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A New Synthetic Approach for Polybenzoxazole and Light-Induced Fluorescent Patterning on Its Film

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ABSTRACT: A new polybenzoxazole containing an adjacent hydroxyphenyl group was synthesized by using Suzuki coupling reaction accompanied by a simultaneous elimination reaction of acetyl protecting group of hydroxyl group. The polymer in solution as well as in the film exhibited a strong emission (520 nm) with a large Stokes shift (about 200 nm) via excited-state intramolecular proton-transfer mechanism. The new conjugated polymer containing 2-(2′-hydroxyphenyl)benzoxazole exhibited a unique fluorescence quenching property upon UV irradiation. We demonstrate simple yet effective fluorescence imaging on the films of the new polymer by means of UV irradiation without aid of any photoacid generator and postprocessing such as baking or etching. The resulting fluorescence image was stable over 100 days of storage in ambient conditions.

Introduction

The use of conjugated fluorescent polymers as active materials in electroluminescence (EL) devices, optical transducers, field effect transistors, plastic lasers, and chemical sensors has been intensively investigated over the past few decades because of their tunable properties through rational molecular design and easy processability.[1−9] Recently, conjugated polymers with heterocyclic moieties, especially those containing nitrogen atoms, have drawn much interest because of their high electron mobility and ability to support a number of charge carriers.[10,11] For example, benzazole polymers including benzoxazole, benzimidazole, and benzothiazole groups are well-known for their excellent mechanical, thermal, and thermooxidative stabilities as well as their high electron mobility.

These heterocyclic compounds, moreover, can be rationally designed to have intramolecular hydrogen bonding with an adjacent free hydroxyl group. Upon excitation, these molecules with intramolecular hydrogen bonding undergo excited-state intramolecular proton transfer (ESIPT).[12] Because ESIPT dissipates absorbed photon energy, heterocyclic compounds with ESIPT capability have been investigated extensively as laser dyes and UV light stabilizers due to their transparency in the visible region and high extinction coefficient in the UV range as well as their excellent stability.[13−18] Furthermore, ESIPT is sensitive to environmental change and can be shut off by chemical reactions, making it an attractive mechanism to design chemical sensors and optical storage devices.[19,20]

Various strategies to develop optical data storage in fluorescence-controlled organic-based systems have been devised. Systems consisting of *tert*-butoxycarbonyl (t-BOC) protected quinizarin or coumarin moieties with photoacid generators (PAG) are an excellent example.[21−23] In these systems, photogenerated acids deprotected the t-BOC protection group, rendering free hydroxyl groups. This process caused the quinizarin to undergo tautomerism, producing strong fluorescence on the exposed area only. The soft lithography technique was also explored to pattern fluorescence images. Thermolytic and acid-catalyzed removal of the bulky tetrahydropyran (THP) group of luminescent polyfluorene derivatives by imprinted acid made the contact area insoluble, allowing fluorescence imaging after selective removal of noncontacted areas.[24]

Photogenerated acids also could be designed to block ESIPT by protonating the nitrogen atom of heterocyclic moieties.[25] In this case, fluorescence emission in the exposed area was selectively quenched allowing fluorescence patterning. Direct UV-cleavable protecting groups combined with an ESIPT system and selective photobleaching of a conjugated polymer also have been used to realize fluorescence imaging.[17,26] However, all have at least one limitation such as slow response, lack of long-term stability, or inevitable requirement of PAG and a subsequent step such as baking or etching. As described in the references, photolytic or thermolytic byproducts as well as remaining PAG in the film after image patterning can reduce the image resolution and deteriorate long-term stability of the patterned image as well. However, the use of PAG is inevitable for fluorescence imaging in the deprotection-induced tautomerism-on systems or the acid−base reaction-induced ESIPT-off systems. Thus, to circumvent the use of PAG, photodegradation-induced fluorescence imaging that uses poly(silylene-*p*-phenylene)s in the absence of PAG was rescently reported. UV irradiation induced oxidation of the exposed area and resulted in fine fluorescent patterns.[27]

Recently, we demonstrated a method to synthesize conjugated benzoxazole polymers with adjacent hydroxyphenyl groups. A benzyl-protected hydroxyl group was used for the polymerization and deprotected by

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Scheme 1. Simultaneous Reactions of Suzuki Coupling Polymerization and Deprotection for Polymer 4

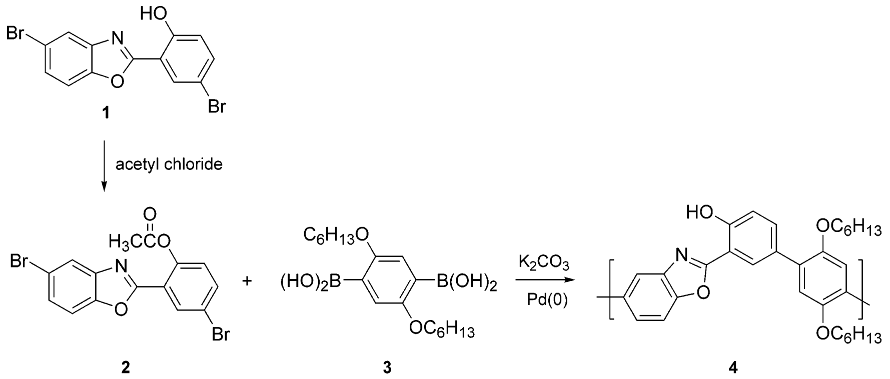
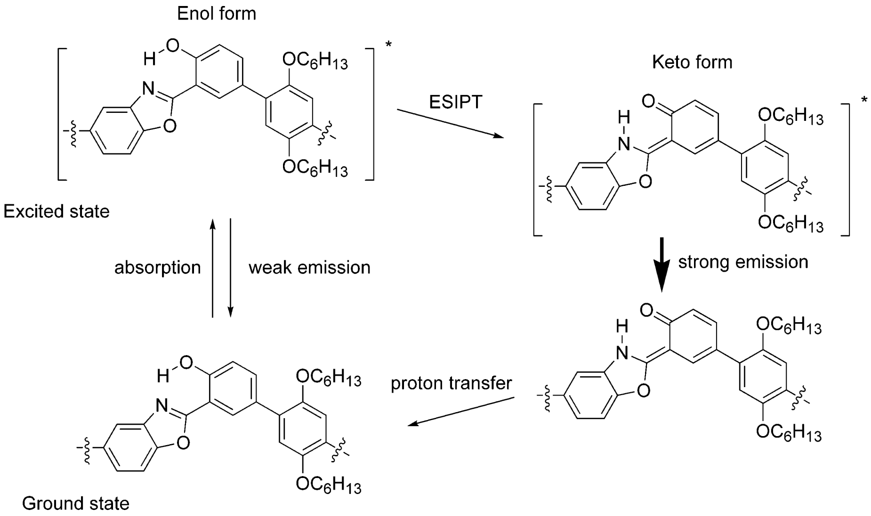


Chart 1. Schematic Representation of the ESIPT Process of 4



eliminating the protecting group.[28] This method requires an additional deprotection step to obtain free hydroxyl groups. Moreover, despite prolonged deprotection reaction times, only about 50% of the protection groups were removed.

In this contribution, we report a simple method to synthesize conjugated benzoxazole polymers with adjacent hydroxyphenyl groups and to fabricate fluorescent images on the polymer films in the absence of PAG. The benzoxazole polymer was prepared through the Suzuki coupling polymerization with simultaneous deprotection of acetyl protection groups during the polymerization. The newly synthesized polymer showed a unique fluorescence quenching property in a thin film upon UV irradiation without presence of any PAG, allowing convenient fluorescence imaging.

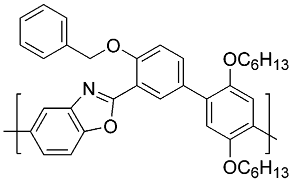
Results and Discussion

Polymer **4** was prepared via the Suzuki coupling reaction between the dibromo monomer **2** and the diboronic acid monomer **3** as shown in Scheme 1.[29] The failure of our initial attempt to synthesize polymer **4** from **1**, which containing a free hydroxyl group, and **3** is likely because the free hydroxyl group inhibits the coupling reaction.[20] Therefore, the acetyl-protected dibromo monomer **2** was eventually used to accomplish the polymerization. The diboronic acid monomer **3** with the long dialkoxy side chains was synthesized according to the method described in the literature.[28] The acetyl group was removed unexpectedly during the polymerization reaction. This deprotection was confirmed by ^{1}H NMR spectrum that did not show any acetyl group at 2.48 ppm after the polymerization. This unexpected deprotection is believed to be due to hydrolysis of the ester group in the presence of potassium carbonate. Under this reaction condition, we obtained the 2-(2′-hydroxyphenyl)benzoxazole polymer derivative **4** with almost 100% free hydroxyl groups.

The number-average and the weight-average molecular weights were determined by gel permeation chromatography (GPC) to be 4500 and 10 700, respectively. DSC analysis of the polymer in a nitrogen atmosphere revealed a T_g of 84.2 °C. Polymer **4** had an off-white color and was soluble in most common organic solvents such as tetrahydrofuran (THF), chloroform, and *N,N*-dimethylformamide (DMF). The polymer could be spin-coated to optical quality films from the solutions. The two long dihexyloxy side chains on the backbone and the fact that a meta-linkage helps prevent aggregation likely contributed to the good solubility. The choice of meta-linkage was also very important in ensuring that ESIPT occurs in the conjugated polymer backbone. It was reported that a 2-(2′-hydroxyphenyl)benzoxazole moiety lost its ESIPT capability when it was incorporated in a highly extended conjugation.[30]

The UV−vis spectrum of polymer **4** has its absorption maximum at 336 nm in chloroform solution and at 334 nm in a film. The emission maximum of the photoluminescence spectrum was observed at 520 nm both in chloroform solution and in film, which resulted from the keto form of 2-(2′-hydroxyphenyl)benzoxazole moieties in the backbone, as shown in Chart 1. In solution,

Chart 2. Benzyl-Protected Polymer 5



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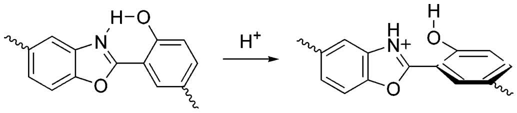
however, the intensity of long wavelength emission from the keto form varies with the polarity of the solvent used, implying that the intramolecular hydrogen bond plays a key role in photoinduced tautomerism.[28,31] Besides the strong emission at 520 nm, a considerably weak emission at a short wavelength around 410 nm was also observed, which resulted from the enol form relaxation as shown in Chart 1. To confirm that the fluorescence emission at 520 nm comes from the keto form and the large Stokes shift is induced by the ESIPT process, we synthesized an analogue of **4** with benzyl-protected hydroxyl groups (Chart 2). The benzyl-protected polymer **5** showed strong emission at 410 nm but no emission at 520 nm due to the lack of intramolecular hydrogen bonding and ESIPT.[20]

Figure 1 shows fluorescence intensity and absorption changes of polymer **4** in chloroform solution upon exposure to trifluoroacetic acid (TFA). Along with fluorescence quenching, a blue shift was facilitated by addition of TFA due to the blocking of keto formation by protonation of the nitrogen atom and the consequent absence of ESIPT as follows (Figure 1a):



The emission maximum shifted to a short wavelength, presumably due to the allowed relaxation from the enol excited state to the enol ground state and prohibited transfer to the keto excited state. The UV spectrum, illustrated in Figure 1b, showed a blue shift of λ_{max} from 336 to 318 nm upon addition of TFA. Originally the absorption at 336 nm was from the $\pi-\pi^*$ transition of the backbone, which was blue-shifted. A new absorption shoulder at around 400 nm appeared, and an isosbestic point was observed at 362 nm. This proves that the acid-induced conversion from neutral to protonated species with no intermediate state and consequently π-conjugated planar structure of hydroxyphenylbenzoxazole was altered within a molecule by protonation with the acid. A similar blue shift in emission maximum was observed from the solution of polymer **4** containing PAG upon UV irradiation, as shown in Figure 1c.

We studied the fluorescence quenching properties of the films of **4**. A spin-cast film composed of polymer **4** and PAG was exposed to UV irradiation at 254 nm for different periods of time. The fluorescence intensity of the film decreased upon exposure to UV irradiation, as shown in Figure 2a. Surprisingly, the same efficient fluorescence quenching was observed in a spin-cast film of **4** without PAG upon UV irradiation although the fluorescence quenching of the film without PAG was slightly slower (Figure 2b). We also used a mercury lamp (50 mW/cm^2) as a power source instead of the monochromatic 254 nm UV lamp (630 μW/cm^2) and observed similar results. However, because of the high intensity of the light source, fluorescence quenching proceeded substantially faster, indicating that the fluorescence quenching occurred more efficiently under stronger irradiation conditions.

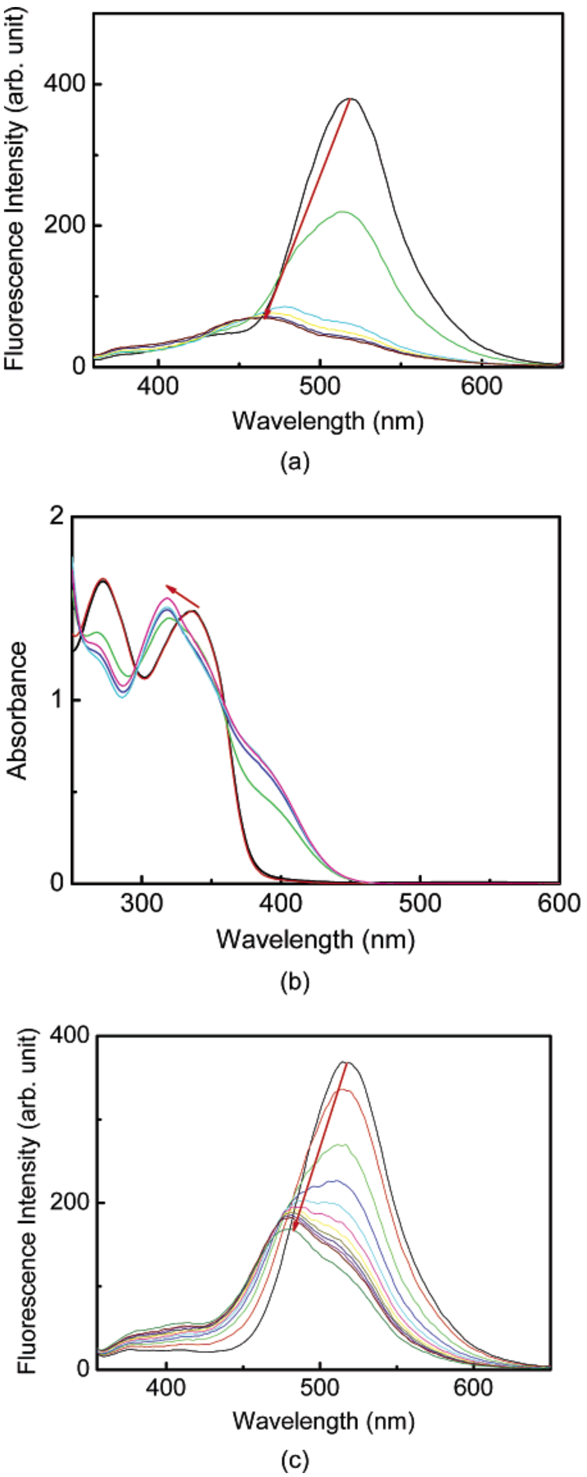


Figure 1. Fluorescence quenching (a) and absorption changes (b) by addition of TFA into polymer **4**/chloroform solution (1.03 × 10^{-6} M). [TFA] = 0, 8.65 × 10^{-3}, 1.73 × 10^{-2}, 2.59 × 10^{-2}, 3.46 × 10^{-2}, and 4.33 × 10^{-2} M. (c) Fluorescence quenching by PAG in polymer **4**/chloroform solution (1.44 × 10^{-7} M). [PAG] = 1.44 × 10^{-6} M (UV irradiation time: 1−15 min).

We investigated the UV absorption spectra of the polymer films in the presence or absence of PAG before and after UV irradiation, as shown in Figure 2. In each case, a small hypochromic shift (decrease in intensity)

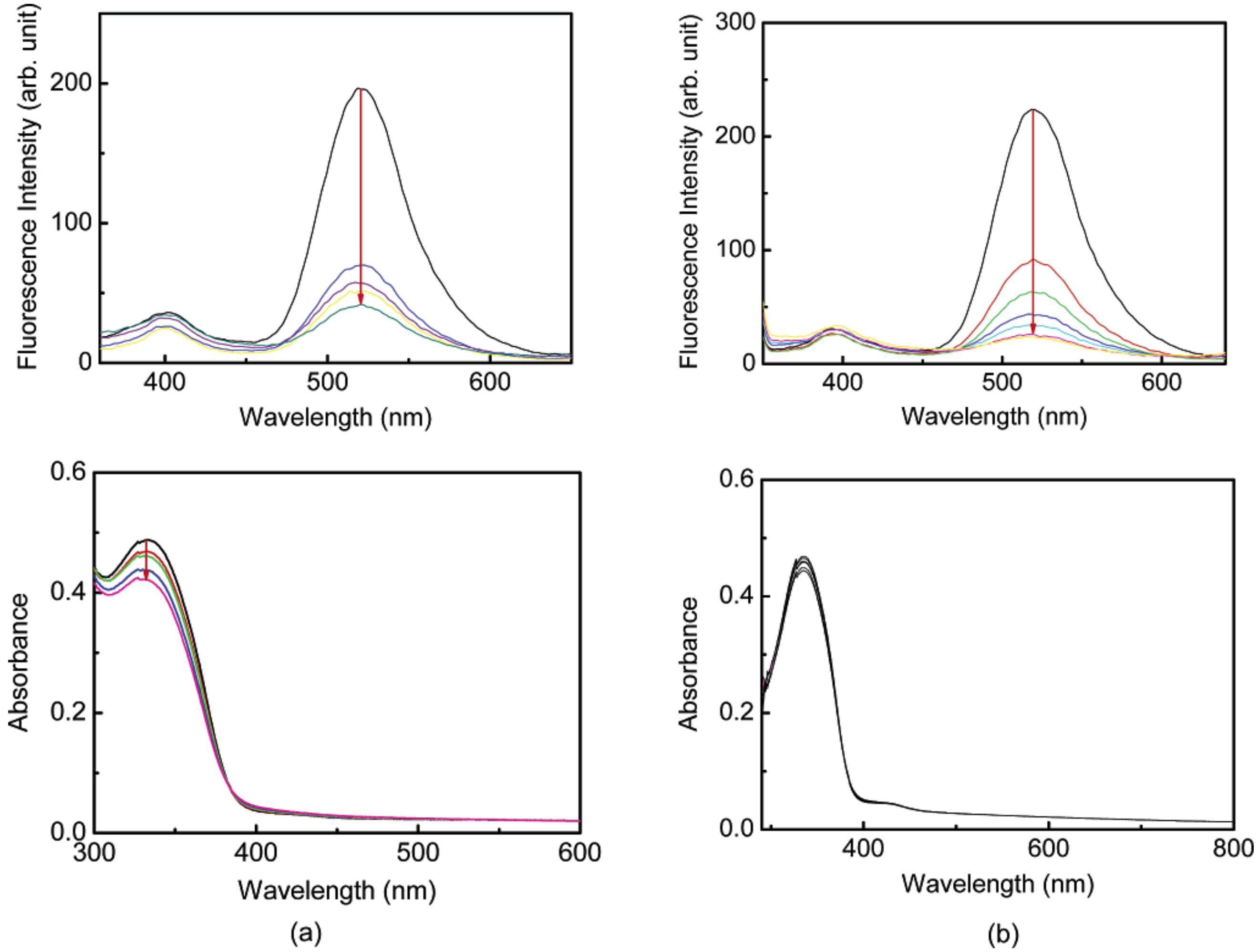


Figure 2. Fluorescence quenching and absorption changes of polymer **4** film upon exposure to 254 nm UV irradiation (a) in the presence of PAG and (b) in the absence of PAG. The concentration of PAG was of 0.05 wt % of polymer. Irradiation time: (a) 0, 3, 6, 9, and 12 min and (b) 0, 5, 10, 15, 20, 25, and 30 min.

of $\lambda_{\max}$ was observed without a blue or red shift even after 30 min of irradiation, contrary to the case in the solution. In the beginning of this study we thought that the small decrease in absorption spectra results from photochemical degradation of benzoxazole units because photochemical degradation and consequent fluorescence quenching of polybenzoxazole model compounds are well-established in the presence of oxygen.[32,33] Various model compounds of polybenzoxazole have shown fluorescence quenching in the solid state, and the degree of quenching was proportional to the concentration of oxygen present. Interestingly, however, in our case, even in a nitrogen atmosphere, films of **4** showed similar fluorescence quenching upon UV irradiation (not illustrated here), suggesting that the presence of oxygen is not essential for fluorescence quenching. This made us to postulate that the fluorescence quenching in the solid is an intermolecular phenomenon. π-Conjugated polymers are known to have a planar structure in the excited state, and this conformational change is the origin of a large Stokes shift of conjugated polymers. Coplanar π-stacking induce ground-state aggregation[4] or an excimer formation,[34] resulting in fluorescence quenching. To test this hypothesis we measured absolute quantum yields of polymer **4** in solution and in the solid state. The fluorescence quantum yield of polymer **4** in chloroform solution and in a thin film was 10.4% and 3.8%, respectively. The thin film was exposed to an UV irradiation to quench the fluorescence down to 1.8%. The polymer film was redissolved in chloroform for quantum yield measurement. The fluorescence quantum yield of the solution was recovered to 9.5%, very close to that of the pristine polymer solution. This fluorescence recovery upon dissolving the quenched polymer into a solution and the oxygen independence of the quenching phenomena strongly support our hypothesis that the fluorescence quenching in the solid state is due to strong π-interactions induced by excited-state planar conformation of the polymer.

We carried out the same experiment of UV irradiation onto the films of polymer **5** fully protected with benzyl groups (Chart 2). In a manner similar to polymer **4**, polymer **5** exhibited fluorescence quenching of the enol emission at 410 nm upon UV irradiation which was likely due to the same π-interactions (Figure 3). We did the same quenching study with poly(methyl methacrylate) (PMMA) films containing 50 wt % monomeric compound **1** and observed minor fluorescence quenching upon exposure to UV irradiation irrespective of the presence of PAG (Figure 4). We believe that the much larger fluorescence quenching in the polymer films is from the fast energy migration along and between the conjugated polymer backbones toward the lower energy π-aggregated sites.

In solution, however, the quenched fluorescence of polymer **4** could not be recovered, suggesting that the

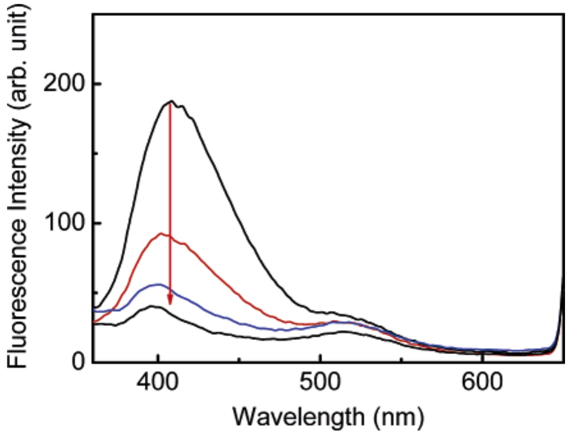
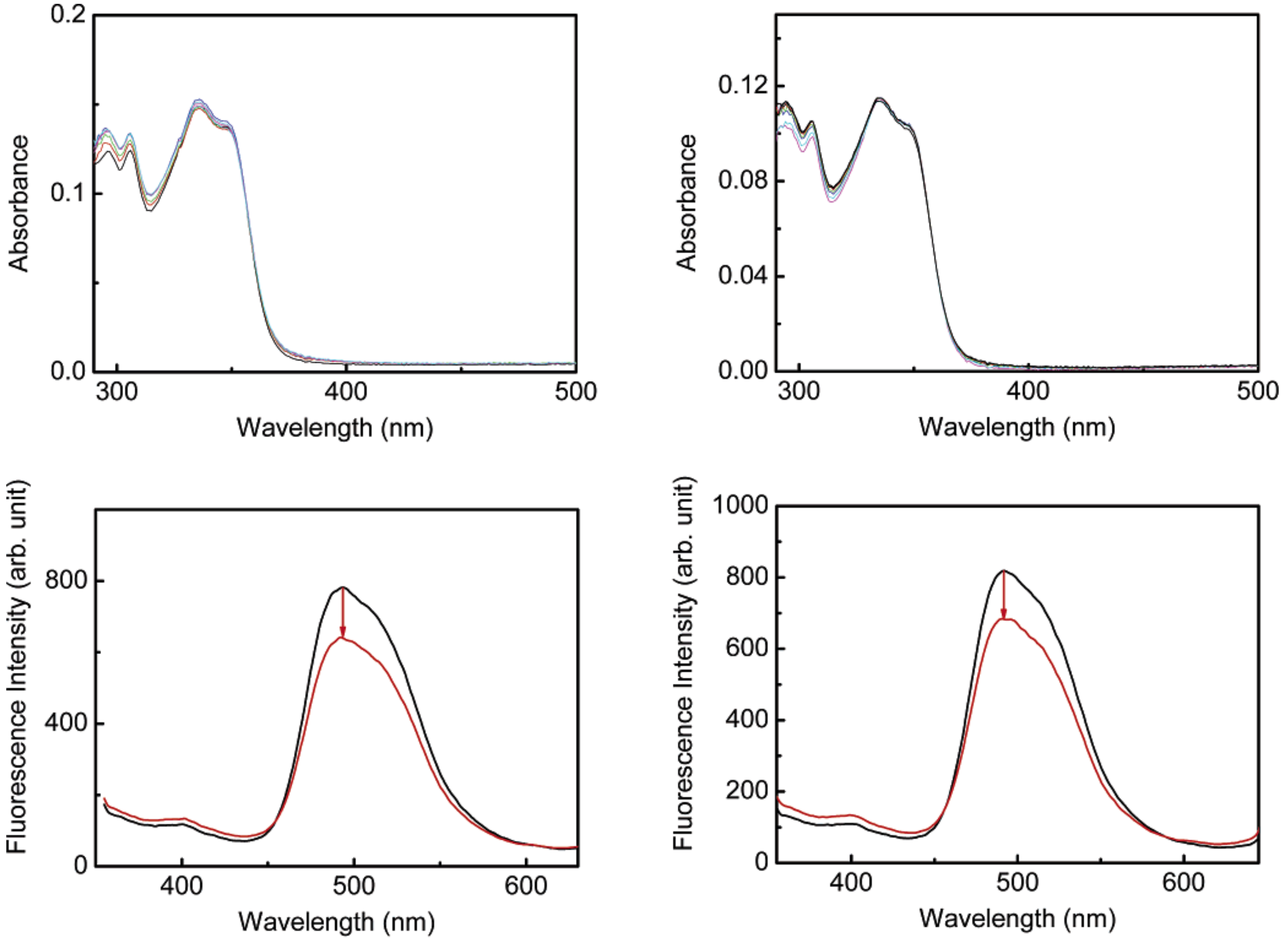


Figure 3. Fluorescence quenching of polymer **5** film upon exposure to 254 nm UV irradiation in the absence of PAG. Irradiation time: 0, 5, 10, and 15 min.

fluorescence quenching in solution is due to backbone degradation. Spectroscopic methods such as FT-IR and NMR as well as X-ray photoelectron spectroscopy (XPS) were employed to investigate the structural changes of polymer **4** before and after UV irradiation without PAG. However, we were not able to find any noticeable changes before and after the UV irradiation in terms of structure and solubility in organic solvents. Although we could not pinpoint the detailed mechanism of photochemical degradation of the polymer in solution, similar photodegradation has been reported in model compound systems, and the degraded products were identified with chromatography and mass spectrometry.[33]

Ultimately, the latent fluorescent images were constructed on a spin-cast film of polymer **4** in the absence of PAG by irradiation from a 254 nm UV lamp for 30 min (Figure 5a) and 10 min (Figure 5b) through photomasks without subsequent processes such as baking or etching. The irradiated films of polymer **4** were no longer emissive, and irradiation through a photomask led to clear fluorescence image inscription. The bright green fluorescent image was made on the unexposed area through the photomask. Fine patterning could be performed with emissive line width of 2 μm according to the photomask used. Because our conjugated polybenzoxazole polymer **4** does not require PAG, we could prepare high-quality spin-cast films, and the films were free from any possible photochemical byproduct or deterioration related to PAG. The patterned image was stable for more than 100 days under ambient light and temperature conditions. Patterns could not be observed under ambient light, while highly resolved fluorescent patterns were clearly seen under UV light.



(a) (b)

Figure 4. Absorption changes and fluorescence quenching of PMMA film containing **1** upon exposure to 254 nm UV irradiation (a) **1**: PAG:PMMA = 0.5:0.05:1 and (b) **1**: PMMA = 0.5:1 by weight; UV spectra: 0−35 min irradiation (interval 5 min); fluorescence spectra: 90 min irradiation.

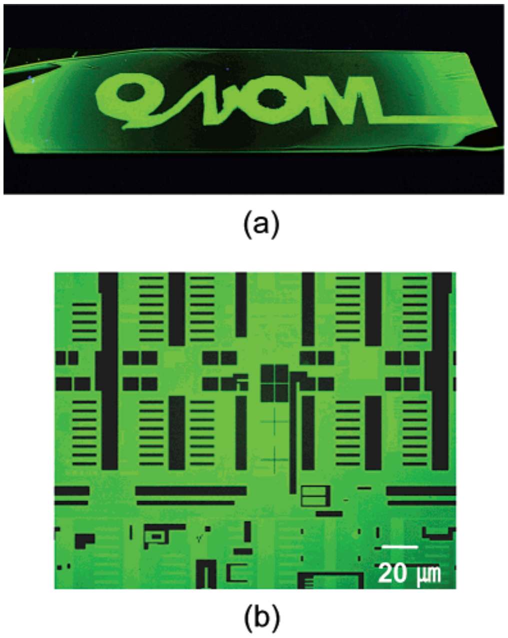


Figure 5. Fluorescence patterned image through photomask (a) on a glass slide by UV irradiation for 30 min and (b) on a silicon wafer by UV irradiation for 10 min. Polymer film was spin-cast from 1 wt % chloroform solution without PAG. Green fluorescence portion was unexposed to UV.

Conclusions

We have developed a new conjugated polymer containing 2-(2′-hydroxyphenyl)benzoxazole from a hydroxyl-protected corresponding polymer by means of the simultaneous reactions of deprotection and Suzuki coupling. The polymer in solutions showed fast fluorescence quenching upon UV irradiation likely due to the photochemical degradation of benzoxazole moieties. The polymer in the solid state also showed fluorescence quenching upon UV irradiation. However, in this case the fluorescence intensity can be recovered by dissolving the quenched polymer film into a solution, suggesting that the fluorescence quenching in the solid state is due to π-interactions induced by excited-state planar conformaion. Patterned latent fluorescence images were easily fabricated by illuminating UV light on a spin-cast film of **4** through a photomask without aid of PAG or any other additional processes. We demonstrated the simplicity and efficiency of our polybenzoazole for fluorescence imaging compared to the conventional methods using PAG. Well-defined synthetic chemistry combined with the ability to construct high-resolution fluorescent images on a polymer film may lead to interesting applications where high information density and good stability are required.

Experimental Section

Characterization. ^{1}H NMR and ^{13}C NMR spectra were collected on a Bruker DRX 300 spectrometer (Korea Basic Science Institute). UV−vis absorption spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer. Luminescence spectra were collected on a Perkin-Elmer LS 45 spectrometer with a xenon lamp as a light source. The elemental analysis (EA) was determined with a CE Instruments EA-1110 elemental analyzer. The absolute quantum yield measurements were carried out by using a fluorescence photometer (QuanaMaster Photon Technology International (PTI)) equipped with an integrating sphere. The molecular weight of the obtained polymer was determined by gel permeation chromatography (GPC) with THF as an eluent and with polystyrene as a standard. Differential scanning calorimetry (DSC) was performed with a Du Pont thermal analyzer model 2100 equipped with a model 2910 DSC in a nitrogen atmosphere with a heating rate of 10 °C/min under nitrogen.

Materials. 2,4-Diaminophenol dihydrochloride (Acros), 5-aminosalicyclic acid (Aldrich), 1,4-benzoquinone (Acros), 1-bromohexane (Aldrich), and trimethyl borate (Aldrich), used for the synthesis of monomers, were used as received. Tetrakis(triphenylphosphine)palladium(0) and butyllithium (1.6 M solution in hexane) were purchased from Aldrich and used as received. The conventional distillation method was employed for purification of tetrahydrofuran (THF) and diethyl ether. The synthesis of 2-(2-hydroxy-5-bromophenyl)-5-bromobenzoxazole (**1**) and polymer **5** was published elsewhere.[20,35]

2-(2-Acetyloxy-5-bromophenyl)-5-bromobenzoxazole (2). Acetyl-protected dibromo compound **2** was prepared via the Sandmeyer reaction from the corresponding diamino compound followed by a protection reaction with acetyl chloride. 2-(2-Hydroxy-5-bromophenyl)-5-bromobenzoxazole, **1** (2.0 g, 5.4 mmol), was dissolved in 30 mL of chloroform under nitrogen. 2.2 mL (27 mmol) of pyridine was slowly added to the flask and cooled to 0 °C using an ice bath. 1.1 mL (16.3 mmol) of acetyl chloride was slowly added to the flask. After 15 min, the mixture was warmed slowly to 40 °C and stirred for 24 h. The reaction mixture was precipitated in n-hexane, filtered, and washed with water. The product recrystallized from ethanol was dried in vacuo (yield 1.0 g, 65.4%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42−7.14 (m, 6H), 2.50 ppm (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 169.76, 159.68, 149.29, 148.62, 143.56, 135.84, 133.07, 129.13, 126.17, 123.67, 121.68, 119.81, 117.80, 112.02, 21.45 ppm. Anal. Calcd for $C_{15}H_9Br_2NO_3$: C, 43.83; H, 2.21; N, 3.41. Found: C, 44.06; H 2.17; N 3.31.

Polymer Synthesis. The polymerization was carried out between **2** and diboronic acid (**3**) with dihexyloxy side chain. **2** (0.73 g, 2.0 mmol), **3** (0.82 g, 2.0 mmol), and 0.13 g (0.113 mmol) of palladium catalyst were placed in a three-necked round-bottom flask charged with 25 mL of THF under nitrogen. The temperature was raised to reflux, and 8 mL of an aqueous 2 M K_2CO_3 solution was added dropwise. After 24 h with stirring, the reaction mixture was cooled and poured into excess methanol. The precipitates were isolated by filtration and washed repeatedly with water and methanol. After drying in a vacuum oven, 0.63 g (64.7%) of product was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.60 (s, 1H), 8.41−7.05 (m, 8H), 4.01 (t, 4H), 1.85−0.82 ppm (m, 22H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 158.10, 150.67, 150.62, 150.54, 148.61, 140.32, 135.91, 135.68, 135.12, 130.40, 130.09, 129.85, 128.59, 128.26, 127.57, 120.34, 117.40, 110.48, 110.04, 69.95, 31.71, 31.64, 29.90, 26.04, 14.16 ppm.

Fluorescence Patterning. Thin films of polymer **4** formulated with in the presence or absence of triphenylsulfonium triflate (0.05 wt %) as a PAG were obtained via spin-casting from 1 wt % chloroform solution on a glass slide or a silicon wafer. After drying in vacuo at 80 °C for 24 h, the film was exposed through a photomask to a monochromatic 254 nm UV light with an intensity of 630 μW/cm^2. The fluorescent image photographs were taken by a digital camera (Nikon Coolpix 3100) and a fluorescence microscope equipped with a cooled CCD camera (Meta Imaging Series 4.6, Universal Imaging Corp.)

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