



## Conjugated polymers containing 2-thiohydantoin: Detection of cuprous ion, hydrogen peroxide and glucose



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### ABSTRACT

A novel poly(phenyleneethynylene) bearing 2-thiohydantoin moieties [poly(**1**)] is synthesized. Cuprous ions quench the fluorescence of the polymer, whereas the addition of cupric ions results in only little change on the fluorescence. Compared with the small molecule counterpart, the Stern–Volmer quenching constant of poly(**1**) caused by  $\text{Cu}^+$  is 94 times greater. When hydrogen peroxide is introduced into the solution containing poly(**1**) and  $\text{Cu}^+$ ,  $\text{Cu}^+$  is oxidized into  $\text{Cu}^{2+}$ , leading to the recovery of the fluorescence. The fluorescence of the poly(**1**)/ $\text{Cu}^+$  solution could also be recovered by the  $\text{H}_2\text{O}_2$  released from glucose oxidation by glucose oxidase (GOD), which means that probe(**1**)/ $\text{Cu}^+$  platform can be used to detect glucose.

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### 1. Introduction

Application of conjugated polymers to detect chemical and biological compounds has attracted considerable attention [1–5]. Compared with small molecule counterparts, the unique  $\pi$ – $\pi^*$  conjugated electronic structure of conjugated polymers provides rapid transfer of excitation along the whole main chain to energy/electron receptors, resulting in the amplified optical response [6–8]. Thus, in the last decade, fluorescent sensors based on conjugated polymers have been developed for various targets including metal ions [9–15], explosives [16–19], saccharides [20–23], proteins [24–28], enzymes [24,29,26,30,31], DNA [32–36] and RNA [37,38]. Based on the conjugated polymer/metal ion system, a novel fluorescent assay was developed to detect the biological analytes. Schanze reported a fluorescent turn-on assay containing carboxylate-substituted poly(phenylene ethynylene) (PPECO2) and cupric ion ( $\text{Cu}^{2+}$ ) to detect phosphatase and alkaline

phosphatase [39]. Jin developed a sensitive assay for detecting hydrogen peroxide and glucose based on the conjugated polymer/ $\text{Fe}^{2+}$  system [40]. We also synthesized poly(phenylene ethynylene) bearing thiourea groups and developed a fluorescent turn-on assay based on thiourea containing poly(phenylene ethynylene) and silver ion to detect ADP [41].

There has been considerable interest in 2-thiohydantoins due to their potential use for medical purposes as anti-convulsant, antimutagenic, anticarcinogenic, antiandrogen and antiviral agents [42–47]. Due to the presence of hydrogen bonding donors and acceptors in the 2-thiohydantoin rings, N–H–O intermolecular hydrogen bonding can be formed, which means that 2-thiohydantoin can act as an anion receptor to detect anions [48–52]. Meanwhile, 2-thiohydantoins also can coordinate the metal ions via nitrogen and/or sulfur donor atom [53].

In the current article, we prepared a new poly(phenylene ethynylene) containing 2-thiohydantoin groups via reaction of diiodo-benzene derivative **1** with *para*-diethynylbenzene. The corresponding small molecule counterpart

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**2** containing 2-thiohydantoin groups (Scheme 1) was synthesized. The interactions between poly(**1**) and metal ions have been investigated. It is very interesting to find that  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  show opposite effects on the fluorescence of poly(**1**).  $\text{Cu}^+$  could effectively quench the fluorescence of poly(**1**), while  $\text{Cu}^{2+}$  at the same concentration caused nearly no change. It is definitely an attractive phenomenon which might be able to be utilized as a potential signal transducer in sensors. Now, we report a fluorescence assay based on the combination of the redox of  $\text{Cu}^{2+}/\text{Cu}^+$  and the subsequent fluorescence recovery of poly(**1**) to detect both oxidant and reductant, as well as their related substrates.

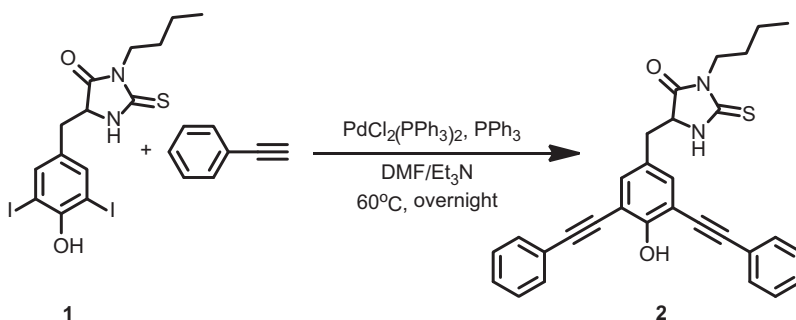
## 2. Experimental section

### 2.1. Measurements

$^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  (100 MHz) NMR spectra were recorded on a Bruker Avance/DMX 400 MHz NMR spectrometer in  $\text{DMSO}-d_6$  and  $\text{CDCl}_3$ , with tetramethylsilane as an internal reference. IR spectra were measured using a Shimadzu FTIR-8100 spectrophotometer. UV–vis spectra were recorded in a quartz cuvettes (thickness: 1.0 cm) at room temperature using a Shimadzu UV-2450 spectrophotometer (Solvent: DMSO, containing 10% water). Fluorescence spectra were obtained using a Hitachi F-4500 spectrofluorometer with a xenon lamp and 1.0 cm quartz cells (Solvent: DMSO, containing 10% water). Melting points (mp) were measured on a digital melting point apparatus (WRS-1B). Elemental analysis were performed on an Eager 300 elemental microanalyzer. The number- and weight-average molecular weights ( $M_n$  and  $M_w$ , respectively) of the polymer were determined using gel permeation chromatography (GPC) on a Jasco Gulliver system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns K804, K805, and J806) and calibrated by polystyrene standards at 30 °C using tetrahydrofuran (THF) as the eluent.

### 2.2. Material

For use as polymerization solvents, N,N-dimethylmethanamide (DMF) and  $\text{Et}_3\text{N}$  were distilled over  $\text{CaH}_2$ . All other reagents were commercially obtained and used as received. **1** was synthesized according to Ref. [54].



Scheme 1. Synthesis of **2**.

### 2.3. Synthesis of **2**

A solution of **1** (2.64 g, 5 mmol) and ethynylbenzene (1.02 g, 10 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (350 mg, 0.5 mmol),  $\text{PPh}_3$  (262 mg, 1 mmol), and  $\text{Et}_3\text{N}$  (10 mL) in DMF (50 mL) was stirred at 60 °C overnight. The filtrate was concentrated by a rotary evaporator and the residue was extracted with 200 mL of  $\text{CH}_2\text{Cl}_2$ . The organic phase was washed with 1 M HCl, saturated aq.  $\text{NaHCO}_3$  and brine. The organic layer was dried over anhydrous  $\text{MgSO}_4$  and evaporated to dryness. The crude product was purified by a silica gel column using hexane/ethyl acetate mixture (4:1 by volume) as eluent. Pale yellow solid was obtained in 83% yield (1.98 g).

Mp 165.3–165.7 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.76(s, 3H;  $\text{CH}_3$ ), 0.89–1.25(m, 2H;  $\text{CH}_2$ ), 1.38(d,  $J = 6.4$  Hz; 2H;  $\text{CH}_2$ ), 2.52–3.36(m, 2H;  $\text{CH}_2$ ), 3.61(s, 2H;  $\text{CH}_2$ ), 4.24(s, H; CH), 6.87(d,  $J = 17.8$  Hz; 1H; NH), 6.97–8.44(m, 12H, Ar H), 9.64(s, 1H; OH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 13.70, 19.98, 29.83, 37.36, 41.22, 60.79, 83.76(C=C), 94.74(C=C), 108.01(Ar), 122.05(Ar), 125.30(Ar), 125.93(Ar), 128.59(Ar), 130.24(Ar), 131.97(Ar), 157.08(Ar), 173.27(C=O), 183.86(C=S); IR (KBr): 3177(m), 2929(m), 2861(m), 2152(w;  $\nu(\text{C}\equiv\text{C})$ ), 1743(s), 1518(m), 1431(w), 1356(w), 1272(w), 1130(w), 915(w), 748(m); Anal. Calcd for  $\text{C}_{30}\text{H}_{26}\text{N}_2\text{O}_2\text{S}$ : C 75.29, H 5.48, N 5.85; found: C 75.12, H 5.27, N 5.94.

### 2.4. Polymerization

A solution of **1** (530 mg, 1.00 mmol) and *para*-diethynylbenzene (126 mg, 1.00 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (35 mg, 50  $\mu\text{mol}$ ),  $\text{PPh}_3$  (26.2 mg, 100  $\mu\text{mol}$ ), and  $\text{Et}_3\text{N}$  (2.00 mL, 14.3 mmol) in DMF (3.00 mL) was stirred at 60 °C overnight. The resulting mixture was poured into MeOH/acetone [4/1 (v/v), 300 mL] to precipitate the polymer. It was separated by filtration using a membrane filter (ADVANTEC H100A047A) and dried under reduced pressure.

### 2.5. Spectroscopic data for the polymer

Poly(**1**): GPC (THF, polystyrene standards):  $M_w = 37291$ ,  $M_n = 15,735$ , PDI = 2.37;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ ): 0.62(s, 3H;  $\text{CH}_3$ ), 0.86(s, 2H;  $\text{CH}_2$ ), 1.25(dd,  $J = 86.1, 113.7$  Hz; 2H;  $\text{CH}_2$ ), 3.26(d,  $J = 65.9$  Hz, 2H;  $\text{CH}_2$ ), 3.46(s, 2H;  $\text{CH}_2$ ), 4.66(s, H; CH), 7.08–8.26(m, 6H, Ar H), 8.99(s, 1H; NH),

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