

熱血格鬥類卡通收視行為對國中生在校霸凌行為影響之研究 = The research of how the viewing behavior of fighting and adventure

戴瑞宏、林朝源

E-mail: 354842@mail.dyu.edu.tw

摘要

共軛高分子是很重要的有機半導體材料，其可應用於發光二極體、光伏電池、場發射傳輸、薄膜電晶體等。高分子光伏電池近年來引起外界注意的目光是因其成本低、重量輕、具可撓性與容易使用溶液製程之製作上的潛力。因此，利用氧化聚合合法合成一系列低規則度的P3HT及交替式H-H、T-T之poly(bithiophen)及其溴化衍生物，藉由兩相臨thiophene上的取代基，溴，利用分子內反應使其在兩相臨thiophene間形成四環狀，藉此提高共軛程度。經由核磁共振光譜儀(NMR)和傅立葉紅外線光譜儀(FT-IR)鑑定其結構，飛行時間法(TOF)鑑定其物理性質，熱重量分析儀(TGA)與微分掃描熱卡儀(DSC)鑑定其熱性質，紫外光可見光吸收光譜儀(UV-Vis)、光激發光譜儀(PL)與光電光譜儀(PESA)鑑定其光學性質。

關鍵詞：溴化、共軛高分子

目錄

Chapter.1 Introduction 1.1 Green Energy resources 1.2 Solar energy 1.3 Organic/Polymer Photovoltaic Theory 1.4 Characteristics general of polymer photovoltaic devices (PV character) 1.5 Structure of organic solar cell device 1.6 Reference review 1.6.1 The development of conjugated polymers 1.7 Polymer Photovoltaic Device Architecture Review [25] 1.7.1 Single layer 1.7.2 Double layer 1.7.3 Bulk heterojunction 1.7.4 Ordered bulk heterojunction 1.8 Motivation Chapter 2 Experimental and Results Synthesis and Properties of Low Regioregularity Random P3HTs and Polybithiophene. 2.1 Materials 2.2 Equipment 2.3 Synthesis of monomers 2.4 Synthesis of polymers 2.5 Identify and Characterization 2.5.1. Nuclear Magnetic Resonance Spectroscopy (NMR) 2.5.2 Fourier Transform Infrared Spectroscopy (FT-IR) 2.5.3MALDI/TOF-TOF 2.5.4Thermogravimetric Analysis (TGA) 2.5.5 Differential Scanning Calorimetry Analysis (DSC) 2.5.6 Absorption and Photoluminescence Spectroscopy (UV&PL) 2.5.7 Photo-electron spectroscopy in air (PESA) Chapter.3 Experimental and Results Synthesis and Properties of bromo-substituted P3HTs and poly(bithiophene). 3.1 Materials 3.2 Equipment 3.3Synthesis of polymers 3.4 Identify and Characterization 3.4.1 Nuclear Magnetic Resonance Spectroscopy (NMR) 3.4.2 Fourier Transform Infrared Spectroscopy (FT-IR) 3.4.3MALDI/TOF-TOF 3.4.4Thermogravimetric Analysis (TGA) 3.4.5 Differential Scanning Calorimetry Analysis (DSC) 3.4.6 Absorption and Photoluminescence Spectroscopy (UV&PL) 3.4.7 Photo-electron spectroscopy in air (PESA) Chapter.4 Synthesis and Properties of cyclization of full bromo -substituted P3HTs and poly(bithiophene). 4.1 Materials 4.2 Equipments 4.3 Synthesis of the Polymers 4.3.1General procedure of preparation of Poly(cyclebutadihexythiophene)(PCBT) 4.4 Identify and Characterization 4.4.1 Differential Scanning Calorimetry Analysis (DSC) Chapter.5 Results and Discussion 5.1 The Polymer Physical Properties 5.2 The Thermal Stability Properties 5.3 Optical properties Chapter.6 Conclusion: Reference List of Figures Fig. 1.1 The spectrum of solar illumination in AM 1.5. Fig. 1.2 The kinds of the air mass. Fig. 1.3 Energy levels and light harvesting. Fig. 1.4. I-V curves of the PV cell under dark (idark) and illuminated (isc) conditions. Fig. 1.5 The architecture in polymer photovoltaic device. Fig. 1.6 Single-layer polymer photovoltaic device. Fig. 1.7 Double-layer polymer photovoltaic device. Fig. 1.8 Bulk heterojunction polymer photovoltaic device. Fig. 1.9 Ordered bulk heterojunction polymer photovoltaic device. Fig. 2.1 Synthesis of 3-hexylthiophene Fig. 2.2 Synthesis of 2-bromo-3-hexylthiophene Fig. 2.3 Synthesis of 3,3' -dihexyl-2,2' -bithiophene Fig. 2.4 Synthesis of RT Random poly(3-hexylthiophene) Fig. 2.5 Synthesis of LT Random poly(3-hexylthiophene) Fig. 2.6 Synthesis of Poly(3,3' -dihexyl-2,2' -bithiophene) Fig. 2.7 1H NMR spectrum of T6. Fig. 2.8 1H NMR spectrum of 2BT6 Fig. 2.9 1H NMR spectrum of C6BiT Fig. 2.10 1H NMR spectrum of RT0 Fig. 2.11 1H NMR spectrum of LT0 Fig. 2.12 1H NMR spectrum of PC6BiT Fig. 2.13 FT-IR spectra of monomers. Fig. 2.14 FT-IR spectra of polymers. Fig. 2.15 MALDI/TOF-TOF spectrum of LT0 Fig. 2.16MALDI/TOF-TOF spectrum of RT0 Fig. 2.17 MALDI/TOF-TOF spectrum of PC6BiT Fig. 2.18 Thermogravimetry analysis (TGA) cureves of P3HTs and poly(bithiophen). Fig. 2.19 Differential Scanning Calorimetry (DSC) curves of P3HTs and poly(bithiophen). Fig. 2.20 Normalized absorption spectra of P3HTs and poly(bithiophen) in solution Fig. 2.21 Normalized absorption spectra of P3HTs and poly(bithiophene) as thin film. Fig. 2.22 Normalized fluorescence spectra of P3HTs and poly(bithiophene) in solution and as thin film. Fig. 2.23 The energy levels of P3HTs and poly(bithiophen). Fig. 3.1 General procedure of Random Poly(3-bromo4-hexylthiophene). Fig. 3.2 Synthesis of Poly(4,4' -dibromo-3,3' -dihexyl-2,2' -bithiophene) Fig. 3.3 1H NMR spectrum of LT50. Fig. 3.4 1H NMR spectrum of LT75. Fig. 3.5 1H NMR spectrum of LT100. Fig. 3.6 1H

NMR spectrum of PC6BiBT. Fig. 3.7 ¹H NMR spectrum of RT50. Fig. 3.8 ¹H NMR spectrum of RT75. Fig. 3.9 ¹H NMR spectrum of RT100. Fig. 3.10 FT-IR spectra of LT bromo-substituted P3HTs. Fig. 3.11 FT-IR spectra of RT bromo-substituted P3HTs. Fig. 3.12 FT-IR spectra of highest bromo-substituted P3HTs and poly(bithiophene). Fig. 3.13 MALDI/TOF-TOF spectrum of LT50 Fig. 3.14 MALDI/TOF-TOF spectrum of LT75 Fig. 3.15 MALDI/TOF-TOF spectrum of LT100. Fig. 3.16 MALDI/TOF-TOF spectrum of RTPC6BiBT Fig. 3.17 MALDI/TOF-TOF spectrum of RT50. Fig. 3.18 MALDI/TOF-TOF spectrum of RT75. Fig. 3.19 MALDI/TOF-TOF spectrum of RT100. Fig. 3.20 Thermogravimetry analysis (TGA) curves of partially bromo-substituted RT P3HTs. Fig. 3.21 Thermogravimetry analysis (TGA) curves of partially bromo-substituted LT P3HTs and poly(bithiophene). Fig.3.22 Differential Scanning Calorimetry Analysis of partially bromo-substituted P3HTs and poly(bithiophene) glass transition temperature. Fig. 3.23 Normalized absorption spectra of partially bromo-substituted P3HTs and PC6BiBT in solution. Fig. 3.24 Normalized absorption spectra of partially bromo-substituted P3HTs and PC6BiBT as thin film. Fig. 3.25 Normalized fluorescence spectra of partially bromo-substituted P3HTs and PC6BiBT in solution Fig. 3.26 Normalized fluorescence spectra of partially bromo-substituted P3HTs and PC6BiBT as thin film. Fig. 3.27 Normalized absorption spectra of LT bromo-substituted P3HTs in solution. Blue line: Dissolved in chloroform. Red line: dissolved in THF. Fig. 3.28 Normalized absorption spectra of LT bromo-substituted P3HTs as thin film. Blue line: Dissolved in chloroform. Red line: dissolved in THF. Fig. 3.29 Normalized absorption spectra of RT bromo-substituted P3HTs in solution. Blue line: Dissolved in chloroform. Red line: dissolved in THF. Fig. 3.30 Normalized absorption spectra of RT bromo-substituted P3HTs as thin film. Blue line: Dissolved in chloroform. Red line: dissolved in THF. Fig. 3.31 The HOMO energy levels (work functions) of P3HTs have obtained determination by PESA. Fig. 4.2 Differential Scanning Calorimetry (DSC) curves of Poly(cyclebutadihexythyophene)s Fig. 5.1 The curves of relation T_d with bromine incorporation ratio. Fig.5.2 The curves of relation \max_{abs} with bromine incorporation ratio. List of Tables Table 1.1 All the solar cell types. Table 2.1 The molecular weight of random P3HTs and Poly(bithiophene). Table 2.2 Thermogravimetric analysis of random P3HTs and Poly(bithiophene) determine by 5% weight loss. Table 2.3 Differential Scanning Calorimetry Analysis of random P3HTs and Poly(bithiophene) glass transition temperature. Table 2.4 Optical Properties of P3HTs and Poly(bithiophene) Table 2.5 The energy levels of P3HTs and poly(bithiophen). Table 3.1 The molecular weight of partially bromo-substituted P3HTs and Poly(bithiophene). Table 3.2 Thermogravimetric analysis of partially bromo-substituted P3HTs and Poly(bithiophene) determine by 5% weight loss. Table.3.3 Differential Scanning Calorimetry Analysis of random P3HTs and Poly(bithiophene) glass transition temperature. Table.3.4 Optical Properties of partially bromo-substituted P3HTs and poly(bithiophene). Table.3.5 UV-vis of partially bromo-substituted P3HTs dissolved in THF and Chloroform. Table.3.6 The energy levels of partially bromo-substituted P3HTs and poly(bithiophene). Table 4.1 Differential Scanning Calorimetry (DSC) of Poly(cyclebutadihexythyophene)s List of Schemes Scheme 2.1 The synthesis of P3HTs and poly(bithiophene) Scheme 3.1 The synthesis of bromo-substituted P3HTs and poly(bithiophene). Scheme.4.1 The synthesis of full bromo-substituted P3HTs and poly(bithiophene).

參考文獻

1. Kevin M. Coakley and Michael D. McGehee, "Conjugated Polymer Photovoltaic Cells", *Chem. Mater.*, 16, 4533 (2004).
2. Adam P. Smith, Rachel R. Smith, Barney E. Taylor, and Michael F. Durstock, "An Investigation of Poly(thienylene vinylene) in Organic Photovoltaic Devices", *Chem. Mater.*, 16, 4687 (2004).
3. Shuxin Tan, Jin Zhai, Meixiang Wan, Qingbo Meng, Yuliang Li, Lei Jiang, and Daoben Zhu, "Influence of Small Molecules in Conducting Polyaniline on the Photovoltaic Properties of Solid-State Dye-Sensitized Solar Cells", *J. Phys. Chem. B*, 108, 18693 (2004).
4. Zhan 'ao Tan, Jianhui Hou, Youjun He, Erjun Zhou, Chunhe Yang, and Yongfang Li, "Synthesis and Photovoltaic Properties of a Donor/Acceptor Double-Cable Polythiophene with High Content of C60 Pendant", *Macromolecules*, 40, 1868 (2007).
5. 張正華, 季陵嵐, 葉楚平, 楊平華, 馬振基, "有機與塑膠太陽能電池" (2007).
6. Holger Spanggaard, Frederik C. Krebs, "A brief history of the development of organic and polymeric photovoltaics", *Solar Energy Materials & Solar Cells*, 83, 125 (2004).
7. Nelson, J., *Phys. Rev. B*, 67, 155209 (2002).
8. H. Antoniadis, B.R. Hsieh, M.A. Abkowitz, S.A. Jenekhe, M. Stolka, Photovoltaic and photoconductive properties of aluminum/poly(p-phenylene vinylene) interfaces, *Synth. Met.*, 62, 265 (1994).
9. G. Yu, C. Zhang, A.J. Heeger, *Appl. Phys. Lett.*, 64, 1540 (1994).
10. R.N. Marks, J.J.M. Halls, D.D.C. Bradley, R.H. Friend, A.B. Holmes, "The photovoltaic response in poly(p-phenylene vinylene) thin-film devices", *J. Phys. Condens. Matter*, 6, 1379 (1994).
11. C.J. Brabec, A. Cravino, D. Meissner, N.S. Sariciftci, M.T. Rispen, L. Sanchez, J.C. Hummelen, T. Fromherz, "The influence of materials work function on the open circuit voltage of plastic solar cells", *Thin Solid Films*, 403,368 (2002).
12. Adam P. Smith, Rachel R. Smith, Barney E. Taylor, and Michael F. Durstock, "An Investigation of Poly(thienylene vinylene) in Organic Photovoltaic Devices", *Chem. Mater.*, 16, 4687 (2004).
13. H. Shirakawa, E.J. Louis, A.G. MacDiramid, C.K. Chiang, A.J. Heeger, *J. Chem. Soc., Chem. Commun.*, 578 (1977).
14. H. Shirakawa, "The Discovery of Polyacetylene Film: The Dawning of an Era of Conducting Polymers (Nobel Lecture)", *Angew. Chem. Int. Engl.*, 40, 2574 (2001).
15. A. G. MacDirmid, *Synthetic Metals: A Novel Role for Organic Polymers (Nobel Lecture)*, *Angew. Chem. Int. Ed. Engl.*, 40, 2581 (2001).
16. A. J. Heeger, "Semiconducting and Metallic Polymers: The Fourth Generation of Polymeric Materials (Nobel Lecture)", *Angew. Chem. Int. Ed. Engl.*, 40, 2591 (2001).
17. G. Tourillon, in *Handbook of conducting of Polymer*, T. A.

Stothenim, Ed. Marcel Dekker, New York, 294 (1986). 18. A. F. Diaz, K. K. Kanazawa, G. P. Gardini, J. Chem. Soc., Chem. Commun., 635 (1979). 19. J. G. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burns and A. B. Holmes, Nature, 247, 539 (1990). 20. (a) K. Y. Jen, R. Oboodi, R. L. Elsenbaumer, Polym. Mater. Sci. Eng. 53, 79 (1985). (b) R. L. Elsenbaumer, K. Y. Jen, R. Oboodi, "Processible and environmentally stable conducting polymers", Synth. Met., 15, 169 (1986). 21. G. G. Miller, R. L. Elsenbaumer, J. Chem. Soc., Chem. Commun. 1346 (1986). 22. J. J. M. Halls and R. H. Friend, in Clean electricity from photovoltaic, edited by M. D. Archer and R. Hill (Imperial College Press, London) 377 (2001). 23. (a) C. D. Dimitrakopoulos, D. J. Mascaro, "Organic Thin Film Transistors for Large Area Electronics", Adv. Mater. 14, 99 (2002) (b) F. Garnier, R. Hajlaoui, A. Yassar, P. Srivastava, "All-Polymer Field-Effect Transistor Realized by Printing Techniques", Science, 265, 1684 (1994). (c) Z. Bao, "Materials and Fabrication Needs for Low-Cost Organic Transistor Circuits", Adv. Mater., 12, 227 (2000). (d) G. H. Gelinck, T. C. T. Geuns, D. M. De Leeuw, Appl. Phys. Lett., 77, 1487 (2000). (e) H. E. A. Huitena, G. H. Gelinck, J. B. P. H. van der Putter, K. E. Kuijk, C. M. Hart, E. Cantatore, P. T. Herwig, A. J. J. M. van Breemen, D. M. de Leeuw, Nature, 414, 599 (2001). (f) B. S. Ong, Y. Wu, P. Liu, S. Gardner, J. Am. Chem. Soc., 126, 3378 (2004). 24. L. Akcelrud, Prog. Polym. Sci., 28, 875 (2003). (b) R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. dos Santos, J. L. Bredas, M. Loglund, W. R. Salaneck, Nature, 397, 121, (1999). (c) A. Kraft, A. Grimsdale, A. B. Holmes, Angew. Chem. Int., 37, 402 (1998). (d) J. R. Sheats, Y. L. Chang, D. B. Roitman, A. Socking, Acc. Chem. Res., 32, 193 (1999). (e) S. Miyata H. S. Nalwa, in Organic electroluminescent materials and devices. Amsterdam: Gordon & Breach (1997). (f) X. Gong, J. C. Ostrowski, M. R. Robinson, D. Moses, G. C. Bazan, A. J. Heeger, Adv. Mater., 14, 581 (2002). (g) R. H. Partridge, Polymer, 24, 733 (1983). 25. (a) J. Christoph, J. Brabec, N. S. Sariciftci, J. C. Hummelen, Adv. Funct. Mater., 11, 15 (2001). (b) J. Xue, S. Uchida, B. P. Rand, S. R. Forrest, Appl. Phys. Lett., 84, 3013 (2004). (c) N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, Science, 258, 1474 (1992). (d) S. Morita, A. A. Zakhidov, K. Yoshino, Solid State Commun., 82, 249 (1992). 26. Yuning Li, George Vamvounis, Steven Holdcroft, "Facile Functionalization of Poly(3-alkylthiophene)s via Electrophilic Substitution", Macromolecules, 34, 141 (2001). 27. Kenneth J. Hoffmann, Eivind Bakken, Emil J. Samuelsen, Per H.J. Carlsen, "Synthesis and polymerization of 3,3'-dialkyl-2,2'-bithiophenes Synthetic Metals", 113, 39(2000). 28. 黃北辰, 高雄應用科技大學化學工程與材料工程所碩士論文, (2007). 29. 李易展, 高雄應用科技大學化學工程與材料工程所碩士論文, (2008). 30. 藍鈺欣, 高雄應用科技大學化學工程與材料工程所碩士論文, (2009).