

**Supporting Information for:**

**Cyclopentadithiophene Based Organic Semiconductors: Effect of Fluorinated  
Substituents on Electrochemical and Charge Transport Properties**

J. Sreedhar Reddy, Tejaswini Kale, Ganapathy Balaji, A. Chandrasekaran,  
S. Thayumanavan\*

Department of Chemistry, University of Massachusetts, Amherst, MA 01003, USA

**Experimental**

*Materials*

The cyclopentadithiophene derivatives shown in Chart 1 were synthesized from common intermediates 2,6-dibromo-4,4-ethylenedioxy-4H-cyclopenta[2,1-*b*:3,4-*b'*] dithiophene and 2-bromo-4,4-ethylenedioxy-4H-cyclopenta[2,1-*b*:3,4-*b'*] dithiophene which were synthesized following literature reported procedures.<sup>1-3</sup> N-bromosuccinimide (NBS) was purchased from Aldrich and recrystallized from water before use. All other reagents were purchased from Aldrich and used without further purification.

*Characterization Techniques*

All molecules were characterized using <sup>1</sup>H NMR, <sup>13</sup>C NMR and high resolution mass spectrometry to confirm the molecular structure. <sup>1</sup>H-NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer using the residual proton resonance of the solvent as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. <sup>13</sup>C-NMR spectra were proton decoupled and recorded on a 100 MHz Bruker spectrometer using carbon signal of the deuterated solvent as the internal standard. Cyclic voltammetry experiments were carried out at room temperature

using a BASi C3 cell stand fitted with three electrodes: a platinum disk working electrode, platinum auxiliary electrode and Ag/Ag<sup>+</sup> reference electrode. The voltammograms were recorded in dry dichloromethane (DCM) using tetrabutylammonium hexafluorophosphate as the supporting electrolyte and ferrocene as the internal standard under nitrogen atmosphere. The scan rate in all experiments was 0.1 V/s. UV-Visible spectra were obtained using a Cary 100 spectrophotometer and fluorescence data were collected using JASCO FP-6500 spectrofluorimeter.

### X-ray Studies

The X-ray crystallographic studies were performed using a Nonius KappaCCD diffractometer and graphite monochromated MoK $\alpha$  radiation ( $\lambda=0.71073$  Å). Data was collected at 293 K,  $\theta_{\text{MoK}\alpha} \leq 25^\circ$ . All data was included in the refinement. The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least squares. Refinements were based on F<sup>2</sup> and computations were performed using SHELXS-86 for solution<sup>1</sup> and SHELXL-97 for refinement.<sup>2</sup> All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the refinement as isotropic scatterers riding in ideal positions on the bonded atoms. The hydrogens on disordered atoms were not included in the calculations. The final agreement factors are based on the reflections with  $I \geq 2\sigma_I$ .

### Mobility Measurements

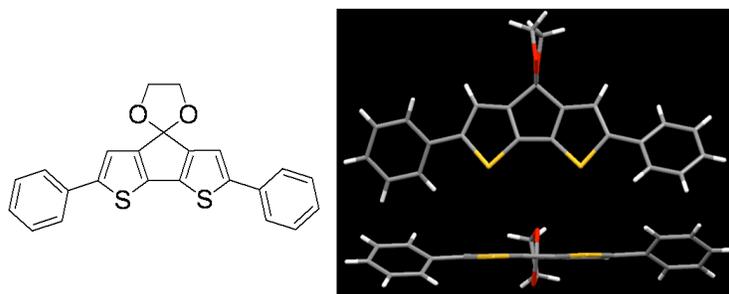
The field effect transistors were constructed using pre-patterned silicon substrates. The transistors were constituted by a heavily n-doped silicon substrate with a 230 nm thermally oxidized silicon dioxide layer with a capacitance of 14.9 nF/cm<sup>2</sup>. Gold

electrodes were deposited on the gate oxide layer to yield the bottom contact FETs. Before deposition of the film, the FET substrates were cleaned with acetone followed by isopropyl alcohol. They were then exposed to HMDS vapor for 1h followed by re-cleaning with isopropyl alcohol. After this, thin films of the samples (~100 nm) were deposited on the surface by spin coating a 0.5 wt% solution in tetrahydrofuran (1500 rpm for 45 seconds). The devices were then annealed for 1 hour at 80 °C. The channel width of all transistors was 10 mm and channel length was 5 μm. All measurements were carried out under inert atmosphere using Agilent 4156C precision semiconductor parameter analyzer.

### *Synthetic Procedures*

#### **Synthesis of 2,6-diphenyl-4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (1)**

A mixture of 2,6-dibromo-4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (0.59 g, 1.5 mmol), **10**, phenyl boronic acid (0.40 g, 3.3 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.17 g, 0.15 mmol) and saturated NaHCO<sub>3</sub> solution (4 mL) in dry dimethoxyethane (DME) (10 mL) was stirred overnight at 80°C. After completion of the reaction, the reaction mixture was transferred to a saturated NH<sub>4</sub>Cl solution in a beaker to yield a yellow suspension. The resulting product was washed with water and extracted into ethyl acetate. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and purified through a silica gel column yielding the diphenylsubstituted product as a yellow solid (0.39 g, 70 % yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.57-7.55 (m, 4H), 7.39-7.35 (m, 4H), 7.29-7.27 (m, 2H), 7.21 (s, 2H), 4.37 (s, 4H) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 150.4, 146.3, 138.2, 134.5, 128.9, 127.5, 125.3, 117.5, 107.9, 65.3 m/z calculated for C<sub>23</sub>H<sub>16</sub>O<sub>2</sub>S<sub>2</sub>: 388.0592, found by EI: 388.0609



### Synthesis of 2,6-diphenyl -4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (2)

A mixture of 2,6-diphenyl-4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (1.5 g, 4.0 mmol) was dissolved with glacial acetic acid at room temperature and HCl (12 M, 3 mL) was added. The reaction was monitored through TLC every 5 minutes until the color changes from a yellow to a dark brown. The reaction was quenched by the addition of water resulting in the formation of a black solid. The solid was collected and washed several times with water and extracted using DCM and purified using a silica gel column yielding a dark brown solid (1.09 g, 72 % yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.55-7.53 (m, 4H), 7.42-7.38 (m, 4H), 7.33-7.31 (m, 2H), 7.22 (s, 2H) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 183.3, 147.9, 147.4, 142.2, 133.6, 129.0, 128.1, 125.1, 116.9 m/z calculated for C<sub>21</sub>H<sub>12</sub>OS<sub>2</sub>: 344.0330 found by EI: 344.0335.

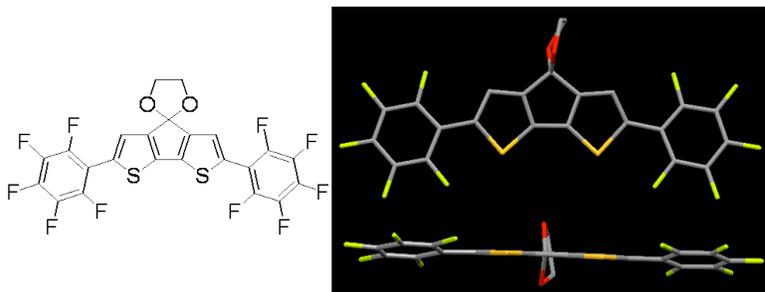
### Synthesis of 2,6-diphenyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-ylidene malononitrile (3)

A mixture of 2,6-diphenyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (115 mg, 0.3 mmol), malononitrile (66 mg, 0.9 mmol) and piperidine (0.2 mL, 1.8 mmol) in CHCl<sub>3</sub> (35 mL) was refluxed for 15 hours. The color of the reaction mixture changed from violet to blue. The reaction mixture was washed with water and extracted into DCM. The mixture was purified by silica gel column to give the title compound as a green solid (79 mg, 69 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.57 (s, 2H), 7.55-7.53 (m, 4H), 7.42-7.38

(m, 4H), 7.35-7.32 (m, 2H)  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 154.8, 147.8, 144.4, 141.3, 133.1, 129.2, 128.5, 125.3, 118.7, 112.5  $m/z$  calculated for  $\text{C}_{24}\text{H}_{12}\text{N}_2\text{S}_2$ : 392.0442 found by EI: 392.0427

**Synthesis of 2,6-bis(pentafluorophenyl)-4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*] dithiophene (4)**

$n\text{BuLi}$  (1.6 M x 1.56 mL, 2.5 mmol) was slowly added at  $-78^\circ\text{C}$  to a solution of 4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene, **9**, (236 mg, 1 mmol) in THF (15 mL). The mixture was kept at this temperature for 20 minutes at which point hexafluorobenzene (1 mL) was added. The resulting mixture was slowly warmed to room temperature over a period of 10 hours. Water was then added and the mixture was extracted into  $\text{CH}_2\text{Cl}_2$  several times. The combined organic extracts were washed with brine and dried over  $\text{Na}_2\text{SO}_4$ . After removal of the volatile components under reduced pressure, the residue was purified by a silica gel column using  $\text{CH}_2\text{Cl}_2$ /hexane as an eluent. This yielded a yellow solid (230 mg, 40 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.45 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 150.8, 145.0, 142.5, 141.1, 139.3, 138.5, 136.8, 128.7, 124.2, 109.9, 107.5, 65.5  $m/z$  calculated for  $\text{C}_{23}\text{H}_6\text{F}_{10}\text{O}_2\text{S}_2$ : 567.9650 found by EI: 567.9622



**Synthesis of 2,6-bis(pentafluorophenyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (5)**

Compound **5** was prepared from the corresponding dioxolane, **4**, 2,6-bis(pentafluorophenyl)-4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene, using a similar procedure as described above for the synthesis of **2**. The title compound was obtained in 62% yield as a reddish brown solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.50 (s, 2H); m/z calculated for C<sub>21</sub>H<sub>2</sub>F<sub>10</sub>OS<sub>2</sub>: 523.9387 found by EI 523.9360

**Synthesis of 2,6-bis(pentafluorophenyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-ylidenemalononitrile (6)**

Compound **6** was prepared from 2,6-bis(pentafluorophenyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one, **5**, using a similar procedure as described above for the synthesis of **3**. The title compound was obtained in 39% yield as a dark blue solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.88 (s, 2H) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 180.1, 153.1, 146.4, 145.2, 142.7, 141.2, 139.4, 136.8, 130.1, 125.6, 112.0, 108.6 m/z calculated for C<sub>24</sub>H<sub>2</sub>F<sub>10</sub>N<sub>2</sub>S<sub>2</sub>: 571.9500 found by EI 571.9501

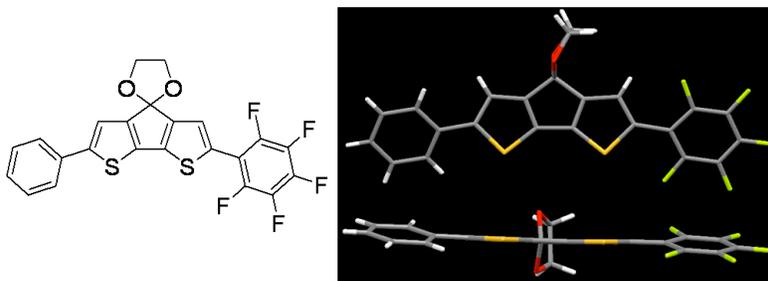
**Synthesis of 2-phenyl-4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (12)**

This compound was prepared from 2-bromo-4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene, **11**, using Suzuki coupling conditions, using 1 eq. of phenyl boronic acid, as described earlier for the synthesis of **1**. The title compound was obtained in 72% yield as a light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.62-7.60 (m, 2H), 7.44-7.40 (m, 2H), 7.34-7.30 (m, 1H), 7.27 (s, 1H), 7.19(d, 1H, J = 4.9 Hz), 7.03(d, 1H, J = 4.9 Hz), 4.39 (s, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 150.8, 149.8, 138.2, 146.0, 139.2, 138.1,

134.5, 128.9, 127.5, 126.4, 125.3, 121.5, 117.6, 107.6, 65.2 m/z calculated for  $C_{17}H_{12}O_2S_2$ : 312.0279 found by EI: 312.0284.

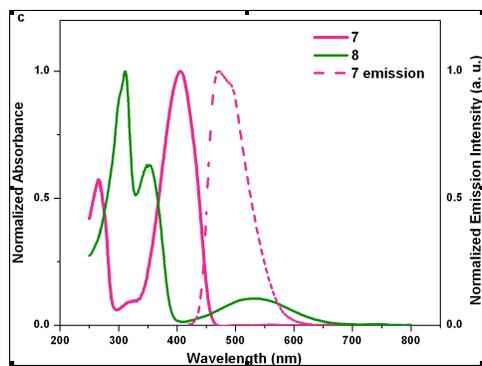
**Synthesis of 2-pentafluorophenyl,6-phenyl-4,4-ethylenedioxy-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (7)**

This compound was prepared from 2-phenyl-4,4-ethylenedioxy-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene, **12**, using the procedure described above for the synthesis of **4**. The title compound was obtained in 52% yield as a dark yellow solid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 7.58-7.56 (m, 2H), 7.43 (s, 1H) 7.39-7.37 (m, 2H), 7.31-7.29 (m, 1H), 7.22 (s, 1H), 4.36 (s, 4H)  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$ : 151.7, 149.6, 147.9, 144.8, 142.3, 139.3, 138.3, 137.1, 134.2, 129.0, 127.8, 127.1, 125.4, 124.2, 124.1, 117.6, 107.7, 65.4 m/z calculated for  $C_{23}H_{11}F_5O_2S_2$ : 478.0121 found by EI: 478.0126



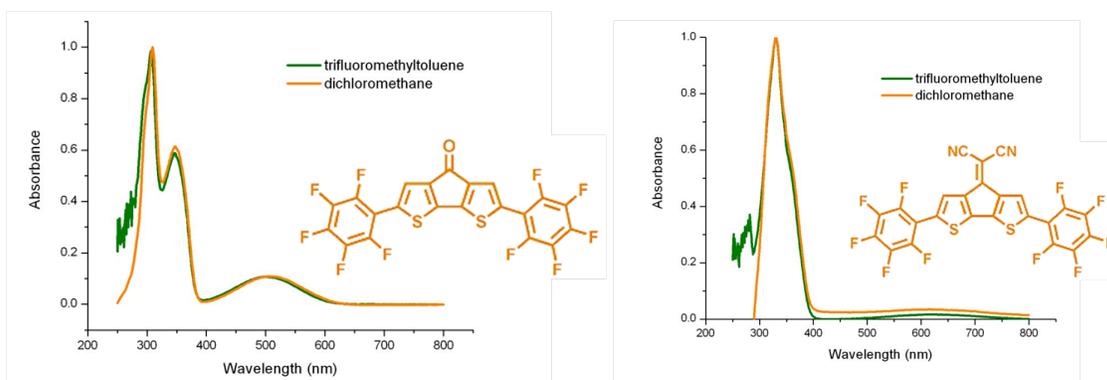
**Synthesis of 2-pentafluorophenyl,6-phenyl-4,4-ethylenedioxy-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (8)**

This compound was prepared from the corresponding dioxolane 2-pentafluorophenyl,6-phenyl-4,4-ethylenedioxy-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene, **7**, using the procedure described for the synthesis of **2**. The title compound was obtained in 64% yield as a grey color solid.  $^1H$  NMR (400 MHz,  $CDCl_3$ , 323K)  $\delta$ : 7.57-7.55 (m, 2H), 7.45 (s, 1H) 7.41-7.39 (m, 2H), 7.35-7.33 (m, 1H), 7.26 (s, 1H) m/z calculated for  $C_{21}H_7F_5OS_2$ : 433.9858 found by EI 433.9821

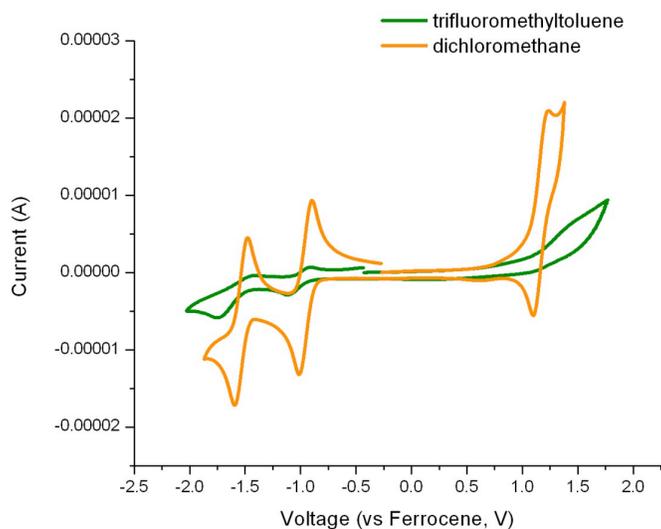


**Figure S1:** UV-vis absorption and emission spectra of **7-8**

*Effect of solvent on optoelectronic properties of molecules containing pentafluorophenyl groups*



**Figure S2:** Comparison of UV-vis absorption spectra recorded in dichloromethane and trifluoromethylbenzene

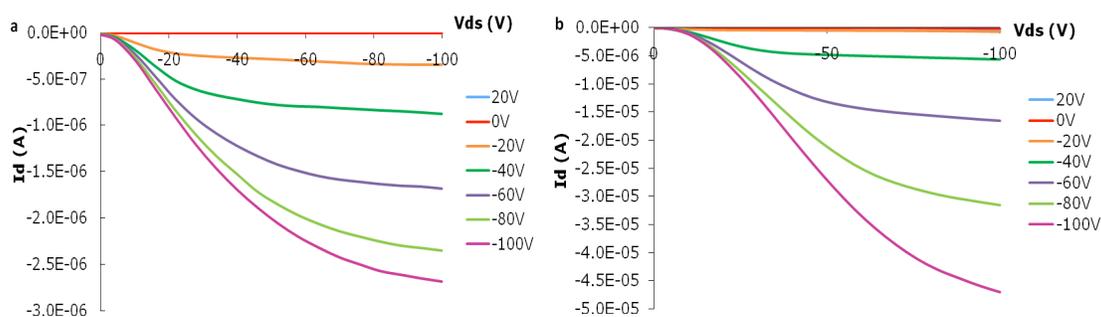


**Figure S3:** Comparison of cyclic voltammograms of **6** recorded in dichloromethane and trifluoromethyl toluene

#### *Mobility Measurement: Output Characteristics*

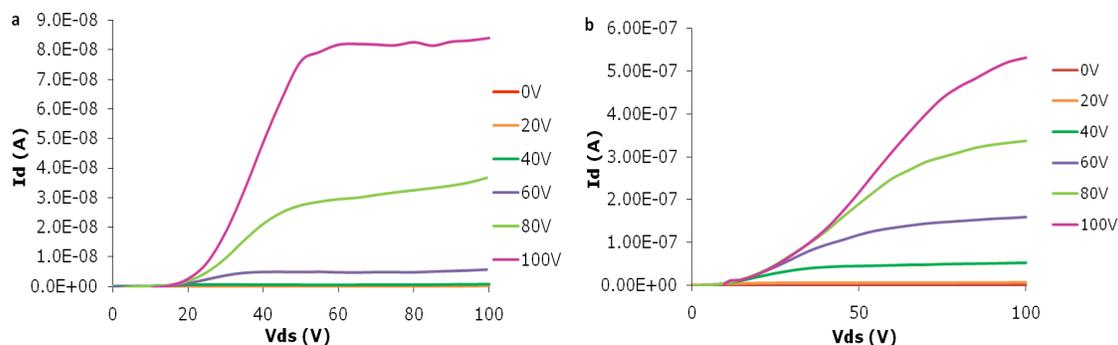
Field effect transistors were fabricated to determine the charge mobility in the molecules. All films were cast for 0.5 wt% solution in tetrahydrofuran, except molecule **2**, which did not yield a film from tetrahydrofuran. Chlorobenzene was used as solvent in this case. All measurements were carried out as  $W/L = 2000$ .

Molecules **2** and **3** are hole transporting materials. Output characteristics for these molecules are shown in Figure S4.



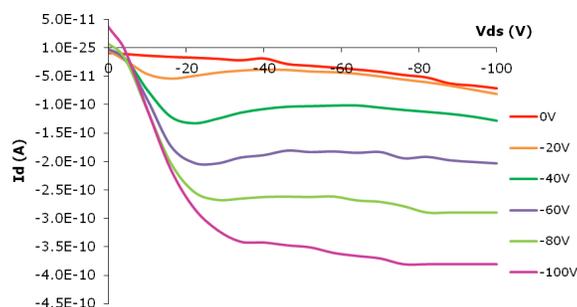
**Figure S4:** Output characteristics of **2** (left) and **3** (right) from the mobility measurements

Molecules **3** and **4** are electron transporting materials. Output characteristics for these molecules are shown in Figure S5.



**Figure S5:** Output characteristics of **5** (left) and **6** (right) from the mobility measurements

Molecule **8** is a hole transporting material. Output characteristics for **8** are shown in Figure S6.



**Figure S6:** Output characteristics of unsymmetrically substituted ketone **8**

### References

- (1) Coppo, P.; Turner, M. L. *J. Mater. Chem.* **2005**, *15*, 1123.
- (2) Roncali, J. *Chem. Rev.* **1997**, *97*, 173.
- (3) Yen, W.; Pal, B.; Yang, J.; Hung, Y.; Lin, S.; Chao, C.; Su, W. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 5044.