

## Conjugated Polymers That Respond to Oxidation with Increased Emission

Dane, E. L.; King, S. B.; Swager, T. M.

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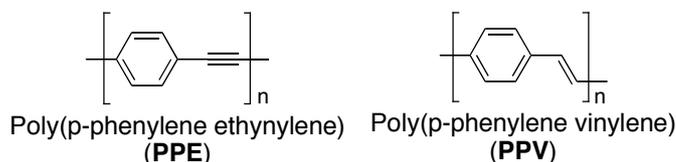
### 1. Introduction

#### 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

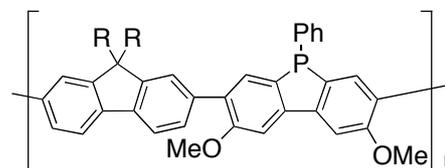
- (Purpose) Prevention of Photobleaching
  - (Strategy)
    - Add antioxidants or triplet quenchers.<sup>1</sup>
    - Increase IPs of polymers by introducing electron-withdrawing perfluoroalkyl groups.<sup>2</sup>
- Achieve higher durability.



**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 oxidation<sup>3</sup> → 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.<sup>4</sup>
- Introduce thioether moiety to polymer backbone.

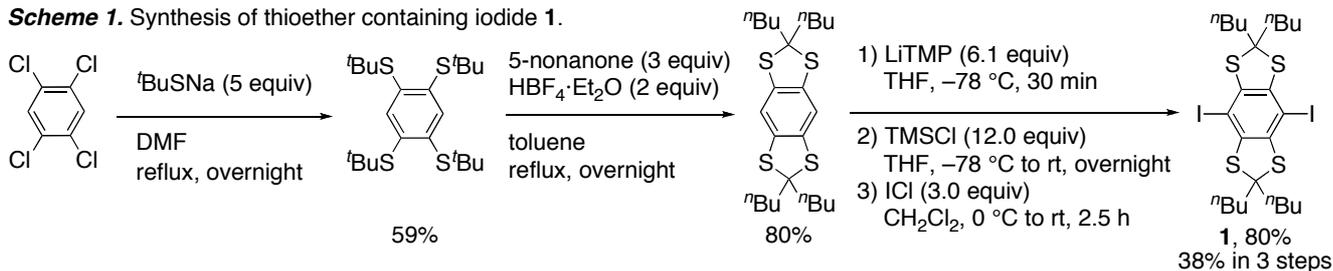


**Figure 2.** Reported phosphorous containing polymer

## 2. Results and Discussion

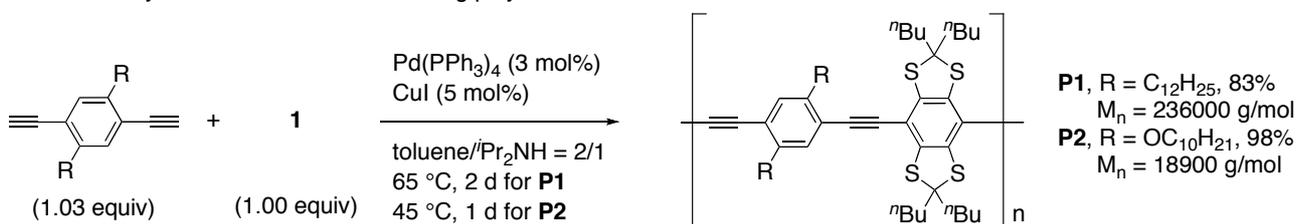
### 2-1. Synthesis

**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).

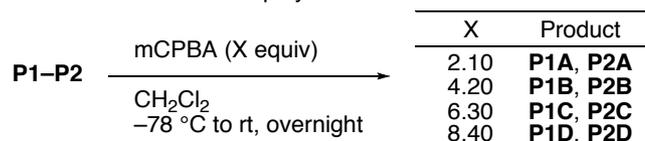
### 2-2. Oxidation of Polymers

• 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).<sup>5</sup>

• **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 CH<sub>2</sub>Cl<sub>2</sub> 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**

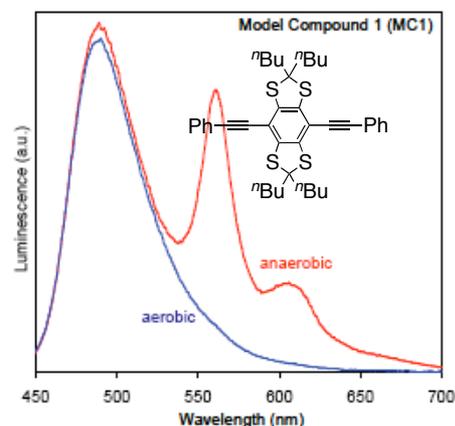
→ Thoroughly degassed solution of polymer model compounds show sharp emission peak in shorter-wavelength region, which is likely to be phosphorescence (Figure 3).

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

**Table 1.** Photophysical Properties of Polymers

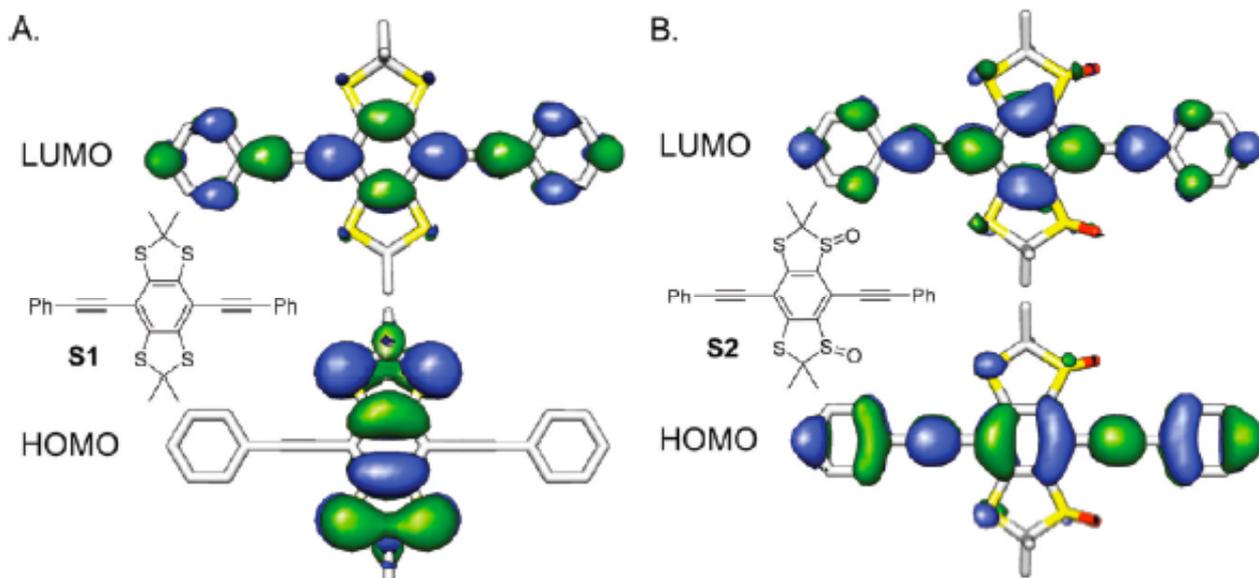
Polymer	$\Phi_F(\text{sol})^a$	$\Phi_F(\text{film})^b$	$\tau_F$ (ns)	$k_F$ ( $\text{ns}^{-1}$ )
<b>P1</b>	0.0096	<0.01	0.13	0.074
<b>P1A</b>	0.35	–	0.67	0.52
<b>P1B</b>	0.53	0.57	0.73	0.72
<b>P1C</b>	0.59	0.70	0.71	0.83
<b>P1D</b>	0.48	–	0.80	0.60
<b>P2</b>	0.0085	<0.01	0.17	0.050
<b>P2A</b>	0.49	0.56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

<sup>a</sup> Quantum yield of polymer solutions in  $\text{CH}_2\text{Cl}_2$ . <sup>b</sup> Quantum yield of films of polymer. <sup>c</sup> Fluorescence lifetime. <sup>d</sup> Rate of fluorescence =  $ff/ft$

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

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

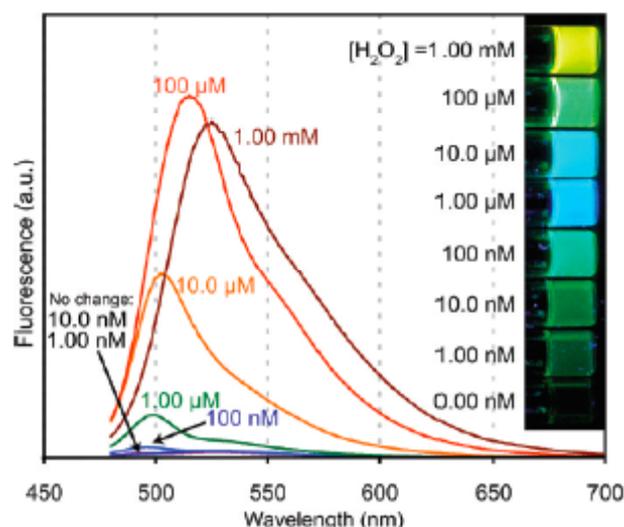
→ Better spatial overlap between HOMO and LUMO (Figure 4. B3LYP6-311+G\*). Especially, in actual polymer cases, the overlap is expected to be greater due to the delocalization of frontier orbitals along to main chain.

**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),<sup>6</sup> **P2** solution showed the same response as the mCPBA oxidation cases, although the reaction rate was slower

**Figure 5.** Fluorescence response of **P2** to  $\text{H}_2\text{O}_2$ .

(Figure 5). → **P2** is said to be applicable for sensors for  $\text{H}_2\text{O}_2$ , 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  $\Phi_F$  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.

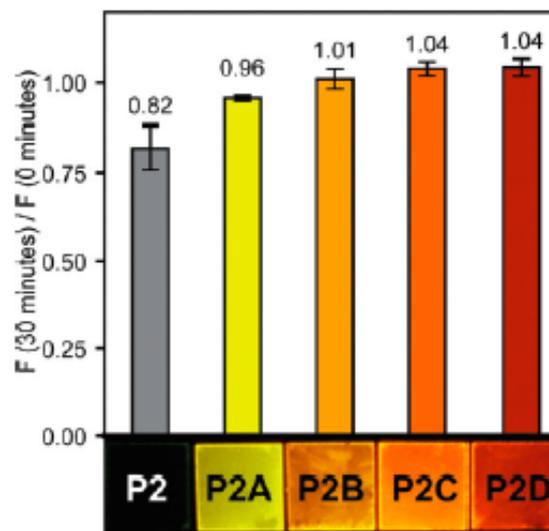


Figure 6. Photostability of **P2** and its oxidized films.

### 3. Conclusions

- Thioether containing polymers, which show large increase in  $\Phi_F$  when oxidized, was synthesized. Films of oxidized polymers are highly resistant to photobleaching.
- The increase of  $\Phi_F$  is due to both increase of  $\tau_F$  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  $\text{H}_2\text{O}_2$  oxidation. → Expected to be applicable for  $\text{H}_2\text{O}_2$  sensor

### 4. References

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