Macromolecules

Electropolymerizable Terthiophene-Terminated Poly(aryl ether) Dendrimers with Naphthalene and Perylene Cores

Ramakrishna Ponnapati, Mary Jane Felipe, and Rigoberto Advincula*

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

ABSTRACT: We describe the synthesis and characterization of a new series of poly(aryl ether) dendrimers with both donor and acceptor moieties. By incorporating p-type terthiophene and n-type perylene and naphthalene diimides into one molecule, we have achieved a dual electrochromic material. These dendrimers were designed to act as electrochemically active precursor polymers, which bear the electroactive terthiophene group that can be cross-linked electrochemically to form conjugated polymer network (CPN) films. Characterization of the optical and redox properties shows that it is possible to incorporate donor and acceptor moieties



in the same molecule with retention of doping properties. The films made by electrochemical polymerization are highly active in both the p- and n-doping processes and have been investigated by spectroelectrochemical methods.

INTRODUCTION

Extensive research is being carried out on electroactive chromophores attached to an emissive core because of their luminescent properties relevant to light-emitting diode applications.¹ Recently, dendrimers were investigated as an alternative source of electroluminescence.² Dendrimers open up new opportunities for precisely placing charge-carrier transporting units at the periphery in a three-dimensional nanoscale construction. One of the attractive properties of electron-rich π -conjugated polymers like polycarbazole, polypyrrole, and polythiophene is their electrical conductivity, which develops during doping of their π -conjugated systems.³ These conjugated polymers are proven to be generally good p-type materials.⁴ Recently, conjugated perylene tetracarboxydiimide (PDI) derivatives have attracted considerable attention owing to their excellent chemical and thermal stability for various applications such as optical switches,⁵ photovoltaic devices,⁶ and dye lasers.⁷ PDI derivatives are well-known n-type (electron acceptor) charge generation sites.8 Incorporation of electron-rich polymer and electron-poor dye molecules within a bulk material may lead to efficient electronic and photonic materials.9

Electrochromism is another important application for these materials. The conjugated polymers used in electrochromic devices are normally of the p-doping type such as polythiophene. The n-doping properties of aromatic diimides like naphthalene tetracarboxydiimide and perylene tetracarboxydiimide have also been reported.⁹ It is well-known that aromatic diimides generally exhibit rather poor solubility in organic solvents. Solubility of these diimides has been increased by attaching long alkyl chains or soluble dendrons to these materials. By incorporating p-type terthiophene and n-type perylene and naphthalene diimides into one molecule, it may be possible to achieve a dual electrochromic material. Herein we report a series of perylene and naphthalene

diimide-based dendrimers, into which the dendron peripheral group terthiophene is introduced as a charge carrier transporting tunable type emitter.¹² These dendrimers are expected to show specific light-antenna capacity and tunable charge carrier transporting characteristics. The benzyl ether backbone increases the solubility of these dendrimers. One advantage of the new terthiophene dendrons is their electropolymerizability to yield polythiophene, to yield Conjugated Polymer Network (CPN) films.

EXPERIMENTAL PART

Materials. Solvents were properly distilled and used immediately. Other reagents and chemicals were commercially available. Analytical grade chemicals were purchased from Aldrich Chemical Co. and were used without further purification.

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 Micro-labs. 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 ($H_2O/H_2O_2/NH_3$: 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) (Scheme 1). The synthesis of 3T ET was carried by

Received:	July 27, 2011
Revised:	September 4, 2011
Published:	September 16, 2011



Scheme 1. Synthesis of Terthiophene Ethanol



first synthesizing ethyl 2-(2,5-dibromothiophen-3-yl)acetate as reported in the literature.^{10a} 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 CH₂Cl₂. The extracted CH₂Cl₂ mixture was dried with Na₂SO₄. 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.^{10a}

Synthesis of 2-(2,5-Di(thiophen-2-yl)thiophen-3-yl)ethanol (3TOH) (Scheme 1). The compound 3T ET (2 g, 5.9 mmol) in 10 mL of THF was added dropwise under nitrogen to an ice-cooled 100 mL THF suspension of LiAlH₄ (0.32 g, 8.4 mmol). Upon addition, the color of the solution immediately turned 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 turned yellow upon neutralization. The solvent was evaporated, and the resulting mixture was extracted three times using CH₂Cl₂. The combined CH₂Cl₂ extracts were further washed with water and brine. The organic layer was dried with Na₂SO₄. After filtering and evaporating CH2Cl2, the reaction mixture was chromatographed using 4:1 CH₂Cl₂:hexane as eluent mixture. 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 $(CDCl_3): (\delta ppm) 7.31-7.04 (m, 7H), 3.88 (q, 2H, J = 6.4 Hz), 3.01$ (t, 2H, J = 6.4 Hz). ¹³C 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 recently by our group.¹² The mixture of alcohol, phenol (or aromatic carboxylic acid), and triphenylphosphine (PPh₃) in minimal THF was cooled to 5 °C with an ice bath and sonicated for 5 min. Under sonication, a solution of diisopropylazodicarboxylate (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 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 layers 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.

General Method for the Conversion of Gn OH to Gn NH₂ (Method C). The conversion of Gn OH to Gn NH₂ was carried by using a modified Gabriel synthesis method. The mixture of alcohol, phthalimide, and PPh₃ in minimal THF was cooled to 5 °C with an ice bath and sonicated for 5 min. Under sonication, a solution of DIAD was added dropwise under nitrogen. The water temperature was allowed to warm to room temperature, and precautions were taken to maintain the temperature. Sonication was performed until the reaction was completed as indicated by TLC. The solvent was evaporated to get the crude product as a white solid. Without further purification, the protecting group was removed by refluxing the crude product in 1:1 THF:MeOH in the presence of hydrazine hydrate. The product was purified by passing through a small pad of silica gel and methylene chloride followed by methanol.

General Method for Dendrimer Synthesis (Method D). A mixture of perylene 3,4,9,10-tetracarboxydianhydride or naphthalene tetracarboxydianhydride, corresponding to Gn NH₂, and zinc acetate dihydrate in *N*-methylpyrrolidinone (NMP) was heated to reflux for 12 h. The warm solution was diluted with water and extracted with methylene chloride. The crude product was purified by column chromatography with methylene chloride and silica gel.

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), 3T OH (3 g, 10.2 mmol), and PPh₃ (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 (CDCl₃): 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 (CDCl₃): 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 (3,5-Bis(4-(9H-carbazol-9-yl)butoxy)phenyl)methanamine (G1 NH₂) (Scheme 3). The general synthesis method C was followed to get G1 NH₂ in 95% yield. ¹H NMR (CDCl₃): δ (ppm) 7.33–7.00 (m, 14H), 6.48 (d, 2H, *J* = 2 Hz), 6.38 (t, 1H, *J* = 2 Hz), 4.15 (t, 4H, *J* = 7 Hz), 3.75 (s, 2H) 3.19 (t, 4H, *J* = 7 Hz). Calcd: C, 61.10; H, 4.25; N, 2.04; O, 4.65; S, 27.96.

Synthesis of G1 Per (Scheme 3). The general synthesis method D was followed to get G1 Per in 60% yield. ¹H NMR (CDCl₃): δ (ppm) 8.35 (d, 4H, *J* = 4 Hz), 8.13 (d, 4H, *J* = 4 Hz), 7.33–7.00 (m, 28H), 6.72 (s, 4H), 6.37 (s, 2H), 5.29 (s, 4H), 4.15 (t, 8H, *J* = 7 Hz), 3.19 (t, 8H, *J* = 7 Hz). Calcd: C, 65.17; H, 3.61; N, 1.62; O, 7.39; S, 22.21. Found: C, 64.73; H, 3.68; N, 2.13; O, 8.97; S, 20.49.

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 4). 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 PPh₃ (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 purification. ¹H NMR (CDCl₃): 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 4). 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 (CDCl₃): 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 (3,5-Bis(3,5-bis(2-(2,5-di(thiophen-2-yl)thiophen-3-yl)ethoxy)benzyloxy)phenyl)methanamine (G2 NH₂) (Scheme 5). The





general synthesis method C was followed to get G2 NH₂ in 95% yield. ¹H NMR (CDCl₃): δ (ppm) 7.33–7.00 (m, 28H), 6.56 (d, 4H, *J* = 2 Hz), 6.54 (d, 2H, *J* = 2 Hz), 6.47 (t, 1H, *J* = 2 Hz), 6.4 (t, 2H, *J* = 2 Hz), 4.91 (s, 4H), 4.16 (t, 8H, *J* = 7 Hz), 3.76 (s, 2H) 3.20 (t, 8H, *J* = 7 Hz). Calcd: C, 62.44; H, 4.15; N, 0.95; O, 6.48; S, 25.98. Found: C, 631.27; H, 4.80; N, 1.37; O, 7.28; S, 23.28.

Synthesis of G2 Per-Dendrimer (Figure 5). The general synthesis method D was followed to get G2 Per-dendrimer in 42% yield. ¹H NMR (CDCl₃): δ (ppm) 8.13 (d, 4H, *J* = 4 Hz), 7.87 (d, 4H, *J* = 4 Hz), 7.33–7.00 (m, 56H), 6.79 (s, 4H) 6.52 (s, 8H), 6.39 (s, 2H), 6.28 (s, 4H) 5.29 (s, 4H), 4.88 (s, 8H) 4.15 (t, 16H, *J* = 7 Hz), 3.19 (t, 16H, *J* = 7 Hz). Calcd: C, 64.42; H, 3.83; N, 0.84; O, 7.71; S, 23.19.

Synthesis of G1 NTCDI (Scheme 6). The general synthesis method D was followed to get G1 NTCDI in 66% yield. ¹H NMR (CDCl₃): δ (ppm) 8.70 (s, 4H), 7.33–7.00 (m, 28H), 6.65 (s, 4H), 6.34 (s, 2H), 5.27 (s, 4H), 4.13 (t, 8H, *J* = 7 Hz), 3.15 (t, 8H, *J* = 7 Hz). Calcd: C, 62.74; H, 3.64; N, 1.74; O, 7.96; S, 23.93.

Electrochemical Synthesis of Cross-Linked Dendrimers. The precursor dendrimers were electropolymerized using the cyclic voltammetry (CV) technique. In a three-electrode cell, 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) was taken as a supporting electrolyte along with 2.5 mM of each dendrimer dissolved in 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 were used as a working electrode and also as a substrate.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthesis of the dendrons was performed using the classical Mitsunobu etherification reaction. However, this reaction is very slow in the case of sterically hindered molecules such as dendrons and dendrimers. In order to achieve fast and synthetically useful yields, we have utilized the sonication-mediated synthesis. The sonicationmediated synthesis drastically reduces the reaction time from weeks or days to only a couple of hours. We have achieved comparable yields to other Fréchet type dendrons using simple Mitsunobu etherification reaction performed under sonication. Although in the past Leopre et al.¹¹ have demonstrated a similar approach using hindered phenols, surprisingly no group has demonstrated the use of sonication chemistry to synthesize dendrimers as in our first report.¹² We have not only optimized these conditions for etherification reactions, but have even extended this method to synthesize imides. The dendrimers with

Scheme 5. Synthesis of G2 Per-terthiophene Dendrimer



Scheme 6. Synthesis of G1 NTCDI Dendrimer



terthiophene groups at the periphery and perylene tetracarboxydiimide at the core were synthesized by a convergent synthetic strategy. First, the Fréchet type dendrons with OH functionality at the focal point were synthesized. The OH groups were converted to amine groups by reacting the corresponding Gn OH with pthalimide in the presence of triphenylphosphine and diisopropyl azodicarboxylate. Pthalimide was deprotected in the presence of hydrazine hydrate according to the literature¹³ and then grafted to the PDI core. To compare the optical properties of these materials, we have also synthesized a first generation terthiophene dendrimer with naphthalene tetracarboxydiimide as a core. It is known that perylene tetracarboxydianhydride (PDA) has very limited solubility in common organic solvents, but when we functionalized with terthiophene dendrons, the solubility of the resulting dendrimers increased drastically. The synthesized dendrimers were characterized using NMR, elemental analysis, and MALDI-TOF mass spectroscopy technique. With increasing dendron generation, the ¹H and ¹³C NMR signals become more complicated and difficult to discern the structures. To assess more clearly the identity of the chemical structures, further characterization was performed using MALDI-TOF mass spectrometry which confirmed exact mass assignment with structure.

Absorption and Luminescent Properties. The optical properties of the terthiophene-functionalized perylene bisimide



Figure 1. UV–vis spectra of first and second generation dendrimers in CH_2Cl_2 solution (optically matched at the perylene region).

dendrimers were investigated by UV—vis absorption as well as fluorescence spectroscopy. Figure 1 shows the absorption spectra of the first and second generation dendrimers optically matched at the perylene region in dichloromethane (ca. 5 × 10⁻⁶ M). As can be seen, both the first and the second generation dendrimers show very similar absorption characteristics. The broad absorption peak at 345 nm is attributed to the $\pi - \pi^*$ transitions of terthiophene¹⁴ while the peaks at 460, 490, and 530 nm are attributed to the perylene diimide core.¹⁵ From the first generation to second generation, the absorbance of the



Figure 2. Emission spectra of first and second generation dendrimers in CH_2Cl_2 solution excited at 345 nm (inset excited at 490 nm).



Figure 3. UV-vis and emission (excited at 340 nm) spectra of G1 NTCDI in CH_2Cl_2 .

terthiophene moiety increased proportionally to the dendrimer generation in an exponential manner consistent with the number of terthiophene groups, e.g., G1 = 4 and G2 = 8, terthiophene units in first and second generation, respectively. The presence of terthiophene units does not influence the absorption behavior of perylene chromophore and vice versa, indicating negligible interaction between the ground states of these two chromophores. Figure 2 shows the fluorescence spectra for these samples excited at 345 nm. In these dendrimers, both the peripheral chromophores and the focal dye are capable of contributing to the absorption of light by the entire macromolecule. In a dendritic antenna, the peripheral donor units collect photons and transfer the excitation energy through space to the core or focal point acceptor. An interesting property to observe here is a possible energy transfer from the peripheral terthiophene to the central perylene unit through a singlet-singlet Förster resonance energy transfer (FRET) mechanism as there is a slight overlap between the emission spectrum of terthiophene and absorption spectrum of perylene.¹⁶ To monitor this phenomenon as a function of dendrimer generation, we have excited these samples at 345 nm which is the terthiophene absorption region and monitored from 360 to 620 nm. Both the first and the second generation dendrimers exhibit perylene bisimide peak at around 540 nm along with an intense emission peak of the terthiophene at around 430 nm. Upon irradiation at 345 nm, the emission peak from perylene chromophore reveals an energy transfer from the terthiophene units to the perylene core. The inset of Figure 2 shows the emission peaks of both dendrimers excited at 490 nm. The emission of the perylene moiety in second generation was drastically quenched more than in the case of first generation. Because of the electron richness of the terthiophene groups, it is not surprising that the emission of the perylene units is quenched by photoinduced electron transfer (PET) process.¹⁷ To further



Figure 4. Cyclic voltammograms for (a) G1 Per and (b) G1 NTCDI.

support PET processes time-resolved emission spectroscopy studies are underway.

Synthesis of G1 NTCDI was carried in a similar manner to the perylene dendrimers. Figure 3 shows the UV–vis absorption and emission spectra of G1 NTCDI in dichloromethane solution. Absorption peak with $\lambda_{\rm max}$ at 345 nm is attributed to the $\pi - \pi^*$ transitions of terthiophene¹⁴ while the peak shoulder at 380 nm is attributed to the naphthalene diimide core. The fluorescence spectrum of G1 NTCDI is very similar to terthiophene itself with an emission peak at 440 nm. Both naphthalene core and terthiophene emit in the same region.

Electrochemical Synthesis of Cross-Linked Dendrimers. Further insight into the electronic properties of these materials was investigated by cyclic voltammetry. The electrochemical polymerization is an important method for forming cross-linked films directly onto a conducting substrate. Our group has been investigating the precursor polymer approach to form conjugated polymer networks (CPN).¹⁸ This approach has recently been applied toward the electrochemical cross-linking and deposition of dendrimers.¹⁹ The resulting cross-linked film is highly robust, mechanically stable, and insoluble in any organic solvents. The electropolymerization of each dendrimer was performed in a three-electrode cell, where the following electrodes were used: platinum as a counter electrode, Ag/AgCl as a reference electrode, and ITO-coated glass substrate as anode/working electrode. The dendrimers were electrodeposited (cross-linked) as films using 2.5 mM concentration in methylene chloride containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte and scanning between 0 and 0.8 V at a scan rate of 50 mV/s.



Figure 5. Cyclic voltammograms of the thin films in monomer free acetonitrile solution (a) G1 Per and (b) G1 NTCDI.

Figure 4 shows the different CV traces for both first generation perylene and naphthalene diimide dendrimers. Both the dendrimers show similar redox behavior with an onset potential of 0.62 V vs Ag/AgCl. From the second scan, the growth of the conducting polymer is reflected by gradually increasing currents in subsequent potential cycles and the simultaneous decrease in the onset potential, which corresponds to the formation of the polythiophene backbone.²⁰ The slight increase in the peak separation potential in the subsequent cycles reflected the increase in the polymer film resistance as the thickness of the film increased with increasing cycles. These films are very robust and showed good stability toward repeated redox cycling. 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.²¹ Subsequently, the redox properties of the dendrimers were investigated by cyclic voltammetry. The electrochemically deposited thin films of G1 Per and G1 NTCDI were washed with dichloromethane and placed into a monomer free electrolyte solution of dichloromethane. Figure 5 shows the cyclic voltammograms of G1 Per and G1 NTCDI dendrimer films. They both exhibit good p- and n-doping processes as these dendrimers were designed to exhibit electrochemical activity in both anodic and cathodic potential scans. When an anodic potential is applied, the polyterthiophene moiety gets oxidized and shows the p-doping properties, whereas in the cathodic potential scan the perylene and naphthalenetetracarboxydiimide moieties get reduced and show n-dpoing characteristics. Moreover, the electrochemical redox processes of the films are very stable in the features of cyclic voltammetry during subsequently repeated scanning. In the p-doping process, the onset oxidation potential is around 0.62 V vs Ag/AgCl for both dendrimers, which is typical for polyterthiophene moiety. In the n-doping process, G1 Per shows a quasi-reversible reductions at -1.6 V, which is typical for the reduction of perylene bisimides



ARTICLE

Figure 6. Spectroelectrochemical changes for (a) G1 Per and (b) G1 NTCDI at different applied voltages.

to anionic species.²² We did not observe a second reduction to form a dianionic species, which is expected for the perylene moiety.²³ In the case of G1 NTCDI, an irreversible reduction at -1.9 V was observed. It is normal for aromatic diimides that the reduction waves become less reversible at scan rates below 0.2 V/s, suggesting that the radical anions undergo slow decomposition.²

To obtain further insight into the redox process of the terthiophene-functionalized perylene and naphthalene bisimides, spectroelectrochemistry of the electropolymerized films was studied by recording their UV-vis absorption at different applied potentials. It is interesting to observe the electrochromic properties of these materials as these materials contain both donor and acceptor moieties. The changes in the absorption spectra induced by p- and n-doping of G1 Per and G1 NTCDI are presented in Figure 6 as a series of UV-vis absorbance curves correlated to different electrode potentials. In the neutral form at 0 V, G1 Per film exhibited strong absorption at a wavelength near 460 nm with two shoulder peaks at 500 and 540 nm. Upon increasing the applied voltage from 0 to 0.6 V, no change was observed in the UV spectrum. The intensities of the peaks at 500 and 540 nm start to decrease at potential around 0.8 V, where the polymer starts to be doped. As the intensities of the peaks decrease, there is a simultaneous appearance of a new band in the longer wavelength region from 600 to 800 nm. This spectral change was attributed to the formation of radical cations of polyterthiophene showing the doped state of the polymer.²⁵ On the other hand, when the electrode potential was decreased from

0 to -1.6 V, the absorption peaks at 460 and 500 nm decrease in favor of new absorption peaks at 570, 610, and 650 nm. Further decrease in the potential did not show any spectral changes. The origin of new peaks was attributed to the formation of radical anions of perylene moieties,²⁶ which is in agreement with the electrochemical data. For G1 NTCDI, a stepwise increase of the electrode potential to 0.8 V drastically quenches the absorption peak at 460 nm with the simultaneous formation of a new absorption band in the longer wavelength region from 600 to 800 nm similar to that of G1 Per which is attributed to the formation of radical cations of polyterthiophene showing the doped state of the polymer.²⁷ On the other hand, a stepwise decrease of the electrode potential from 0 to -1.6 V allows a complete recovery of the absorption peak without any other changes in the absorption spectrum. Further reduction in the electrode potential to -2.5 V did not change the absorption spectrum. The electrochemical reduction of naphthalene diimide to the corresponding radical anion state leads to a change in the absorption with the appearance of new peak at 470 nm. In this case, this change was not visible as the polyterthiophene has an intense absorption in this region. In case of G1 Per, the fabricated films shows a clear dual electochromism by showing electrochromic activity in both anodic and cathodic potential scans. These spectral changes observed in the UV-vis spectrum are difficult to see with the naked eye, especially during cathodic scan as the shift in the wavelength is very small. However, this study reveals protocols for making libraries of materials that can be tailored to act as dual electrochomic materials and leading to multifunctional electrochromic films. It will be interesting to investigate the electroluminescence behavior of these materials as well.

CONCLUSION

In conclusion, we have synthesized terthiophene-terminated dendrons and dendrimers with naphthalene and perylene diimide cores. Characterization of the optical and redox properties of the novel materials shows that it is possible to design materials with donor and acceptor moieties in the same molecule which will retain their individual properties. Electrochemical polymerization of these materials provided polymer films which have been investigated by spectroelectrochemical methods. The films obtained are highly active in both the p- and n-doping processes. G1 Per with perylene core and terthiophene dendron periphery showed dual electrochromism by showing the electrochromic activity in both cathodic and anodic potential scans. Further investigation of these materials is still underway.

AUTHOR INFORMATION

Corresponding Author

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

ACKNOWLEDGMENT

The authors acknowledge funding from NSF CBET-0854979, DMR-10-06776, and Robert A. Welch Foundation, E-1551. Technical support from INFICON Inc. and Metrohm is also acknowledged.

REFERENCES

(1) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. Angew. Chem., Int. Ed. **1998**, 37, 402. (b) Neher, D. Macromol. Rapid Commun. **2001**, 22, 1365.

(2) (a) Furuta, P.; Brooks, J.; Thompson, M. E.; Frechet, J. M. J. J. Am. Chem. Soc. 2003, 125, 13165. (b) Kwok, C. C.; Wong, M. S. Macromloecules 2001, 34, 6821. (c) Wang, P. W.; Liu, Y. J.; Devadoss, C.; Bharathi, P.; Moore, J. S. Adv. Mater. 1996, 8, 237.

(3) (a) Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds. *Handbook of Conducting Polymers*, 2nd ed.; Dekker: New York, 1998. (b) Kanatzidis, M. G. *Chem. Eng. News* **1990**, *68*, 36. (c) MacDiarmid, A. G. *Angew. Chem.* **2001**, *113*, 2649.

(4) (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.; Jastrabík, L. *Phys. Rev. Lett.* **1997**, *78*, 326.

(5) O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L., III; Wasielewski, M. R. *Science* **1992**, *257*, 63.

(6) Schelettwein, D.; Wöhrle, D.; Karmann, E.; Melville, U. Chem. Mater. **1994**, *6*, 3.

(7) Sadrai, M.; Hadel, L.; Sauers, R. R.; Husain, S.; Krogh-Jespersen, K.; Westbrook, J. D.; Bird, G. R. *J. Phys. Chem.* **1992**, *96*, 7988.

(8) Popovic, Z. D.; Loutfy, R. O.; Hor, A. M. Can. J. Chem. 1985, 63, 134.

(9) (a) Mitschke, U.; Bäuerle, P. J. Mater. Chem. 2000, 10, 1471. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. Angew. Chem., Int. Ed. 1998, 37, 402. (c) Würthner, F.; Wortmann, R.; Meerholz, K. ChemPhysChem 2002, 3, 17. (d) Brabéc, C. J.; Sariciftci, N. S.; Hummelen, J. C. Adv. Funct. Mater. 2001, 11, 15.

(10) (a) Taranekar, P.; Fulghum, T.; Baba, A.; Patton, D.; Advincula,
R. *Langmuir* 2007, 23, 908. (b) Yassar, A.; Moustrou, C.; Youssoufi,
H. K.; Samat, A.; Guglielmetti, R.; Garnier, F. *Macromolecules* 1995, 28, 4548.

(11) Lepore, S. D.; He, Y. J. Org. Chem. 2003, 68, 8261.

(12) (a) Taranekar, P.; Fulghum, T.; Baba, A.; Patton, D.; Ponnapati, R.; Clyde, G.; Advincula, R. J. Am. Chem. Soc. 2007, 129, 12537. (b) Ponnapati, R.; Felipe, M. J.; Park, J.; Vargas, J.; Advincula, R. Macromolecules 2010, 43, 10414. (c) Sebastian, R.; Caminate, A.-M.; Majoral, J.; Levillain, E.; Huchet, L.; Roncali, J. Chem. Commun. 2000, 507–508.

(13) Hammerschmidt, F.; Hanbauer, M. J. Org. Chem. 2000, 65, 6121.

(14) Jang, S.; Sotzing, G. A. Macromolecules 2002, 35, 7293.

(15) Tian, H.; Liu, P.; Zhu, W.; Gao, E.; Wu, D.; Cai, S. J. Chem. Mater. 2000, 10, 2708.

(16) (a) Guldi, D. M.; Luo, C.; Swartz, A.; Gómez, R.; Segura, J. L.; Martín, N. J. Phys. Chem. A 2004, 108, 455. (b) Yamanaka, K.; Fujitsuka, M.; Araki, Y.; Ito, O.; Aoshima, T.; Fukushima, T.; Miyashi, T. J. Phys. Chem. A 2004, 108, 250. (c) Förster, T. Ann. Phys. 1948, 2, 55. (d) Schenning, A. P. H. J.; v. Herrikhuyzen, J.; Jonkheijm, P.; Chen, Z.; Würthner, F.; Meijer, E. W. J. Am. Chem. Soc. 2002, 124, 10252. (e) Qu, J.; Pschirer, N. G.; Liu, D.; Stefan, A.; De Schryver, F. C.; Müllen, K. Chem.—Eur. J. 2004, 10, 528. (f) Würthner, F.; Thalacker, C.; Sautter, A. Adv. Mater. 1999, 11, 754.

(17) (a) Würthner, F.; Vollmer, M. S.; Effenberger, F.; Emele, P.; Meyer, D. U.; Port, H.; Wolf, H. C. J. Am. Chem. Soc. 1995, 117, 8090.
(b) Vollmer, M. S.; Würthner, F.; Effenberger, F.; Emele, P.; Meyer, D. U.; Stümpfig, T.; Port, H.; Wolf, H. C. Chem.—Eur. J. 1998, 4, 260.
(c) González-Rodríguez, D.; Torres, T.; Guldi, D. M.; Rivera, J.; Echegoyen, L. Org. Lett. 2002, 4, 335. (d) Serin, J. M.; Brousmiche, D. W.; Fréchet, J. M. J. J. Am. Chem. Soc. 2002, 124, 11848.

(18) (a) Taranekar, P.; Baba, A.; Fulghum, T. M.; Advincula, R. *Macromolecules* **2005**, *38*, 3679. (b) Taranekar, P.; Fulghum, T. M.; Baba, A.; Patton, D.; Advincula, R. *Langmuir* **2007**, *23*, 908.

(19) Taranekar, P.; Park, J.-Y.; Fulghum, T.; Patton, D.; Advincula, R. *Adv. Mater.* **2006**, *18*, 2461.

(20) Schäferling, M.; Bäuerle, P. J. Mater. Chem. 2004, 14, 1132.

(21) Wei, Z.; Xu, J.; Nie, G.; Du, Y.; Pu, S. J. Electroanal. Chem. 2006, 589, 112.

(22) Parker, V. D. J. Am. Chem. Soc. 1976, 98, 98.

(23) (a) Lee, S. K.; Zu, Y.; Herrmann, A.; Geerts, Y.; Müllen, K.; Bard, A. J. J. Am. Chem. Soc. **1999**, *121*, 3513. (b) You, C.-C.; Würthner, F. J. Am. Chem. Soc. **2003**, *125*, 9716.

(24) Viehbeck, A.; Goldberg, M. J.; Kovac, C. A. J. Electrochem. Soc. **1990**, 137, 1460.

(25) 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.

(26) MacKinnon, S. M.; Wang, Z. Y. J. Polym. Sci., Part A: Polym. Chem. 2000, 38, 3467.

(27) Zheng, J.; Qiao, W.; Wan, X.; Gao, J. P.; Wang, Z. Y. Chem. Mater. 2008, 20, 6163.