# Synthesis of novel arylamine containing perfluorocyclobutane and its electrochromic properties<sup>†</sup>

Bogyu Lim,<sup>*a*</sup> Yoon-Chae Nah,<sup>*ab*</sup> Jin-Taek Hwang,<sup>*c*</sup> Jieun Ghim,<sup>*a*</sup> Doojin Vak, $\S^a$  Jin-Mun Yun<sup>*a*</sup> and Dong-Yu Kim<sup>*a*</sup>

Received 3rd October 2008, Accepted 19th January 2009 First published as an Advance Article on the web 23rd February 2009 DOI: 10.1039/b817303f

A new electrochromic oligomer based on an arylamine compound containing a perfluorocyclobutane (PFCB) ring has been synthesized *via* 2 + 2 cyclodimerization. A new N,N,N',N'-tetraphenyl-biphenyl-4,4'-diamine (TPD) with PFCB (**TPD-PFCB**) showed high thermal stability with a decomposition temperature (T<sub>d</sub>) of 435 °C. Cyclic voltammograms of **TPD-PFCB** films coated onto an indium–tin oxide substrate showed two reversible redox steps during a potential scan between 0.7 and 1.2 V. The spectroelectrochemical series of **TPD-PFCB** films exhibited color change from colorless to yellow and then to greenish blue during the oxidation reaction of **TPD-PFCB**. This oligomer exhibited a high electrochromic coloration efficiency (602 cm<sup>2</sup>/C) and a comparable response speed (coloring and bleaching time at 700 nm were 0.71 and 0.12 s, respectively).

# Introduction

Since their discovery, conjugated polymers and organic semiconductors have attracted tremendous attention because of their suitability for a wide range of promising electronic, optical, and electrochemical applications such as organic light-emitting diodes,<sup>1</sup> photovoltaic cells,<sup>2</sup> organic thin-film transistors,<sup>3</sup> and electrochromic devices.<sup>4</sup> Compared to other applications, organic electrochromic devices are inexpensive and simple to fabricate.<sup>5</sup> Also, organic electrochromic devices have many advantages such as the realization of multiple colors with the same material, the promise of high contrast ratios, a long lifetime, a rapid switching time, and color tuning through chemical modification.<sup>5</sup> Therefore, a wide range of organic semiconducting materials has been reported in the literature for electrochromic applications.

Arylamine-based derivatives are well known electron-rich compounds that are widely used in hole transporting materials, and light emitters in the field of optoelectronics such as organic light-emitting diodes.<sup>6</sup> The family of arylamines also has many good properties such as redox properties, ion transfer processes, and photoelectrochemical behavior as well as their excellent electronic properties.<sup>7,8</sup> In addition, it has been reported that

Parkville, Victoria 3010, Australia

2380 | J. Mater. Chem., 2009, 19, 2380-2385

arylamine compounds also have strong electrochromic properties when they are oxidized.<sup>5,7</sup> The mechanism of anodic oxidation of arylamine has been well studied.<sup>9</sup> The cation radical of arylamine is not stable and it forms a dimer. However, with a *p*-substitution, the cation radical of arylamine can be stabilized.<sup>10</sup> To apply the electrochromic device using organic semiconductors such as arylamine compounds, thermal and chemical stability should be further enhanced. Liou *et al.* reported polyimides bearing arylamine as an electrochromic compounds with high thermal and mechanical stability.<sup>7b</sup> The polymers have high glass transition and decomposition temperature. Furthermore, these polymers could be tough and flexible films with good mechanical properties.

In this paper, we report the synthesis and characterization of a new N,N,N',N'-tetraphenyl-biphenyl-4,4'-diamine (TPD) containing a perfluorocyclobutane (PFCB) oligomer such as **TPD-PFCB** (Scheme 1), and its electrochromic properties. PFCB-based polymers have been studied as a peculiar class of fluoropolymers. PFCB polymers are easily polymerized neat or in solution without the need for a catalyst or initiator, by the radical-mediated thermal cyclopolymerization of trifluorovinyl ethers (TFVE), resulting in conversions in excess of 99%.<sup>11</sup> These polymers have excellent properties such as high thermal stability, chemical resistance, high glass-transition temperature, processability, durability, low dielectric constant, and optical transparency.<sup>11,12</sup> Thus, PFCB polymers are suitable for use in various applications such as polymer photonic devices,<sup>13</sup> low dielectric coatings,<sup>14</sup> light-emitting diodes,<sup>6a,15</sup> and electrochromic devices. However, to our knowledge, electrochromic devices based on PFCB materials have not been reported so far. In the present work, thermal, optical, electrochemical, and electrochromic properties of the obtained polymer were investigated. In its undoped state, the TPD-PFCB has high thermal, chemical stability and optical transparency. In addition, this oligomer exhibits strong electrochromic contrast. These results suggest that the introduction of PFCB to organic electrochromic chromophores such as thiophene and pyrrole derivatives could also

<sup>&</sup>lt;sup>a</sup>Heeger Center for Advanced Materials, Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, 1 Oryong-Dong, Buk-Gu, Gwangju 500-712, Republic of Korea. E-mail: kimdy@gist.ac.kr; Fax: +82-62-970-2304; Tel: +82-62-970-2319

<sup>&</sup>lt;sup>b</sup>Department of Materials Science, WW4-LKO, University of Erlangen-Nuremberg, 91058 Erlangen, Germany

<sup>&</sup>lt;sup>c</sup>R&D Center, e-Polymers Co., Ltd., 217-4, Hwapyung-ri, Ganam-myun, Yeoju-gun, Gyunggi-do, Korea

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: <sup>1</sup>H NMR and <sup>19</sup>F NMR spectra of **TPD-TFVE**, and a cyclic voltammogram of the **TPD-PFCB** film. See DOI: 10.1039/b817303f

<sup>‡</sup> Present address: Advanced R&D Center, Electronic Components Group, Senior Research Engineering, LS Cable, Ltd., 555 Hogye-dong, Dongan-gu, Anyang-si, Kyungki-do 431-080, Republic of Korea § Bio21 Institute, University of Melbourne, 30 Flemington Road,



Scheme 1 Synthesis scheme for TPD-TFVE and TPD-PFCB

enhance the thermal, chemical stability and optical transparency, so that the lower thermal stability of organic electrochromic chromophore could be improved.

## Experimental

#### Materials

All starting materials were purchased from Aldrich Chemical Co. and used without further purification. Tetrahydrofuran (THF) and diethyl ether were dried over calcium hydride, and distilled prior to use.

#### Synthesis

4-[(trifluorovinyl)oxy]bromobenzene (TFVE, **2**) was synthesized according to literature procedures<sup>6a</sup> and is commercially available from Oak-wood Chemicals, Inc.

# N,N'-Bis[(p-trifluorovinyloxy phenyl)]-N,N'-bis(phenyl) benzidine (TPD-TFVE)

A solution of tris(dibenzylideneacetone)dipalladium (0.023 g, 0.025 mmol), tri-*tert*-butylphosphine (0.051 g, 0.25 mmol), sodium *tert*-butoxide (1.922 g, 20 mmol), **1** (1.682 g, 5 mmol), and **2** (3.036 g, 12 mmol) in 100 mL of toluene was refluxed under nitrogen for 24 h. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over anhydrous MgSO<sub>4</sub>. The solution then was concentrated. The reaction mixture was purified by chromatography on silica gel using hexane:EA = 95:5 as the eluent. The resulting yellowish viscous liquid was obtained in 85% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.45 (d, 4H, J = 8.62 Hz), 7.28 (t, 4H, J = 7.33, 8.43 Hz), 7.13 (m, 18H). <sup>19</sup>F NMR (282.65 MHz, CDCl<sub>3</sub>):  $\delta$  – 135.01~-134.42 (1F, dd, CF = CF<sub>2</sub>, F<sub>c</sub>), -128.36~-127.63 (1F, dd, trans-CF = CF<sub>2</sub>, F<sub>b</sub>), -121.35~-120.80 (1F, dd, cis-CF = CF<sub>2</sub>, F<sub>a</sub>). Elemental

analysis: calcd: for  $C_{40}H_{26}F_6N_2O_2$ : C, 70.59; H, 3.85; N, 4.12. Found: C, 70.50; H, 4.10; N, 4.06%, GCMS (DI): *m*/*z* 680, calcd 680.19

#### Preparation of the oligomer and the films

**TPD-TFVE** was cyclopolymerized in a vacuum oven at 180 °C for 4 h. The mixture was bulk-oligomerized by isothermal heating under nitrogen. After oligomerization, the number-average molecular weight ( $M_n$ ) was 3000. The **TPD-PFCB**-oligomer was subsequently dissolved in chlorobenzene and filtered using a 0.2  $\mu$ m PP filter. The **TPD-PFCB**-oligomer was spin-coated with a 1 wt% solution in chlorobenzene on an ITO substrate cleaned by a conventional process<sup>1a</sup> and dried at 120 °C for 30 min, with additional polymerization at 180 °C for 1 h in a vacuum oven. The film thickness and sample area after post-polymerization were 30 nm and 1.8 cm<sup>2</sup>, respectively.

#### Characterization and measurements

Materials were characterized by <sup>1</sup>H, <sup>19</sup>F NMR spectroscopy (JEOL JNM-LA300WB 300 MHz). Thermo-gravimetric analysis (TGA) was performed using a TA Instrument 2050 series. Differential scanning calorimetry (DSC) was carried out on a TA Instrument 2010 series at a heating rate of 10 °C/min under a nitrogen atmosphere. Samples were scanned in the range of 40– 350 °C. Elemental analyses were carried out by the Korea Basic Science Institute, Seoul Branch Analytical Laboratory (Elemental analysis; CE Instruments Flash EA 1112 series). Absorption spectra were measured using a UV/Vis spectrophotometer (Varian spectrometer, Carry1E). Molecular weight was confirmed by gas chromatography mass spectrometry (GC/MS; Shimadzu, GCMS-QP2010) and by gel permeation chromatography (GPC, Futecs, NS2001). All electrochemical tests were performed using an Autolab PGSTAT30 Potentiostat/Galvanostat. **TPD-PFCB**/ITO (indium-tin oxide) film, a Pt wire and a Ag wire were used as the working, counter and reference electrodes, respectively. A 0.1 M solution of lithium perchlorate (LiClO<sub>4</sub>) in propylene carbonate (PC) was used as the liquid electrolyte. The cyclic voltammetry (CV) measurement was performed in the range of 0.7 V to 1.2 V at a scan rate of 50 mV/s. In order to investigate the charge densities and response time during the redox reactions, the chronoamperometric measurement was performed at 0.7 V and 1.2 V with intervals of 10 s, respectively. Transmittance was simultaneously measured *in situ* during all experiments using a UV/Vis spectrophotometer. The transmittance of the ITO/glass with the electrolyte and the cell window was assumed to be 100%.

# **Results and discussion**

#### Synthesis and characterization

Synthesis of a TPD-TFVE was carried out by the procedure shown in Scheme 1. 2 was prepared using a procedure as described in the literature.<sup>6a</sup> TPD-TFVE was prepared in 85% yield from 1 and 2 using a palladium-catalyzed C-N bond forming reaction.<sup>16</sup> **TPD-TFVE** was obtained as a slightly yellowish viscous liquid. In general, arylamines can be synthesized by the Ullmann reaction using a copper-catalyst or a palladium-catalyzed C-N bond forming reaction. In the latter case, however, reaction conditions and yield are favorable. TPD-TFVE was purified by column chromatography, with hexane:EA = 95:5 as an eluent, and fully characterized using  ${}^{1}H$  NMR,  ${}^{19}F$ NMR, mass spectrometry, and elemental analysis (ESI, Fig. S1).† As the molecular weight of TPD-TFVE was too low to form thin film layers using solution processes such as spin coating, PFCB oligomers were prepared by bulk oligomerization via 2 + 2 cyclodimerization. The oligomerization of **TPD-TFVE** was carried out in a vacuum oven at 180 °C for 4 h, as shown in Scheme 1. When the TPD-TFVE was oligomerized at 180 °C for 5 h, the **TPD-PFCB** oligomer had poor solubility in organic solvents such as chloroform or chlorobenzene, which made it difficult to form the thin film using solution process. On the other hand, when TPD-TFVE was oligomerized for 4 h at 180 °C, it showed better solubility. After cyclodimerization, the peak at around -120--136 ppm disappeared in <sup>19</sup>F-NMR, which shows the formation of PFCB ring groups. The molecular weight of the oligomer was estimated by GPC relative to polystyrene standards. The number-average molecular weight  $(M_n)$  was 3000. The molecular weight of TPD-PFCB was sufficient to fabricate the film on a substrate using a solution process such as spin coating. The low molecular weight may be due to the relatively short reaction times (4 h) and low polymerization temperature (180 °C). In general, the degree of polymerization of the PFCB polymer is determined by the polymerization conditions such as reaction time and temperature.<sup>13a</sup> The temperature required for dimerization depends on the electronic structure of the aryl groups, and is typically in the range 150-250 °C.<sup>13a</sup> After spincoating, the film was dried at 120 °C for 30 min, and the TPD-PFCB oligomers were additionally polymerized at 180 °C for 1 h in a vacuum oven. After post-polymerization, thermal, chemical stability and the solvent resistance could be enhanced due to the increase of molecular weight.6a,15



Fig. 1 (a) DSC thermogram of TPD-TFVE (—) and  $T_g$  of TPD-PFCB (---) and (b) TGA curve of TPD-PFCB polymer.

# Thermal properties

Thermal properties were investigated by means of TGA and DSC. As shown in Fig. 1(a), the broad exothermic peak (solid line) of the DSC curve corresponds to the thermal polymerization of **TPD-TFVE**. Exothermic peaks were found at about  $T_{onset} = 160$  °C and  $T_{max} = 238$  °C, which are typical in PFCB ring formation temperature.<sup>13</sup> After polymerization, **TPD-PFCB** has a high glass transition temperature ( $T_g$ ). DSC analysis shows that **TPD-PFCB** has a  $T_g$  of 175 °C (dashed line). In addition, **TPD-PFCB** shows high thermal stability with a decomposition temperature ( $T_d$ ) of 435 °C (Fig. 1(b)). Thermal stability of **TPD-PFCB** was estimated by TGA scanning from 40 to 800 °C at 10 °C/min. The high thermal stability of **TPD-PFCB** is caused by the introduction of PFCB.

# Optical and electrochemical properties

The optical properties of **TPD-PFCB** were investigated using UV-vis and photoluminescence (PL) spectroscopy. Fig. 2 shows the UV-vis absorption and PL spectra of **TPD-PFCB** films. The films were prepared by spin-coating using 1 wt% **TPD-PFCB** oligomer solution in chlorobenzene onto an ITO glass substrate, followed by drying at 120 °C for 30 min and additional polymerization at 180 °C for 1 h in a vacuum oven. The absorption maximum and absorption onset peaks of **TPD-PFCB** in the solid state appeared at 356 nm and 405 nm, respectively. From the absorption spectrum, the optical band-gap of the **TPD-PFCB** is



Fig. 2 UV-vis absorption and photoluminescence (PL) spectra of TPD-PFCB film on the indium-tin oxide-coated glass substrate.



Fig. 3 Cyclic voltammogram of **TPD-PFCB** film onto the indium-tin oxide-coated glass substrate.

estimated to be 3.06 eV. The PL spectrum of the **TPD-PFCB** film shows that an emission maximum is at wavelength of 502 nm.

To investigate the electrochemical properties of TPD-PFCB films, CV measurements were performed in a solution of propylene carbonate with 0.1 M LiClO<sub>4</sub>. The CV curve of the TPD-PFCB/ITO film is shown in Fig. 3. During the potential scan between 0.7 and 1.2 V, two reversible redox peaks are present. One sharp oxidation peak and another broad peak appear at 1.06 and 1.11 V, respectively, which is likely to be due to the two amine units of TPD-PFCB. The two oxidation peaks indicate that **TPD-PFCB** has the potential ability to show two coloration states. The highest occupied molecular orbital (HOMO) energy was calibrated using the half-wave potential of ferrocene/ferrocenium (Fc) redox coupling, which is 4.8 eV under vacuum. The HOMO level appears at 5.14 eV, and the LUMO energy level of the polymer is determined to be 2.08 eV which is estimated from the optical band-gap. In addition, the results of CV measurements of the polymer thin films on ITO substrates show very good reversibility, indicating that TPD-PFCB has good electrochemical stability (ESI, Fig. S2).† The reason for this is probably due to the introduction of PFCB structure which could enhance the chemical stability.

#### **Electrochromic properties**

The electrochromic absorptions of **TPD-PFCB** thin films were monitored by UV-vis spectroscopy at different applied voltages. The spectroelectrochemical series for **TPD-PFCB** films are



**Fig. 4** Spectroelectrochemisty of the **TPD-PFCB** film on the indium–tin oxide-coated glass substrate at applied potentials from 0 V to 1.2 V.

shown in Fig. 4. When the applied potential increases from 0.0 to 1.0 V, the peak of absorption at 365 nm decreases with the formation of a new band at 490 nm. In this voltage range, the color of the film changes to yellow from transparent state. When the applied potential further increases to 1.05 V, the peak of absorption at 365 nm decreases rapidly, while the absorption peaks at 490 and 715 nm increases and the color of the thin film is changed from yellow to greenish blue. As the potential is applied to more positive direction from 1.05 to 1.2 V, the peak of absorption at 715 nm further increased, but the two bands grown at 490 and 365 nm decreased. These two-step colorations (yellow and greenish blue) can be attributed to the two oxidation reactions which are shown by CV measurement. When the voltage is applied in reverse, the color returns to transparent from greenish blue, *via* a yellow-colored intermediate state.

To quantitatively explore the electrochromic properties of **TPD-PFCB**, chronoamperometric and transmittance measurements were performed. Fig. 5(a) shows the current density-time



Fig. 5 (a) Current-time curves of the **TPD-PFCB** film for chronoamperometric measurements at 0.7 V and 1.2 V (b) Corresponding *in situ* transmittance curves of **TPD-PFCB** film.

curves of TPD-PFCB thin films obtained during chronoamperometric measurement applied between 0.7 V and 1.2 V. We calculated the charge density  $(Q_d)$  by integration of the current density and time obtained from the graph of Fig. 5(a) to investigate the amount of charge incorporated during the redox reactions. The amount of  $Q_d$  is 0.299 mC/cm<sup>2</sup> and 0.308 mC/cm<sup>2</sup> for oxidation and reduction process, respectively. The ratio of the charge density is 0.97, indicating that charge injection/ extraction is highly reversible during the electrochemical reactions. Fig. 5(b) shows the corresponding percentage transmittance of TPD-PFCB film monitored at a wavelength of 700 nm. Transmittance difference ( $\Delta T\%$ ) is 33.2%. The relatively low  $\Delta T\%$ is thought to be due to a very thin film thickness of about 30 nm. However, the coloration efficiency (CE), which is calculated by following equation:  $\log(T_{\text{bleaching}}/T_{\text{coloring}})/Q_d$ , is about 602 cm<sup>2</sup>/C. This value is much higher compared to electrochromic compounds based on arylamine.<sup>5,7,8</sup> Also, response time, which is defined as time needed to reach 90% of  $\Delta T$ %, was 0.71 s and 0.12 s for the coloring and bleaching processes, respectively. Considering that electrochromic polymers typically have a response rate less than 1 s, our results are comparable or better than other reports.<sup>17</sup>

## Conclusions

In summary, we synthesized PFCB containing an arylamine polymer *via* a 2 + 2 cyclodimerization and investigated its electrochromic properties. The new electrochromic polymer, **TPD-PFCB**, showed high thermal stability ( $T_d = 435$  °C) due to the incorporation of stable PFCB. During the electrochemical reactions, the color of the **TPD-PFCB** thin films changed from transparent to greenish blue through yellow intermediate colors, and *vice versa*. Also, highly reversible charge injection/extraction reactions took place during the redox reaction. Compared to other arylamine-based compounds, **TPD-PFCB** exhibited a higher electrochromic coloration efficiency and comparable response time. We believe that this new polymer can find applications in electrochromic devices. Further investigation into fabrication of multilayer electrochromic films using a PFCB-based cross-linking agent is currently underway.<sup>6a</sup>

#### Acknowledgements

This work was financially supported by the Ministry of Education of Korea through the Brain Korea 21 (BK21) program, the National Research Laboratory (NRL) Program of the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korean government (MEST) (M10500000077-06J0000-07710), the Bio Imaging Research Center at GIST, and the Program for Integrated Molecular Systems (PIMS) at GIST.

# References

- (a) D. Vak, C. Chun, C. L. Lee, J.-J. Kim and D.-Y. Kim, J. Mater. Chem., 2004, 14, 1342; (b) J. Liu, Z. Xie, Y. Cheng, Y. Geng, L. Wang, X. Jing and F. Wang, Adv. Mater., 2007, 19, 531; (c) D. Vak, B. Lim, S.-H. Lee and D.-Y. Kim, Org. Lett., 2005, 7, 4229.
- 2 (a) P. Ravirajan, S. A. Haque, J. R. Durrant, D. D. C. Bradly and J. Nelson, Adv. Funct. Mater., 2005, 15, 609; (b) L. H. Nguyen, H. Hoppe, T. Erb, S. Günes, G. Gobsch and N. S. Sariciftei, Adv. Funct. Mater., 2007, 17, 1071; (c) N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletete, G. Durocher, Y. Tao and M. Leclerc, J. Am. Chem. Soc., 2008,

**130**, 732; (*d*) M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, *Adv. Mater.*, 2006, **18**, 789; (*e*) J. Jo, D. Vak, Y.-Y. Noh, S.-S. Kim, B. Lim and D.-Y. Kim, *J. Mater. Chem.*, 2008, **18**, 654.

- 3 (a) C. Müller, S. Goffri, D. W. Breiby, J. W. Andreasen, H. D. Chanzy, R. A. J. Janssen, M. M. Nielsen, C. P. Radano, H. Sirringhaus, P. Smith and N. Stingelin-Stutzmann, *Adv. Funct. Mater.*, 2007, **17**, 2674; (b) Y. Li, Y. Wu, P. Liu, M. Birau, H. Pan and B. S. Ong, *Adv. Mater.*, 2006, **18**, 3029.
- 4 (a) B. D. Reeves, E. Unur, N. Ananthakrishnan and J. R. Reynolds, Macromolecules, 2007, 40, 5344; (b) C.-G. Wu, M.-I. Lu, S.-J. Chang and C.-S. Wei, Adv. Funct. Mater., 2007, 17, 1063; (c) Y.-C. Nah, S.-S. Kim, J.-H. Park, H.-J. Park, J. Jo and D.-Y. Kim, Electrochemistry Communications, 2007, 9, 1542; (d) Y.-C. Nah, S.-S. Kim, J.-H. Park and D.-Y. Kim, Electrochem. Solid-State Lett., 2007, 10, j12; (e) Y.-C. Nah, W. S. Choi and D.-Y. Kim, Sol. Energy Mater. Sol. Cells, 2008, 92, 1547.
- 5 K. Choi, S. J. Yoo, Y.-E. Sung and R. Zentel, *Chem. Mater.*, 2006, 18, 5823.
- 6 (a) B. Lim, J.-T. Hwang, J. Y. Kim, J. Ghim, D. Vak, Y.-Y. Noh, S.-H. Lee, K. Lee, A. J. Heeger and D.-Y. Kim, *Org. Lett.*, 2006, 8, 4703;
  (b) H. Yan, P. Lee, N. R. Armstrong, A. Graham, G. A. Evmenenko, P. Dutta and T. J. Marks, *J. Am. Chem. Soc.*, 2005, 127, 3172.
- 7 (a) S. J. Yeh, C. Y. Tsai, C.-Y. Huang, G.-S. Liou and S.-H. Cheng, Electrochemistry Communication, 2003, 5, 373; (b) S.-H. Cheng, S.-H. Hsiao, T.-H. Su and G.-S. Liou, Macromolecules, 2005, 38, 307; (c) T.-H. Su, S.-H. Hsiao and G.-S. Liou, J. Polym. Sci. Part A: Polym. Chem., 2005, 43, 2085; (d) M.-Y. Chou, M.-K. Leung, Y. O. Su, C. L. Chiang, C.-C. Lin, J.-H. Liu, C.-K. Kuo and C.-Y. Mou, Chem. Mater., 2004, 16, 654.
- 8 (a) H. Tanaka, S. Tokito, Y. Taga and A. Okada, Chem. Commun., 1996, 2175; (b) Y. Shirota, J. Mater. Chem., 2000, 10, 1.
- 9 (a) C.-W. Chang, G.-S. Liou and S.-H. Hsiao, J. Mater. Chem., 2007, 17, 1007; (b) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy and R. N. Adams, J. Am. Chem. Soc., 1966, 88, 3498.
- 10 A. Ito, H. Ino, K. Tanaka, K. Kanemoto and T. Kato, J. Org. Chem., 2002, 67, 491.
- (a) D. W. Smith, Jr. and D. A. Babb, *Macromolecules*, 1996, **29**, 852;
   (b) S. T. Iacono, S. M. Budy, J. Jin and D. W. Smith, Jr., *J. Polym. Sci. Part A: Polym. Chem.*, 2007, **45**, 5705.
- 12 (a) A. P. Kennedy, D. A. Babb, J. N. Bremmer and A. J. Pasztor, Jr., J. Polym. Sci., Part A: Polym. Chem., 1995, 33, 1859; (b) D. W. Smith, Jr., D. A. Babb, H. V. Shah, A. Hoeglund, R. Traiphol, D. Perahia, H. W. Boone, C. Langhoff and M. Radler, J. Fluorine Chem., 2000, 104, 109; (c) R. Traiphol, H. Shah, D. W. Smith, Jr. and D. Perahia, Macromolecules, 2001, 34, 3954; (d) D. W. Smith, Jr., S. Chen, S. M. Kumar, J. Ballato, C. Topping, H. V. Shah and S. H. Foulger, Adv. Mater., 2002, 14, 1585; (e) C. Chun, J. Ghim, M.-J. Kim and D.-Y. Kim, J. Polym. Sci., Part A: Polym. Chem., 2005, 43, 3525; (f) B. K. Spraul, S. Suresh, J. Jin and D. W. Smith, Jr., J. Am. Chem. Soc., 2006, 128, 7055; (g) G. A. Kumar, R. E. Riman, S. Banerjee, A. Kornienko, J. G. Brennan, S. Chen, D. W. Smith, Jr. and J. Ballato, Appl. Phys. Lett., 2006, 88, 091902.
- 13 (a) J. Ghim, D.-S. Lee, B. G. Shin, D. Vak, D. K. Yi, M.-J. Kim, H.-S. Shim, J.-J. Kim and D.-Y. Kim, *Macromolecules*, 2004, **37**, 5724;
  (b) J. Ghim, H.-S. Shim, B. G. Shin, J.-H. Park, J.-T. Hwang, C. Chun, S.-H. Oh, J.-J. Kim and D.-Y. Kim, *Macromolecules*, 2005, **38**, 8278; (c) S. Wong, H. Ma, R. Barto, C. W. Frank and A. K.-Y. Jen, *Macromolecules*, 2004, **37**, 5578; (d) M.-C. Oh, M.-H. Lee, J.-H. Ahn, H.-J. Lee and S. G. Han, *Appl. Phys. Lett.*, 1998, **72**, 1559; (e) B. K. Spraul, S. Suresh, S. Glaser, D. Perahia, J. Ballato and D. W. Smith, Jr., *J. Am. Chem. Soc.*, 2004, **126**, 12772.
- 14 (a) D. A. Babb, B. R. Ezzell, K. S. Clement, W. F. Richey and A. P. Kennedy, J. Polym. Sci., Part A: Polym. Chem., 1993, 31, 3465; (b) R. Schwödiauer, G. S. Neugschwandtner, S. Bauer-Gogonea and S. Bauer, Appl. Phys. Lett., 1999, 75, 3998; (c) J. Ghim, K.-J. Baeg, Y.-Y. Noh, S.-J. Kang, J. Jo, D.-Y. Kim, S. Cho, J. Yuen, K. Lee and A. J. Heeger, Appl. Phys. Lett., 2006, 89, 202516.
- 15 (a) X. Gong, D. Moses, A. J. Heeger, S. Liu and A. K.-Y. Jen, Appl. Phys. Lett., 2003, 83, 183; (b) S. Liu, X. Jiang, H. Ma, M. S. Liu and A. K.-Y. Jen, Macromolecules, 2000, 33, 3514; (c) X. Jiang, S. Liu, M. S. Liu, H. Ma and A. K.-Y. Jen, Appl. Phys. Lett., 2000, 76, 2985; (d) X. Jiang, S. Liu, M. S. Liu, P. Herguth, A. K.-Y. Jen, H. Fong and M. Sarikaya, Adv. Funct. Mater., 2002, 12, 745;

- 16 M. Nishiyama, T. Yamamoto and Y. Koie, *Tetrahedron Lett.*, 1998, 39, 617.
- 17 (a) D. M. DeLongchamp, M. Kastantin and P. T. Hammond, *Chem. Mater.*, 2003, **15**, 1575; (b) C. A. Cutler, M. Bouguettaya and J. R. Reynolds, *Adv. Mater.*, 2002, **14**, 684; (c) S. Liu, H. Möhwald, D. Volkmer and D. G. Kurth, *Adv. Mater.*, 2002, **14**, 225; (d) D. M. DeLongchamp and P. T. Hammond, *Adv. Mater.*, 2001, **13**, 1455.

This journal is © The Royal Society of Chemistry 2009