Sensors

Design of a Modular-Based Fluorescent Conjugated Polymer for Selective Sensing**

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We have designed and synthesized a new modular-based fluorescent polymer **1** with a binding domain and a signaling domain. They are coupled together through an electron-conducting backbone for highly selective sensing of the Pd^{II}

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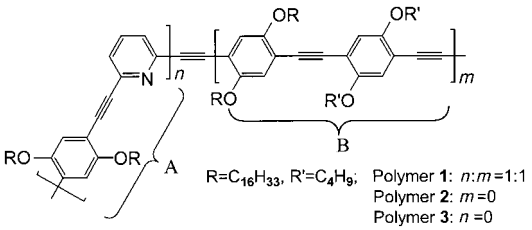
ion. The *meta*-substituted monopyridyl improves the spatial matching for selective binding, whereas the poly(*p*-phenylene ethynylene) derivative provides the additional amplification for sensing. With the increase in the number of applications for optical sensors, the design and synthesis of new sensing materials with high sensitivity and selectivity is a critical challenge.[1,2] Recently, "molecular-wire effects" of conjugated polymers have shown great potential in signaling molecular-recognition processes,[2,3] thus making them ideal for the development of highly sensitive sensing materials used to monitor ions, organic molecules, and even biomolecules.[2–6] Among the fluorescent conjugated polymers reported to date, there is a diversity of properties such as conductivity, charge transfer, redox, and energy transfer. This diversity has been accomplished by tuning the conjugated polymers,[5–7] however, selective sensing of ions by electrostatic action or ligand coordination has remained unsatisfactory.[4a–b,5,6] The challenging selection requirements of the conjugated polymer are usually associated with properties such as special binding or spatial matching. For spatial-matching interactions, a flexible backbone and conformational freedom are indispensable to build a binding pocket and to offer a high affinity for analyte, which is common in biological macromolecules. However, for a conjugated polymer a rigid structure is preferable for efficient electron transfer. To resolve the conflicting architectural requirements, an important goal that has not yet been achieved satisfactorily is to develop a generic approach for linking a flexible part of binding domain and a rigid part of the signaling domain together in a range of polymers to be used in chemical sensing. By this modular-based design, many specific-binding domains with less or even no optical expression and those signaling domains that have excellent energy-transfer properties but without selective-binding properties can all be sufficiently used to avoid their specific flaws in each case. Herein we report a new modular-based conjugated polymer for detecting Pd^{II} ions, the design of which exploits molecular architecture, the intrinsic nature of the domains, and the properties of functional groups to yield a molecule capable of selective and sensitive sensing.

In this research, we designed and synthesized a new fluorescent polymer **1** (Scheme 1) comprising two separate functional parts (**A** and **B**), one part to introduce specific binding and the other to signal the response. Part **B**, a poly(*p*-phenylene ethynylene) derivative, was chosen as the signaling domain for its excellent photophysical and conductive properties.[2,3] Its rigid structure is also capable of reducing intramolecular association. Part **A** was chosen as the binding domain because the monopyridyl group has a great affinity for the Pd^{II} ion and should selectively bind by self-assembly.[8]



Scheme 1. The structures of polymers **1**–**3**.

The *meta* linkage of the monopyridyl can regulate the flexibility of the backbone and may provide potential spatial matching for interpolymer binding by using an ion as the linker. The synthetic method to produce **1** (Ex/Em = 415 nm/475 nm, $\Phi = 0.34$, $M = 3.6 \times 10^4$, where Ex is the excitation wavelength, Em is the emission wavelength, Φ is the quantum yield and M is the average weight) involves the Sonogashira coupling. To ensure the desirable flexibility of the backbone, the reactants and their ratio were carefully considered. H NMR spectra of **1** confirm that monopyridyl groups have been separately incorporated into the polymer.[9] To address the role of the different modular domains played in the selective metal binding, **2** (Ex/Em = 380 nm/425 nm, $\Phi = 0.12$, $M = 4.3 \times 10^3$) and **3** (Ex/Em = 453 nm/475 nm, $\Phi = 0.42$, $M = 5.7 \times 10^4$) were also prepared by a similar procedure. According to the experimental results, **1** with an appropriate modular-based polymer can truly form an interchain interaction through palladium–pyridyl coordination that results in dramatic fluorescence quenching and provides an excellent selectivity for Pd^{II} over other heavy and transition-metal ions.

The Pd^{II}-ion-responsive properties of polymers and the monomeric model 2,6-di(phenylethynyl)-pyridine (Dpp) were monitored in THF by using fluorescence emission spectroscopy. In the case of **1**, the Stern–Volmer data (Stern–Volmer quenching constant $K_{sv} = 4.34 \times 10^5\ L\,mol^{-1}$) reveals that the best amplification quenching by Pd^{II}, which is ≈ 56 times greater than that of the Dpp ($K_{sv} = 7.72 \times 10^3\ L\,mol^{-1}$ not shown). This result indicates that the specially designed molecular wire (i.e., the conjugated polymer chain) significantly amplifies the quenching. Figure 1 shows a comparison of fluorescence quenching of polymers **1**–**3** with various concentrations of Pd^{II}. To examine the effect of the binding domain (**A**) on the fluorescence quenching properties, the luminescence behavior of **3** in response to Pd^{II} was also investigated. Although **3** has a longer effective conjugated length[3] than **1**, its Stern–Volmer quenching constant on Pd^{II} is only $3.79 \times 10^3\ L\,mol^{-1}$, which is even less than that of Dpp. This suggests that the A part of **1** functions as a necessary sensitive domain for Pd^{II} binding, and only the B part of **1** cannot bring out the amplification sensitivity. From Figure 1, we can also learn that **2** shows far less sensitivity than **1** and its

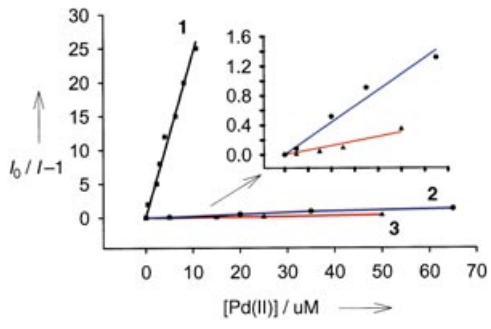


Figure 1. Fluorescence quenching of polymer **1** (■ λex/λem = 415 nm/476 nm), **2** (● λex/λem = 380 nm/425 nm) and **3** (▲ λex/λem = 453 nm/475 nm) by various concentration of Pd^{II} ions, in which I_0 and I denote the intensity of the fluorescence signal of the sensing materials in the absence and presence of the analyte, respectively (the scale and legend of the *x*-axis of the inset is similar to those of the figure).

Stern–Volmer quenching constant ($K_{sv} = 2.18 \times 10^4\ L\,mol^{-1}$) is only 2.8 times greater than that of monomeric model Dpp, although it provides slightly more efficient quenching than **3**. The great disparity in the response efficiency of **1** and **2** demonstrates that the B domain in **1** provides a remarkable amplification, that is, the binding of Pd^{II} with the **A** domain can lead to a significant quenching of the **B** domain. Despite the attraction of special binding of the **A** domain, the excessive distortion in the conjugated polymer of **2** decreases the quantum yield, the average weight, thus the sensitivity, and even the selectivity are seriously reduced. From these results, we believe that neither specific-binding domain, **A**, nor the signaling domain, **B**, could achieve the desired sensitivity. A combination of them together, however, leads to high sensitivity.

In contrast to those of **2** and **3**, the selectivity of **1** for Pd^{II} is excellent. Figure 2 shows that many transitional-metal and main-group ions such as Ru^{III}, Rh^{III}, Co^{II}, Ni^{II}, Zn^{II}, Fe^{III}, Sn^{II}, Pb^{II}, Cu^{II}, Hg^{II}, Ag^{I}, Na^{I}, Mg^{II}, and Mn^{II} have little effect on

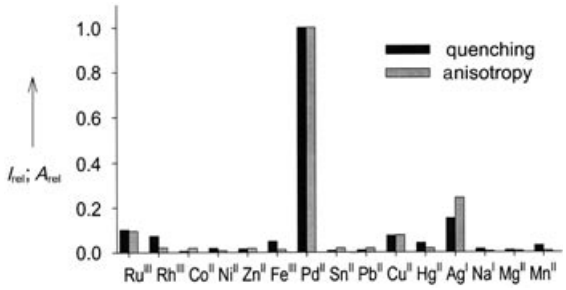


Figure 2. The relative fluorescence quenching and anisotropy changes of **1** with different metal ions.

the fluorescence of **1**. Compared with previous reports,[5,6] the modular-based conjugated polymer **1** provides better selectivity for Pd^{II} ions. That means proper flexibility of the backbone mainly contributes to the selective response. Other elements such as the varying coordination ability or mode (mono- or multi-dentate) between the ion and pyridyl group may also influence the selectivity. The trend of fluorescence quenching of **1** by ions is similar to that of Dpp, but **1** enlarges the discrimination. Compound **1** thus exhibits high selectivity towards Pd^{II} ions and provides an excellent avenue for designing conjugated fluorescent polymers for sensing applications. We also investigated fluorescence quenching with Pt^{IV} ions. The experimental results suggest that with Pt^{IV} ions with compound **1** give a similar effect although its quenching is about 58.1 % and fluorescence anisotropy changes about 68.4 % of that of Pd^{II} at the concentration of $1.5 \times 10^5\ mol\,L^{-1}$. This suggests that Pt^{IV} has a much stronger response than most of the other ions tested.

To further clarify the relationship between the structural arrangement of a conjugated polymer and its specific response, detailed investigations of the mechanism were carried out by using absorption measurements and fluorescence anisotropy. At room temperature, the significant spectroscopic variations that occur as Pd^{II} ions interact with **1** can be observed within a few minutes by progressively adding a solution containing Pd^{II} ions into a solution of **1**. The corresponding excitation band is red-shifted from 415 nm to 444 nm, whereas the emission band is only slightly red-shifted (≈3 nm). Consistent with the excitation variation, the absorption band at 415 nm of **1**, which is attributed to the conjugated backbone, is also red-shifted by ≈30 nm upon adding an appropriate quantity of Pd^{II} ions (Figure 3). The

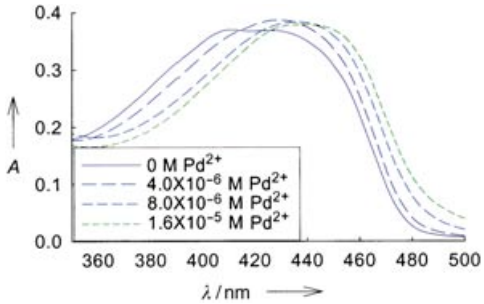
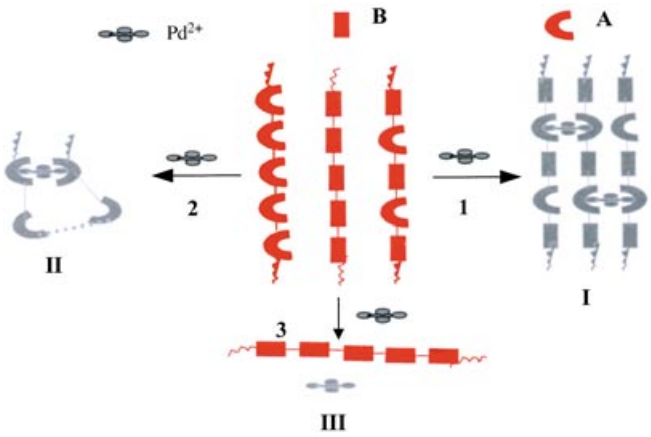


Figure 3. Absorption spectra of **1** in THF (5.0×10^{-6} M) as a function of different concentrations of Pd^{II} ions.

absorptive bands of **2** and **3** display no obvious changes. These spectroscopic results clearly show that there is a difference in the energy state of **1** in the presence and absence of Pd^{II} ions. The red-shift absorption of **1** suggests that the species formed is on average conjugated over a greater length, which may be ascribed to the interpolymer interaction by Pd^{II}-pyridyl binding (**I** in Scheme 2). As for the excessive distortion backbone of **2**, its lower absorption shift results indicate that intrachain linkage may take place (**II** in Scheme 2) instead of interchain linkage. For **3**, without the binding domain **A**, the interchain linkage by the association between Pd^{II} and pyridyl can not produce at all (**III** in Scheme 2) and which is confirmed by the no changes of absorption. The almost unchanged emission spectra of **1** demonstrate the facile energy transfer that can occur along the different segments of the backbone and even through the interchain system. Stronger ligands than pyridine, such as CN^- ions, were added into a solution of **1** to complex the Pd^{II} ions. Consequently, the fluorescence of the conjugated polymer almost fully recovered, thus indicating the reversibility of the sensing property of this molecule.



Scheme 2. Schematic interaction of the different polymer structures (**1**, **2**, and **3**) with Pd^{II} ions.

Fluorescence anisotropy was used to identify the link joining the chains of polymer **1** as this method has been used for studying molecular interactions, particularly in cases in which there is a significant change in molecular weight upon binding or interaction.[11] We used it to study the aggregation of **1** due to the binding of Pd^{II} ions through the pyridyl groups. Figure 4 shows the effects of varying concentrations of Pd^{II} ions on the observed fluorescence anisotropy and quenching of **1**. As expected, the fluorescence anisotropy of **1** increased linearly when a solution containing Pd^{II} ions was gradually added into the diluted polymer solution. The enhanced anisotropy values clearly indicated that the polymer chains coupled, that is, a complex with a larger molecular weight formed, which hindered the rotational diffusion rate of the polymer.[12] Anisotropy value reached a plateau when a concentration of Pd^{II} ions rose above 20 μM, which indicated that saturated aggregation of **1** had occurred. With the increase of anisotropy, fluorescence quenching was correspondingly decreased. The interaction of **1** and Pd^{II} ions was also found to be highly specific by using anisotropy measurements (Figure 2). Further experiments indicate that a stronger ligand such as CN^- could also restore the anisotropy value of **1** in the presence of Pd^{II} ions. Under the same experimental conditions, however, the fluorescence anisotropy of **2** and **3** changed very little even at high concentrations of Pd^{II} ions, thus indicating that interactions between polymer chains do not occur.[9] These results confirm that the high sensitivity and selectivity of **1** closely correlates with the ability of the polymer chains to interact, which, in turn is closely related to its modular-based design.

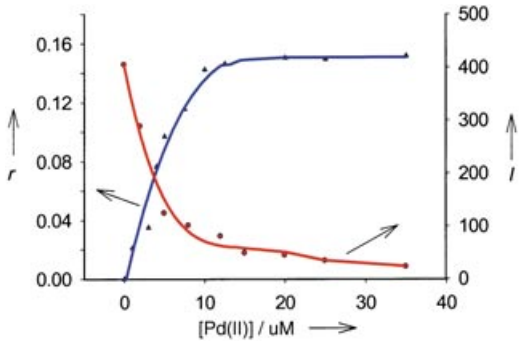


Figure 4. Fluorescence anisotropy (▲) and quenching (●) of **1** with various concentrations of Pd^{II} ions (*r* is the fluorescence anisotropy).

In summary, we report a novel and general method to design a modular-based conjugated polymer with a flexible structure of a binding domain and a rigid structure of a signaling domain. The appropriate selection of the different modules can provide excellent selectivity and high sensitivity. By using this general approach, we synthesized a new fluorescent conjugated polymer for Pd^{II} ion detection with high specificity and excellent sensitivity. This new macromolecule design demonstrates the feasibility of varying the structures to fine-tune the molecular spatial binding properties of the resulting conjugated polymers. The process will enhance the versatility of these sensing systems and their applications. This new design will provide an excellent approach to efficiently and simply regulate the optical and electronic properties of conjugated polymers, which is essential to make them useful for electrical devices and bio/chemical sensors.

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