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A Polymer-Based Ultrasensitive Metal Ion Sensor

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The development of highly sensitive and selective chemosensory materials for the detection of metal ions in environmental or biological systems has gained tremendous attention in recent years.[1] In particular, many attempts have focused on the design of sensing systems with unique optical properties as output signals[2] that provide real-time monitoring capabilities.[3] Preparation and utilization of small molecules that show selective binding to the target metal ions constitute one practical route toward this goal.[4] Nevertheless, many of these probes suffer from one or more limitations, including irreversibility, slow response, low selectivity, and low sensitivity. Swager et al. have demonstrated that delocalizable, π-electronic conjugated "molecular wire" polymers exhibit pronounced sensitivity enhancement in the fluorescence quenching due to facile energy migration.[5] For the detection of transition metal ions, quenching sites are typically generated through the integration of coordination sites.[6,7] In spite of extensive investigations, the question as to how the local structure surrounding the coordination site affects the sensing efficacy remains largely unaddressed. This issue is of fundamental significance for the design of optimized metal ion detection systems. Previously constructed polymers are dominated by the use of 2,2′-bipyridyl (bpy) and terpyridyl (tpy) groups, incorporated either as the main-chain or side-chain entity.[3a,6d,8] We are interested in expanding the structural space of intelligent chemical systems through the rational design of molecular architectures. A selective metal ion-sensing system in the weak binding monomer regime has therefore been developed out of these efforts.[2b] However, the selectivity offered by the approach is accompanied by only a modest sensitivity, an undesired feature for real applications. Moreover, previous exhaustive investigations on bpy- and tpy-substituted polymers did not yield any sensing systems with satisfactory sensitivity, even compared with many small molecule-based architectures.[3a,9] Therefore, the fulfillment of "molecular wire" strategy as an effective guiding principle for achieving highly sensitive polymer platform has become an urgent goal. To develop such a platform, we have turned our attention to a uniquely structured functional unit, dipyrido[3,2-*a*:2,3-*c*]phenazine (dppz). Dppz has been used extensively in the construction of substitutionally inert transition metal complexes, especially for probing DNA-related photophysical and photochemical processes.[10] The extended π-conjugation/rigid conformation, coupled with the chelation site in the molecule, is expected to provide unique quenching response toward transition metal ions if incorporated into the backbone of a conjugated polymer. Herein, we report on the fabrication of a dppz-based selective metal ion-sensing system with picomolar sensitivity. Prior to this work, a 1,10-phenanthroline (phen) unit has been harnessed as the coordination site in replacement of bpy.[6f,11] The electron density variations on the polymer backbone upon the metal ion binding have been used to account for the fluorescence quenching behavior.

Besides the extended conjugation associated with monomer unit, the design of dppz-containing poly(arylene ethynylene) (PAE) is based on the following considerations: (1) The coordination site is distally located from the polymer backbone, thus presenting a fundamentally distinct architecture from typical bpy-based frameworks. (2) The AE unit offers a rigid linking motif that exhibits good photophysical characteristics.[12] (3) The ability to intercalate into DNA from dppz provides potential biological sensing possibility.[13] (4) The ability to form the foldamer structure from properly configured, meta-linking PAE framework could offer guest binding cavity.[14] As the first demonstration of the functional attributes of **P1**, we present the extraordinary metal ion sensing capacity of this multifunctional polymer. In particular, a detection limit of 6.5×10^{-12} M has been achieved for Ni^{2+}, at least 3 orders of magnitude lower than typical fluorescence-based chemosensors.[6h−j,9]

P1 was conveniently synthesized by the Suzuki coupling[15] between 10,13-dibromodipyrido[3,2-*a*:2,3-*c*]phenazine[16,17] and 1,4-bis(trimethylsilylethynyl)-2,5-bis(butyloxy)benzene.[9,15] Polymers **P2**, **P3**, and **P4** were also synthesized in an analogous fashion (Scheme 1 and Schemes S1 and S2). All polymers were purified by precipitation from methanol and obtained as slightly black solids. The purified polymers were characterized by ^{1}H NMR, providing conclusive evidence for the well-controlled incorporation of both monomers within target structures (Figures S1−S19). The molecular weights and polydispersity index (PDI) of these polymers were determined by size exclusion chromatography (SEC), with polystyrene as the reference (Table S1).

Absorption and emission spectra were collected for all polymer systems in THF at room temperature (Figures S20 and S21). **P1** displays absorption peaks at 253, 320, and 381 nm and a broad band around 500 nm. These features are associated with various localized and delocalized $\pi-\pi^*$ electronic transitions. Vibronic structures can be clearly seen for peaks at 320 and 381 nm. The complexity of the spectrum is mirroring that from the constituent unit, dppz (Figures S22 and S23).[18] Similarly, **P2** exhibits pronounced absorption at 250, 311, and 378 nm and a broad band around 490 nm. This is understandable because of the cognate repeating units comprising the backbone of **P2** as compared with **P1**. The similarity also suggests that the four peaks in **P1** are not associated with the chelating nitrogen atoms. One major peak characterizing the $\pi-\pi^*$ transition of the polymer backbone is observed for both **P3** and **P4**. All polymers are emissive in the visible region under UV irradiation (365 nm). Whereas **P3** and **P4** are yellowish-green, **P1** and **P2** appear red and yellow, respectively. The emission of **P1** is red-shifted compared with **P3**, consistent with the extended conjugation offered by dppz in the main chain.

Ion-responsive properties of **P1** are investigated by UV−vis absorption spectroscopy. The change of the absorption spectrum in the case of addition of Ni^{2+} is presented in Figure 1. Most notably, the high-energy bands (around 253 and 320 nm) experienced a red shift, ultimately reaching 13 and 12 nm at

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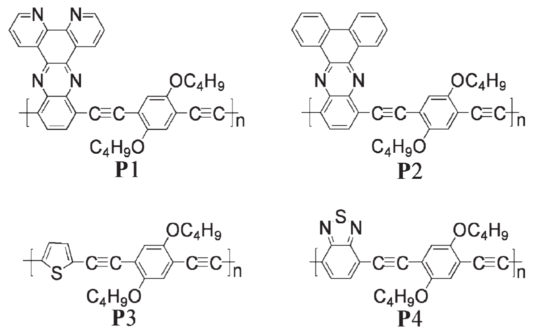
Scheme 1. Structures of Polymers P1−P4



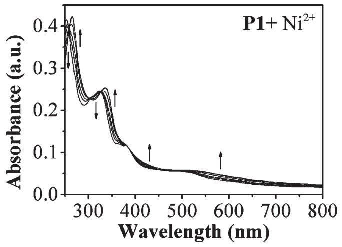


Figure 1. UV−vis absorption spectra of a THF solution of **P1** (2×10^{-5} M, with respect to the receptor unit) after the addition of Ni^{2+}. $[Ni^{2+}] = (1, 2, 3, 4, 5) \times 10^{-7}$ M.

elevated Ni^{2+} concentrations, respectively. The clear isosbestic point found in the titration experiment implies the interaction of Ni^{2+} with the chelating site of dppz receptor in **P1**. This is supported by a control experiment with **P2**, which shows virtually no change of the absorption spectrum upon the addition of Ni^{2+}. Thus, these findings demonstrate the essential role played by dppz moiety in the ion recognition process and rule out the coordination from the phenazine nitrogen atoms. The rigid planar structure of the dppz unit prevents conformational change of the polymer backbone upon metal ion binding, thus supporting the notion that conformational change is not required for achieving ionochromic response. Analogous to **P2**, no isosbectic point and shift of the spectrum are observed for **P3** and **P4** that lack metal recognition sites (Figures S24−S26).

The ion-responsive fluorescence quenching behavior of **P1** at a dppz concentration of 2×10^{-5} M was recorded in THF (Figure 2). Thus, at a Ni^{2+} concentration as low as 5×10^{-12} M, one could already observe a 3% emission intensity decrease. The emission intensity is attenuated to 50% of the initial value at about 1×10^{-7} M and is further diminished to about 5% at 5.0×10^{-7} M. In contrast, no change of the fluorescence intensity was observed for **P2** (Figure S27). This suggests that the observed fluorescence quenching involves the participation of chelating site of dppz and the formation of the **P1**−Ni^{2+} complex. The virtually identical fluorescence spectrum in the absence and presence of Ni^{2+} for **P3** and **P4** (Figures S28 and S29) provides further evidence that the chelating unit of dppz is essential for achieving highly sensitive metal ion-sensing response.

To gain insight into the fluorescence quenching characteristics, a Stern−Volmer plot is presented for the analysis of concentration-dependent behavior. Thus, the steady-state emission graph for **P1** in the presence of Ni^{2+} is shown in Figure S30. A linear Stern−Volmer relationship indicates the dominance of one type of quenching process. It is interesting to note the presence of three linear regions at low Ni^{2+} concentrations, indicating three distinctive operating mechanisms. The Stern−Volmer constants are determined to be 2.57×10^{9} M^{-1} [$(0.0005-0.004) \times 10^{-8}$ M], 2.63×10^{7} M^{-1} [$(0.03-0.3) \times 10^{-8}$ M], and 8.27×10^{6} M^{-1} [$(1-20) \times 10^{-8}$ M].[19] Although the exact nature of the concentration-dependent quenching process has yet to be determined, the extraordinary sensing capability has been established. An upwardly positive deviation was observed at higher concentrations, suggesting the presence of combined quenching actions at this concentration range. The ability to completely quench the fluorescence **P1** by Ni^{2+} can be attributed to the electron-transfer interactions between the conjugated polymer backbone and metal ion.[3c,6d,g] Indeed, metal ions with an open shell electronic structure such as Ni^{2+} (d8) may enable the occurrence of strong metal−ligand orbital interactions, forming a low-lying metal-to-ligand (ML) or ligand-to-metal (LM) charge transfer state and causing strong fluorescence quenching. Metal ions with a full occupancy or half occupancy outer-shell orbital, which generally show weak metal−ligand orbital interactions, might cause weak fluorescence quenching as in the case of Zn^{2+} (d10) and Cd^{2+} (d10) (vide infra). The coordination strength of dppz is not likely the sole reason that leads to a highly sensitive quenching response. After all, other polypyridyl-containing conjugated polymers with similar metal ion binding capability did not exhibit such a pronounced effect.[3g,6d,h,8a,11b,20] Most probably, energy- or electron-transfer rate between the polymer and metal ion and nonradiative excitation decay rate of the complex play a dictating role.

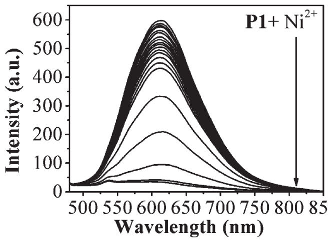


Figure 2. Emission spectra of a THF solution of **P1** (2×10^{-5} M with respect to the receptor unit) after the addition of Ni^{2+}. $[Ni^{2+}] = (0.005, 0.009, 0.01, 0.02, 0.03, 0.04, 0.1, 0.2, 0.3, 1, 2, 3, 10, 20, 30, 100, 200, 300, 400, 500) \times 10^{-9}$ M. Excitation wavelength: 462 nm.

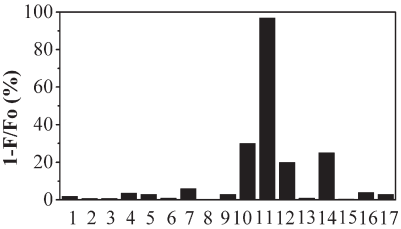


Figure 3. Fluorescence quenching degrees ($1 - F/F_0$) of a THF solution **P1** (2×10^{-5} M, with respect to the receptor unit) in the presence of various metal ions (5.0×10^{-7} M). F and F_0 are taken as the fluorescence intensity at 614 nm. 1, Zn^{2+}; 2, Na^{+}; 3, K^{+}; 4, Ag^{+}; 5, Mg^{2+}; 6, Cr^{3+}; 7, Pb^{2+}; 8, Cd^{2+}; 9, Hg^{2+}; 10, Co^{3+}; 11, Ni^{2+}; 12, Mn^{2+}; 13, Al^{3+}; 14, Cu^{2+}; 15, Ca^{2+}; 16, Fe^{3+}; 17, Fe^{2+}.

The selectivity of **P1** response toward Ni^{2+} against other metal ions was carefully examined next. Virtually no fluorescence intensity change was observed after the addition of Zn^{2+}, Na^{+}, K^{+}, Ca^{2+}, Pb^{2+}, Cr^{3+}, Fe^{3+}, Fe^{2+}, Cd^{2+}, Hg^{2+}, Ag^{+}, Mg^{2+}, and Al^{3+}. The emission intensity was decreased to 70%, 75%, and 80% of the initial value at a concentration of 5.0×10^{-7} M for Co^{3+}, Cu^{2+}, and Mn^{2+}, respectively. In comparison, under identical conditions, a drastically more significant intensity decrease (to 5% of the original value) was discerned for Ni^{2+} (Figure 3 and Figure S31). A detection limit of 6.5×10^{-12} M was established for Ni^{2+} using the 3σ method. Therefore, a highly sensitive and selective metal ion sensing polymer system has been developed. Moreover, an instant color change from light red to colorless upon the addition of Ni^{2+} (5.0×10^{-7} M) was observed for a THF solution of **P1**. Notably, in this way, Ni^{2+} can be readily distinguished from the other 16 metal ions by the naked eye. To exclude the synergistic effect exerted by the combination of metal ions and therefore the potential interference from ionic mixtures, further experiments have been conducted (Figure S32). The first group of metal ions, containing only weakly responsive Zn^{2+}, Na^{+}, K^{+}, Pb^{2+}, Fe^{3+}, Mg^{2+}, and Al^{3+}, generates a merely 7% reduction in the **P1** emission intensity. Even in the presence of Zn^{2+}, Na^{+}, K^{+}, Pb^{2+}, Fe^{3+}, Mg^{2+}, Al^{3+}, Co^{3+}, and Mn^{2+}, much less reduction in the emission intensity as compared with Ni^{2+} was observed. The lack of pronounced effect from this group of metal ions is also evidenced by the fact that really weak influence could be further imposed on the fluorescence intensity of Ni^{2+}-added **P1**. This indicates that the addition of other metal ions results in very little disturbance to the selective sensing of **P1** toward Ni^{2+}.

In summary, we have designed and synthesized a dppz-based metal ion-sensing conjugated polymer with high sensitivity and selectivity. The incorporation of a repeating unit with an extended conjugation structure has proven to be beneficial to the performance of the sensor. An unprecedented picomolar sensitivity has been achieved for the polymer with such a rigidly planar structure. The results presented herein provide important insight into the polymer−metal ion interactions and should enable the expansion of the structural space for the preparation of next-generation intelligent polymer systems.

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Supporting Information Available: ^{1}H NMR of monomers; ^{13}C NMR of monomers; ^{1}H NMR of polymers **P1−P4**; molecular weights of polymers **P1−P4**; optical data of polymers **P1−P4** in THF; absorption and emission spectra of polymers **P1−P4** in THF; UV−vis absorption and emission spectra of THF solutions of **P2−P4** after the addition of Ni^{2+}. This material is available free of charge via the Internet at http://pubs.acs.org.

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