Articles

Chemically and Photochemically Stable Conjugated Poly(oxadiazole) Derivatives: A Comparison with Polythiophenes and Poly(*p*-phenyleneethynylenes)

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ABSTRACT: We have designed and synthesized highly stable conjugated poly(oxadiazoles) derivatives (**PO1** and **PO2**). The oxadiazole-containing conjugated polymers have a strong photoluminescent property and are completely soluble in organic solvents. **PO1** and two commonly used conjugated polymers, PPE and P3HT, were tested under strong acidic condition and strong UV irradiation condition to investigate their chemical and photochemical stability. **PO1** turned out to be intact through the harsh treatments while the two control polymers were severely damaged in their conjugated backbone and lost their emissive property. Protonation of the oxadiazole unit of **PO1** by acids induced backbone planarization of **PO1**, resulting in emission color change from blue to green. Reversible color change by adding and removing trifluoroacetic acid (TFA) to **PO1** and latent fluorescent patterning by using a photoacid generator and UV irradiation through a photomask were demonstrated. The results provide a design principle to develop highly stable conjugated polymers for various applications where photobleaching and oxidation are a common challenging problem.

Introduction

For the past three decades, organic conjugated polymers have attracted much attention as an active component for their potential applications such as organic transistors,[1-4] polymer light-emitting devices,[5-7] photovoltaic cells,[8] and chemical and biological sensors.[9-12] A wide range of conjugated polymers, for example, polythiophenes,[13-19] poly(*p*-phenylenes),[20,21] poly-(*p*-phenylenevinylenes),[22-24] poly(*p*-phenyleneethynylenes),[25-29] and polyfluorenes,[30-32] have been reported in the literature as promising materials for these applications. One of the greatest advantages of conjugated polymers over inorganic materials or heavy metal-based organic molecules are their easy processing and nontoxic property. However, the critical disadvantage found in currently available conjugated polymers is their poor stability compared to inorganic materials because they are vulnerable to photodegradation and oxidation in the presence of strong UV, oxygen, and acids. Unfortunately, these harsh conditions are required either as an operating condition or during the fabrication procedures of the above-mentioned devices. For example, long time direct exposure to strong sunshine is the ideal condition to maximize energy harvesting and produce useful electricity in solar cell application but a least desirable condition in point of polymer stability. Many biological applications require bioconjugation with peptides or nucletides, and their synthetic

procedures involve UV irradiation, photoacid generator, and/or TFA (trifluoroacetic acid) deprotection. These are detrimental conditions for conjugated polymers.

In this contribution, we report the systematic investigation about the stability and pH-sensitive properties of our newly developed poly(oxadiazole-*co*-phenylene-*co*-fluorene) derivatives (**PO*x*, *x* = 1, 2**). PO*x* showed a highly emissive and stable property against long time UV exposure and strong acidic condition. In these harsh conditions, the emissive properties of **PO*x*** were comparatively investigated with other two frequently used conjugated polymers, poly(*p*-phenyleneethynylene)s (**PPE**) and poly(3-hexylthophenes) (**P3HT**).

Oxadiazole-containing polymers and organic small molecules are a topic of interest due to their unique properties arising from the presence of its nitrogen-containing heterocyclic aromatic structure. The electron-deficient oxadiazole moiety has been used in the molecule design of organic optoelectronic materials to improve the electron mobility.[33] Incorporating oxadiazole-containing organic materials in the electroluminescence devices constituted of multilayered organic thin films can greatly improve the overall device efficiency by making the balance of charge mobility in the active organic components.[34,35] Very recently, we have synthesized a series of oxadiazole-containing organic molecules and investigated the role of the oxadiazole unit in terms of conjugation and emissive property as well.[36] The oxadiazole moiety is also known to provide enhanced thermal stability, redox stability, and good film-forming properties.[37,38]

Our oxadiazole-containing conjugated polymer is composed of three different units for their own role and designed for signal-
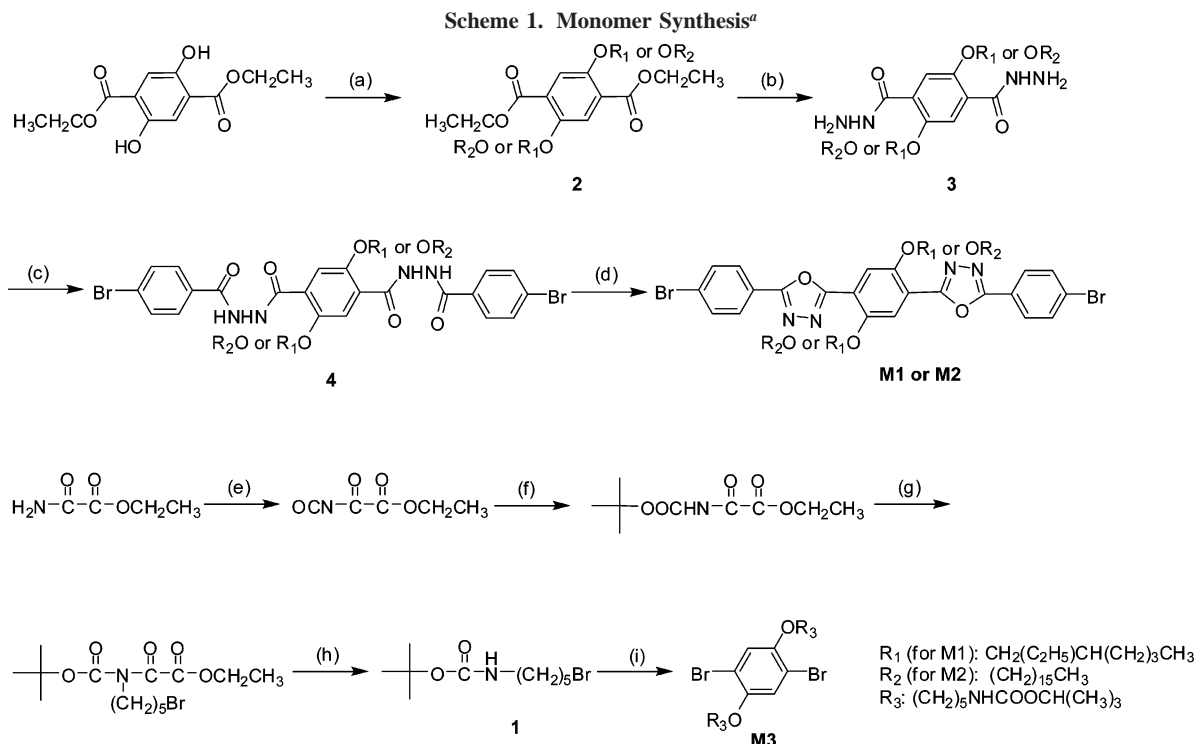
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Scheme 1. Monomer Synthesis[a]

[a] (a) 2-Ethylhexyl bromide (for R$_1$) or 1-bromohexadecane (for R$_2$), K$_2$CO$_3$, DMF, 80 °C, 48 h; (b) H$_2$NNH$_2$, ethanol, 78 °C, 24 h; (c) 4-bromobenzoyl chloride, triethylamine, chloroform, 12 h; (d) POCl$_3$, reflux, 12 h; (e) oxalyl chloride, methylene chloride, 0 °C → 25 °C, 12 h; (f) *tert*-butanol, toluene, 0 °C → 40 °C, 15 min; (g) 1,5-dibromopentane, *t*-BuOK, DMF, 40 °C, 1 h; (h) LiOH, THF, water, RT, 3 h; (i) 2,5-dibromohydroquinone, K$_2$CO$_3$, DMF, 70 °C, 48 h.

amplifying DNA microarray development.[39] The amine functional group is for polymer tethering to a solid support and solid-state DNA synthesis at the same time. The fluorene unit is to improve the solubility and color tuning of the polymer. The oxadiazole unit is to enhance the stability of the polymer during the solid-state DNA synthesis which requires UV irradiation and strong photoacid generators.

Experimental Methods

Materials and Methods. All solvents and reagents were used without further purification as received from Sigma-Aldrich Chemical Co. Compounds **2** and **3** were prepared by the literature procedure with slight modification.[39,40] Gel permeation chromatography (GPC) was used to determine the number- and weight-average molecular weights and the molecular weight distributions with respect to polystyrene standards (Waters Corp.) in tetrahydrofuran as an eluent. UV/vis absorption spectra were recorded with a Varian Cary50 UV/vis spectrophotometer. Photoluminescence spectra and quantum yield in solution and the solid state were obtained by using PTI QuantaMaster spectrofluorometers equipped with an integrating sphere. Fluorescence lifetimes of the **M1** were measured with PTI TimeMaster fluorescence lifetime spectrometer. ^{1}H NMR spectra (400 or 500 MHz) were obtained from Varian Inova 400 or 500 NMR instrumentation. Polymer film was coated by the spin-casting method (3000 rpm for 1 min) on the glass or HMDS-coated glass using 1 mg/mL of polymer solution (**PO1** in chloroform and **PPE** or **P3HT** in tetrahydrofuran).

Synthesis of Compound 4 Having C$_{16}$ Chain. To a 100 mL two-neck round-bottom flask were added compound **3** (0.29 g, 0.429 mmol), 4-bromobenzoyl chloride (0.198 g, 2.1 × 0.429 mmol), triethylamine (0.24 mL), and 25 mL of chloroform. During vigorous stirring precipitation was observed due to the limited solubility of **4** in chloroform. Even though 10 mL of tetrahydrofuran was added to the solution, the solution was still hazy. The reaction further continued overnight for completion. The solid product was filtered to collect the dihydrazide compound **4**. However, compound **4** showed a limited solubility in organic solvents, so reaction

proceeded without further characterization. ^{1}H NMR (400 MHz, CDCl$_3$): δ/ppm 11.70, 10.40 (broad s, 4H, NH), 7.85 (s, 2H, aromatic), 7.75, 7.67 (dd, *J* = 32, 8 Hz, 8H, aromatic), 4.27 (t, 4H, CH$_2$), 2.02 (m, 4H, CH$_2$), 1.10−1.50 (m, 52H, CH$_2$), 0.83 (t, 6H, CH$_3$).

Monomer M2 C$_{16}$ Chain. The synthesis and characterization of monomer **M1** have been reported in another publication.[39] **M2** was prepared according to the same procedure as **M1**. 0.37 g of compound **4** was dissolved in 150 mL of phosphorus oxychloride, and the solution was refluxed for 24 h. The mixture was poured into 1500 mL water, and the appearing solids were collected by filtration and drying in vacuo. White powder product (**M2**) was obtained from recrystallization in benzene (yield: 87%). ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm 8.04, 7.69 (dd, *J* = 175, 11 Hz, 8H, aromatic), 7.80 (s, 2H, aromatic), 4.08 (t, 4H, CH$_2$), 1.88 (m, 4H, CH$_2$), 1.15−1.43 (m, 52H, CH$_2$), 0.85 (t, 6H, CH$_3$).

Synthesis of PO1 and PO2. **PO2** synthesis was done according to the synthetic route of polymer **PO1** in the literature reported previously with a slight modification.[39] To a 50 mL of Schlenk flask were added **M2** (50.0 mg, 49.75 μmol), **M3** (31.8 mg, 49.75 μmol), **M4** (42.4 mg, 100 μmol), THF (3 mL), and 1 M K$_2$CO$_3$ (2 mL). Degassed tetrakis(triphenylphosphine)palladium(0) (5 mol %) in THF (1 mL), prepared in a separate Schlenk, was transferred to the monomer mixture by cannula, and the monomer solution was degassed by several cycles of vacuum and argon purging. Polymerization was carried out at 80 °C for 36 h. The solution of the reaction mixture was precipitated in 30 mL of methanol and filtered. It was further wash with methanol, acetone, water, and hexane (3 × 10 mL each) and dried. Further purification was done by extraction with chloroform/water to give precursor polymer. 2.5 mL of trifluoroacetic acid (TFA) was carefully added to the polymer in chloroform (5 mL), and the polymer solution was stirred at room temperature for 6 h to cleave the *t*-BOC group. After evaporation of solvent and TFA, the polymer was redissolved in chloroform and washed with 1 M KOH solution, followed by NaCl, and deionized water to give yellow polymer (**PO2**) (yield: 73 mg). ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm 8.28 (d, 4H, aromatic), 7.91 (d, 4H, aromatic), 7.40−7.74 (broad m, 14H, aromatic), 7.36 (s, 2H,

aromatic), 4.25 (t, 4H, CH$_2$), 4.00 (t, 4H, CH$_2$), 2.68 (m, 4H, CH$_2$), 2.11 (broad s, 4H, NH$_2$), 1.99 (m, 8H, CH$_2$), 1.90−1.01 (broad m, 100H, CH$_2$), 0.88 (t, 6H, CH$_3$), 0.78 (t, 12H, CH$_3$). The number/weight-average molecular weight was calculated with the polymer before cleavage of *t*-BOC due to the limited solubility of **PO2** in tetrahydrofuran as a GPC eluent; M_n = 35 000, PDI = 3.7.

Results and Discussion

Monomers **M1** and **M2** were prepared according to the synthetic routes illustrated in Scheme 1. The ethylhexyl or hexadecane group was attached to diethyl 2,5-dihydroxyterephthalate by Williamson ether synthesis to give a good solubility in organic solvents to the final polymer. A hydrazine reaction followed by the 4-bromobenzoyl treatment gave a dihydrazide compound **4**. Compound **4** showed a limited solubility in organic solvents, so the reaction proceeded without further characterization. Compound **4** having a hydrazide group was converted to an oxadizole group through intramolecular ring closure reaction by refluxing **4** at phophorus oxychloride. We initially tried to make the conjugated polymer containing an oxadiazole unit by ring-closing reaction of the hydrazide group after the polymerization of the linear polymer. However, we failed to make the conjugated polymer having oxadiazole units due to the solubility problem and side reaction during the ring closure reaction in phosphorus oxychloride. We overcame these problems by conducting the ring closure reaction in the monomer state. **M1** and **M2** were obtained as a pale yellow powder at a yield of ca. 75%. **M1** and **M2** showed a good solubility in organic solvents such as chloroform and tetrahydrofuran (>15 mg/mL). We also prepared several other monomers having different length of alkyl chains (hexyl or octyl group) and polymerized them to make polyoxadiazole derivatives (data not included). However, we noticed that the polymers having short alkyl side chains showed limited solubility in organic solvents due to the strong backbone rigidity that is in good agreement with the results from Wu et al.[40] To prepare **M3**, ethyl oxamate was first reacted with oxalyl chloride to give ethyloxalyl isocyanate. The isocyanate group was blocked with the BOC group, and introduction of the bromopentyl group was achieved by the nucleophilic reaction with *tert*-butoxide. Finally, the removal of the ethyloxalyl group gave **M3** having a *t*-BOC-protected diamino group.
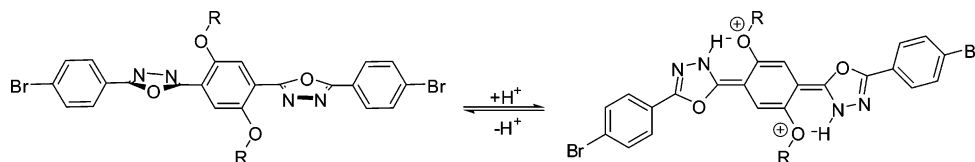
Photophysical properties of **M1** and **M2** were investigated by means of UV−vis and PL analysis. **M1** and **M2** showed similar physical and photophysical behaviors. In Figure 1a, the UV−vis spectrum of **M1** has two absorption maxima at 307 and 373 nm, and the emission maximum of the photoluminescence spectrum was observed at 413 nm in chloroform. The main-chain conjugation is responsible for the absorption peak at 373 nm, and the central *p*-dialkoxyphenyl ring creates another chromophore and produces the absorption peak at 307 nm.[36] The quantum yield of **M1 and M2** was 44% (e.g., at 313 nm) and 76% (e.g., at 370 nm) in chloroform, respectively. We investigated the stability of **M1** by analyzing the effect of acidic environment on the photophysical property of **M1**. The emission spectrum of **M1** gradually red-shifted without losing intensity as TFA was added into the **M1** solution in chloroform. We believe that the observed red shift is due to the acid-induced planarization of **M1** main chain, as illustrated in Figure 2.[36,41,42] The nitrogen atoms in the oxadiazole ring are prone to be protonated in the presence of TFA because the lone pair electrons in nitrogen are not participated in the aromatic sextet. There are several works which revealed the relationship the planar structure and fluorescence lifetime due to the keto−enol formation of heterocylic ring.[41−43] The lifetime of **M1** character-
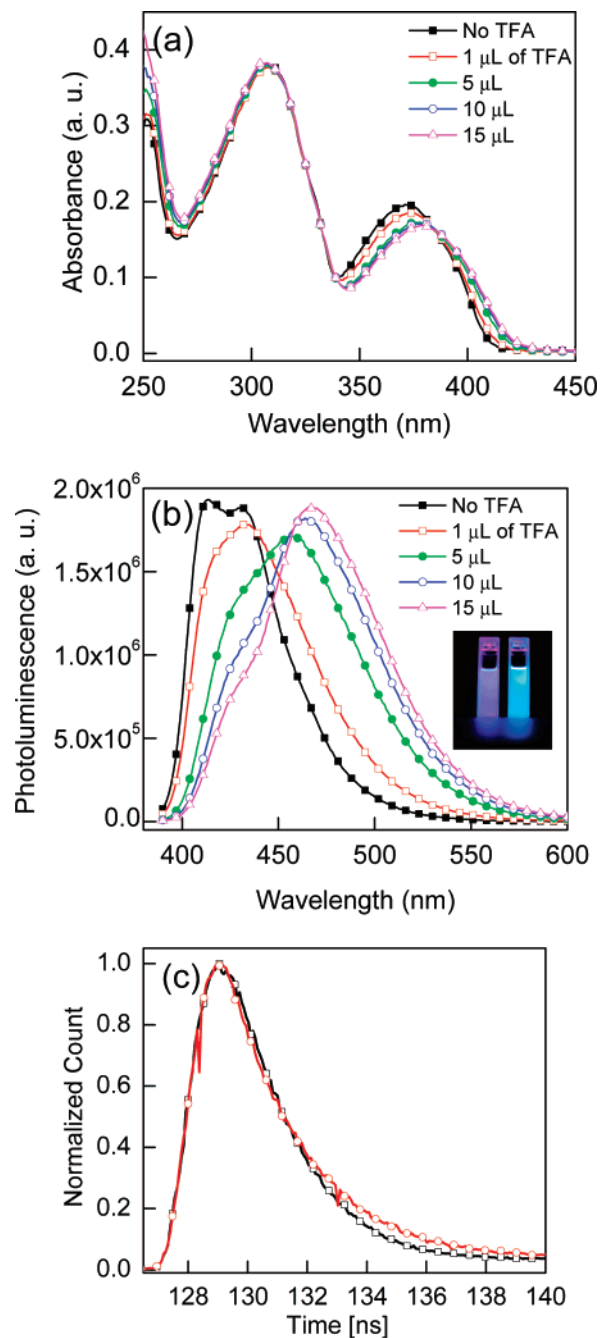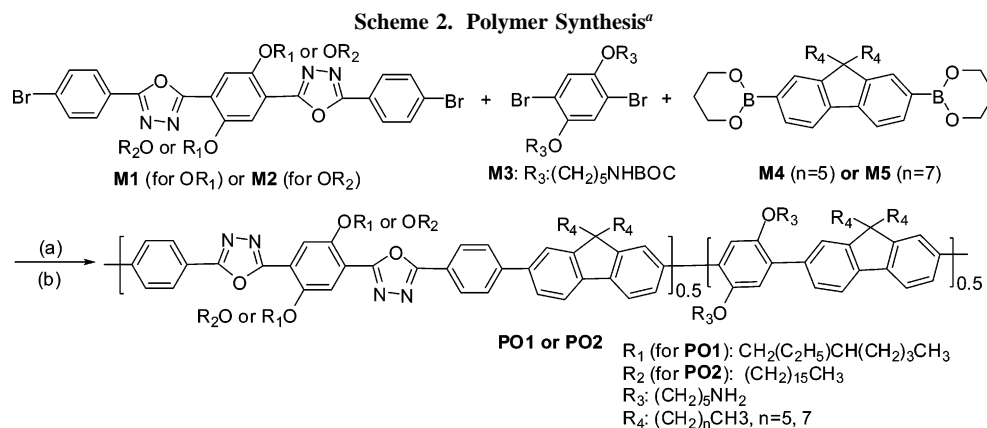

Figure 1. (a) UV−vis and (b) PL spectrum profiles of **M1** in chloroform upon TFA treatment. (c) Fluorescence lifetime results of **M1** (1 mg/L) characterized by time-resolved fluorescence spectroscopy before (□, emission at 413 nm) and after (○, emission at 468 nm) adding 10 μL of TFA in 3 mL of chloroform upon excitation at 386 nm. The protonation of the aromatic dioxadiazole unit induces the planarization of the structure by forming a stable six-membered ring structure and causes the blue to green fluorescence shift.

ized by time-resolved fluorescence spectroscopy increased from 2.1 and 2.4 ns after adding TFA, showing a good agreement with the reported results that a planar structure induces the longer fluorescence lifetime. Moreover, we did not observe the bathochromic shifts from the oxadiazole derivatives without alkoxy side chains which cannot form the proposed stable six-membered ring structure, supporting our hypothesis.
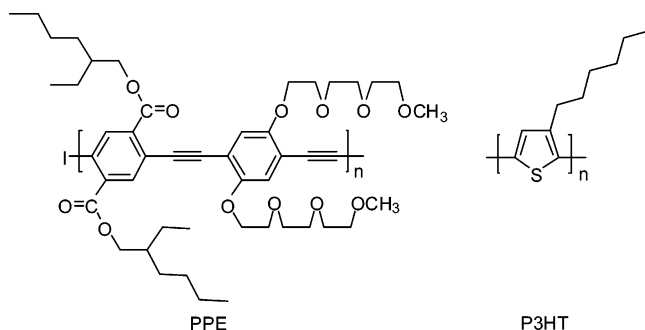
The polymers **PO1** and **PO2** were prepared via the Suzuki cross-coupling reaction of the oxadizole monomer **M1** (or **M2**), the diamine monomer **M3**, and a fluorene monomer having borolene unit **M4** (or **M5**), as shown in Scheme 2.[39,44] The

Figure 2. A proposed planarization mechanism induced by TFA.

Scheme 2. Polymer Synthesis[a]

M1 (for OR₁) or **M2** (for OR₂) + **M3**: R₃:(CH₂)₅NHBOC + **M4** (n=5) or **M5** (n=7)

PO1 or PO2 R₁ (for **PO1**): CH₂(C₂H₅)CH(CH₂)₃CH₃
R₂ (for **PO2**): (CH₂)₁₅CH₃
R₃: (CH₂)₅NH₂
R₄: (CH₂)ₙCH3, n=5, 7

[a] (a) THF, water, Pd(PPh₃)₄, K₂CO₃, 80 °C, 36 h; (b) 50% TFA in CHCl₃.

Figure 3. Chemical structure of poly(*p*-phenyleneethynylene)s (**PPE**) and polythiophene (**P3HT**).

photophysical and chemical properties of the resulting oxadiazole-containing conjugated polymers turned out to be independent of the length of the alkyl side chain on the fluorene unit and the oxadiazole unit. **PO1** showed better solubility in chloroform than **PO2**. Therefore, we will focus the discussion on **PO1**. Molecular weights of these copolymers were determined by gel permeation chromatography (GPC) using monodisperse polystyrenes as the standard. The number (M_n) and weight (M_w) average molecular weight of **PO1** before cleavage of *t*-BOC was 51 000 g/mol and 224 000 g/mol, respectively, and the polydispersity indices (PDI) was 4.4. **PO1** before deprotection of *t*-BOC had an off-white color and was soluble in organic solvents such as tetrahydrofuran (THF) and chloroform but almost insoluble in polar solvents like *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). After deprotection of *t*-BOC, **PO1** was still soluble in chloroform, but its solubility in THF was significantly decreased.

We compared the photopysical properties and particularly stability of **PO1** with a poly(*p*-phenyleneethynylene) (**PPE**) and poly(3-hexylthiophene) (**P3HT**), commonly used conjugated polymers (Figure 3). The **PPE** was synthesized by using the palladium-catalyzed Sonogashira–Hagihara reaction (detailed synthesis is in the Supporting Information), and the **P3HT** was prepared by the conventional procedure.[27,45] Both conjugated polymers were soluble in THF and chloroform.

The optical characteristics of the polymers were investigated by UV–vis and PL spectra in the solution and the film state.

Photophsical data of the conjugated polymers are summarized in Table 1. The polymers were spin-cast to form optical quality films from the chloroform (**PO1,** 1 mg/mL) or tetrahydrofuran (**PPE** or **P3HT**, 1 mg/mL) solution. As shown in Figure 4a, the absorption λ_{max} of **PO1** was observed at 385 nm both in chloroform and in the film while the emission λ_{max} was located at 413 nm in chloroform solution and 425 nm in the film. We also observed the broad tailing band from the solid film, which implies that **PO1** aggregated in the solid state likely due to $\pi-\pi$ backbone stacking. Figure 4b,c shows the absorption and emission spectra of **PPE** and **P3HT**. The absorption (emission) maximum of **PPE** and **P3HT** in THF was at 445 nm (486 nm) and 430 nm (567 nm), respectively. One can see the significant red shift from the solution to the film. The quantum yield in the solid state decreased accordingly.

We investigated the stability of **PO1** films in acidic condition and under strong UV illumination condition, respectively, and used **PPE** and **P3HT** as a control. First, the polymer films were placed in 1 M hydrochloric acid (HCl) solution at room temperature for 1 h. The UV–vis spectra of the polymers before and after the HCl treatment are shown in Figure 5a. **PO1** showed a slight decrease in absorption intensity while the absorption intensity of **PPE** and **P3HT** decreased significantly to 74% and 86% of the original value, respectively. Absorption λ_{max} of **PPE** and **P3HT** also blue-shifted from 482 to 464 nm for **PPE** and from 513 to 499 nm for **P3HT**, implying a backbone damage by the strong acid. Moreover, the fluorescence emission spectra in Figure 5b clearly demonstrate that the emissive property of **PO1** is intact during the HCl treatment but that of **PPE** and **P3HT** is severely damaged by the strong acid treatment: **PPE** showed 41% quenching and **P3HT** showed 74% quenching.

We also tested stability of each polymer in the presence of a strong acid and under UV irradiation condition. 1 wt % of triphenylsulfonium triflate, a photoacid generator (PAG), was added to each polymer solution in chloroform (**POx**) or tetrahydrofuran (**PPE** and **P3HT**). Thin layer films of the polymers were fabricated by spin-casting and subsequently exposed to 254 nm of strong UV irradiation (4 W) for 1 h to activate the PAG. The UV–vis spectra of each film before and the after the UV irradiation are shown in Figure 6a. The absorption intensity of **PO1** decreased 16%, while that of **P3HT**

Table 1. Photophysical Data of PO1, PPE, and P3HT Used in This Study

| polymer | E_g/eV^b | solution[a] | | film | | Φ (CHCl$_3$)[c] | Φ (film)[c] |
		$\lambda_{max,abs}/nm$ $\lambda_{max,em}/nm$	Stokes shift/ cm^{-1},	$\lambda_{max,abs}/nm$ $\lambda_{max,em}/nm$	Stokes shift/ cm^{-1}		
PO1	2.83	385 413	1760	385 425	2440	0.94	0.05
PPE	2.50	445 486	1900	482 546	2430	0.6	0.17
P3HT	2.25	430 567	5620	513 645	3990	0.12	0.00016

[a] UV−vis and PL data were measured in chloroform (1 mg/L) for **PO1** and tetrahydrofuran (1 mg/L) for **PPE** and **P3HT**. [b] The optical HOMO−LUMO energy gap is based on the low-energy onset in the solution-state UV−vis spectra. [c] Quantum yield is absolute quantum value measured by using an integrating sphere.
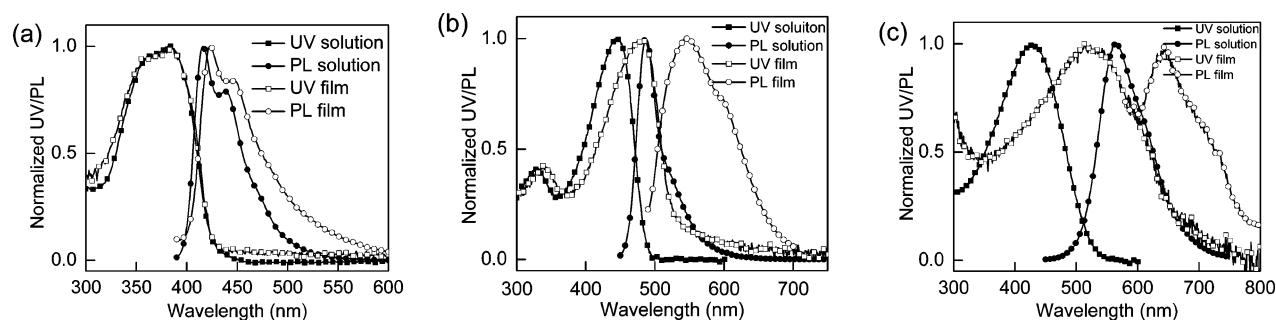

Figure 4. UV−vis (■, solution; □, film) and PL (●, solution; ○, film) spectra of (a) **PO1**, (b) **PPE**, and (c) **P3HT** in solution and in the film.
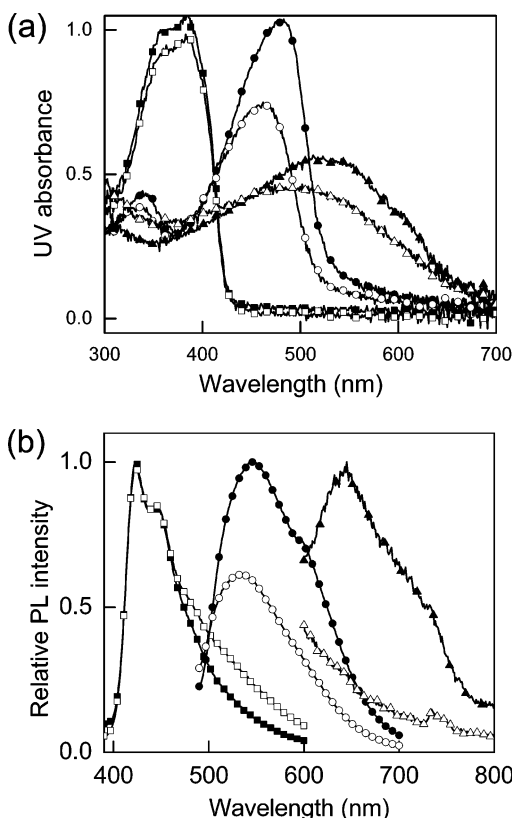

Figure 5. (a) UV−vis and (b) PL spectra of the polymer films before (■, **PO1**; ●, **PPE**; ▲, **P3HT**) and after (□, **PO1**; ○, **PPE**; △, **P3HT**) the HCl treatment. All polymer-coated slides were dipped in 1 M HCl solution at room temperature for 1 h.

decreased 27%. **P3HT** also showed a blue shift of its absorption λ_{max} from 510 to 490 nm likely due to the reduced conjugation length resulting from backbone damage. As for **PPE**, its main chain looked to be completely degraded by UV irradiation because the film essentially did not show any chromophore absorption. It is believed that the weak backbone triple bond was completely photobleached by UV irradiation. Furthermore,
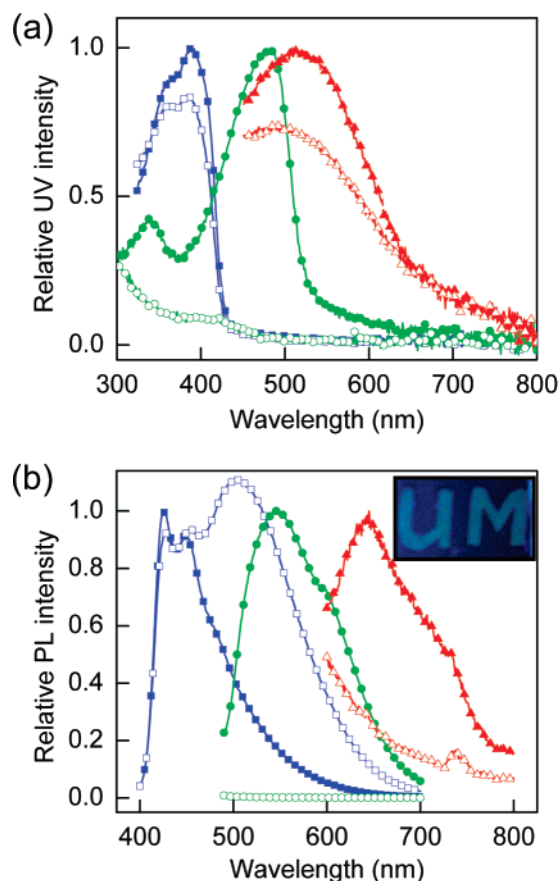

Figure 6. Change in (a) UV and (b) PL spectra before (■, **PO1**; ●, **PPE**; ▲, **P3HT**) and after (□, **PO1**; ○, **PPE**; △, **P3HT**) UV irradiation (254 nm, 6 W, 1 h) in the presence of photogenerated acid (PGA), UV irradiation condition: 254 nm, 6 W, 1 h. Inset: patterned images of **PO1** after 1 h UV exposure. The area of the character "UM" was exposed to 254 nm of UV light for 1 h.

the photoluminescence (PL) spectra in Figure 6b clearly show that the main-chain conjugation of **PPE** and **P3HT** is significantly damaged by UV irradiation and the acid. The fluorescence

emission of **PPE** was completely quenched, and that of **P3HT** was 77% quenched. However, interestingly after the UV irradiation the PL intensity of **PO1** at 425 nm remained constant, and surprisingly a new even stronger band emerged at 500 nm. We believe that the oxadiazole unit was protonated by the strong acid generated upon UV irradiation and the protonation-induced backbone planarization and produced the new emission band at 500 nm. The reason why we did not observe a strong new emissive band formation from the same **PO1** film upon HCl treatment is likely that aqueous HCl cannot penetrate into the **PO1** while PAG was evenly distributed in the **PO1** film. In fact, the PL spectrum of the **PO1** film after the HCl treatment shows only small shoulder formation above 480 nm (Figure 6b). Interestingly, we could pattern a fluorescent image on a spin-cast film of **PO1** by using a photomask (Figure 6b inset). The UV-exposed letter area shows green emission while the unexposed background emits blue fluorescence.

To confirm the stability of **PO1** and our acid-induced planarization hypothesis, we additionally investigated the absorption and emission properties of **PO1** in chloroform solution by using TFA. TFA was added and homogeneously mixed into the **PO1** solution. Figure 7 shows the UV−vis and PL spectra of the solution upon addition of TFA. From Figure 7a we can see slight red shift as TFA was gradually added. The solution color was changed from transparent to light yellow, an indication of aggregation/planarization.[46−50] Consistently, PL spectra also show a new band formation at 500 nm and significant fluorescence quenching by TFA. It is believed that the quinoid structure of **PO1** due to the protonation of oxadiazole unit induces backbone planarization (Figure 2). The protonation also charges **PO1** and decreases the solubility of **PO1** in chloroform. Therefore, the planarization and the decreased solubility of **PO1** cause polymer aggregation in the solution and resulting fluorescence quenching. However, in the film structure the mobility of the chain is suppressed by adjacent polymer chains, and therefore we did not observe fluorescence quenching but an emerging new strong band in Figure 6b. Another piece of evidence supporting our hypothesis is the reversibility test we conducted. We removed TFA from the **PO1** chloroform solution by vacuum, and the fluorescence emission of the solution was completely recovered. We repeated the addition and removal of TFA and observed completely reversible increase and decrease of the emission λ_{max} at 415 nm, as shown in Figure 7c.

The presented strong acid and UV irradiation studies evidently show that **PO1** is remarkably stable in harsh conditions such as under strong acidic and UV irradiation conditions. Particularly, because all the experiments were conducted in ambient condition, we can emphasize that **PO1** is not vulnerable to oxidation that is the common degradation mechanism of conjugated polymers. The unique stability of **PO1** made its application for our recent development of signal-amplifying DNA microarrys.[39]

Conclusion

We have synthesized conjugated polymers containing oxadiazole moiety and examined the stability of the polymers in harsh conditions like strong acid and prolonged UV exposure. The poly(oxadiazole) derivative, **PO1**, showed an exceptional stability in the harsh conditions, and its emissive property was intact while the two control polymers, **PPE** and **P3HT**, were significantly damaged and their emissive property was completely ruined. The oxadiazole unit of **PO1** is believed to be protonated in a strong acidic environment and induces backbone
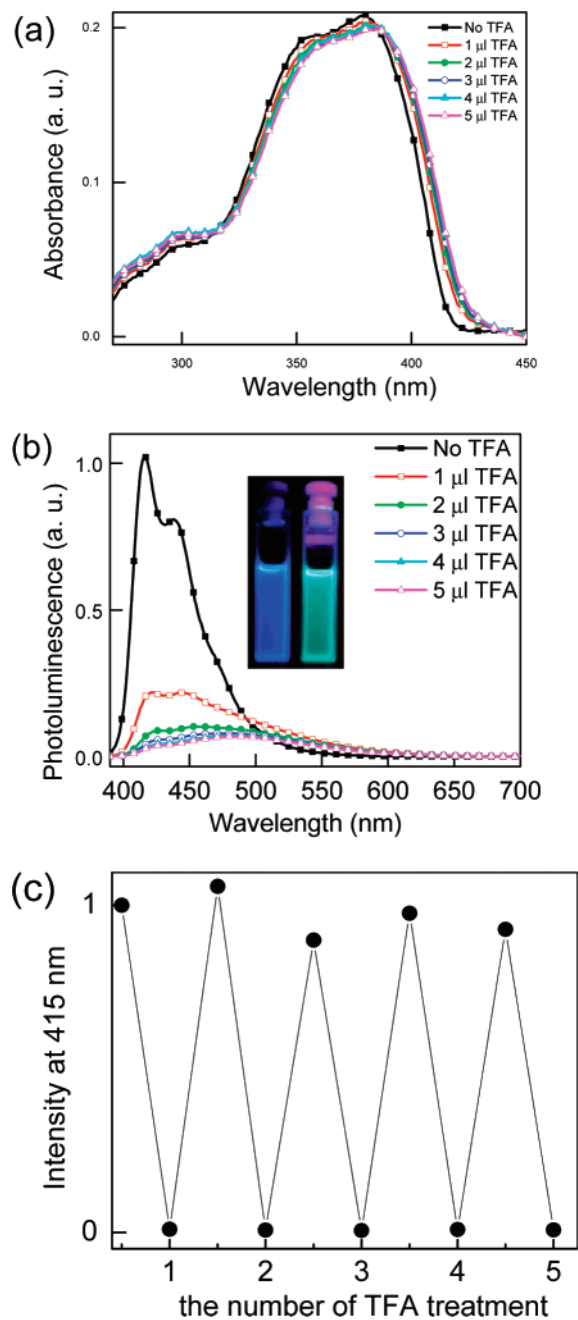
Figure 7. (a) UV−vis and (b) photoluminescence spectra of **PO1** solution in chloroform (1 mg/L) upon addition of TFA. (c) Reversible feature of the emission change of **PO1** in chloroform by adding and removing of TFA (TFA was added and removed by vacuum repeatedly).

planarization of **PO1**. Cycles of addition and removal of TFA in **PO1** solution produced completely reversible fluorescence emission change from blue to green due to the protonation and subsequent planarization of the conjugated polymer backbone, demonstrating the chemical stability of **PO1**. Latent fluorescence patterning on a **PO1** film was also demonstrated by using a photoacid generator and UV irradiation through a photomask. The outstanding chemical and photochemical stability of **PO1** can provide a molecular design principle to develop conjugated polymers having unique stability for various optoelectronic device applications and biosensor array development.[39]

Supporting Information Available: Details for the PPE synthesis and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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