

Conjugated Polymers That Respond to Oxidation with Increased Emission

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1. Introduction

1-1. Fluorescent Conjugated Polymers (Fluorescent CPs)

- Fluorescent CPs, such as PPV and PPE (Figure 1), have potentials for application of OLEDs, detections of the trace amount of the specific chemicals, such as TNT, *etc.*
- Most fluorescent CPs become less emissive under an aerobic atmosphere (Photobleaching), due to the oxidation of the multiple bonds, to form carbonyl groups *etc.*, of CPs. → Oxidative atmosphere disturbs the use of fluorescent CPs.

1-2. Authors' Previous Work

- (Purpose) Prevention of Photobleaching
- (Strategy)
 - Add antioxidants or triplet quenchers.¹
 - Increase IPs of polymers by introducing electron-withdrawing perfluoroalkyl groups.²
- Achieve higher durability.

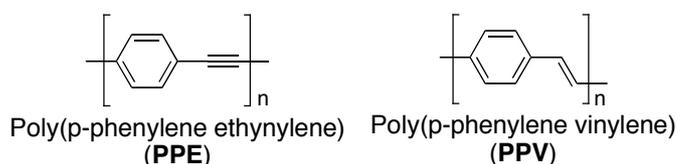


Figure 1. Examples of Fluorescent CPs

1-3. This Work

- (Purpose) Prepare polymers, whose emission increase after oxidation → Potentials for application to oxidation sensing materials
- (Previous Report) P-containing polymer (Figure 2) → almost same emission efficiency before/after oxidation³ → P was selectively oxidized in the presence of multiple bonds. → Prevent photobleaching
- (Authors' Strategy) Introduce sulfur-containing moieties to PPE polymer backbone
 - Sulfur atoms can be selectively oxidized in the presence of alkynes → Sulfur atoms can prevent the oxidation of main chain like phosphorous, and keep the fluorescent property.
 - Electron withdrawing nature of oxidized sulfur atoms (sulfoxide and sulfone moieties) is expected to cause changes of spectra and may increase the emission due to the donor-acceptor interactions?
 - In general, thioether, sulfoxide, and sulfone based CPs were less investigated than thiophene-based CPs.⁴
- Introduce thioether moiety to polymer backbone.

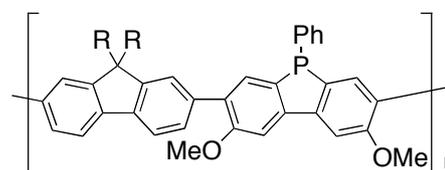
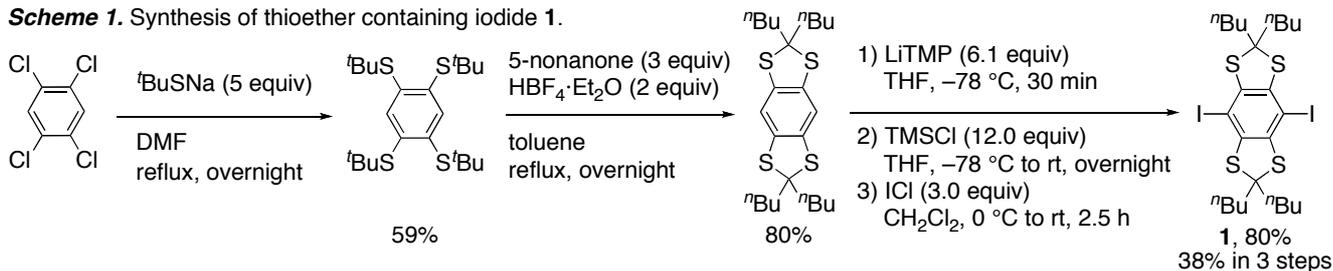


Figure 2. Reported phosphorous containing polymer

2. Results and Discussion

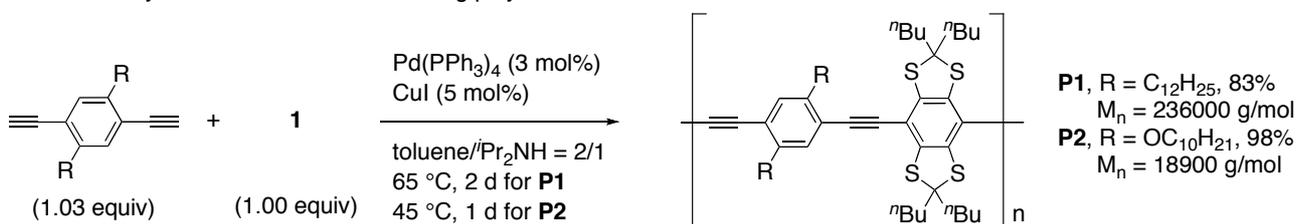
2-1. Synthesis

Scheme 1. Synthesis of thioether containing iodide **1**.



• Thioether containing iodide **1** was prepared from readily available 1,2,4,5-tetrachlorobenzene (Scheme 1).

Scheme 2. Synthesis of thioether containing polymer **P1** and **P2**.



• Two polymers were synthesized via Sonogashira cross-coupling from **1** and corresponding dialkynylbenzene (Scheme 2).

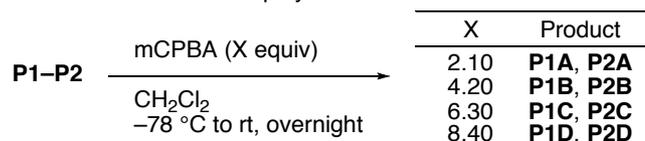
2-2. Oxidation of Polymers

• Oxidized polymers were prepared with various equivalents of mCPBA (Scheme 3).

• According to FT-IR analysis, polymers are first oxidized to sulfoxides (S=O) on four positions and then oxidized to sulfones (O=S=O).⁵

• **P2** is more easily to be oxidized to sulfones because of the existence of electron-donating groups.

Scheme 3. Oxidation of polymer **P1** and **P2**.



2-3. Properties of the Solutions of Polymer and Oxidized Polymer (Table 1)

• Both **P1** and **P2** solution in CH₂Cl₂ are relatively non-emissive ($\Phi_F < 0.01$). Once the polymers are oxidized, its quantum yields increase dramatically (**P1A** and **P2A**)

- **Reason 1.** Shorter fluorescence lifetime of **P1** and **P2**

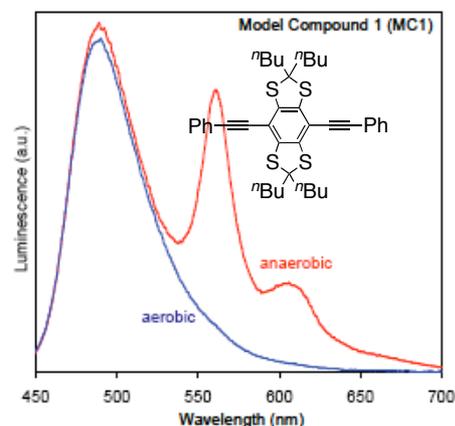
→ Thoroughly degassed solution of polymer model compounds show sharp emission peak in shorter-wavelength region, which is likely to be phosphorescence (Figure 3).

→ Thioether promotes intersystem crossing, and phosphorescence process disturbed fluorescence process.

Table 1. Photophysical Properties of Polymers

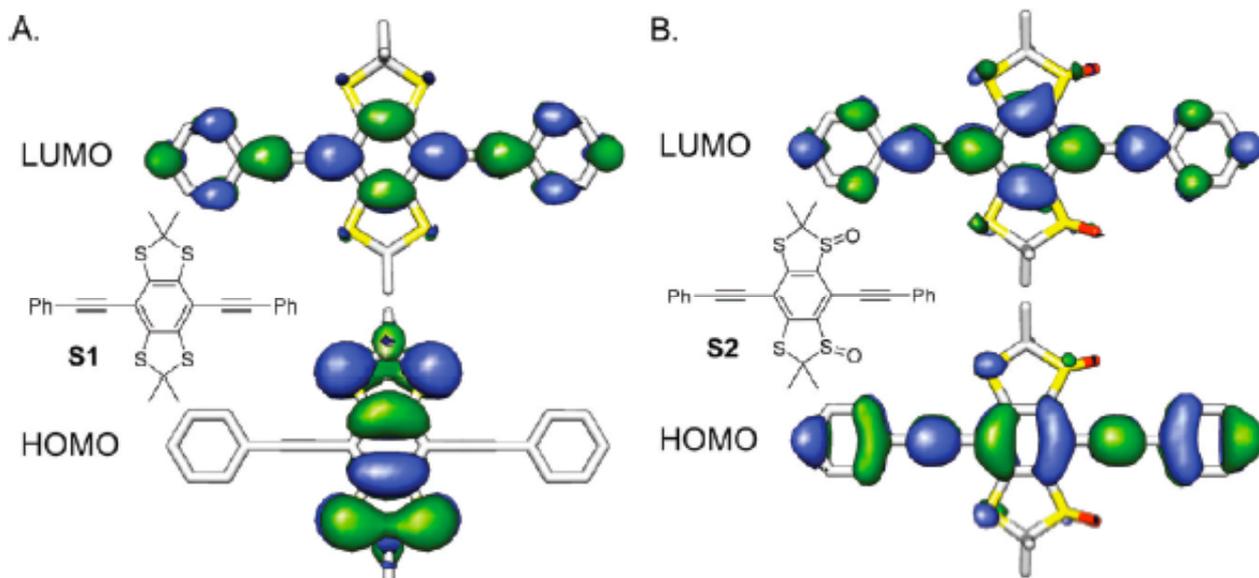
Polymer	$\Phi_F(\text{sol})^a$	$\Phi_F(\text{film})^b$	τ_F (ns)	k_F (ns ⁻¹)
P1	0.0096	<0.01	0.13	0.074
P1A	0.35	–	0.67	0.52
P1B	0.53	0.57	0.73	0.72
P1C	0.59	0.70	0.71	0.83
P1D	0.48	–	0.80	0.60
P2	0.0085	<0.01	0.17	0.050
P2A	0.49	0.56	1.35	0.36
P2B	0.28	<0.10	1.51	0.19
P2C	0.25	<0.10	1.66	0.15
P2D	0.19	<0.10	1.72	0.11

^a Quantum yield of polymer solutions in CH₂Cl₂. ^b Quantum yield of films of polymer. ^c Fluorescence lifetime. ^d Rate of fluorescence = ff/τf

**Figure 3.** Emission spectra of model compound of **P1**.

- **Reason 2.** Higher rate of fluorescence of **P1A** and **P2A**

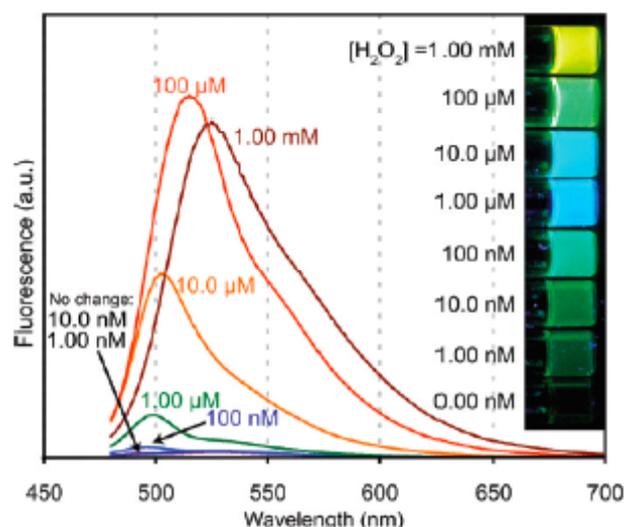
→ Better spatial overlap between HOMO and LUMO (Figure 4. B3LYP6-311+G*). Especially, in actual polymer cases, the overlap is expected to be greater due to the delocalization of frontier orbitals along to main chain.

**Figure 4.** Calculated HOMO and LUMO of model compounds of **P1** before (A) and after (B) oxidation.

- Further oxidation causes the decrease in quantum yield in both cases, especially in **P2** case. → The formation of sulfone moieties seems to disturb the fluorescence process.

- Oxidation causes the continuous spectral changes in emission (Figure 5).

- In the presence of methylrhenumtrioxide (MTO),⁶ **P2** solution showed the same response as the mCPBA oxidation cases, although the reaction rate was slower

**Figure 5.** Fluorescence response of **P2** to H₂O₂.

(Figure 5). → **P2** is said to be applicable for sensors for H_2O_2 , which plays important biological roles, such as disease markers and signaling molecules.

2-5. Properties of the Films of Polymer and Oxidized Polymer

- Thin films of each polymer were prepared by spin-casting a chloroform solution, and following annealing at $120\text{ }^\circ\text{C}$ for 10 min.
- Each film showed the similar behaviors to that of solutions (For Φ_F values, see Table 1). The films of moderately oxidized polymers showed the good emission. There were no signs of aggregation.
- The films of **P2** did not show any increase of emission when irradiated in air (Figure 6). → Oxidation did not proceed under air? Or the oxidation mediated by air is so minimal that any oxidized moieties are effectively quenched by the remaining unoxidized segments.
- Films of oxidized polymers of **P2** (**P2A–P2D**) retained more than 95% fluorescence than that of their original polymer (Figure 5). → These films are highly photostable.

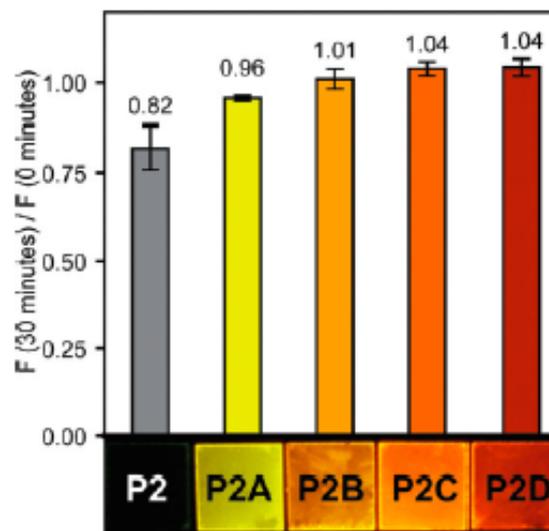


Figure 6. Photostability of **P2** and its oxidized films.

3. Conclusions

- Thioether containing polymers, which show large increase in Φ_F when oxidized, was synthesized. Films of oxidized polymers are highly resistant to photobleaching.
- The increase of Φ_F is due to both increase of τ_F due to the disappearance of phosphorescence involvement and the increase of k_F due to greater overlap of frontier orbitals.
- Polymer **P2** is sensitive to H_2O_2 oxidation. → Expected to be applicable for H_2O_2 sensor

4. References

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