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A Quinoliene-Containing Conjugated Polymer-Based Sensing Platform for Amino Acids

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Supporting Information

8-Quinolinol and its derivatives have attracted increasing attention during the past few decades due to their important applications in organic light-emitting diodes (OLEDs), solar cells, energy conversion materials, etc.[1,2] The excellent chelation of 8-quinolinol to metal ions makes them fine "acceptor−analyte" pairs in fabricating novel chemosensors.[3] Recently, larger conjugation systems, particularly conjugated polymers (CPs), showed unparalleled advantages as sensing elements due to the so-called "molecular wire effect", "superquenching effect", and/or "one point contact and multiple points response effect".[4] Therefore, it is reasonable to expect that introduction of a quinolinol structure into CPs may significantly enhance the sensing properties of the CPs because this structure can function as an acceptor to trap metal ions. Actually, CPs with their main chains containing 8-quinolinol have been synthesized and reported by Yamamoto and co-workers.[5] As expected, the polymers exhibit strong attraction to metal ions, and the fluorescence properties of the polymers are greatly altered by the combination of metal ions. However, as pointed out by the authors, the quinolinol-containing CPs have not received enough attention.[6]

Recently, CPs-based fluorescent chemosensors developed via a "turn-on" strategy have received special attention since these sensors possess not only high selectivity but also good sensitivity.[7] It is known that 8-quinolinol has a strong tendency to chelate Cu^{2+}, and furthermore, Cu^{2+} is one of the best-known fluorescence quenchers.[8,9] Therefore, it is expected that complexation of Cu^{2+} by the 8-quinolinol residues contained in a CP must result in quenching of the fluorescence emission from the polymer. No doubt, once Cu^{2+} is combined by a more stronger chelate, an analyte, the quenched fluorescence should recover. In other words, this kind of Cu^{2+}−CPs may be used as a platform to detect target analytes. A similar idea has been employed for the development of sensing methods for Fe^{2+},[10] CN^-,[7d,11] F^-,[12] and some "neutral" analytes, such as NO,[13] and even protease[7c] with high sensitivity and good selectivity. However, sensing methods for amino acids are rarely reported.[14,15] Accordingly, three quinolinol-containing CPs were purposely designed and synthesized. The structures of the polymers are shown in Scheme 1. The three polymers containing bromine, imidazole, and hydroxyl structures are denoted as **P1**, **P2**, and **P3**, respectively. The synthetic procedures and the characterization data are presented in the Supporting Information.

As examples, the UV−vis absorption and fluorescence spectra of **P2** are shown in Figure S2. The maximum absorption of **P2** in THF appears at 410 nm, and the emission centers at 460 nm with a shoulder appearing at 485 nm. The solution of **P1** in THF exhibits similar absorption and emission spectra (cf. Figures S1 and S2). **P3** in the same solvent, however, displays a little bit different absorption and emission spectra if compared to those of **P1** and **P2** (cf. Figure S3).

Figure 1 displays the fluorescence emission spectra of **P2** in THF and in the presence of different concentrations of Cu^{2+}. It is seen that the emission is quenched to 10% of its initial value when the concentration of Cu^{2+} reaches 1.6 μmol/L. The quenching results were further treated with the Stern−Volmer equation, $I_0/I = 1 + K_{sv}[Cu^{2+}]$, where I_0, I, and K_{sv} stand for the fluorescence intensity of the polymer in the absence and presence of Cu^{2+} and the Stern−Volmer constant, respectively. The result from the treatment is shown in the inset of Figure 1. Similarly, **P1** and **P3** were also used to detect Cu^{2+}. Figure S4 shows the fluorescence spectra of **P1** in THF containing different concentrations of Cu^{2+}. It is seen that the fluorescence emission is rarely affected even though the concentration of Cu^{2+} reached to 1.6 μmol/L. In contrast, **P3** exhibits notable responses to Cu^{2+} (cf. Figure S5). Different response behaviors of the three polymers to Cu^{2+} reveal the important role of the functional groups contained in the polymer to the sensing process. **P1** has no functional group which possesses specific affinity to Cu^{2+}, and thereby, Cu^{2+} barely quenches its fluorescence emission. The imidazole-functionalized polymer, **P2**, and 8-hydroxyquinoline-containing polymer, **P3**, however, have a strong tendency to combine Cu^{2+} due to the presence of the groups, and spontaneously, their emissions are remarkably quenched by Cu^{2+}.

It is known that compared to imidazole amino acids are stronger chelates to Cu^{2+}, and thereby the quenched fluorescence of Cu^{2+}−**P2** may be recovered by the addition of amino acids. As expected, addition of glycine, a typical amino acids, into the Cu^{2+}−**P2** systeme did result in recovery of the quenched fluorescence (see Figure 2). The extent of the recovery depends on the concentration of the amino acid. The detection limit of Cu^{2+}−**P2** to Gly was determined by employing a standard method as described in the literature,[16] and the result is 7.7×10^{-9} M. In contrast, addition of glycine into Cu^{2+}−**P3** showed little effect to the fluorescence emission of the system (cf. Figure S6). The difference may be rationalized by considering the stability of the polymer−Cu^{2+} complexes. It is well-known that

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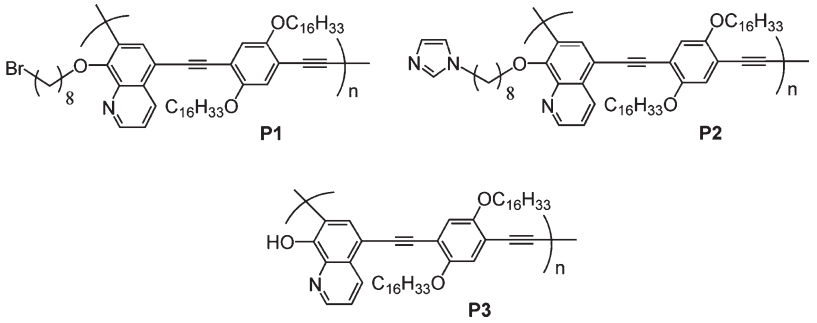
Scheme 1. Structures of the Three Polymers



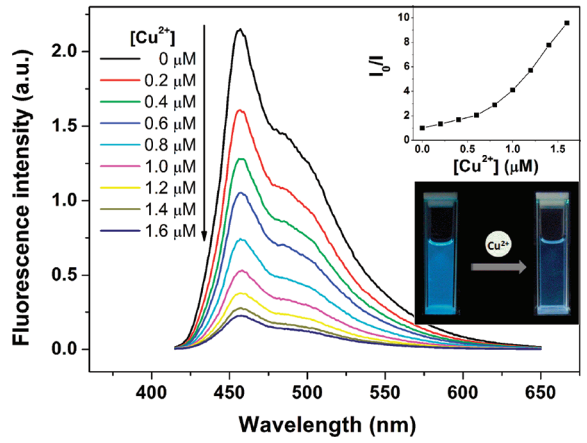


Figure 1. Fluorescence emission spectra of **P2** in THF in the presence of different concentrations of Cu^{2+} (from top to bottom, 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, and 1.6 μM) (λ_{ex} = 410 nm), [**P2**] = 1×10^{-6} M. Inset is the plot of I_0/I measured at 460 nm against the concentration of Cu^{2+}.

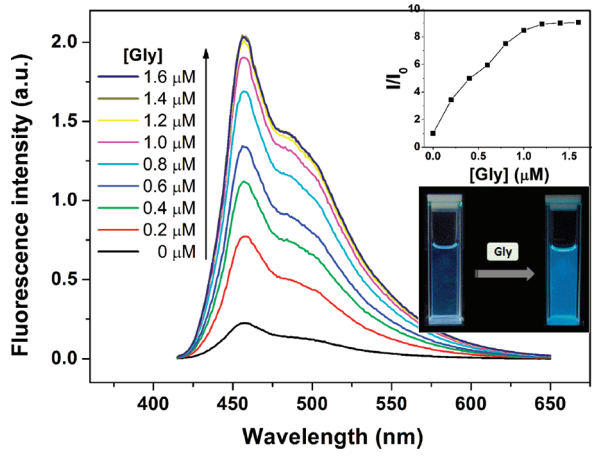


Figure 2. Fluorescence emission spectra of the **P2** + Cu^{2+} in the presence of different concentrations of Gly (from top to bottom, 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, and 1.6 μM) in THF (λ_{ex} = 410 nm), [**P2**] = 1×10^{-6} M. [Cu^{2+}] = 1.6 μM. Inset is the plot of I/I_0 measured at 460 nm against the different concentration of Gly.

8-hydroxyquinoline is a much stronger chelate to Cu^{2+} than that of amino acids, and thereby, the amino acid cannot snatch Cu^{2+} from the Cu^{2+}—polymer complex, of which 8-hydroxyquinoline

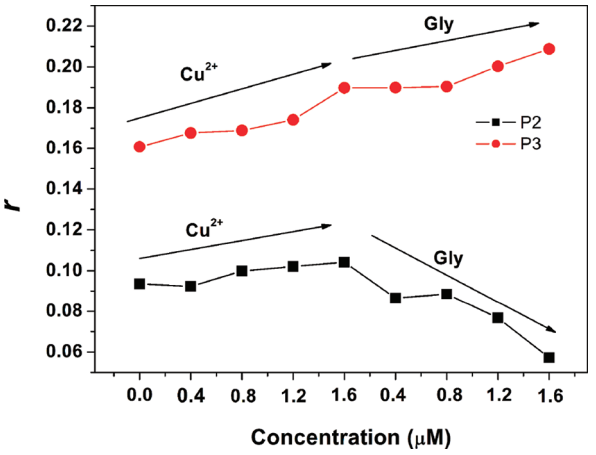


Figure 3. Fluorescence anisotropy of the polymers in THF in the presence of different concentrations of Cu^{2+} and glycine: **P2** (■) and **P3** (●), [**P2**] = [**P3**] = 1×10^{-6} M.

is the cation binding site. It is to be noted that Cu^{2+}—**P2** is also a good sensing platform for other amino acids, such as aspartic acid, cysteine, glutamic acid, etc. (cf. Supporting Information).

To understand the interaction between Cu^{2+} and the polymers, UV—vis measurements were conducted to examine the "turn-off" and "turn-on" process, and the results are shown in Figures S13 and S14, respectively. Reference to the figures, it is seen that both the intensity and the profile of the absorption of **P2** in THF do not change very much along with increase of the quencher, Cu^{2+}, concentration. On the contrary, the absorption spectra of **P3** exhibit remarkable changes when Cu^{2+} was introduced. The maximum of the absorption of **P3** red-shifts from 420 to 455 nm (cf. Figure S15). Existence of an isoabsorption point in the spectra suggests two absorption species in the system, indicating formation of a Cu^{2+}—**P2** complex, which possesses an absorption centering at 455 nm. Addition of glycine shows little effect to the UV—vis absorption of the Cu^{2+}—**P3** solution suggests that the cation is still combined by the polymer (cf. Figure S16). Furthermore, UV—vis measurements revealed that complexation of Cu^{2+} by the 8-hydroxyquinoline structure, a component of the main chain of **P3**, alters the main chain structure of the polymer and thereby its photophysical behavior. For **P2**, however, the combination was realized by the imidazole structure, which was affixed to the side chains of the polymer and thereby

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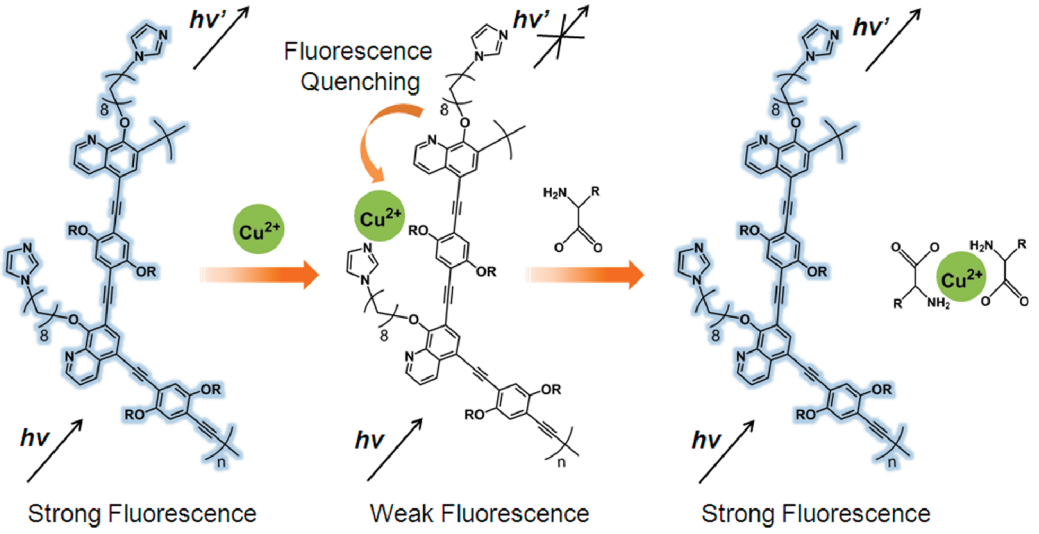
Scheme 2. Schematic Representation of Detection of Amino Acid



showed little effect to the absorption of the polymer. Results from fluorescence anisotropy measurment is also in support of the assumption.

Fluorescence anisotropy is an effect way to study molecular interactions, particularly in cases in which there is a significant change in molecular weight upon binding or interaction.[17] As shown in Figure 3, the values of the fluorescence anisotropy (r) of **P2** and **P3** increase along with increasing the conentration of Cu^{2+}. However, introduction of glycine results in different results for the two systems. For the system of **P2**, the value of r decreases along with increasing the amino acid concentration. On the contrary, for **P3**, the value increases with increase of the amino acid concentration. This difference might be understood by considering that for the system of Cu^{2+}—**P2** the cation might be freed due to complexation with the amino acid, and thereby the polymer became more mobile, corresponding to lower r values. For Cu^{2+}—**P3**, however, the cation could not be freed from the polymer in the presence of amino acid due to the reason described already, explaining why the r value did not decrease along with addition of the amino acid. As for the increase of the r value, it might be a result of association of the amino acid to the polymer backbone due to its affinity to Cu^{2+}.

On the basis of the results described above, a possible sensing mechanism of Cu^{2+}—**P2** to amino acid is proposed and schematically shown in Scheme 2.

In conclusion, a copper(II)-conjugated polymer complex, Cu^{2+}—**P2**, has been developed into a fluorescent sensing platform for amino acids using a "turn-on" strategy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Details of synthesis and characterization of monomers and **P1**, **P2**, and **P3**; UV—vis and fluorescence studies of the systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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