

行政院國家科學委員會補助專題研究計畫 成果報告

官能性高分子 (2/2)

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計畫主持人：許慶豐

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行政院國家科學委員會專題研究計畫成果報告

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執行機構及單位名稱：國立交通大學應用化學系

一、中文摘要

Part 1: 我們合成新型的芴共聚物，將缺電子的基團 4-*tert*-butylphenyl-1,3,4-oxadiazole 置放於每一間隔芴的碳-9 位置，形成三維的 cardo 結構。由於剛性的 cardo 結構，使得此共聚物有很高的玻璃轉移溫度 (213 °C) 及好的熱安定性，也導致於高分子膜在高溫熱處理後 (150 °C, 20 小時)，在測量螢光時，沒有發現 aggregate 或 excimer 的形成。利用這高分子為發光層的電激光二極體可發出藍光，它的起始電壓為 5.3 伏特；在 10.8 伏特時，亮度為 2770 cd/m²。最大外部量子效率為 0.52%，當電壓為 7.4 伏特，當時的亮度為 537 cd/m²。

Part 2: 我們的合成及鑑定一系列含有懸垂各種階層 benzyl-ether 楔形物的聚芴高分子。我們先合成各種階層 benzyl-ether 楔形物的芴單體，然後進行 Suzuki 反應，來形成我們所要的芴共聚物。這些芴聚合物的螢光性質受到在側鏈上楔形物的大小影響，由於遮護效應，高階層的楔形物使得高分子有較佳的螢光效率及安定性。

關鍵詞：聚芴高分子；電激光二極體；楔形物。

Abstract

Part 1: A novel polyfluorene copolymer (PF-OXD) was synthesized by attaching two electron-deficient, 4-*tert*-butylphenyl-1,3,4-oxadiazole groups onto the C-9 position of the alternating fluorene unit to form a 3-D cardo-structure. This polymer possesses a very high T_g (213 °C) and very good thermal stability due to its rigid cardo-linkage. The results from the photoluminescence measurements of the isothermal heated

PF-OXD thin film (150 °C for 20 h) show that the commonly observed aggregate/excimer formation in polyfluorenes is very effectively suppressed in this polymer due to its 3-D structure and high T_g . A double-layer LED device using this polymer as the emitting layer shows a bright blue emission with a low turn-on voltage at 5.3 V and a high brightness of 2770 cd/m² at a drive voltage of 10.8 V. The maximum external quantum efficiency is 0.52 % at 537 cd/m² with a bias of 7.4 V. The improved device performance over that of POF may be due to better charge injection and transport from PF-OXD and the efficient energy transfer from OXD side chain to the polyfluorene main chains. (Wu, F. -I.; Reddy, D. S.; Shu, C. -F.; Liu, M. S.; Jen, A. K. -Y. "A Novel Oxadiazole-Containing Polyfluorene with Efficient Blue Electroluminescence" *Chem. Mater.* **2003**, *15*, 269.)

Part 2: A series of polyfluorenes containing pendant poly(benzyl ether) dendritic wedges of different generations was synthesized via the macromonomer approach, and then characterized by their structures and properties. The dendritic monomers were prepared by coupling benzyl bromide-functionalized dendrons with 9,9-bis(4-hydroxyphenyl)-2,7-dibromofluorene and were subsequently copolymerized with a 9,9-dioctylfluorene diboronate derivative by the Suzuki coupling reaction to give the target alternating copolymers. Photophysical studies reveal that the photoluminescent properties of the dendronized polymers are greatly affected by the size of the dendritic side chains. Polymers appended with higher generation dendrons exhibit an enhanced

photoluminescence efficiency and an improved luminescent stability. This is attributed to the shielding effect induced by the bulky dendrimer side chains, which prevent self-quenching and suppress the formation of aggregates/excimers. (Chou, C. -H.; Shu, C. -F. "Synthesis and Characterization of Dendronized Polyfluorenes" *Macromolecules* **2002**, *35*, 9673.)

Keywords: polyfluorene; LED device; dendrons.

二、Introduction

Part 1: Since the discovery of polymer-based light-emitting diodes (PLEDs) in 1990,¹ considerable progress has been made in the development of new conjugated polymers and exploration of their applications in displays.² Organic luminescent polymers are attractive due to the flexibility in fine-tuning their luminescent properties through the manipulation of chemical structures, and the feasibility of combining spin-coating and printing processes for large-area flat panel displays. In full color display applications, polymer with large energy band gap that can efficiently emit blue light and can also serve as the energy-transfer donor in the presence of lower energy fluorophores is highly desirable.³ Polyfluorenes (PF), with their high photoluminescence (PL) and electroluminescence (EL) efficiencies, are among the most promising candidates as blue-emitting polymers.⁴ The facile functionalization at the C-9 position of the fluorene unit provides the opportunity to improve both the solubility and processability of the resulting polymers, while offering the ability to reduce inter-chain interactions,⁵ and cross-linking side reactions.⁶ It also offers a good mechanism to improve the charge-injecting or -transporting properties of the polymers if either an electron- or a hole-transporter can be directly attached onto this position. Herein, we report the synthesis and

characterization of a fluorene-based alternating copolymer containing oxadiazole moieties with their phenyl end group directly attached to the C-9 carbon in every alternating fluorene unit. Our motivation for the synthesis of this novel copolymer can be explained in 3-fold. First, since PF has been proved to be a better hole-transporting polymer, the incorporation of an electron-deficient oxadiazole group will result in an increased electron affinity and transporting properties of the polymer, leading to a more balanced charge recombination in the polymer emissive layer.⁷ Second, the 3-D cardo-oxadiazole structure linked on the C-9 position may help preventing π -stacking between polymer chains and suppressing the formation of excimers in the solid state. Furthermore, the rigidity of the main chain will be preserved, yielding a polymer with a much higher glass transition temperature and better thermal stability. Third, the sp³ carbon (C-9) serves as a spacer to effectively block the conjugation between the oxadiazole side chains and the polymer backbone.⁸ Thus, the conjugation and the integrality of the emission spectrum of the PF main chain will be remain unperturbed.

Part 2: Since the discovery of polymer-based light emitting diodes (PLEDs) in 1990,¹ considerable progress has been made in the development of new conjugated polymers and in the performance of related LEDs.² Organic luminescent polymers are attractive due to the flexibility in fine tuning their luminescent properties through the manipulation of chemical structures, along with the feasibility of utilizing spin-coating and printing processes for large area display devices. Polymers with large energy band gaps that emit blue light efficiently are of special interest; these materials are desired for full color display applications and also serve as energy-transfer donors in the presence of lower energy fluorophores.³ Due to their high photoluminescence and electroluminescence efficiencies, polyfluorenes are among the most promising

candidates for blue-emitting polymers.⁴ However, a major problem with polyfluorenes concerns their tendency to form long-wavelength aggregates/excimers in the solid state upon heating.⁵ This leads to issues of color instability of the light emitted from LEDs fabricated with polyfluorenes.

Dendritic macromolecules are characterized by a central polyfunctional core, from which monomeric units with branching points arise successively. This results in a nearly entanglement-free, highly branched polymeric structure with a well defined three-dimensional architecture.⁶ Dendronized polymers, consisting of a linear, polymeric core appended with dendrons or dendrimers, form another class of macromolecules which is presently being given considerable attention.⁷ There are two principally different synthetic routes to dendronized polymers. In the macromonomer route, the desired dendrons are attached to the monomer unit before polymerization.⁸ In the attach-to route, the polymers which become the core in the final product possess anchor groups to either convergently or divergently attach a dense sequence of dendrons.⁹ The dendronized approach has been applied to polymers with conjugated polymer backbones such as poly(*p*-phenylene),¹⁰ poly(*p*-phenylene-vinylene),¹¹ poly(*p*-phenyleneethynylene),¹² and poly(thiophene).¹³ Recently, Müllen et al. reported polyfluorenes appended with polyphenylene dendrons, anticipating that the incorporation of the three-dimensional dendritic side chain to the light-emitting polymer would improve its luminescent activity.¹⁴ While this paper was in preparation, Carter et al. reported the synthesis of dendronized polyfluorenes containing “Fréchet-type” dendrons, with their focal benzyl group directly bonded to the C-9 carbon of the fluorene units.^{15,16} Both groups demonstrated that the shielding effect provided by the dendritic side chains on the conjugated polyfluorene backbone suppresses the formation of aggregates/excimers.^{14,16} More recently,

Fujiki group reported an unsymmetrically substituted polyfluorene bearing a bulky poly(benzyl ether) dendron and a less bulky 3,6-dioxaoctyl group in the C-9 position and showed that this polymer gives a pure bluish photoluminescence with negligible excimer emission around 520 nm.¹⁷

The facile functionalization at the C-9 position of the fluorene unit provides the opportunity to improve both the solubility and processability of the resulting polymers, while offering the ability to control interchain interactions,^{14,16} cross linking,¹⁸ and the charge-injecting or -transporting properties of the polymers.^{19,20} Herein, we report the synthesis and characterization of fluorene-based alternating copolymers containing poly(benzyl ether) dendritic wedges as side chains, with their benzyl focal point attached through a 4-hydroxyphenylene spacer to the C-9 carbon in every alternating fluorene unit. The extended 9,9-bis(4-hydroxyphenyl)-fluorenyl core is easily accessible, and will offer the following advantages. First, it avoids the direct attachment of benzyl groups to the fluorene unit. The benzyl linkages at the C-9 position of polyfluorenes are potentially susceptible to photooxidation, which may cause polymer degradation and device failure in polymer LEDs.^{2a,14} Second, the extended core reduces steric hindrance and offers easy access to the introduction of high generation dendrons with bulky frameworks into the fluorene unit.²¹ In addition, the coupling of “Fréchet-type” dendrons with the extended fluorenyl core is readily available via the Williamson ether synthesis to afford the desired macromonomers. Third, the insertion of a rigid phenylene spacer between the dendritic side chain and the polymer backbone may lead to a more efficient shielding effect on the polyfluorene main chain, while not blocking the reaction sites of the macromonomer from the palladium-catalyzed polymerization reaction.

三、Results and Discussion

Part 1: We have developed a novel polyfluorene copolymer with two electron-deficient, 4-*tert*-butylphenyl-1,3,4-oxadiazole groups functionalized on the C-9 position of the alternating fluorene unit to form a 3-D cardo-structure. This polymer possesses a very high T_g (213 °C) and very good thermal stability. The results from the photoluminescence measurements of the isothermal heated PF-OXD thin film (150 °C for 20 h) show that the commonly observed aggregate/excimer formation is very effectively suppressed in this polymer due to its 3-D structure and high T_g . A double-layer LED device using this polymer as the emitting layer shows a bright blue emission with a low turn-on voltage at 5.3 V and a high brightness of 2770 cd/m² at a drive voltage of 10.8 V. The maximum external quantum efficiency is 0.52 % at 537 cd/m² with a bias of 7.4 V. The improved device performance over that of POF may be due to better charge injection and transport from PF-OXD and the efficient energy transfer from OXD side chain to the polyfluorene main chains.

Part 2: Using the macromonomer approach, we have synthesized dendronized polymers consisting of a conjugated polyfluorene backbone appended with different generations of poly(benzyl ether) dendritic wedges.¹⁵ The dendritic monomers were prepared by coupling “Fréchet-type” benzyl bromide dendrons with 9,9-bis(4-hydroxyphenyl)-2,7-dibromofluorene (**2**) via the Williamson ether synthesis, and then copolymerized with the diboronate (**4**) by the Suzuki coupling reaction to afford the alternating copolymers. Photophysical studies revealed that the size of the dendrimer side chain has a significant influence on the luminescence activity of the dendronized polymers. The large framework of higher generation dendrons, such as [**G3**], is likely to sufficiently encapsulate the conjugated backbone as a “shell.” This not only prevents

self-quenching, but also suppresses aggregate/excimer formation, leading to an enhancement in PL efficiency and luminescent stability. These results demonstrate that **PF-G3** is a promising candidate for blue-emitting polymer LEDs. The application of this polymer as an emitting material in electroluminescent devices is currently under study.

四、References

Part 1:

- (1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
- (2) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem. Int. Ed.*, **1998**, *37*, 402. (b) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121. (c) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737. (d) Mitschke, U.; Bäurele, P. *J. Mater. Chem.* **2000**, *10*, 1471.
- (3)(a) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1994**, *64*, 815. (b) Kido, J.; Shionoya, H.; Nagai, K. *Appl. Phys. Lett.* **1995**, *67*, 2281. (c) McGehee, M. D.; Bergstedt, T.; Zhang, C.; Saab, A. P.; O'Regan, M. B.; Bazan, G. C.; Srdanov, V. I.; Heeger, A. J. *Adv. Mater.* **1999**, *11*, 1349. (d) Chen, F. -C.; Yang, Y.; Thompson, M. E.; Kido, J. *Appl. Phys. Lett.* **2002**, *80*, 2308.
- (4) (a) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416. (b) Leclerc, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2867. (c) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1365. (d) Becker, S.; Ego, C.; Grimsdale, A. C.; List, E. J. W.; Marsitzky, D.; Pogantsch, A.; Setayesh, S.; Leising, G.; Müllen, K. *Synth. Met.* **2002**, *125*, 73.
- (5) (a) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946. (b) Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 6965.
- (6) Klärner, G.; Lee, J.-I.; Lee, V. Y.; Chan, E.; Chen, J.-P.; Nelson, A.; Markiewicz, D.; Siemens, R.; Scott, J. C.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1800.
- (7) (a) Huang, W.; Meng, H.; Yu, W.-L.; Gao, J.; Heeger, A. J. *Adv. Mater.* **1998**, *10*, 593. (b) Yu, W.-L.; Meng, H.; Pei, J.; Huang, W.; Li, Y.;

- Heeger, A. J. *Macromolecules* **1998**, *31*, 4838.
- (c) Peng, Z.; Bao, Z.; Galvin, M. E. *Chem. Mater.* **1998**, *10*, 2086. (d) Huang, W.; Meng, H.; Yu, W.-L.; Pei, J.; Chen, Z.-K.; Lai, Y.-H. *Macromolecules* **1999**, *32*, 118. (e) Peng, Z.; Zhang, J. *Chem. Mater.* **1999**, *11*, 1138. (f) Lee, Y. -Z.; Chen, X.; Chen, S. -A.; Wei, P. -K.; Fann, W. -S. *J. Am. Chem. Soc.* **2001**, *123*, 2296. (g) Zheng, M.; Ding, L.; Gürel, E. E.; Lahti, P. M.; Karasz, F. *Macromolecules* **2001**, *34*, 4124. (h) Zhan, X.; Liu, Y.; Wu, X.; Wang, S.; Zhu, D. *Macromolecules* **2002**, *35*, 2529.
- (8) Chiang, C. -L.; Shu, C. -F. *Chem. Mater.* **2002**, *14*, 682.
- Part 2:**
- (1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
- (2) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem. Int. Ed.*, **1998**, *37*, 402. (b) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121. (c) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737. (d) Mitschke, U.; Bäurele, P. *J. Mater. Chem.* **2000**, *10*, 1471.
- (3) (a) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1994**, *64*, 815. (b) Kido, J.; Shionoya, H.; Nagai, K. *Appl. Phys. Lett.* **1995**, *67*, 2281. (c) McGehee, M. D.; Bergstedt, T.; Zhang, C.; Saab, A. P.; O'Regan, M. B.; Bazan, G. C.; Srdanov, V. I.; Heeger, A. J. *Adv. Mater.* **1999**, *11*, 1349. (d) Chen, F. -C.; Yang, Y.; Thompson, M. E.; Kido, J. *Appl. Phys. Lett.* **2002**, *80*, 2308.
- (4) (a) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416. (b) Leclerc, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2867. (c) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1365. (d) Becker, S.; Ego, C.; Grimsdale, A. C.; List, E. J. W.; Marsitzky, D.; Pogantsch, A.; Setayesh, S.; Leising, G.; Müllen, K. *Synth. Met.* **2002**, *125*, 73.
- (5) (a) Lee, J. I.; Klaerner, G.; Miller, R. D. *Synth. Mat.* **1999**, *101*, 126. (b) Teetsov, J.; Fox, M. A. *J. Mater. Chem.* **1999**, *9*, 2117. (c) Weinfurter, K. -H.; Fujikawa, H.; Tokito, S.; Taga, Y. *Appl. Phys. Lett.* **2000**, *76*, 2502. (d) Yu, W. -L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 828.
- (6) (a) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138. (b) Mekelburger, H.-B.; Jaworek, W.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1571. (c) Fréchet, J. M. J. *Science* **1994**, *263*, 1710. (d) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681. (e) Frey, H.; Lach, C.; Lorenz, K. *Adv. Mater.* **1998**, *10*, 279. (f) Smith, D. K.; Diederich, F. *Chem. Eur. J.* **1998**, *4*, 1353.
- (7) (a) Frey, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2193. (b) Schlüter, A. D.; Rabe, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 864.
- (8) (a) Kaneko, T.; Horie, T.; Asano, M.; Aoki, T.; Oikawa, E. *Macromolecules* **1997**, *30*, 3118. (b) Jahromi, S.; Coussens, B. Meijerink, N.; Braam, A. W. M. *J. Am. Chem. Soc.* **1998**, *120*, 9753. (c) Jahromi, S.; Litvinov, V.; Coussens, B. *Macromolecules* **2001**, *34*, 1013.
- (9) Yin, R.; Zhu, Y.; Tomalia, D. A. *J. Am. Chem. Soc.* **1998**, *120*, 2678. (b) Shu, L.; Schäfer, A.; Schlüter A. D. *Macromolecules* **2000**, *33*, 4321. (c) Grayson, S. M.; Fréchet, J. M. J. *Macromolecules* **2001**, *34*, 6542.
- (10)(a) Karakaya, B.; Claussen, W.; Gessler, K.; Saenger, W.; Schlüter, A. D. *J. Am. Chem. Soc.* **1997**, *119*, 3296. (b) Stocker, W.; Karakaya, B.; Schürmann, B. L.; Rabe, J. P.; Schlüter, A. D. *J. Am. Chem. Soc.* **1998**, *120*, 7691. (b) Bo, Z.; Zhang, C.; Severin, N.; Rabe, J. P.; Schlüter A. D. *Macromolecules* **2000**, *33*, 2688.
- (11)(a) Bao, Z.; Amundson, K. R.; Lovinger, A. J. *Macromolecules* **1998**, *31*, 8647. (b) Jakubiak, R.; Bao, Z.; Rothberg, L. *Synth. Mat.* **2000**, *114*, 61.
- (12) Sato, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 10658.
- (13) Malenfant, P. R. L.; Fréchet, J. M. *Macromolecules* **2000**, *33*, 3634.
- (14) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946.
- (15) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.
- (16) Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 6965.
- (17) Tang, H. -Z.; Fujiki, M.; Zhang, Z. -B.; Torimitsu, K.; Motonaga, M. *Chem. Commun.* **2001**, 2426.
- (18) Klärner, G.; Lee, J.-I.; Lee, V. Y.; Chan, E.; Chen, J.-P.; Nelson, A.; Markiewicz, D.; Siemens, R.; Scott, J. C.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1800.
- (19) Ego, C.; Grimsdale, A. C.; Uckert, F.; Yu, G.; Srdanov, G.; Müllen, K. *Adv. Mater.* **2002**, *14*, 809.
- (20) Wu, F. -I.; Reddy, S.; Shu, C. -F.; Liu, M. S.; Jen, A. K.-Y. *Chem. Mater.* submitted.
- (21) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018.