the solution emission spectra than the G0 D and G2 D, which indicate less pairing of the terthiophene units.

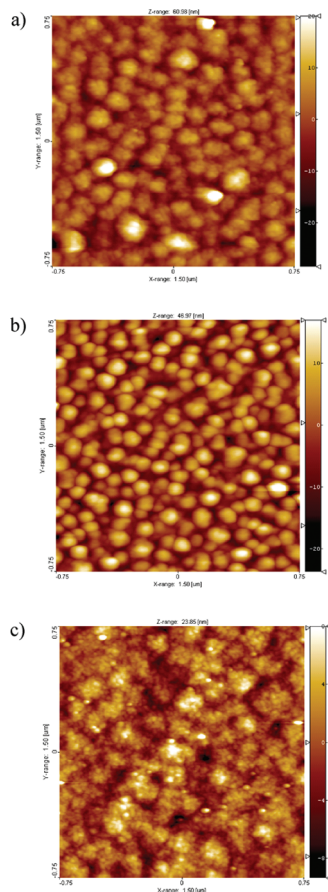


Figure 5. AFM images of the cross-linked dendrimer films: (a) G0 D, (b) G1 D, and (c) G2 D.

It is possible that the eventual film formation has a correlation to the inability of G1D to form more intermolecular cross-linking, i.e., reaction of the terthiophenes with another dendrimer. This is also evident in the fluorescence behavior of the films as discussed in the next section. The cross-linked solid-state films obtained by electropolymerization have been characterized spectroscopically by UV–vis and fluorescence or photoluminescence (PL) measurements likewise to understand their optical properties. The extent of increasing π -orbital overlap between neighboring repeat units on conjugated polymers can be directly assessed from their electronic spectra.²⁰ The extent of electronic π -conjugation directly affects the observed energy of the π – π^* transition, which appears as the absorption maxima in these materials.²³

As seen from Figure 6a, all three generations show broad absorption peaks from 300 to 600 nm with a λ_{max} value around 440 nm, attributed to π – π^* transitions in a π -conjugated polymer. These values are comparable to the absorption maxima of typical polyterthiophenes obtained by electropolymerization²¹ and, in general, that of polythiophenes.²⁴ Although the average conjugation length cannot be determined from this data alone, the red-shifted absorption relative to the terthiophene monomer (oligomer of three thiophene units) indicates a significant increase in conjugation length. It is also consistent with the measured band gap, E_g , in Figure 2. Figure 6b shows the PL spectra of the cross-linked dendrimer films excited at 440 nm. The results of the photoluminescence of these cross-linked films are more interesting. The λ_{max} values for G0 D, G1 D, and G2 D are 590, 525, and 660 nm, respectively, and are normalized. For G0 D film, the photoluminescence peak appears as a single broad peak with a Stokes shift of 150 nm while G2 D shows

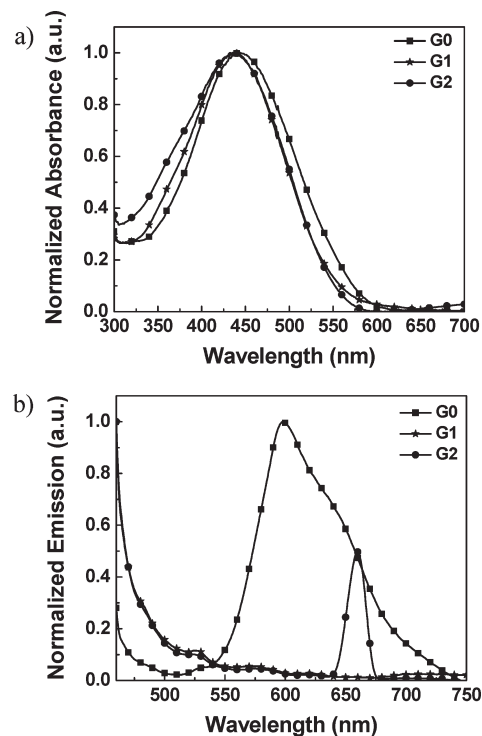


Figure 6. Optical studies of electropolymerized dendrimers in solid state thin films: (a) UV–vis absorption spectra and (b) emission spectra of the different films excited at 440 nm.

relatively sharper peak and appears to have the highest Stokes shift around 210 nm, indicating a large difference in the ground and excited states. This G2D behavior is rather peculiar since the narrow half-width maximum is less than 100 nm and may indicate a very narrow distribution of conjugated species. On the other hand, G1 D shows only two weak peaks with λ_{max} at 525 nm with a shoulder at 590 nm. The peak at 525 nm indicates a limited intermolecular cross-linking leading to a relatively smaller amount of fluorescing conjugated units at this particular excitation.²² This behavior may again be related to the inability of the terthiophene units in G1 D to “reach out” to neighboring dendrimeric species but have a tendency to react only intramolecularly or within the dendrimer surface alone. This is in contrast to what has been observed with polybenzylether dendrimers bearing carbazole peripheral units in solution and solid-state films, where electropolymerizability and the PL properties are highly correlated.^{9b} PL properties should also be a function of effective conjugation length and effective torsional strain between thiophene units such that this can be correlated with the inter- and intramolecular cross-linking properties of the dendrimers.²⁴ Future studies will include other modes of excitation and fluorescence lifetime studies in order to further probe the distinction of the respective PL behavior of the different generations and the narrow peak observed with G2 D. Again, it will be interesting to correlate with molecular modeling the dendrimer conformation in distinguishing these spectral features.

To understand this electrochemical cross-linking process better, we have electropolymerized G1 D with various concentrations of the thiophene monomer, a copolymerization process that introduces more intermolecular linking and extends the amount of π -conjugated species. The emission behavior for the electrodeposition of the monomer (terthiophene) alone is shown in the Supporting Information. Electropolymerization of G1 dendrimer with thiophene monomer was done using the same conditions used for the G1

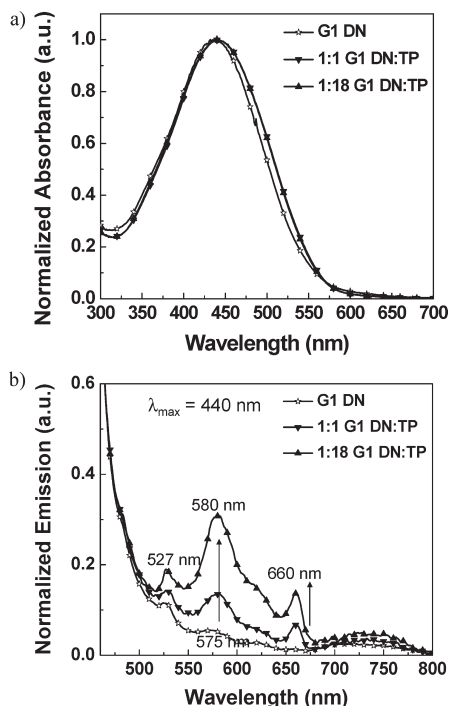


Figure 7. Optical properties of electropolymerized films of G1 with thiophene monomer: (a) UV-vis absorption spectra and (b) emission spectra excited at 440 nm for various ratios.

dendrimer itself. We have made three different films by electrochemical synthesis from pure G1 dendrimer as well as 1:1 and 1:18 molar ratios of G1 dendrimer and thiophene monomer. The CV traces showed similar behavior to the G1 dendrimer alone for all three films. Interestingly, the current density of the film during scanning abruptly decreases with the thiophene monomers are added, which does not follow the equation for the current-concentration proportionality relationship. This may be due to the relatively slow electron transfer of thiophene monomers and intermolecular cross-linking with G1 dendrimers. Nevertheless, Figure 7a shows the absorption spectra of all three different films made from G1 D and thiophene monomer which are very similar to G1 dendrimer itself. Figure 7b shows the photoluminescence spectra of the cross-linked dendrimer films excited at 440 nm. Interestingly, as we increase the concentration of thiophene monomer, we can see an increase in the intensity of the peaks at 580 and 660 nm, indicating the formation of more linear π -conjugated species. This is a good indication that the limited intermolecular cross-linking ability of the G-1 dendrimer is extended by copolymerization with monomeric species. Interestingly, the fine spectra also indicate specific conjugated segments or species were formed with copolymerization, which are usually the domain of PL spectral tuning with the use of various side chain derivatives or by introducing head-to-tail stereoregularity in polythiophenes.²⁴ Another method is by the use of polymer blends or block copolymer formation.²⁴ These results indicate that the dendrimer structure plays an interesting role when electrodeposited to form distinct π -conjugated polymer species in a film. In principle, facile control on the inter- and intramolecular cross-linking with the use of dendrimers can potentially lead to another route toward tuning the electro-optical property of polythiophene films.²⁴ The concept in general may be applicable to spectral tuning of other linear π -conjugated polymers. Finally, all cross-linked films formed were optically clear and uniform and therefore could be well suited for OLED and

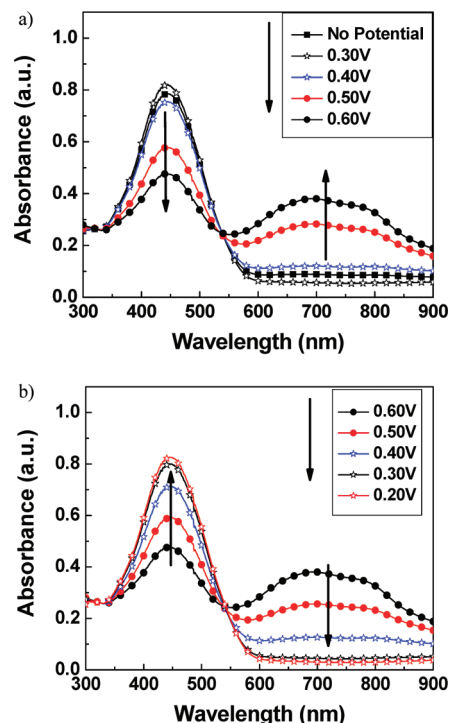


Figure 8. Spectroelectrochemical changes for the G1 D at different constant voltages (a) forward and (b) backward directions.

other flat display device or “sandwich type” thin film device or sensor applications.

Electrochromic devices are another possible application for these materials. The electrochromic properties of the G1 dendrimer were evaluated using spectroelectrochemistry. For these investigations, the G1 dendrimer film was electropolymerized on an ITO-coated glass slide. The cross-linked G1 D film was analyzed under monomer-free conditions by applying a constant potential. The results from the G1 D film are presented in Figure 8 as a series of UV-vis absorbance curves correlated to electrode potentials. In the neutral form at 0 V, the film exhibited strong absorption at a wavelength near 445 nm, which is characteristic of a polythiophene solid-state film.¹⁶ Upon oxidation of the G1 film (increasing the applied voltage from 0 to 0.6 V), the intensity of the absorption at 445 nm gradually decreased while a new broad band having its maximum absorption wavelength at 805 nm gradually increased in intensity. We attribute this spectral change toward the near IR to the formation of a stable radical cation or polaronic and bipolaronic species.²² The observed UV-vis absorption changes in the film of G1 D at various potentials are fully reversible, as shown in Figure 8b, and are associated with strong color changes going from bluish-green to orangish-red, which can even be seen by the naked eye. Therefore, the electrochromic switching behavior appears to be a highly reversible process for these thin film materials. Further studies will be made to compare their switching rates with PEDOT derivatives.

Conclusion

In conclusion, poly(benzyl ether)-based terthiophene peripheral-terminated dendrons and dendrimers have been successfully synthesized by Mitsunobu coupling under sonication conditions. All the characterization results, NMR, GPC, MALDI-TOF, and elemental analysis confirmed the structures proposed in the schemes. Optical studies of the thin films made by the electropolymerization of these materials show that the dendrimer structure

and generation play an important role when depositing these materials to form a cross-linked conjugated polymer network film. In particular, the generation of the dendrimer enabled selective energy transfer behavior that contributed to variations in spectral emission as a function of cross-linking and dendrimer generation. Moreover, copolymerization with monomeric species can enable spectral tuning of the emission properties by facilitating more intermolecular reactions. Conversely, linear pi-conjugated polymer species can be spectroscopically tuned by the addition of dendrimeric species. Spectroelectrochemistry studies of these materials show that the electrochromic switching behavior is a highly reversible process. These materials are currently being systematically investigated for their optical, redox behavior under potential cycling and electropatterning as thin films

Acknowledgment. The authors acknowledge funding from the Robert A. Welch Foundation, E-1551. Technical support from Agilent Technologies (formerly Molecular Imaging) and Malvern Instruments (formerly Viscotek) is acknowledged.

Supporting Information Available: Electropolymerized thiophene monomer film and its fluorescence spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) (a) Furuta, P.; Brooks, J.; Thompson, M. E.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2003**, *125*, 13165. (b) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, *18*, 1701. (c) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819. (d) Ma, D.; Lupton, J. M.; Beavington, R.; Burn, P. L.; Samuel, I. D. W. *Adv. Funct. Mater.* **2002**, *12*, 507.
- (2) (a) MacDiarmid, A. G. *Angew. Chem.* **2001**, *113*, 2649. (b) Heinze, J. In *Encyclopedia of Electrochemistry*; Bard, A. J., Stratmann, M., Schéfer, H. J., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 8, p 605. (c) Roncali, J. *Chem. Rev.* **1992**, *92*, 711. (d) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 885.
- (3) (a) Brédas, J. L.; Thémans, B.; Fripiat, J. G.; André, J. M.; Chance, R. R. *Phys. Rev. B* **1984**, *29*, 6761. (b) Samukhin, A. N.; Prigodin, V. N.; Jastrabik, L. *Phys. Rev. Lett.* **1997**, *78*, 326.
- (4) Xu, Z. F.; Moore, J. S. *Angew. Chem.* **1993**, *105*, 1394.
- (5) Deb, S. K.; Maddux, T. M.; Yu, L. P. *J. Am. Chem. Soc.* **1997**, *119*, 9079.
- (6) Xia, C.; Fan, X.; Locklin, J.; Advincula, R. C.; Gies, A.; Nonidez, W. J. *J. Am. Chem. Soc.* **2004**, *126*, 8735.
- (7) Wiesler, U. M.; Weil, T.; Müllen, K. *Dendrimers III* **2001**, *212*, 1.
- (8) (a) Meerholz, K.; Heinze, J. *Synth. Met.* **1993**, *55*, 5040. (b) Heinze, J.; Tschuncky, P. In *Electronic Materials, The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998; p 479.
- (9) (a) Taranekekar, P.; Fulghum, T.; Baba, A.; Patton, D.; Advincula, R. *Langmuir* **2007**, *23*, 908. (b) Taranekekar, P.; Fulghum, T.; Baba, A.; Patton, D.; Ponnampati, R.; Clyde, G.; Advincula, R. *J. Am. Chem. Soc.* **2007**, *129*, 12537.
- (10) Taranekekar, P.; Park, J.; Patton, D.; Fulghum, T.; Ramon, G. J.; Advincula, R. *Adv. Mater.* **2006**, *18*, 2461.
- (11) (a) Lepore, S. D.; He, Y. *J. Org. Chem.* **2003**, *68*, 8261. (b) Gholap, A. R.; Venkatesan, K.; Daniel, T.; Lahoti, R. J.; Srinivasan, K. V. *Green Chem.* **2003**, *6*, 693. (c) Chen, M.-Y.; Lu, K.-C.; Lee, A. S.-Y.; Lin, C.-C. *Tetrahedron Lett.* **2002**, *43*, 2777. (d) Adewuyi, Y. G. *Ind. Eng. Chem. Res.* **2001**, *40*, 4681.
- (12) (a) Tierney, J. P.; Lidstrom, P. *Microwave Assisted Organic Synthesis*; Blackwell Publishing: Oxford, UK, 2005; Vol. 280, p 89. (b) Wang, X.; Kim, Y.-G.; Drew, C.; Ku, B.-C.; Kumar, J.; Samuelson, L. A. *Nano Lett.* **2004**, *4*, 331. (c) Tong, H.; Wang, L.; Jing, X.; Wang, F. *Macromolecules* **2003**, *36*, 2584. (d) Murphy, C. B.; Zhang, Y.; Troxler, T.; Ferry, V.; Martin, J. J.; Jones, W. E., Jr. *J. Phys. Chem. B* **2004**, *108*, 1537.
- (13) (a) Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nature Mater.* **2006**, *5*, 222. (b) Wang, F.; Gu, H.; Swager, T. M. *J. Am. Chem. Soc.* **2008**, *130*, 5392. (c) Sivula, K.; Luscombe, C. K.; Thompson, B. C.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2006**, *128*, 13988.
- (14) Taranekekar, P.; Baba, A.; Park, J.; Fulghum, T.; Advincula, R. *Adv. Funct. Mater.* **2006**, *16*, 2000.
- (15) Alvarez, J.; Sun, Li.; Crooks, R. M. *Chem. Mater.* **2002**, *14*, 3995.
- (16) Jang, S.; Sotzing, G. A. *Macromolecules* **2002**, *35*, 7293.
- (17) (a) Freeman, A. W.; Koene, S. C.; Malenfant, P. R. L.; Thompson, M. E.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2000**, *122*, 12385. (b) Barron, J. A.; Bernhard, S.; Houston, P. L.; Abruna, H. D. *J. Phys. Chem. A* **2003**, *107*, 8130. (c) Tomalia, D. A. *High Perform. Polym.* **2001**, *13*, S1–S10. (d) Glazier, S.; Barron, J. A.; Morales, N.; Ruschak, A. M.; Houston, P. L.; Abruna, H. D. *Macromolecules* **2003**, *36*, 1272.
- (18) Schäferling, M.; Bäuerle, P. *J. Mater. Chem.* **2004**, *14*, 1132.
- (19) Bockris, J. O. M.; Khan, S. U. M. *Surface Electrochemistry. A Molecular Level Approach*; Kluwer Academic/Plenum Publishers: New York, 1993.
- (20) Dai, J.; Sellers, J. L.; Nofle, R. E. *Synth. Met.* **2003**, *139*, 81.
- (21) (a) Yassar, A.; Moustrou, C.; Korri, H. Y.; Samat, A.; Guglielmetti, R.; Garnier, F. *Macromolecules* **1995**, *28*, 4548. (b) Roncali, J.; Garnier, F.; Lemaire, M.; Garreau, R. *Synth. Met.* **1986**, *15*, 323.
- (22) Pomerantz, M.; Cheng, Y.; Kasim, R. K.; Elsenbaumer, R. L. *J. Mater. Chem.* **1999**, *9*, 2155.
- (23) Galand, E. M.; Kim, Y.; Mwaura, J. K.; Jones, A. G.; McCarley, T. D.; Shrotriya, V.; Yang, Y.; Reynolds, J. R. *Macromolecules* **2006**, *39*, 9132.
- (24) Perepichka, I.; Perepichka, D.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281.