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Synthesis and Photophysical Properties of Polymers Containing a Novel Class of Light Emitters

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Introduction. The development of light-emitting diodes (LEDs) based on π-conjugated organic materials has been the subject of intense research due to their potential applications in full-color, flat-panel organic displays.[1] Two key challenges currently remain for the fabrication of high-performance organic electroluminescent devices: design and synthesis of blue light-emitting materials, on one hand,[2] and of materials capable of good electron injection and transport properties, on the other one.[3]

Many photoluminescent conjugated polymeric materials have been investigated, leading to polymeric light-emitting devices (PLEDs). Among these polymers, blue electroluminescence was observed from poly(*p*-phenylene), polyfluorene, polycarbazole derivatives, and ladder-conjugated polymers.[4] However, it should be noted that for these conjugated homo- and copolymers (i) the light-emitted wavelength depends on the extension of the conjugated length, a parameter hard to control, and (ii) most of these materials are better hole than electron carriers. Therefore, to achieve blue emission and/or electron injection, other types of emitting polymers have been investigated: partially conjugated alternating main-chain copolymers (*alt*MCPs), in which a well-defined active conjugated chromophore is covalently bound along the main chain to nonconjugated segments,[5] and side-chain polymers (SCPs), which have the conjugated moiety linked via a spacer to a nonconjugated backbone.[6]

In this framework, there is a major challenge in designing and synthesizing (i) chromophores exhibiting efficient blue light emission, on one hand, and electron injection ability (high electron affinity), on the other one, as well as (ii) blue light-emitting polymers (*alt*MCPs and SCPs) based on these chromophores.

In previous papers,[7] a novel class of conjugated chromophores based on a 3,3′-bipyridine core was described. It was shown that some of them (**I** and **II** in Scheme 1) exhibit not only high electron affinity (EA ∼ 3.0 eV), as expected from the electron deficiency of the pyridinic ring, but also intense fluorescence emission in the blue wavelength region. Then, an efficient pure blue-emitting LED incorporating (**I**) was fabricated (CIE coordinates: 0.148; 0.157).[7b] The main performances of the device at 10 mA/cm^2 are a luminous efficiency of 3.9 cd/A, a power efficiency of 1.4 lm/W, and an external quantum efficiency of 2.9%. In this context, we were interested in seeing whether it is possible to translate results obtained with a molecular material as emitting moiety to polymeric materials incorporating the same emitting structure.

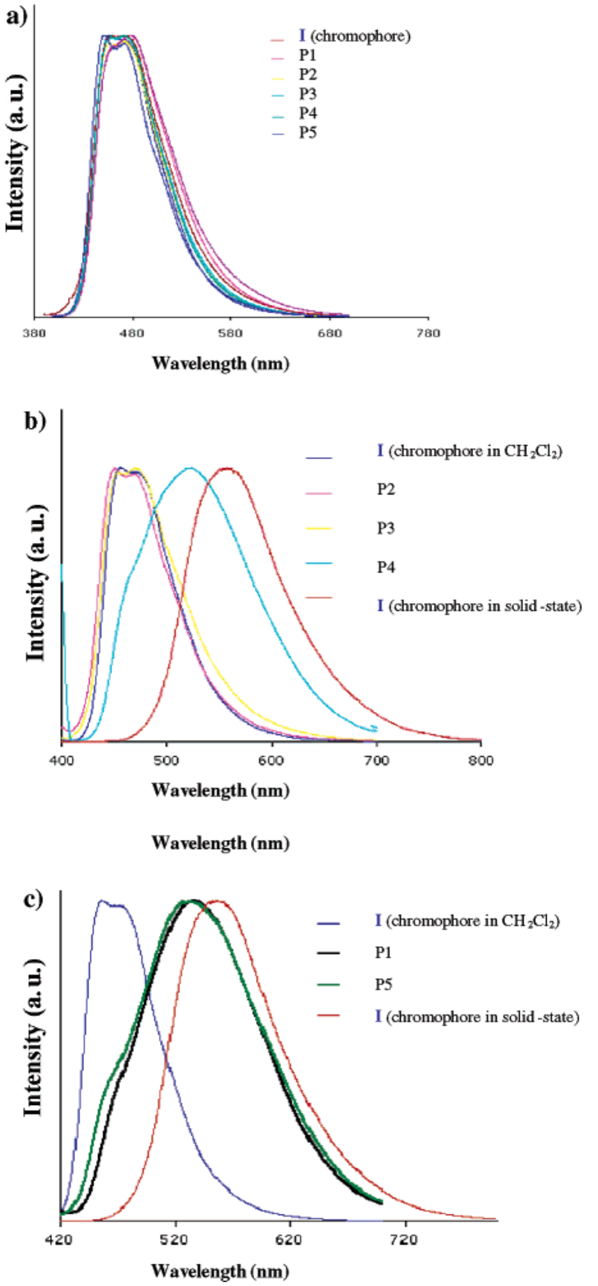

Figure 1. Emission spectra (a) of copolymers **P1**−**P5** in CH$_2$Cl$_2$ solution, (b) of copolymers **P2**−**P4** in thin film, and (c) of copolymers **P1** and **P5** in thin film.

In the present communication, starting from **I** and **II** as key emitting moieties, we report our first results on syntheses of derived monomers (**M1** and **M2**, respectively) and copolymers bearing the active chromophore in the main chain (**P1**) and as side group (**P2**−**P4**, **P5**, and **P5′**) (Scheme 2). Copolymers were obtained by free radical polymerization and the Mitsunobu reaction. We also present some preliminary photophysical properties of the copolymers in relation to their topology and composition.

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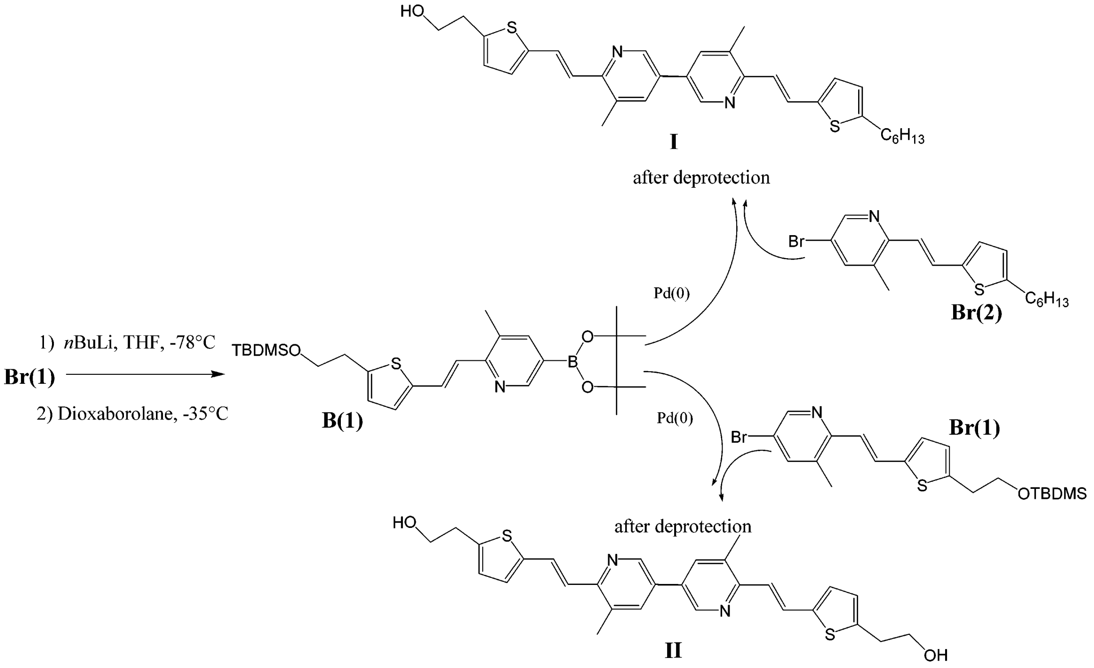
Scheme 1. Syntheses of Monofunctionalized Chromophore (I) and Difunctionalized Chromophore (II)



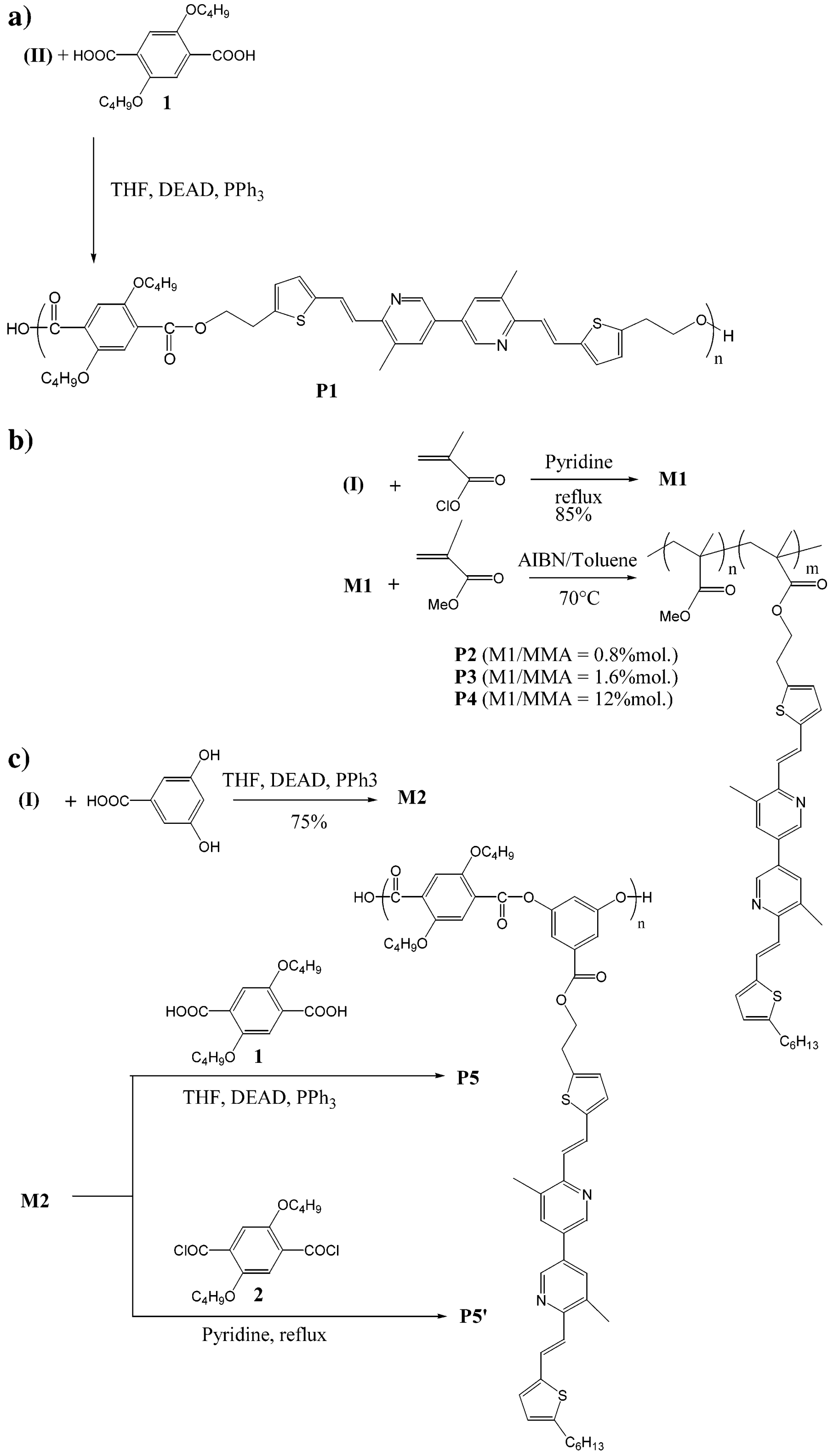
Results and Discussion. The simplest way to obtain an alternating main-chain copolymer was to synthesize a polyester from the polymerization between an aromatic di(carbonyl chloride) and **II** as diol. As conventional polyesterification methods failed, a polycondensation via a Mitsunobu reaction was used leading to **P1** (Scheme 2a).[8] To prepare suitable polymer systems with the emitting chromophore as pendant group, two synthetic strategies have been used, leading to copolymers **P2**−**P4** and **P5**, **P5′** respectively. For **P2**−**P4**, a free radical polymerization process was chosen in combination with methyl methacrylate units as polymerizable groups (Scheme 2b). For **P5** and **P5′**, the synthetic route involved either a Mitsunobu reaction or a conventional polyesterification, respectively (Scheme 2c).

As shown in Scheme 1, the strategy for the obtention of chromophores **I** and **II** is based on (i) the synthesis of π-conjugated 6-substituted-3-bromopyridine building blocks Br(1) and Br(2) incorporating the electron-rich thienyl ring and (ii) borylation of Br(1) by using a boronic diester.[7] The resulting boronated building block B(1) was then coupled with building blocks Br2 and Br1, giving, after deprotection, chromophores **I** and **II**, respectively, in 70−76% yield and multigram scale. The monofunctional methacrylate monomer **M1** was prepared by direct esterification of **I** with methacryloyl chloride, in a quantitative yield, as reported in Scheme 2b. As conventional esterification methods failed, the difunctional monomer **M2** was obtained by Mitsunobu esterification between hydroxyl groups of **I** and acidic groups of 3,5-dihydroxybenzoic acid (**1**), in a 75% yield.[8a] Regarding the comonomers **1** and **2** (2,5-dibutoxyterephthalic acid and 2,5-dibutoxyterephthaloyl chloride, respectively), they were synthesized according to procedures reported in the literature.[9] The butoxy side groups were introduced to ensure solubility of the polymers. All these compounds have been characterized by ^{1}H and ^{13}C NMR spectroscopies and elemental analysis (see Supporting Information).

On one hand, two novel polyesters (**P1** and **P5**) were prepared from the polymerization reaction between the diacid (**1**) and diol (chromophore **II** or **M2**, respectively) by the Mitsunobu reaction, using diethyl azodicarboxylate (DEAD) and triphenylphosphine (PPh_3) in anhydrous tetrahydrofuran (THF) solvent at room temperature (Schemes 2a and 2c, respectively). The use of the Mitsunobu reaction, previously reported for the synthesis of polyimides,[8b,c] has not been previously published to obtain polyesters, at our knowledge. Regarding the copolymer **P5′**, it was obtained by conventional polyesterification. Whatever the previous route, the comonomer feed ratio is 50:50. On the other hand, a series of novel copolymers **P2**−**P4** with emissive chromophore as pendant group were obtained by copolymerizing **M1** and methyl methacrylate in the desired ratio, as indicated in Scheme 2b, the free radical copolymerizations being initiated with *N*,*N*-azobis(isobutyronitrile) (AIBN) in toluene at 70 °C over 24 h. The copolymers **P2**−**P4** were characterized by ^{1}H NMR. The relative integrals of the two different units in the copolymers (signals for pyridinic ring and OMe at ca. δ 8.6 and 3.6 ppm) allowed to determine the molar ratio (Figure 1S, see Supporting Information). These values are in broad agreement with the feed ratio of monomers used in the copolymerization as listed in Table 1.

The physical and photophysical properties of all the copolymers are listed in Table 1. Concerning the polyesters obtained by polycondensation, the resulting polymers **P1**, **P5**, and **P5′** are partially soluble in THF. Size exclusion chromatography (SEC) data (measured against monodisperse polystyrene standards) indicate that the number-average molecular weights (M_n) of the soluble fraction are 9360, 5350, and 3110 g mol^{-1} with a polydispersity (I_p) of 2, 1.2, and 1.4, respectively. These low molecular weights can be partly related with the low solubility of these polymers. Differential scanning calorimetry (DSC) measurements indicate that **P1**, **P5**, and **P5′** have T_g of around 80 °C. It should be noted that the synthetic route does not significantly influence the characteristics of **P5** and **P5′**. On the contrary, the polymers obtained by free radical polymerization (**P2**−**P4**) are highly soluble in common organic solvents, such as THF and chloroform, and can be processed by spin-coating to yield thin films. SEC measurements reveal

Scheme 2. Syntheses of Monomers M1 and M2 and Polymers P1, P2–P4, P5, and P5′



unimodal distributions, with number-average molecular weights variying from 10 500 to 26 000 g mol^{-1} and polydispersity ranging from 1.5 to 2.2. The M_n values are higher than those of the polymers obtained by the Mitsunobu reaction. All these polymers present a glass transition temperature T_g higher than that of atactic poly(methyl methacrylate) (PMMA). Moreover, it is worth noting that all these polymeric materials are amorphous, which should lead to a good mechanical stability up to 100 °C. This parameter may become particularly important for their future use in light-emitting diodes.

The solution and solid-state optical properties of all polymers have been investigated. Results are reported in Table 1. In solution or as thin films, the absorption spectra of all the polymers result in a strong and intense low-lying absorption band around 390–400 nm, as shown in Figure 1a,b.

Table 1. Composition, Molecular Weights, and Thermal and Photophysical Properties of the Copolymers

copolymers	M_n ($\times 10^3$ g mol^{-1})	M_w ($\times 10^3$ g mol^{-1})	I_p	DP$_n$	T_g (°C)	absorption λ_{max} (nm) solution[b] and film	emission λ_{max} (nm) film
P1	9.4	18.6	2	12	81	383	535
P2 (M1/MMA: 0.8 mol %; 2 wt %)[a]	10.5	17.2	1.6	119	103	391	455
P3 (M1/MMA: 1.6 mol %; 8 wt %)[a]	11.3	17.0	1.5	123	108	392	476
P4 (M1/MMA: 17 mol %; 49 wt %)[a]	26.0	56.6	1.7	155	107	390	528
P5	5.3	6.3	1.2	5.7	75	385	537
P5′	3.1	4.4	1.4	3.3	77	385	537

[a] Calculated from ^{1}H NMR data. [b] Determined in CH_2Cl_2.

In dilute solution (Figure 1a), upon radiative excitation at 390 nm, **P1**−**P5** exhibit an intense blue emission with a maximum at 460 nm, as observed for the chromophores **I** or **II**. More indicative are the emission spectra of thin films prepared from the copolymers (Figure 1b,c). For **P2** and **P3** the emission maximum is located at 455 and 476 nm, respectively, in the blue region, whereas for **P1, P4,** and **P5** a yellowish emission at 528 and 535 nm, respectively, is observed. This red shift accompanied by large emission band could be explained either by intramolecular aggregation between laterals chromophore units within the same chain with the increasing amount of chromophore (**P4**−**P5**) or by interaction between chromophores in different main chains (**P1**).

Conclusion. We successfully designed and synthesized monomers derived from blue-emitting chromophores. Polymethacrylate- and polyester-based copolymers have been obtained by using free radical polymerization or the Mitsunobu reaction, respectively. All the copolymers, incorporating the fluorescent center either as repeating units in main chain or as lateral groups are soluble in organic solvents. Copolymers **P2** and **P3** emit blue light whereas **P1**, **P4**, and **P5** are yellowish emitters. All these results make these polymers potential candidates for the fabrication of PLEDs. Introducing longer alkyl chains into the terephthalic derived comonomers and using controlled radical copolymerizations should reduce inter- and intrachains interactions and consequently allow to obtain blue light-emitting polymers.

Supporting Information Available: Syntheses details; NMR and elemental analysis data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) *Organic Electroluminescent Materials and Devices*; Miyata, S., Nalwa, H. S., Eds.; Gordon and Breach: New York, 1997.

(2) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.

(3) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jeneckhe, S. A. *Chem. Mater.* **2004**, *16*, 4556.

(4) (a) Shim, H. K.; Jin, J. I. *Adv. Polym. Sci.* **2001**, *158*, 193. (b) Morin, J. F.; Leclerc, M. *Macromolecules* **2001**, *34*, 4680. (c) Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1853.

(5) (a) Somolik, I.; Yang, Z.; Karasz, F. E.; Morton, D. C. *J. Appl. Phys.* **1993**, *74*, 3584. (b) Yang, Z.; Somolik, I.; Karasz, F. E. *Macromolecules* **1993**, *26*, 1188. (c) Zyunh, T.; Hwang, D. H.; Kang, I. N.; Shim, H. K.; Hwang, W. Y.; Kim, J. J *Chem. Mater.* **1995**, *7*, 1966.

(6) (a) Aguiar, M.; Hu, B.; Karasz, F. E.; Akcelrud, L. *Macromolecules* **1996**, *29*, 3161. (b) Bouché, C. M.; Berdagué, P.; Facoetti, H.; Robin, P.; Le Barny, P.; Schott, M. *Synth. Met.* **1996**, *81*, 191. (c) Baigent, D. R.; Friend, R. H.; Schrock, R. R. *Synth. Met.* **1995**, *81*, 2171. (d) Li, X. C.; Cacialli, F.; Giles, M.; Grüner, J.; Friend, R. H.; Holmes, A. B.; Moratti, S. C.; Yong, T. M. *Adv. Mater.* **1995**, *7*, 898.

(7) (a) Leclerc, N.; Serieys, I.; Attias, A.-J. *Tetrahedron Lett.* **2003**, *44*, 5879. (b) Leclerc, N.; Sanaur, S.; Galmiche, L.; Mathevet, F.; Attias, A.-J.; Fave, J.-L.; Roussel, J.; Hapiot, P.; Lemaître, N.; Geffroy, B. *Chem. Mater.* **2005**, *17*, 502−513.

(8) (a) Mitsunobu, O. *Synthesis* **1981**, 1. (b) Kim, T.-D.; Lee, K.-S.; Lee, G. U.; Kim, O.-K. *Polymer* **2000**, *41*, 5237. (c) Lee, K.-S.; Moon, K.-J.; Woo, H. Y.; Shim, H.-K. *Adv. Mater.* **1997**, *9*, 978.

(9) Ballauff, M. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 407.

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