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Novel Blue-Light-Emitting Polymers Containing Dinaphthylanthracene Moiety

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The discovery of electroluminescent (EL) polymers for light-emitting devices (LEDs) has stimulated tremendous research activity in the development of LEDs for display applications.[1−3] The colors that the polymers emit can be easily tailored by chemical modification of the polymer structures. However, efficient, highly bright, and stable blue-light-emitting materials are still under intensive research because blue light is necessary for full color EL display applications. With blue-light-emitting polymers as primary materials, it is possible to generate other colors by a downhill energy transfer process.[4] Several classes of conjugated polymers have been demonstrated to emit blue light.[5−9]

An effective approach to achieve wide energy band gaps for blue light is to control the conjugation length. For example, well-defined conjugated chromophores can be incorporated in the side chains[10] or the main chains of the polymers. In the latter case, the conjugation length of the chromophores can be controlled by introducing flexible nonconjugated spacer groups to tune the optical properties of the polymers. The spacer groups usually prevent the extended conjugation and contribute to the solubility and film-forming properties of the polymers. This approach has been demonstrated in several examples including PPV, polythiothene, PPP, and poly(oxadiazoles).[11−14]

In this paper, we report on the design, synthesis, and characterization of blue-light-emitting polymers, **P1**−**P3,** containing a novel chromophore 9,10-di(2-naphthyl)-anthracene (Figure 1). This chromophore has proved to be particularly useful for the fabrication of efficient and stable blue EL devices.[15] Polymers incorporating such chromophores are expected to be highly fluorescent and emit blue light. **M1** is a model compound for the polymers and was synthesized for the comparison of optical properties.

The synthesis of the monomers and polymers is illustrated in Figure 1. The flexible spacer group is incorporated into monomer 2.[16] Its precursor, compound 1**,** was synthesized according to a modified literature procedure.[17,18] Monomer 5 is a highly fluorescent crystalline material and was synthesized in three steps.[19] **M1** was synthesized via a cross-coupling reaction,[20] and the polymers were synthesized via the Suzuki coupling reaction in the presence of a phase transfer reagent.[21] **M1** and the polymers are highly fluorescent materials. **M1**, **P1**, and **P2** are fluorescent blue while **P3** is fluorescent greenish blue. Polymers are readily soluble in common organic solvents, and a pinhole-free thin film can be obtained easily by spin-coating. The molecular weights of the polymers were determined by size-exclusion chromatography (SEC) by using polystyrene standards in THF. Polymers show weight-average molecular weights (M_w) of 15 700, 10 000, and 17 600 and polydispersities of 2.08, 1.62, and 1.60 for **P1**, **P2**, and **P3**, respectively.

All polymers are thermally stable and show onset decomposition temperature, T_d, above 390 °C. **P1** has a

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(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) Sheats, J. R.; Antoniadis, H.; Hueschen, M.; Leonard, W.; Miller, J.; Moon, R.; Roitman, D.; Stocking, A. *Science* **1996**, *273*, 884.

(3) Spreitzer, H.; Becker, H.; Kluge, E.; Kreuder, W.; Schenk, H.; Demandt, R.; Schoo, H. *Adv. Mater.* (*Weinheim, Ger.*) **1998**, *10*, 1340.

(4) Kido, J.; Hongawa, K.; Nagai, K. *Macromol. Symp.* **1994**, *84*, 81.

(5) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys., Part 2* **1991**, *20*, L1941.

(6) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.

(7) Grem, G.; Paar, C.; Stampfl, J.; Leising, G.; Huber, J.; Scherf, U. *Chem. Mater.* **1995**, *7*, 2.

(8) Gebler, D. D.; Wang, Y. Z.; Blatchford, J. W.; Jessen, S. W.; Lin, L. B.; Gustafson, T. L.; Wang, H. L.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *J. Appl. Phys.* **1995**, *78*, 4264

(9) Huang, W.; Meng, H.; Yu, W.-L.; Gao, J.; Heeger, A. J. *Adv. Mater.* **1998**, *10*, 593.

(10) Lee, J.-K.; Schrock, R. R.; Baigent, D. R.; Friend, R. H. *Macromolecules* **1995**, *28*, 1966.

(11) Zheng, S.; Shi, J.; Mateu, R. *Chem. Mater.* **2000**, *12*, 1814.

(12) Andersson, M. R.; Berggren, M.; Inganaes, O.; Gustafsson, G.; Gustafsson-Carlberg, J. C.; Selse, D.; Hjertberg, T.; Wennerstroem, O. *Macromolecules* **1995**, *28*, 7525.

(13) Pei, Q.; Yang, Y. *Adv. Mater.* **1995**, *7*, 559.

(14) Hilberer, A.; Brouwer, H.-J.; van der Scheer, B.-J.; Wildeman, J.; Hadziioannou, G. *Macromolecules* **1995**, *28*, 4525.

(15) (a) Shi, J.; Tang, C. W.; Chen, C. H. U.S. Patent 5,935,721, 1999. (b) Shi, J.; Tang, C. W. Eur. Pat. Appl. 1009041, 2000. (c) Shi, J.; Tang, C. W.; Klubek, K. P. Eur. Pat. Appl. 1009044, 2000. (d) Hosokawa, C.; Higashi, H.; Fukuoka, K.; Ikeda, H. PCT Int. Appl. WO 0121729, 2001.

(16) The crude product was recrystallized from hexane to give off-white needlelike crystals at 57% yield (in two steps). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.85 (t, $J = 6.9$ Hz, 3H), 1.02 (s, 12H), 1.24−1.34 (m, 18H), 1.58−1.65 (m, 2H), 3.71 (t, $J = 6.6$ Hz, 2H), 3.79 (s, 8H), 4.11−4.16 (m, 1H), 4.24−4.36 (m, 4H), 7.17 (s, 2H), 7.14 (d, $J = 8.5$ Hz, 2H), 7.67 (dd, $J = 8.2$ Hz, 2H), 7.75 (d, $J = 8.8$ Hz, 2H), 7.8 (d, $J = 8.3$ Hz, 2H), 7.91 (s, 2H); ^{13}C NMR ($CDCl_3$): 14.11, 21.93, 22.68, 26.07, 29.35, 29.47, 29.63, 29.66, 30.06, 31.92, 67.83, 71.15, 72.37, 76.47, 106.77, 118.61, 125.77, 128.62, 130.26, 130.66, 134.80, 136.13, 157.38; mp 59−61 °C; FD-MS: *m*/*z* 726 (M^+).

(17) Scherf, U.; Mullen, K. *ACS Symp. Ser.* **1997**, *672*, 358.

(18) Compound **1**: The crude product was purified by column chromatography on silica gel using CH_2Cl_2/hexane (15:85) as eluent to give pure product as white powder. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.87 (t, $J = 6.9$ Hz, 3H), 1.25−1.39 (m, 18H), 1.60−1.70 (m, 2H), 3.73 (t, $J = 6.6$ Hz, 2H), 4.13−4.18 (m, 1H), 4.26−4.37 (m, 4H), 7.16 (d, $J = 2.2$ Hz, 2H), 7.19 (dd, $J_1 = 8.9$ Hz, $J_2 = 1.8$ Hz, 2H), 7.48 (dd, $J_1 = 8.8$ Hz, $J_2 = 1.8$ Hz, 2H), 7.57 (d, $J = 8.8$ Hz, 2H), 7.63 (d, $J = 8.9$ Hz, 2H), 7.91 (d, $J = 1.4$ Hz, 2H); ^{13}C NMR ($CDCl_3$): 14.10, 22.67, 26.05, 29.33, 29.44, 29.61, 29.65, 30.03, 31.90, 67.76, 71.16, 76.40, 106.95, 117.22, 119.85, 128.35, 128.51, 129.64, 130.13, 132.94, 156.92; mp 99−101 °C; FD-MS: *m*/*z* 668 (M^+).

(19) Monomer **5**: The crude product was purified by column chromatography on silica gel with hexane as an eluent to give yellow flaky crystals (30% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.93−1.70 (m, 14H, alkyl), 1.81−1.89 (m, 1 H, alkyl), 3.12 (d, $J = 5.4$ Hz, 2H, OCH_2), 7.34 (d, $J = 9.2$ Hz, 2H), 8.00 (d, $J = 9.2$ Hz, 2H), 8.71 (s, 2H); ^{13}C NMR ($CDCl_3$): 11.12, 14.10, 23.08, 23.93, 29.15, 30.52, 39.88, 72.76, 107.74, 117.02, 125.27, 129.51, 129.75, 130.12, 152.87; mp 103−105 °C; FD-MS: *m*/*z* 590 (M^+).

(20) **M1:** The crude product was purified, by refluxing it in methylene chloride, and filtered. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.97 (s, 6H), 7.29 (dd, $J_1 = 8.9$ Hz, $J_2 = 2.4$ Hz, 2H), 7.40 (d, $J = 6.9$ Hz 2H), 7.41 (d, $J = 6.9$ Hz, 2H), 7.53 (d, $J = 2.2$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 2H), 7.64 (d, $J = 6.8$ Hz, 2H), 7.65 (d, $J = 6.8$ Hz, 2H), 7.94 (d, $J = 9$ Hz, 2H), 7.97 (s, 2H), 8.10 (d, $J = 8.4$ Hz, 2H); FD-MS: *m*/*z* 490 (M^+).

(21) Inbasekaran, M.; Wu, W.; Woo, E. P. U.S. Patent 5 777 070, 1998.

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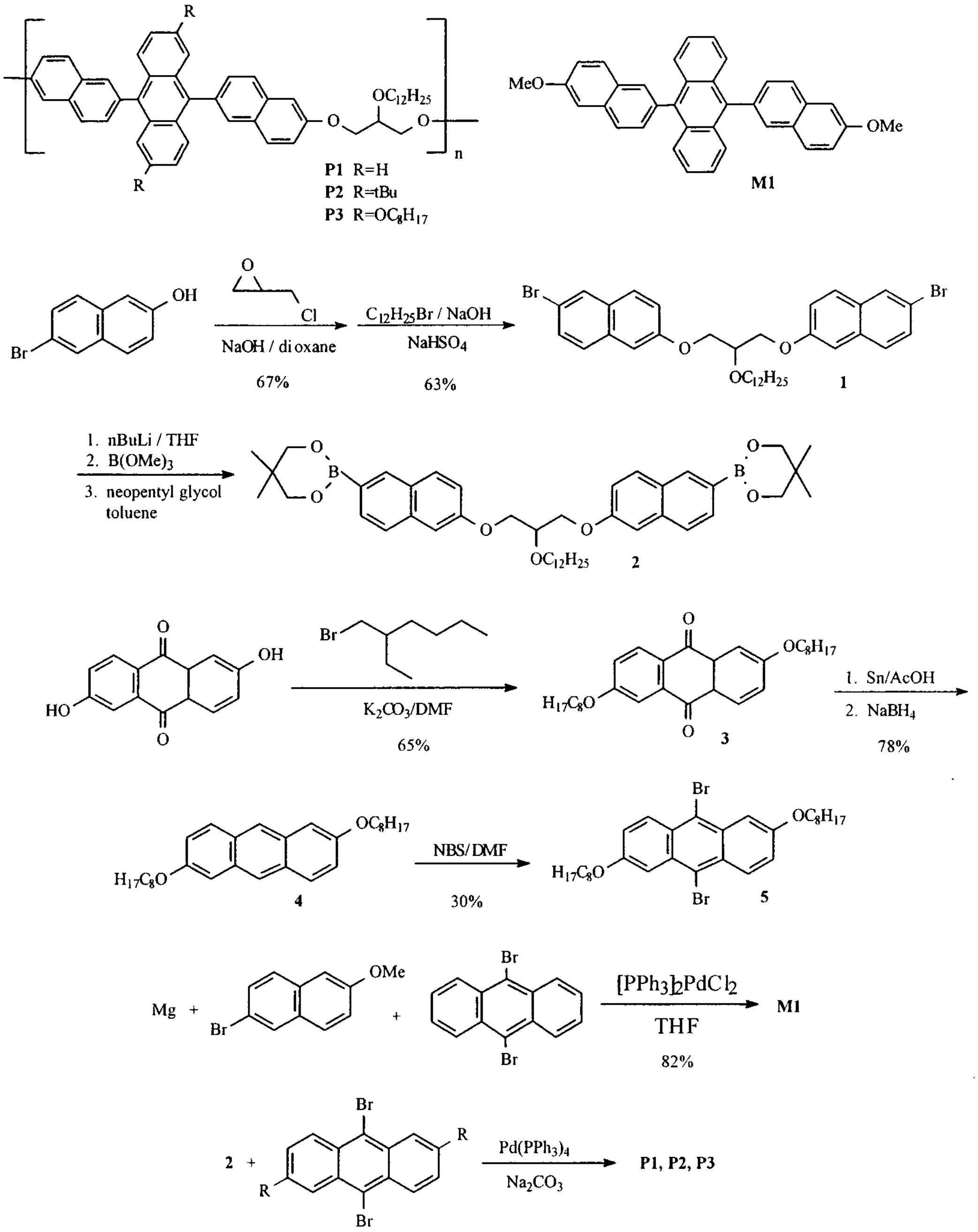

Figure 1. Chemical structures and syntheses of model compound and polymers.

T_d of 418 °C and a glass transition temperature, T_g, of 90 °C, and **P2** shows a similar T_d of 412 °C and a higher T_g of 112 °C. **P3** has a lower T_g of 46 °C due to both the long side chain and the flexible spacer group.

The absorption spectra of the model compound and the polymers in dilute toluene solutions (5 μg/mL, which corresponds to 5.3, 6.3, and 7.3 μM for **P1**−**P3** and 10 μM for **M1**) are shown in Figure 2. **P1** and **P2** show similar absorption spectra in dilute solutions, and the spectra are similar to that of **M1**. **M1** shows strong absorption peaks at 379 and 398 nm, which are attributed to the anthracene moiety. However, in **P3**, the absorption peaks are less resolved and red-shifted because of the strong electron-donating characteristic of the alkoxy side chain. The presence of aggregation phenomena of **P3** in toluene solution was ruled out by the almost identical normalized absorption spectra at various concentrations ranging from 2.5 to 50 μg/mL and absorbance at 413 nm ranging from 0.04 to 0.4. Furthermore, the possibility of intramolecular charge transfer induced by the more polar alkoxy group was eliminated by the study of absorption spectra of **P1**−**P3** in methylene chloride, a more polar solvent. For each polymer, the spectra in both solvents are almost identical.

Emission spectra of the polymers and **M1** in solution are compared in Figure 3. **M1** emits blue light at 432 nm, and **P1** shows almost identical emission peaks at 430 nm. This suggests that the spacer groups in **P1** have no effect on the optical properties of the polymer. The emission peaks, 440 nm for **P2** and 457 nm for **P3,** are red-shifted due to the electron-donating nature of alkyl and alkoxy side chains on the anthracene moiety. However, the emission spectrum of **P3** is more resolved than those of **P1** and **P2**. To explain this unusual difference, the excitation spectra of the polymers in both

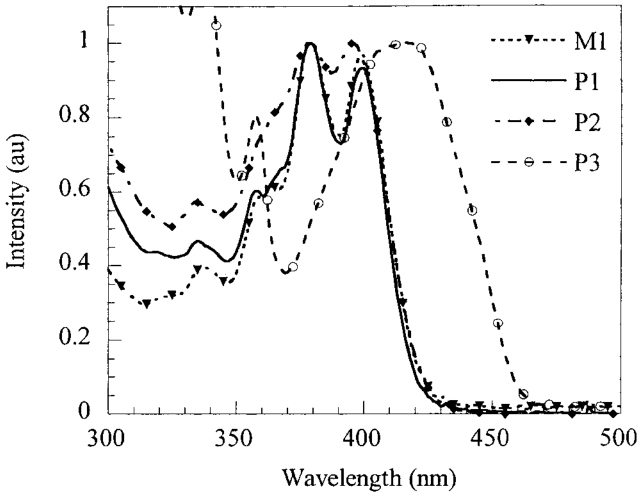

Figure 2. Absorption spectra of model compound and polymers in dilute toluene solution.

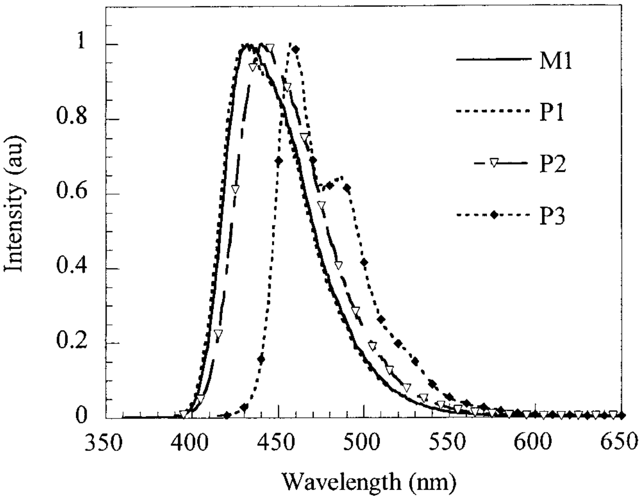

Figure 3. Emission spectra of model compound and polymers in dilute toluene solution.

toluene and methylene chloride solutions are compared with the absorption spectra. For each polymer, the excitation and absorption spectra in each solvent are almost identical. The results indicate that there is only one component involved in the absorption for each polymer. At this point, it is not clear why **P3** has a more resolved emission spectrum. The fact that the absorption and emission spectra do not change with time rules out the possibility of light-induced chemical structure changes in the emissive materials. In solid thin films, the emission peaks of the polymers shift to longer wavelength. **P1**, **P2**, and **P3** shows photoluminescence (PL) at 441, 449, and 464 nm, respectively. The quantum efficiency of the thin films is high with an efficiency of 22 and 37% for **P1** and **P2**, respectively.

The EL properties of the polymers are investigated by evaluation of the single-layer LED devices, indium–tin oxide (ITO)/polymer/Mg:Ag. The preliminary device data are reported here. The current and light output vs the voltage were measured in forward bias. All the devices exhibited typical diode behavior. The forward current was observed to increase superlinearly with the increase of applied voltage after exceeding the turn-on voltage. The absorption, emission, and EL spectra of **P1** are shown in Figure 4. **P1** shows blue EL at 444 nm, which is very close to the PL in solid thin film. Similarly, **P2** emits blue light at 468 nm. The threshold voltage of the device for light emission from **P2** is 4.9 V. The results suggest that our polymer shows relatively low turn-on voltages compared with other polymers with flexible spacer groups.[22] A common issue related to blue-light-emitting polymers is the difficulty of charge injection into the polymer leading to lower device efficiency. One strategy is to modify the contact between the polymer and the ITO with a thin interlayer of PEDOT.[23] For example, the luminous efficiency of a device from **P2** was improved from 0.01 to 0.4 Cd/A at 20 mA/cm^2.

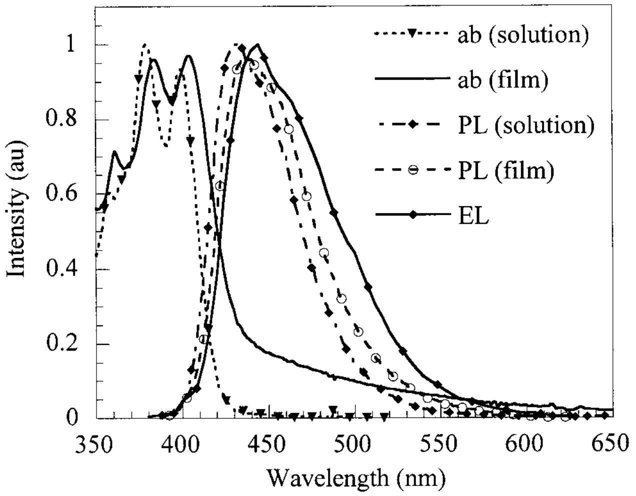

Figure 4. Absorption, emission, and EL spectra of **P1**.

In summary, we have synthesized and characterized novel blue-light-emitting polymers containing blue chromophore 9,10-di(2-naphthyl)anthracene. These polymers show good solubility and excellent thermal stability. The absorption and emission spectra indicate that the active chromophores in the polymers are 9,10-di(2-naphthyl)anthracenes. Polymers show efficient blue PL in solution and solid state. Preliminary device evaluation indicates that single-layer LED devices emit blue light with low turn-on voltages. Future work will focus on improving device efficiency by optimizing device structures.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] Kim, H. K.; Ryu, M.-K.; Kim, K.-D.; Lee, S.-M.; Cho, S.-W.; Park, J.-W. *Macromolecules* **1998**, *31*, 1114.

[23] Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. *Adv. Mater.* **2000**, *12*, 481.