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

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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.¹ Among these applications, organic light-emitting diodes (OLEDs) have been most widely investigated.² While many chromophores have been designed and synthesized for potential OLEDs,³ 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.⁴ Among the polymers, conjugated and nonconjugated polymers have been used, such as poly(*p*-phenylene-vinylene) (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.⁵ 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.^{5a} Initially, the *tert*-butyl ester of PPB was selectively hydrolyzed with trifluoroacetic acid (TFA)⁶ 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)phosphoric chloride (BOP-Cl)⁷ 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 AIBN⁸ to afford polymers (PPS, PPM1, and PPM2) (Schemes 1 and 2). These polymers were soluble in halogenated solvents such as CH₂Cl₂, ClCH₂CH₂Cl, 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)

| polymer | <i>T</i> _g (°C) | decomposition (°C) ^a | <i>M</i> _w (<i>M</i> _w / <i>M</i> _n) ^b |
|---------|----------------------------|---------------------------------|--|
| PPS | 140 | 330 | 3.15 × 10 ⁵ (9.9) |
| PPM1 | 126 | 325 | 5.79 × 10 ⁵ (30.3) |
| PPM2 | 118 | 180 (5% loss), 290 | 5.00 × 10 ⁵ (3.4) |

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

^b Determined by GPC, relative to polystyrene standards.

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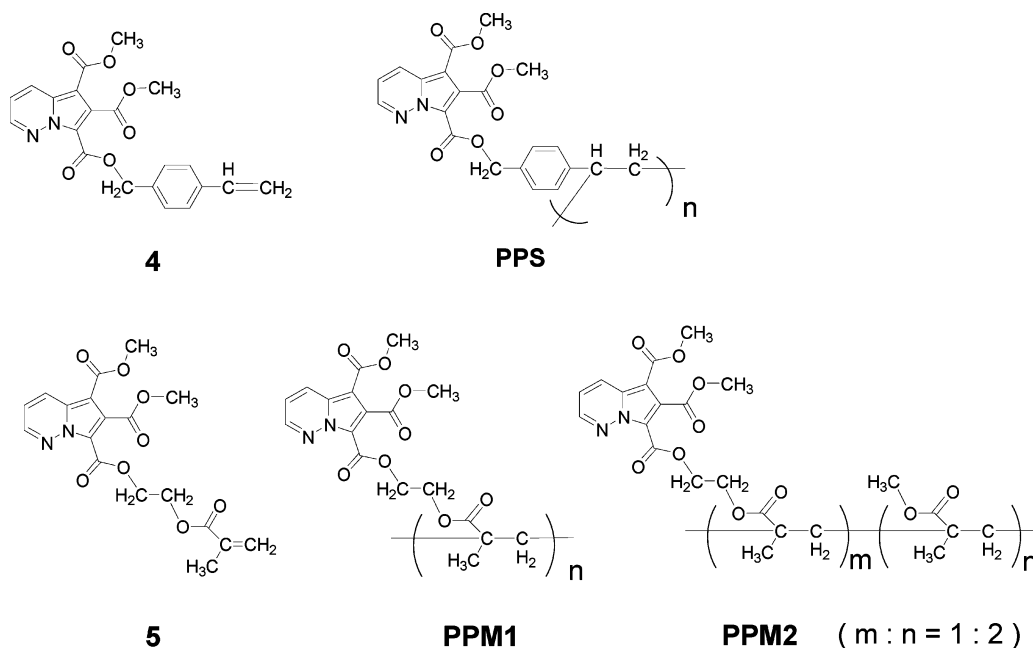
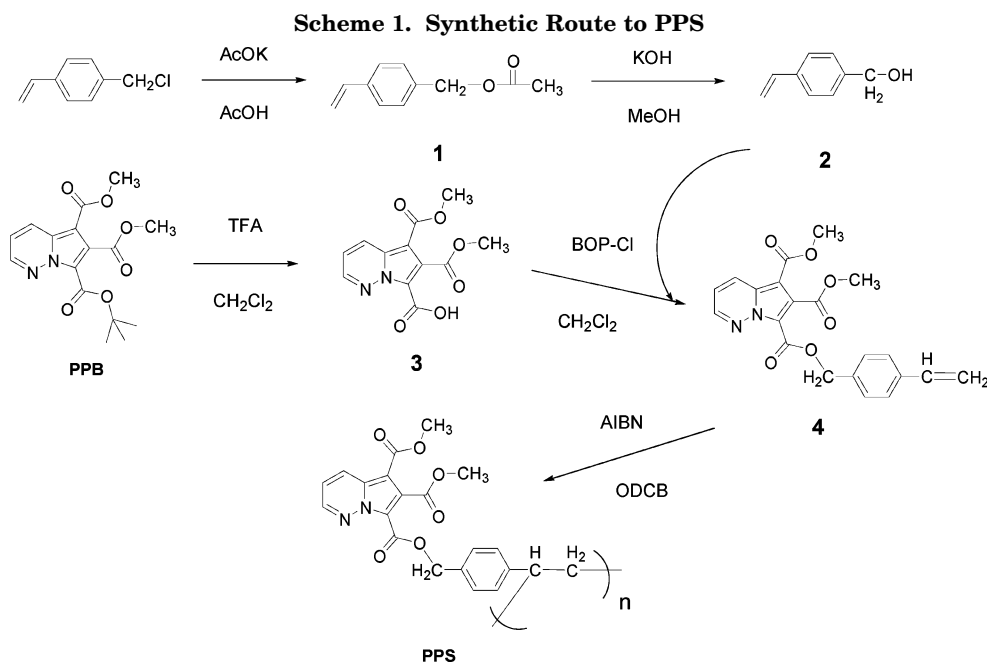


Figure 1. Structures of the monomers and the polymers reported in this paper.



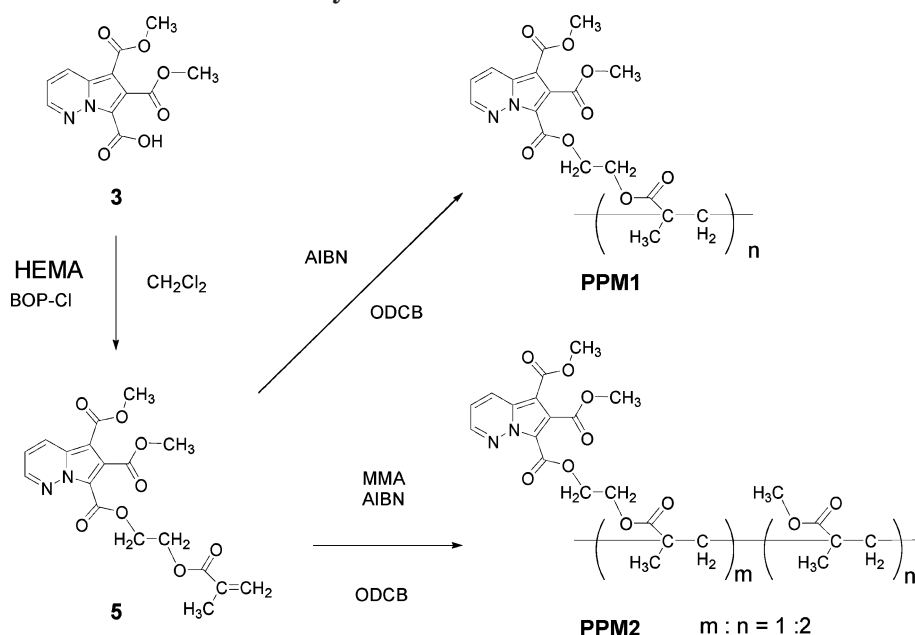
except the first 5% of weight loss in PPM2 (discussed later). The glass transition temperatures (T_g) are much higher than those of the backbone polymers, polystyrene and poly(methyl methacrylate) (PMMA). The T_g of PPS is 140 °C, while that of atactic polystyrene is 100 °C.^{9,10} The T_g of PPM1 (126 °C) and PPM2 (118 °C) is also much higher than the reported values of PMMA (~100 °C).^{10,11} 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 (λ_{\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_2Cl_2) to 13% (in DMSO), possibly due to aggregation of PPS in DMSO that enhances the self-quenching.¹⁵

Scheme 2. Synthetic Route to PPM1 and PPM2



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

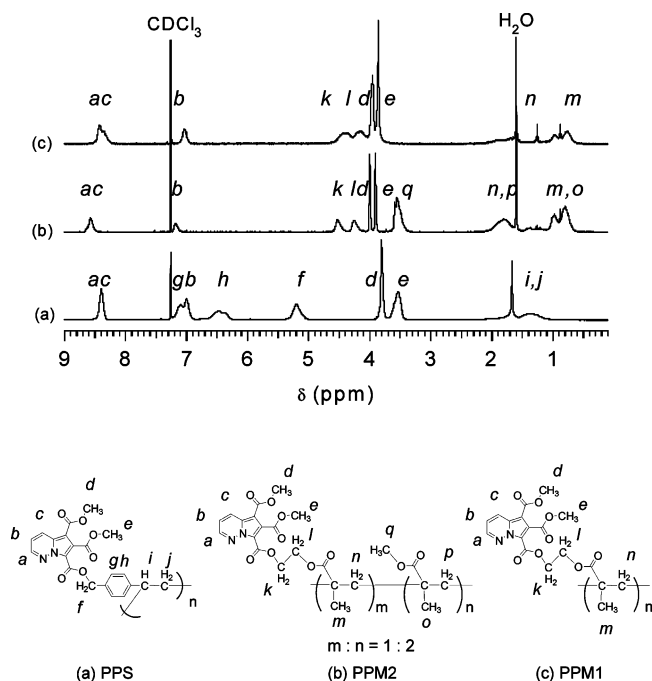


Figure 2. ^1H NMR spectra of polymers (PPS, PPM1, PPM2).

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.

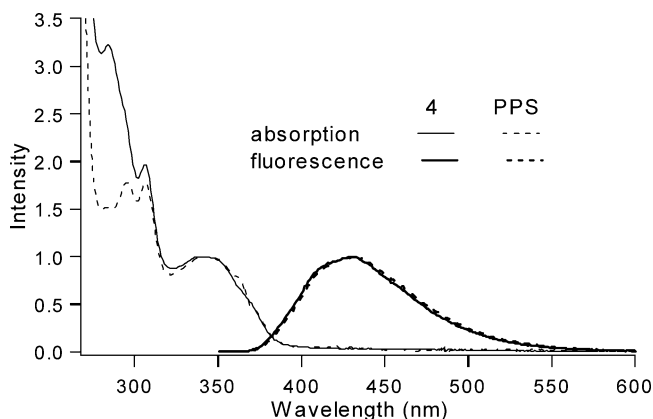


Figure 3. Absorption and fluorescence spectra of monomer **4** and PPS in CH_2Cl_2 .

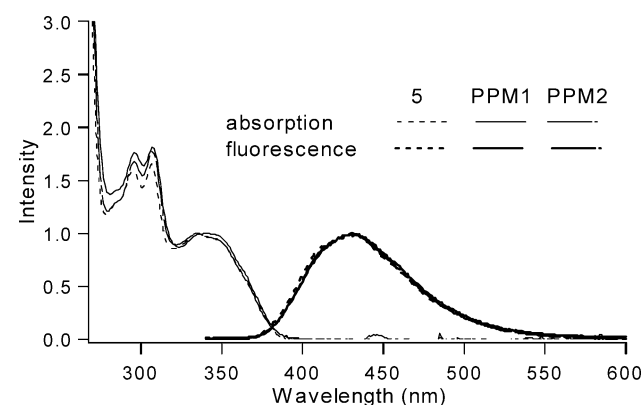


Figure 4. Absorption and fluorescence spectra of monomer **5** and PPM1 and PPM2 in CH_2Cl_2 .

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

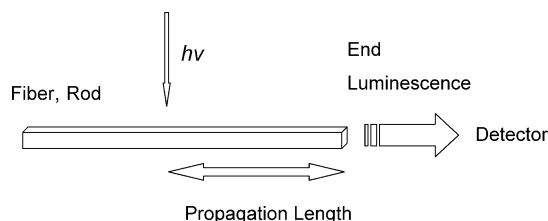
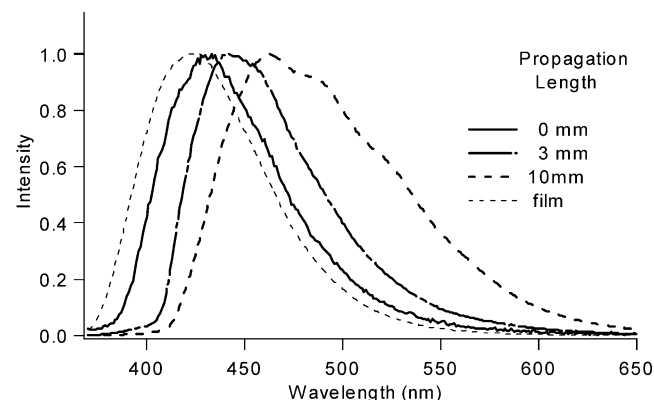
| compound | absorption (λ_{max} /nm) | | | | fluorescence (λ_{max} /nm) (quantum efficiency (%)) | | | |
|----------|--|----------|---------------------------------|----------|---|----------|---------------------------------|----------|
| | DMSO | MeOH | CH ₂ Cl ₂ | hexane | DMSO | MeOH | CH ₂ Cl ₂ | hexane |
| 4 | 331 | 334 | 339 | 345 | 433 (51) | 429 (77) | 431 (74) | 429 (75) |
| PPS | 332 | <i>a</i> | 343 | <i>a</i> | 434 (13) | <i>a</i> | 430 (61) | <i>a</i> |
| 5 | 331 | 333 | 338 | 344 | 432 (48) | 430 (86) | 430 (64) | 428 (91) |
| PPM1 | 332 | <i>a</i> | 340 | <i>a</i> | 433 (32) | <i>a</i> | 430 (40) | <i>a</i> |
| PPM2 | 333 | <i>a</i> | 339 | <i>a</i> | 433 (45) | <i>a</i> | 430 (54) | <i>a</i> |

^a Insoluble.

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.¹⁸ The absorption coefficients (ϵ) are around 4400 (dm³/(cm mol)) for the monomers and around 3900 (dm³/(cm mol)) for the polymers, and to the first order, the cross section for stimulated emission is the same as that for absorption.¹⁹

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 CH₂Cl₂. 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.

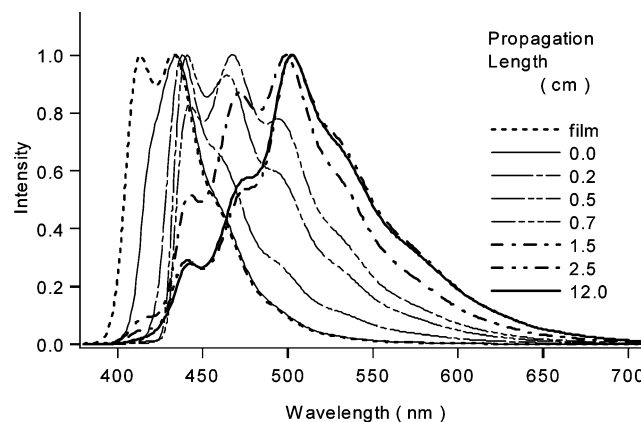
To investigate this phenomenon, we made a thick rod of a composite consisting of 9,10-diphenylanthracene

**Figure 5.** End luminescence.

Observed peak intensities. 0mm: 100, 3mm: 40, 10mm: 2

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

and polystyrene. The luminescence from the end changed from blue to orange (Figure 7) as the excitation spot was



Observed peak intensities. 0.0cm: 100, 0.2cm: 42, 0.5cm: 17, 0.7cm: 10, 1.5cm: 2.3

Figure 7. Normalized end luminescence from the rod of composite made of polystyrene and 9,10-diphenylanthracene.

moved away from the end of the rod. The off-resonance absorption²⁰ 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

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 pyrrolopyridazines 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 343 nm, 9,10-diphenylanceracene was excited at 377 nm, and the width of the light source was 0.2 mm. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC Pyris instrument at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TAC 7/DX Thermal Analyst system at a heating rate of 10 °C/min under a flow of N₂. All solvents were distilled before use as set forth by standard techniques.²⁴ Melting points were measured by using a capillary melting point apparatus and were uncorrected. Elemental analyses were performed by Desert Analytics. Molecular weights of the polymers were determined by gel-permeation chromatography relative to polystyrene standards, using PL gel columns that were connected in series, eluting with chloroform.

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) (8.58 g, 87.5 mmol). The color turned yellow gradually. As the reaction proceeded, precipitate increased. The mixture was poured to ice and extracted with ethyl acetate (100 mL). The organic extracts were washed with aqueous NaHCO₃ (2 × 50 mL) and H₂O (2 × 50 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 → 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, 11.0, 17.8 Hz, 1H), 5.77 (dd, 17.8, 0.8 Hz, 1H), 5.27 (dd, 0.8, 11 Hz, 1H), 5.10 (s, 2H), 2.11 (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 NH₄Cl (2 × 50 mL) and H₂O (2 × 50 mL) and dried over Na₂SO₄. The solvent was removed under reduced pressure to afford a pale yellow oil. The residue was chromatographed on silica gel (500 g), with (hexane/ethyl acetate = 5:1 → hexane/ethyl acetate = 3:1) to obtain a colorless oil (4.95 g, 36.8 mmol) in 81% yield. ¹H NMR (CDCl₃): δ 7.40 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.72 (dd, J = 11.0, 17.9 Hz, 1H), 5.76 (dd, J = 17.9 Hz, 0.9 Hz, 1H), 5.25 (dd, J = 0.9 Hz, 11.0 Hz, 1H), 4.65 (s, 2H), 1.90–2.10 (br, 1H). ¹³C NMR (CDCl₃): δ 140.5, 137.0, 136.5, 127.2, 126.4, 113.9, 65.0.

5,6-Bis(methoxycarbonyl)pyrrolo[1,2-*b*]pyridazine-7-carboxylic Acid (3). Pyrrolo[1,2-*b*]pyridazine-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) was dropped in at 0 °C. The reaction was allowed to proceed to room temperature, and the solution was stirred for 3 h. The solvent was evaporated and then stored under vacuum for 12 h to afford a pale yellow solid. Purification was accomplished by dissolving the powder in aqueous NaHCO₃ and washing with CH₂Cl₂. Acidification of the aqueous layer with 1 M HCl to pH = 3.5 afforded a white solid that was isolated by filtration and dried under reduced pressure to afford a white solid (11 g, 40 mmol) in 89% yield; mp 193 °C (decomp). ¹H NMR (CDCl₃): δ 8.76 (dd, J = 1.5, 7.7 Hz, 1H),

8.53 (dd, J = 1.5, 3.1 Hz, 1H), 7.26 (dd, J = 3.1, 7.7 Hz, 1H), 4.05 (s, 3H), 3.93 (s, 3H). ¹³C NMR (CDCl₃): δ 164.6, 162.3, 157.5, 144.0, 130.7, 130.6, 120.0, 117.4, 116.2, 104.3, 53.4, 52.2 MS (EI+) m/z : 278.1. Elemental analysis for C₁₂H₁₀N₂O₆: Calcd C, 51.55; H, 3.80; N, 10.22. Found C, 51.80; H, 3.62; N, 10.07. IR: ν (C=O) 1724, 1707, 1692 cm⁻¹.

Pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic Acid 5,6-Dimethyl Ester 7-(4-Vinylbenzyl) Ester (4). 5,6-Bis(methoxycarbonyl)pyrrolo[1,2-*b*]pyridazine-7-carboxylic acid (3) (2.5 g, 7.48 mmol) and 4-vinylbenzyl alcohol (2) (1.03 g, 7.48 mmol) were dissolved in distilled CH₂Cl₂ (20 mL). Triethylamine (1.51 g, 14.96 mmol) and bis(2-oxo-3-oxazolidinyl)phosphonium chloride (BOP-Cl) (1.904 g, 7.47 mmol) were added to this solution. The white reagent (BOP-Cl) was getting dissolved in 20 min. The mixture was stirred for 4 h, and aqueous NaHCO₃ (20 mL) was added. The organic layer was extracted with CH₂Cl₂. The organic extracts were washed with H₂O (2 × 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 (CH₂Cl₂ → CH₂Cl₂:ethyl acetate = 4:1). The fraction corresponding to the monomer was evaporated to afford a white solid (2.5 g). Purification was accomplished by dissolving the solid in CH₂Cl₂ (5 mL) and being precipitated with pentane (50 mL) to afford a white powder that was isolated by filtration and dried under vacuum for 12 h (2.21 g, 5.41 mmol) in 72% yield; mp 116.5–117.5 °C. ¹H NMR (CDCl₃): δ 8.63 (dd, J = 1.9, 4.5 Hz, 1H), 8.57 (dd, J = 9.2, 1.9 Hz, 1H), 7.42 (dd, J = 12.1, 8.7 Hz, 4H), 7.15 (dd, J = 9.2, 4.5 Hz, 1H), 6.72 (dd, J = 17.6, 10.9 Hz, 1H), 5.76 (dd, J = 0.8, 17.6 Hz, 1H), 5.26 (dd, J = 0.8, 10.9 Hz, 1H), 5.35 (s, 2H) 3.89 (s, 3H), 3.66 (s, 3H). ¹³C NMR (CDCl₃): δ 165.4, 162.7, 157.8, 145.1, 137.8, 136.3, 132.0, 129.0, 128.4, 126.4, 117.7, 114.4, 102.8, 66.9, 52.7, 51.9. MS (EI+) m/z : 394.1. Elemental analysis for C₂₁H₁₈N₂O₆: Calcd C, 63.91; H, 4.80; N, 7.10. Found C, 64.01; H, 4.70; N, 7.01. IR: ν (C=O) 1738, 1714, 1706 cm⁻¹.

Pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic Acid 5,6-Dimethyl Ester 7-[2-(2-Methylacryloyloxy)ethyl] Ester (5). 5,6-Bis(methoxycarbonyl)pyrrolo[1,2-*b*]pyridazine-7-carboxylic acid (3) (1.25 g, 3.74 mmol) and 2-hydroxyethyl methacrylate (HEMA) (0.53 g, 4.11 mmol) were dissolved in distilled CH₂Cl₂ (80 mL). Triethylamine (0.75 g, 7.48 mmol) and BOP-Cl (0.952 g, 3.79 mmol) were added to this solution. The white reagent (BOP-Cl) was getting dissolved in 1 h as the mixture increased viscosity. The mixture was stirred for 8 h, and aqueous NaHCO₃ (20 mL) was added to this solution. The organic layer was extracted with CH₂Cl₂, and the extracts were washed with H₂O (2 × 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 (CH₂Cl₂ → hexane:CH₂Cl₂ = 1:1). The fraction corresponding to the monomer was evaporated to afford a white solid. Purification was accomplished by dissolving the solid in CH₂Cl₂ (5 mL) and being precipitated with pentane (50 mL) to obtain a white powder that was isolated by filtration and dried under vacuum for 3 days (0.56 g, 1.67 mmol) in 45% yield; mp 114.0–115.0 °C. ¹H NMR (CDCl₃): δ 8.63 (dd, J = 7.3, 1.9 Hz, 1H), 8.55 (dd, J = 1.9, 2.7 Hz, 1H), 7.16 (dd, J = 2.6, 7.3 Hz, 1H), 6.19 (d, J = 1.5 Hz, 1H), 5.61 (d, J = 1.5 Hz, 1H), 4.60 (t, J = 3.2 Hz, 2H), 4.45 (t, J = 3.2 Hz, 2H), 3.96 (s, 3H), 3.91 (s, 3H), 1.80 (s, 3H). ¹³C NMR (CDCl₃): δ 165.4, 157.7, 147.8, 145.1, 135.9, 132.1, 129.1, 128.4, 126.4, 117.8, 62.8, 62.2, 53.0, 52.0, 18.3. MS (EI+) m/z : 362.1. Elemental analysis for C₁₇H₁₈N₂O₇: Calcd C, 56.35; H, 5.01; N, 7.73. Found C, 56.40; H, 5.30; N, 7.47. IR: ν (C=O) 1746, 1738, 1730, 1704 cm⁻¹.

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 CH_2Cl_2 (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 CH_2Cl_2 (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(pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid 5,6-dimethyl ester 7-(4-vinylbenzyl) ester) (PPS). In 44% yield. ^1H NMR (CDCl_3): δ 8.5–8.3 (br, 2H), 7.3–6.9 (br, 3H), 6.7–6.2 (br, 2H), 5.4–5.0 (br, 2H), 3.9–3.7 (br, 3H), 3.7–3.4 (br, 3H), 2.2–0.9 (br, 3H). ^{13}C NMR (CDCl_3): δ 165.2, 162.5, 158.8, 145.0, 133.0, 131.7, 129.1, 127.5–128.4 (br), 117.7, 116.8, 102.6, 66.7, 52.4–52.8 (br), 51.8, 40.0–40.5 (br). Elemental analysis for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_6$: Calcd C, 63.91; H, 4.80; N, 7.10. Found C, 63.32; H, 4.37; N, 6.85. IR: ν (C=O) 1735, 1722, 1710 cm^{-1} .

Poly(pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid 5,6-dimethyl ester 7-[2-(2-methylacryloyloxy)ethyl] ester) (PPM1). In 44% yield. ^1H NMR (CDCl_3): δ 8.5–8.2 (br, 2H), 7.1–6.9 (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 $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_7$: Calcd C, 56.35; H, 5.01; N, 7.73. Found C, 56.72; H, 4.71; N, 7.28. IR: ν (C=O) 1739, 1722, 1709 cm^{-1} .

Poly(pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid 5,6-dimethyl ester 7-[2-(2-methylacryloyloxy)ethyl] ester-co-methyl methacrylate) (1:2) (PPM2). Pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid 5,6-dimethyl ester 7-[2-(2-methylacryloyloxy)ethyl] ester (5) (181 mg, 0.5 mmol) and methyl methacrylate (100 mg, 1.0 mmol) were used together as monomers, and PPM2 was obtained in 38% yield according to the general method of polymerization. ^1H NMR (CDCl_3): δ 8.6–8.4 (br, 2H), 7.2–7.0 (br, 1H), 4.6–4.4 (br, 2H), 4.4–4.1 (br, 2H), 4.05–3.95 (br, 3H), 3.95–3.85 (br, 3H), 3.7–3.3 (br, 6H), 2.2–1.1 (br, 6H), 1.1–0.6 (br, 9H). Elemental analysis for $\text{C}_{27}\text{H}_{34}\text{N}_2\text{O}_{11}$: Calcd C, 57.64; H, 6.09; N, 4.98. Found C, 56.85; H, 5.84; N, 4.91. IR: ν (C=O) 1724, 1711 cm^{-1} .

Fabrication of Waveguides. (1) Fiber of PPS. A 5 mL vessel was charged with polymer PPS (100 mg) in CH_2Cl_2 (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 $0.5 \times 0.5 \times 30$ 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 $2 \times 2 \times 200$ mm.

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- (22) 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.
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- (25) Compound PPB was prepared according to our procedure (ref 5a).

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