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Pendant structure governed the selectivity of Pd^{2+} using disubstituted polyacetylenes with sulfur functions and the application of thiophanate-methyl detection

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ABSTRACT

A series of disubstituted polyacetylenes-based fluorescent chemosensors for Pd^{2+} has been designed and synthesized. The optimization of sensing performance for Pd^{2+} ions is realized through modulating the coordination mode, type and number of coordination atoms in pendant groups. The receptor groups containing both N and S atoms (Poly [1-phenyl-2-[3-(2-pyridylmercapto)propyl]acetylene] (**P2**) and Poly [1-phenyl-2-[3-(5-methyl-1,3,4-thiadiazole-2-mercapto)propyl]acetylene] (**P4**)) can respond simultaneously for Pd^{2+} and $Pt^{4+/2+}$ ions, and the only introduction of sulfur as the ligand atoms (Poly [1-phenyl-2-[3-(*p*-methylphenylthio)propyl]acetylene] (**P1**) and Poly [1-phenyl-2-[3-(2-Thienylthio)propyl]acetylene] (**P3**)) can exhibit high selectivity for Pd^{2+}. **P3** containing double sulfur atoms in pendants exhibits more high selectivity and sensitivity toward Pd^{2+} than that of **P1** containing single sulfur atom. Aforementioned results were illustrated by fluorescence titration, Ksv fitting and cyclic voltammetry (CV) analysis. The emission of **P3**–Pd^{2+} complex can be turned on by the addition of thiophanate-methyl (TM) without the interference from other anions and pesticides. Thus, **P3**–Pd^{2+} complex can work as the novel Pd^{2+}–mediated conjugated polymer-based fluorescent (CPF) chemosensors platform for thiophanate-methyl detection. The “on-off-on” sensing mechanism was supported by MALDI-TOF mass analysis, density functional theory (DFT) calculations and the association constants *Ka* fitting.

1. Introduction

The study of the fluorescent/colorimetric chemosensors for the detection of precious metal ions (including gold, silver, ruthenium, rhodium, osmium, iridium, platinum and palladium ions) has attracted significant attention because of their widely industrial applications, as well as the adverse effects to the environment and in biological systems. To date, some kinds of chemosensors were used to detect these precious metal ions in solid and solution, such as small molecule chemosensors [1–3], chemosensors based on quantum dots or nanoparticles [4–6], macromolecular sensing systems [7], polymer-based sensing systems [8], and chemosenors based on mesoporous materials [9], etc.

Among these precious metal ions, Palladium (Pd), as an important metal of platinum group elements, has been widely used in the applications such as medical instruments, dental crowns, jewellery, automobile catalytic converters and fuel cells, due to its inertness biocompatibility and versatility as a catalyst [10–12]. To achieve a rapid analytical method for Pd^{2+} residues at trace levels, a series of small molecule colorimetric/fluorescent chemosensors for Pd^{2+} based on the formation of Pd^{2+}–complex [13–17] or Pd–catalyzed [18–34] reaction were developed in recent years.

However, compared with the systematic study of small molecule chemosensors for Pd^{2+} detection, the reports regarding to conjugated polymer-based fluorescent (CPF) chemosensors for the detection of trace Pd^{2+} are very limited [35–40], and selective sensing of Pd^{2+} has remained unsatisfactory. Bai group [35–37] synthesized 2,6-bis(2-Thienyl)pyridine –containing and 2,6-dithienyl-4-phenylpyridine-containing fluorescent polymers (**P-1** and **P-A**) for Pd^{2+} detection. However, the selectivity of **P-1** and

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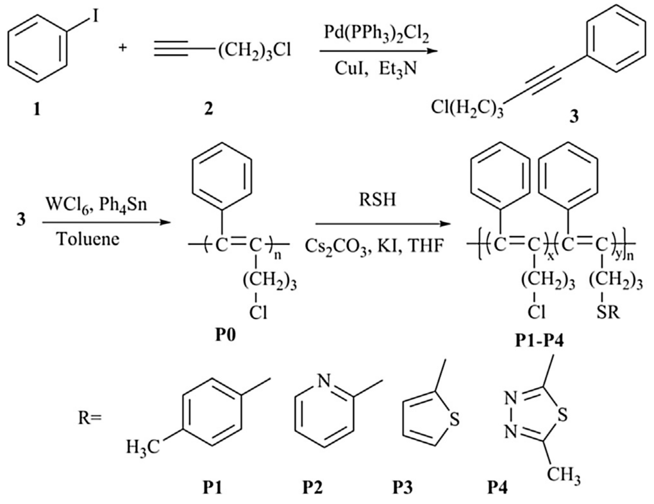

Scheme 1. Synthetic routes of **P0**, **P1**, **P2**, **P3** and **P4**.

P-A was suffered from the interference of Pt^{4+}. Wang [40] designed a poly(*p*-phenylene ethynylene) derivative with monopyridyl moiety to form Pd^{2+}-pyridyl coordination, resulting in significant fluorescence quenching for Pd^{2+}. However, Pt^{4+} induced a similar fluorescence quenching of polymer.

Generally speaking, the high selectivity requirements of the conjugated polymer are usually associated with properties such as special binding or spatial matching [8]. Study finds that most of reported CPF chemosensors for Pd^{2+} detection without satisfactorily selectivity have two reasons: (1) the rigid receptor in conjugated backbone induces the limited spatial matching; (2) systematic modification of by different receptor groups is not easy, due to the complicated synthesis route. To resolve the requirements of high selectivity for Pd^{2+} detection, an ideal goal is to develop a generic and convenient approach for linking a flexible part of binding domain as a receptor and a conjugated part of the signalling domain together in the structures of polymers to be used in chemical sensing.

As a kind of well-known conjugated polymers, disubstituted polyacetylene (PA) with the pendant group prepared by the post-functionalization approach may be a competitive candidate [41,42]. Tang and Li developed a series of disubstituted PA–based fluorescent chemosensors with pendant groups, which were designed as different fluorescent sensing receptor units, and the detection of metal ions (Cu^{2+}, Hg^{2+}) [43,44] and anions (CN^-, S^{2-}) [45,46] as well as neutral species (α-amino acids) [47] was realized. Hence, by modulating the structure of pendant group to develop a PA-based fluorescent chemosensor for selective detection of Pd^{2+} over $Pt^{4+/2+}$ would be advantageous.

Encouraged by this strategy, along with the relative work of functionalized PAs in our group [48,49], we designed and synthesized four novel PAs with strong photoluminescence (**P1**–**P4**, Scheme 1). Through the nucleophilic substitution reaction of **P0**, the sulfur-containing functional groups were introduced as pendants to the PA backbones to obtain **P1**–**P4**. Sulfur-containing moieties were often used for binding transition metal cations such as Pd^{2+}, due that a sulfur atom is considered as a “soft” donor atom and has the strong affinity and high selectivity for “soft” Pd^{2+}. We focused on governing the structures of sulfur functions in PAs, including adjusting the coordination mode, type and number of coordination atoms in pendant groups, to effect on their recognition abilities for Pd^{2+}. It’s desirable to gain the novel disubstituted PA-based fluorescent chemosensors for Pd^{2+} detection with the high sensitivity and selectivity, and to eliminate the interference of other commonly coexistent metal species (including $Pt^{4+/2+}$).

On the other hand, our group newly developed two disubstituted PA-based fluorescent chemosensors (TZP and PBP) with *N*-heterocycles as the side groups [50], both of whose emissions were turned off by Cu^{2+}. Subsequently, the quenched **TZP**/Cu^{2+} and **PBP**/Cu^{2+} complexes were utilized as a new sensing platform and exhibited the distinct “turn on” sensing signals for monitoring glyphosate (Glyp, an organophosphorus herbicide widely used in agriculture). The sensing mechanism is that Glyp exhibited the higher affinity to Cu^{2+} than that of TZP/PBP to Cu^{2+}, and the fluorescence of PA/Cu^{2+} complexes was recovered with addition of Glyp. Considering the similarity between the PA/Pd^{2+} complexes in this work and the reported PA/Cu^{2+} ones, we speculated that our polyacetylene containing Pd^{2+} complexes might have the capability for pesticides determination. After the initial selectivity experiment by testing several common pesticides listing in chart S1, results showed the quenched luminescence of PA/Pd^{2+} complexes could be turned on by thiophanate-methyl (TM) only.

Thiophanate methyl (dimethyl 4,4′-(*o*-phenylene)bis(3-thioallophanate)) is one member of extensively used pesticides in agriculture to control important fungal diseases of crops, vegetables and fruits, etc. But, the residues of TM may cause the potential hazards to environment and human health [51–55]. Therefore, it’s an urgent need to develop a sensitive and selective sensing platform for the determination of TM. To date, several conventional detection techniques were employed for TM analysis, including gas chromatography-mass spectrometry (GC–MS) [56], high-performance liquid chromatography-ultraviolet (HPLC-UV) [57], high-performance liquid chromatography–mass spectrometry/mass spectrometry (HPLC–MS/MS) [58], high-performance liquid chromatography-diode array detection (HPLC-DAD) [59], along with some new analytical methods of TM, such as a liquid chromatography method with post-column photoinduced chemiluminescence (PICL) detection and surface-enhanced Raman scattering (SERS) imaging coupling with multivariate analysis [60,61]. Nevertheless, such used methods need the expensive instrumentation, long analysis time and trained personnel. Correspondingly, luminescence spectroscopy is more suitable for in situ and real-time detection of TM. Due to the slight fluorescent intensity of TM itself (Fig. S1), the sulfur-containing PAs as the novel Pd^{2+}-mediated sensing platform for thiophanate-methyl is a better choice.

In this paper, the “off-on” sequential sensing response for Pd^{2+} and TM was achieved by using the disubstituted PAs with sulfur functions as the sensing platform. We not only provided some useful ideas for designing the polyacetylenes as the highly selective CPF chemosensors for Pd^{2+}, but also supplied a simple and effective method for thiophanate-methyl detection utilizing PA–Pd^{2+} complex as the novel CPF sensing platform for pesticides.

2. Experimental section

2.1. Materials and measurements

The polymerization reaction that required oxygen-free conditions was conducted under an atmosphere of dry nitrogen using standard Schlenk techniques. Toluene and tetrahydrofuran (THF) were dried and distilled over Na under an atmosphere of dry nitrogen. All other reagents were of analytical reagent grade and used without further refinement. Distilled water was used for all experiments. Solutions of metal ions came from Na_2PdCl_4, $NiSO_4{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $MgCl_2{\cdot}6H_2O$, $HgCl_2$, $Fe(NO_3)_3{\cdot}9H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, $ZnCl_2$, $PtCl_2$, $Ce_2(CO_3)_3$, $Na_2PtCl_6{\cdot}6H_2O$, $AgNO_3$, $CuSO_4{\cdot}5H_2O$. Solutions of anions came from $NaNO_3$, Na_2SO_4, $CH_3COONa{\cdot}3H_2O$, K_2HPO_4, Na_2S, $Na_2S_2O_3$, NaHS. Glyphosate (Gly), Chlorpropham (Chl), Prometryn (Pro), Tetramethylthiuram