Synthesis and Color Tuning Properties of Blue Highly Fluorescent Vinyl Polymers Containing a Pendant Pyrrolopyridazine

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Received September 15, 2004; Revised Manuscript Received March 24, 2005

ABSTRACT: We report here the synthesis, polymerization, and properties of highly fluorescent vinyl polymers containing pendant pyrrolopyridazines. Their luminescence quantum efficiencies can be as high as 60%, and all polymers showed strong luminescence even in the solid state, which is indicative of little self-quenching in these systems. The polymers were processable into films, fibers, and rods that were suitable for several device applications. The fibers and rods showed interesting end luminescence whose colors were tunable by manipulating their geometries.

Introduction

Light-emitting organic compounds continue to arouse strong interest because of their fascinating functions as electroluminescent materials, sensors, lasers, and other semiconductor devices. Among these applications, organic light-emitting diodes (OLEDs) have been most widely investigated. While many chromophores have been designed and synthesized for potential OLEDs, it is essential to find materials that exhibit high fluorescence quantum efficiency, little self-quenching, proper energy levels, pure RGB color, and high stability.

Two types of organic materials, small molecules and polymers, are commonly used for OLEDs. Compared to small molecules, polymers have the advantage of facile processability, high flexibility, and thermal stability. Polymers also have lower production costs and can afford uniform films with large areas due to inexpensive solution processing, such as spin-coating. Polymer light-emitting diodes have various advantages and have been the subject of intense research since their discovery. Among the polymers, conjugated and nonconjugated polymers have been used, such as poly(p-phenylenevinylene) (PPV) derivatives and poly(9-vinylcarbazole) (PVK), respectively. The quantum efficiency is often decreased by self-quenching, making it difficult to obtain highly fluorescent polymers. Moreover, pure-blue-emitting polymers are still rare.

Recently, we synthesized a series of blue highly fluorescent pyrrolopyridazines which are expected to be good chromophores for highly efficient OLEDs. These compounds show high luminescence even in the solid state, which indicates that there is little interaction of the excited state species in the high-density environment of the films. This suggests that it is imperative to incorporate the heterocycles into polymers where the chromophores are located close to each other. Here we report new vinyl polymers with pendant pyrrolopyridazines that exhibit highly efficient pure-blue light. We have successfully obtained three novel polymers and studied their optical and thermal properties. An unusual color modulation with sample geometry, due to waveguiding, was observed and investigated.

Results and Discussion

Synthesis. The new organic monomers and polymers reported in this paper are presented in Figure 1. Strategies for the synthesis and polymerizations are depicted in Schemes 1 and 2.

The starting material, pyrrolo[1,2-b]pyridazine-5,6,7-tricarboxylic acid 7-tert-butyl ester 5,6-dimethyl ester (PPB), was prepared according to the published procedure. Initially, the tert-butyl ester of PPB was selectively hydrolyzed with trifluoroacetic acid (TFA) at low temperature (0 °C) to afford 3. Acid 3 was allowed to react with 4-vinylbenzyl alcohol (2) using bis(2-oxo-3-oxazolidinyl)phosphilic chloride (BOP-Cl) as a coupling reagent to afford monomer 4 in good yield. This method afforded better results than the reaction between chloromethyl-4-vinylbenzene and acid 3 (the best yield was only 45%). Compound 2 was prepared from commercially available chloromethyl-4-vinylbenzene via acetate 1. The acrylate monomer 5 was prepared similarly using 2-hydroxyethyl methacrylate (HEMA) in place of 2. The radical polymerization of the monomers was initiated with AIBN to afford polymers (PPS, PPM1, and PPM2) (Schemes 1 and 2). These polymers were soluble in halogenated solvents such as CH2Cl2, CHCl3, and o-dichlorobenzene. The solutions had high viscosity, and 1H NMR spectra (Figure 2) showed broad peaks that are typical for high molecular weight polymers. The polymers were easily processed into films, fibers, and rods, a direct consequence of their high molecular weights. The molecular weights of the polymers (Table 1) were determined by gel permeation chromatography (GPC), relative to polystyrene standards (see Table 1).

As shown in Table 1, all the polymers have high thermal stability. The decomposition temperatures are around 300 °C by thermogravimetric analysis (TGA),

Table 1. Thermal Data and Properties of Polymers (PPS, PPM1, PPM2)

<table>
<thead>
<tr>
<th>polymer</th>
<th>Tg (°C)</th>
<th>decomposition (°C)</th>
<th>Mw (Mn/Mw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPS</td>
<td>140</td>
<td>330</td>
<td>3.15 x 10^5 (9.9)</td>
</tr>
<tr>
<td>PPM1</td>
<td>126</td>
<td>325</td>
<td>5.79 x 10^4 (30.3)</td>
</tr>
<tr>
<td>PPM2</td>
<td>118</td>
<td>180 (5% loss), 290</td>
<td>5.00 x 10^3 (3.4)</td>
</tr>
</tbody>
</table>

* The temperature for onset of the primary mass loss by TGA.

a Determined by GPC, relative to polystyrene standards.

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10.1021/ma048091y CCC: 1530.25 © 2005 American Chemical Society Published on Web 04/29/2005
except the first 5% of weight loss in PPM2 (discussed later). The glass transition temperatures ($T_g$) are much higher than those of the backbone polymers, polystyrene and poly(methyl methacrylate) (PMMA). The $T_g$ of PPS is 140 °C, while that of atactic polystyrene is 100 °C.$^9,10$ The $T_g$ of PPM1 (126 °C) and PPM2 (118 °C) is also much higher than the reported values of PMMA ($\sim$100 °C).$^9,11$ These results indicate that the introduction of the pendant pyrrolopyridazines makes the polymers harder. In general, high thermal stability and high $T_g$ are very important for the device stability.$^{12}$ Polymer PPM2 exhibits a two-step decomposition, indicating that some parts of the copolymer may be subject to depolymerization at 180 °C to cause the 5% weight loss.

**Optical Properties.** The absorption and fluorescence spectra of monomers (4, 5) and polymers (PPS, PPM1, PPM2) were recorded in DMSO, methanol, methylene chloride, and hexane solutions at room temperature.$^{13}$ Figures 3 and 4 show the optical spectra of monomers (4, 5) and polymers (PPS, PPM1, PPM2) in methylene chloride. Quantum yields were determined relative to 9,10-diphenylanthracene in degassed hexane ($\Phi = 0.96$)$^5$ as a reference. As shown in Table 2, the pyrrolopyridazines are very intense blue emitters ($\lambda_{\text{max}}$ of fluorescence around 430 nm). The quantum efficiencies of the monomers reach up to 91%, and those of the polymers can be as high as 61%.

The quantum efficiency of PPS decreased slightly compared with monomer 4. This might be because of self-quenching between the chromophores in PPS, but the decrease is relatively small and the quantum efficiencies are considerably higher than conventional fluorescent polymers.$^{14}$ These results demonstrate that the self-quenching between pyrrolopyridazines in PPS is relatively small. Interestingly, the quantum efficiency is solvent dependent, changing from 61% (in CH$_2$Cl$_2$) to 13% (in DMSO), possibly due to aggregation of PPS in DMSO that enhances the self-quenching.$^{15}$
The fluorescence quantum efficiencies of PPM1 are also lower than those of monomer 5. This is also because of self-quenching. Upon diluting the chromophore, the quantum efficiencies of PPM2 improved. The quantum efficiency of PPM1 is lower than that of PPS in methylene chloride, which indicates that polystyrene is a better backbone for improved fluorescence in low polarity solvents. Interestingly, in polar solvents such as DMSO, all the pyrrolopyridazines showed blue-shifted absorptions without significant change in luminescence.16

Figures 3 and 4 show that the absorption and fluorescence spectra are all identical, which indicates that the chromophores in the polymer do not strongly interact and behave independently. The absorption band (around 290 nm) of monomer 4 decreased after polymerization. This band corresponds to the absorption of the styrene unit in monomer 4.17

We reasoned that due to their high solid-state fluorescence quantum efficiency, the pyrrolopyridazines may have potential for use as laser dyes. Furthermore, the Stokes shifts are relatively large (ca. 100 nm) (Table 2), and the overlap of the absorption and the luminescence spectra is small (Figures 3 and 4), so that the emitted light is not likely to be quenched or absorbed by unexcited chromophores.

![Scheme 2. Synthetic Route to PPM1 and PPM2](image)

**Figure 2.** $^1$H NMR spectra of polymers (PPS, PPM1, PPM2).

**Figure 3.** Absorption and fluorescence spectra of monomer 4 and PPS in CH$_2$Cl$_2$.

**Figure 4.** Absorption and fluorescence spectra of monomer 5 and PPM1 and PPM2 in CH$_2$Cl$_2$. 
The pyrrolopyridazines, however, do not show any signs of stimulated emission, even under strong pump conditions. The reason for the absence of lasing is that the excited-state absorption is larger than the stimulated emission at any wavelength under the fluorescence band, resulting in a net absorption from the excited state. The absorption coefficients ($\varepsilon$) are around 4400 (dm$^3$/cm mol) for the monomers and around 3900 (dm$^3$/cm mol) for the polymers, and to the first order, the cross section for stimulated emission is the same as that for absorption.

**Waveguide Study.** As mentioned above, the polymers are easily processed into waveguide structures such as fibers and rods by pultrusion from a viscous solution such as the melt or concentrated solutions in CH$_2$Cl$_2$. The waveguides show an interesting phenomenon; the color and intensity of the fluorescence from the end of the fiber (end luminescence) were tunable according to the position of the pump along the fiber (Figure 5). When the side of the fiber was excited, the end luminescence was similar to that of the film or solution. As the excitation position moved farther from the end facing the detector, the emission color that was propagated through the guide showed increasing shifts to the red (Figures 5 and 6). As well as the color, the absolute intensity decreases with increasing propagation length.

To investigate this phenomenon, we made a thick rod of a composite consisting of 9,10-diphenylanthracene and polystyrene. The luminescence from the end changed from blue to orange (Figure 7) as the excitation spot was moved away from the end of the rod. The off-resonance absorption$^{20}$ of the material and scattering losses in the waveguide red shift the end luminescence;$^{21}$ light of shorter wavelengths is easily absorbed or scattered during propagation, while light of longer wavelengths propagates in the waveguide with little loss. The absolute intensity of luminescence also decreases with increasing propagation length.

This loss of blue emission from wave guiding provides information that makes structure in the tail of the emission band clear. Originally, there is only one clear peak (430 nm) in fluorescence from films of PPS (Figure 6) and two (413 and 433 nm) in the composite of 9,10-diphenylanthracene and polystyrene (Figure 7). As the propagation length becomes longer, the tail of the fluorescence is relatively enhanced, and several new peaks become obvious.$^{22}$ As with Figures 6 and 7, there are spectral evolutions of the emissions. This phenomenon is also interesting because a single uniform fiber or rod can produce tunable color simply by switching the pump position. This means that such waveguides have potential to be used in optical devices such as switches or modulators.$^{23}$

**Conclusion**

Three new vinyl polymers based on the pyrrolopyridazine unit were prepared, and their optical properties were studied. The polymers exhibited intense blue emission with quantum efficiencies up to 60%, which demonstrates that there is little self-quenching between chromophores even in condensed phase. These design strategies are very important for synthesis of new organic polymers for electronic applications, such as OLEDs. We also have shown that the emission color is

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**Table 2.** $\lambda_{\text{max}}$ (nm) of Absorption Spectra, $\lambda_{\text{max}}$ (nm) of Fluorescence Spectra, and Relative Quantum Efficiency (%) of Monomers (4, 5) and Polymers (PPS, PPM1, PPM2)

<table>
<thead>
<tr>
<th>Compound</th>
<th>DMSO</th>
<th>MeOH</th>
<th>CH$_2$Cl$_2$</th>
<th>Hexane</th>
<th>DMSO</th>
<th>MeOH</th>
<th>CH$_2$Cl$_2$</th>
<th>Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>331</td>
<td>334</td>
<td>339</td>
<td>345</td>
<td>433</td>
<td>429</td>
<td>431</td>
<td>429</td>
</tr>
<tr>
<td>PPS</td>
<td>332</td>
<td>a</td>
<td>343</td>
<td>a</td>
<td>434</td>
<td>430</td>
<td>430</td>
<td>428</td>
</tr>
<tr>
<td>5</td>
<td>331</td>
<td>333</td>
<td>338</td>
<td>344</td>
<td>432</td>
<td>430</td>
<td>430</td>
<td>428</td>
</tr>
<tr>
<td>PPM1</td>
<td>332</td>
<td>a</td>
<td>340</td>
<td>a</td>
<td>433</td>
<td>430</td>
<td>430</td>
<td>428</td>
</tr>
<tr>
<td>PPM2</td>
<td>333</td>
<td>a</td>
<td>339</td>
<td>a</td>
<td>433</td>
<td>430</td>
<td>430</td>
<td>428</td>
</tr>
</tbody>
</table>

* Insoluble.

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**Figure 5.** End luminescence.

**Figure 6.** Normalized end luminescence from the fiber of polymer PPS.

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**Figure 7.** Normalized end luminescence from the rod of composite made of polystyrene and 9,10-diphenylanthracene.
tunable using a waveguide geometry, providing the potential to use such geometries in devices such as optical switches or modulators.

**Experimental Section**

Synthetic procedures for the pyrrolyridazines are depicted in Schemes 1–5.

**General.** Nuclear magnetic resonance (NMR) spectra were taken by using CDCl3 solutions at 400 MHz with TMS as the internal reference (δ = 0.00 ppm). FT-IR spectra were recorded by the drift method. UV–vis spectra and fluorescence spectra were obtained by using DMSO, MeOH, hexane, and methylene chloride. For end luminescence, PPS was excited at 345 nm, 9,10-diphenylacene was excited at 377 nm, and the width of the light source was 0.2 mm. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC Pyris instrument at a heating rate of 10 °C/min under a nitrogen atmosphere. DSC thermograms were obtained by using DMSO, MeOH, hexane, and methylene chloride as the internal reference (δ = 0.0 ppm). DSC scans were corrected for the background heat flow with Ar. The mixture was warmed to 80 °C. The viscosity was increased gradually. The mixture was stirred for 2 h and cooled to room temperature. The mixture was dissolved in CH2Cl2 (10 mL) and dried over Na2SO4.

**Synthesis of 4-Vinylbenzyl Acetate (1).** Chloromethyl-4-vinylbenzene (7.5 g, 50 mmol) in glacial acetic acid (30 mL) was refluxed for 7 h with potassium acetate (AcOK) (8.5 g, 87.5 mmol). The color turned yellow gradually. As the reaction proceeded, precipitate increased. The mixture was poured to ice and extracted with ether (3 × 100 mL). The organic extracts were washed with aqueous NH4Cl (20 mL) and dried over Na2SO4. The solvent was removed under reduced pressure to afford a white solid. The solid was chromatographed on silica gel (300 g) with (hexane → ethyl acetate = 5:1) to afford a colorless oil (8.3 g, 4.7 mmol) in 94% yield. 1H NMR (CDCl3): δ 7.41 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 6.72 (dd, J = 11.0, 17.8 Hz, 1H), 5.77 (dd, J = 0.8, 11 Hz, 1H), 5.27 (dd, J = 11.0, 17.8 Hz, 1H), 5.10 (s, 1H), 5.07 (s, 1H), 4.65 (s, 2H), 2.12 (s, 3H). 13C NMR (CDCl3): δ 170.9, 137.6, 136.3, 135.4, 128.6, 126.4, 114.4, 66.1, 21.0.

**4-Vinylbenzyl Alcohol (2).** Acetic acid 4-vinylbenzyl ester (8.0 g, 45.5 mmol) and KOH (8.6 g 154 mmol) in MeOH (40 mL) and H2O (12 mL) was refluxed for 6 h. The color of the solution changed from pale yellow to yellow. The reaction mixture was poured to ice and extracted with ether (3 × 100 mL). The organic extracts were washed with aqueous NaHCO3 (20 mL) and dried over Na2SO4. The solvent was removed under reduced pressure to give a brown oil. The residue was chromatographed on silica gel (300 g) with (hexane → ethyl acetate = 5:1) to afford a colorless oil (8.3 g, 4.7 mmol) in 94% yield. 1H NMR (CDCl3): δ 7.41 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 6.72 (dd, J = 11.0, 17.8 Hz, 1H), 5.77 (dd, J = 0.8, 11 Hz, 1H), 5.27 (dd, J = 11.0, 17.8 Hz, 1H), 5.10 (s, 1H), 5.07 (s, 1H), 4.65 (s, 2H), 2.12 (s, 3H). 13C NMR (CDCl3): δ 170.9, 137.6, 136.3, 135.4, 128.6, 126.4, 114.4, 66.1, 21.0.

**Pyrrolo[1,2-b]pyrazidine-5,6,7-tricarboxylic Acid (3).** Pyrrolo[1,2-b]pyrazidine-5,6,7-tricarboxylic acid 7-tert-butyl ester 5,6-dimethyl ester (PPB)25 (15 g, 44.9 mmol) and dry CH2Cl2 (80 mL) were charged in a round-bottom flask. Trifluoroacetic acid (TFA) (6.39 g, 56.1 mmol) and dry CH2Cl2 (80 mL) were charged in a round-bottom flask. Trifluoroacetic acid (TFA) (6.39 g, 56.1 mmol) and dry CH2Cl2 (80 mL) were charged in a round-bottom flask. Trifluoroacetic acid (TFA) (6.39 g, 56.1 mmol) and dry CH2Cl2 (80 mL) were charged in a round-bottom flask. Trifluoroacetic acid (TFA) (6.39 g, 56.1 mmol) and dry CH2Cl2 (80 mL) were charged in a round-bottom flask. Trifluoroacetic acid (TFA) (6.39 g, 56.1 mmol) and dry CH2Cl2 (80 mL) were charged in a round-bottom flask. Trifluoroacetic acid (TFA) (6.39 g, 56.1 mmol) and dry CH2Cl2 (80 mL) were charged in a round-bottom flask. Trifluoroacetic acid (TFA) (6.39 g, 56.1 mmol) and dry CH2Cl2 (80 mL) were charged in a round-bottom flask.

**General Method for Polymerization.** A monomer (1.5 mmol) and distilled 1,2-dichlorobenzene (0.40 mL) were charged in a round-bottom flask. The mixture was degassed by the freeze-and-thaw method three times. The flask was charged with Ar. The mixture was warmed to 80 °C. The monomer was dissolved completely. AIBN (3 mg, 0.018 mmol) was added to this mixture under Ar. The viscosity increased gradually. The mixture was stirred for 2 h and cooled to room temperature. The mixture was dissolved in CH2Cl2 (10 mL) and added MeOH.
(20 mL). The precipitate was centrifuged, and the solid was collected. The solid was dissolved in CHCl₃ (10 mL), and the solution was added to MeOH (50 mL) with stirring. The precipitate was separated by centrifuging and dried under reduced pressure for 24 h. Purification was accomplished by dissolving the solid in CHCl₃ (10 mL) and being precipitated with 2-propanol (50 mL) to afford a white powder that was isolated by filtration and dried under vacuum for 4 days at 60 °C.

Poly(1,2-bispyridazine-5,6,7-tricarboxylic acid 5,6-dimethyl ester 7-[4-vinylbenzyl] ester) (PPM1). In 44% yield. ¹H NMR (CDCl₃): δ 8.5–8.2 (br, 2H), 7.7–6.9 (br, 1H), 4.6–4.0 (br, 4H), 4.0–3.9 (br, 3H), 3.9–3.8 (br, 3H), 2.3–1.2 (br, 2H), 1.1–0.6 (br, 3H). Elemental analysis for C₃₇H₂₉N₂O₁₆: Calcd C, 63.91; H, 4.80; N, 7.10. Found C, 63.32; H, 4.37; N, 6.85. IR: 1739, 1722, 1710 cm⁻¹.

Fabrication of Waveguides. (1) Fiber of FPS. A 5 mL vessel was charged with polymer FPS (100 mg) in CHCl₃ (0.5 mL). The mixture was stirred with a glass rod (diameter 0.3 cm) for 10 min. From the viscous mixture a fiber was pulled up slowly (30 mm/1 min) with the glass rod. The size of the obtained fiber was 0.5 × 0.5 × 30 mm.

(2) Rod of 9,10-Diphenylanthracene and Polystyrene. A 5 mL vessel was charged with polystyrene (190 mg) and 9,10-diphenylanthracene (10 mg). The mixture was stirred with a glass rod (diameter 0.3 cm) and heated around 150 °C for 10 min. From the viscous melt a rod was pulled up slowly (100 mm/1 min) with the glass rod. The size of the obtained rod was 2 × 2 × 200 mm.

Acknowledgment. We are grateful to Dr. M. Bendikov (Department of Chemistry and Biochemistry, UCLA) for DSC and TGA measurements and Prof. Y. Yang (Department of Engineering, UCLA) for instructive discussion. We are grateful to Mitsubishi Chemical Corp. for support of T.M. We also thank the ONR for support through a grant (N00014-97-1-0835).

References and Notes


From the fluorescence spectra, PPS has bands at 424, 463, 484, and 518 nm and 9,10-diphenylanthracene has bands at 413, 434, 468, 503, 530, and 572 nm.


Compound PPB was prepared according to our procedure (ref 5a).