

Bi-8-carboxamidoquinoline Derivatives for the Fluorescent Recognition of Zn²⁺

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Abstract Three fluorescent sensors which were composed of a phendiol (*o*-, *m*-, *p*-isomers) and two carboxamidoquinolines have been synthesized and characterized. Research on the Zn²⁺-sensing properties of the three sensors was carried out, and the results showed a significant difference in the recognition performance for Zn²⁺. The fluorescence intensity ($I_{510\text{ nm}}$) of ortho isomeric sensor binding to Zn²⁺ was enhanced 23-fold, the meta 15-fold, the para 8-fold. As the distance between two carboxamidoquinolines became longer, the fluorescence enhancement decreased. In addition, the selectivity of sensors got poor and the detection limit became higher with rising the distance between two receptors.

Keywords Carboxamidoquinolines · Fluorescent sensor · Zinc ion · Recognition · Isomeric

Introduction

As the second most abundant transition metal ion in the human body [1], zinc ion involves in multiple biological processes and has close relationship with many diseases [2, 3]. Based on the above facts, it is very necessary to monitor zinc

ion. Fluorescence detection owing to their high sensitivity, selectivity, versatility and relatively simple handling has been widely implemented in biology and clinical medicine [4–7], especially for the detection of zinc ion.

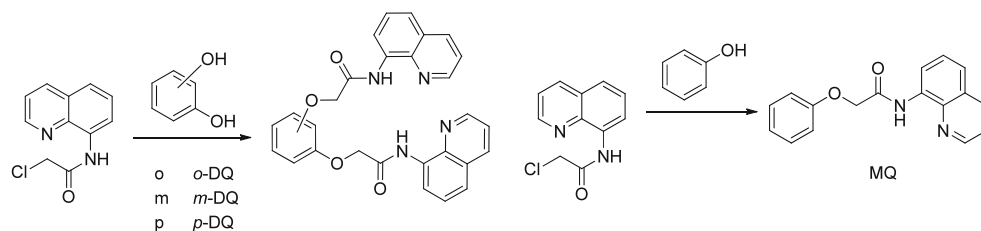
The fluorescent sensors are the key to perform fluorescence detection. Thus, zinc ion fluorescent sensors have sparked the scientists' interest recently [8–10]. For satisfying the distinct demands, different kinds of fluorescent sensors for Zn²⁺ have been reported. So far, the reported Zn²⁺ sensors have commonly utilized coumarin [11, 12], naphthalimide [13], quinoline [14, 15], pyrene [16], anthracene [17, 18] etc. as fluorophores, and employed di-2-picolyamine [19], Schiff base [20, 21] and triazole [22, 23] etc. as the receptors. Among these, Zn²⁺ sensors based on carboxamidoquinoline developed quickly [24–26], owing to simple synthesis, certain binding ratio, good water-solubility, and ratio detection. In our previous research, the nitrogen atom at α position of the acetyl group was necessary to chelate Zn²⁺ [27]. Recently a combination of dual carboxamidoquinolines which have no the nitrogen atom at α position of the acetyl group could bind to Zn²⁺ successfully [28, 29].

It is generally known that the receptor with suitable distance of coordination atoms, matching shape and proper binding sites can improve the luminescent properties of a fluorescent sensor [30]. Herein, four fluorescent sensors (MQ, *o*-DQ, *m*-DQ and *p*-DQ) were synthesized through the introduction of carboxamidoquinoline on phenol and three isomers of phendiol (as shown in Scheme 1). The strategy is to modulate the distance and the number of coordination atoms by changing the number of carboxamidoquinolines and varying their substituent positions, and consequently the structure-function relationships of the sensors were discovered. The synthesis of the sensors followed the procedures in Scheme 1.

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Scheme 1 The synthesis of the sensors



Experimental Section

Reagents and Apparatus

All solvents and reagents (analytical grade) were obtained commercially and used as received without further purification. Double-distilled water and HEPES buffer were used throughout the experiments. The metal ion solutions were prepared from NaCl, KCl, $Mg(ClO_4)_2$, $Ca(NO_3)_2$, $Cr(NO_3)_2$, $Fe_2(SO_4)_3$, $CoSO_4$, $NiSO_4$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $AgNO_3$, $CdSO_4$, $HgCl_2$, $Pb(NO_3)_2$, $AlCl_3$ in distilled water with a concentration of 0.05 M. All spectroscopic experiments were carried out at room temperature and pH is 8.3 in methanol/water (9:1, v/v) mixed solvent.

1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE-600 spectrometer and referenced to internal tetramethylsilane. Infrared spectral data were measured with Nicolet Avatar-370. Mass spectra were obtained on a Waters Xevo G2-S QT. Melting points were measured using an X-6 microscopic melting point apparatus (Beijing, China). The UV–vis spectra were measured on a Puxi TU-1901 (Beijing, China) spectrophotometer. Fluorescence measurements were made on a Hitachi F-7000 (Tokyo, Japan). The excitation and emission slit widths were kept at 2.5 and 5.0 nm, respectively.

Preparation of 2-chloro-*N*-(quinol-8-yl)acetamide

2-Chloro-*N*-(quinol-8-yl)acetamide was synthesized by a modified procedure [31], 8-aminoquinoline 1.286 g (8.93 mmol) and potassium carbonate 3.703 g (26.79 mmol) were mixed in CH_2Cl_2 (25 mL), then the solution of the 2-chloroacetyl chloride 1.513 g (13.40 mmol) in dichloromethane (10 mL) was slowly added under cooling by ice. The resulting mixture was allowed to stir 2 h at room temperature. After filtration, the solvent was concentrated under vacuum. The crude products were purified by column chromatography using CH_2Cl_2 as eluant to afford a white solid. Yield: 1.691 g (85.9 %), mp: 132.1–132.6 °C.

Preparation of the Target Sensors

Phenol 0.051 g (0.53 mmol), potassium carbonate 0.147 g (1.06 mmol) and 2-chloro-*N*-(quinol-8-yl)acetamide 0.129 g (0.58 mmol) were mixed in anhydrous DMF (5 mL), the resulting mixture was kept stirring under N_2 atmosphere at 100 °C for 1 h. Then it was diluted by water and extracted with CH_2Cl_2 . The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The crude

Fig. 1 Absorption spectra of sensors (10 μ M). **a** MQ **b** *o*-DQ **c** *m*-DQ **d** *p*-DQ (methanol/water=9:1, v/v, 0.01 M HEPES, pH=8.3)

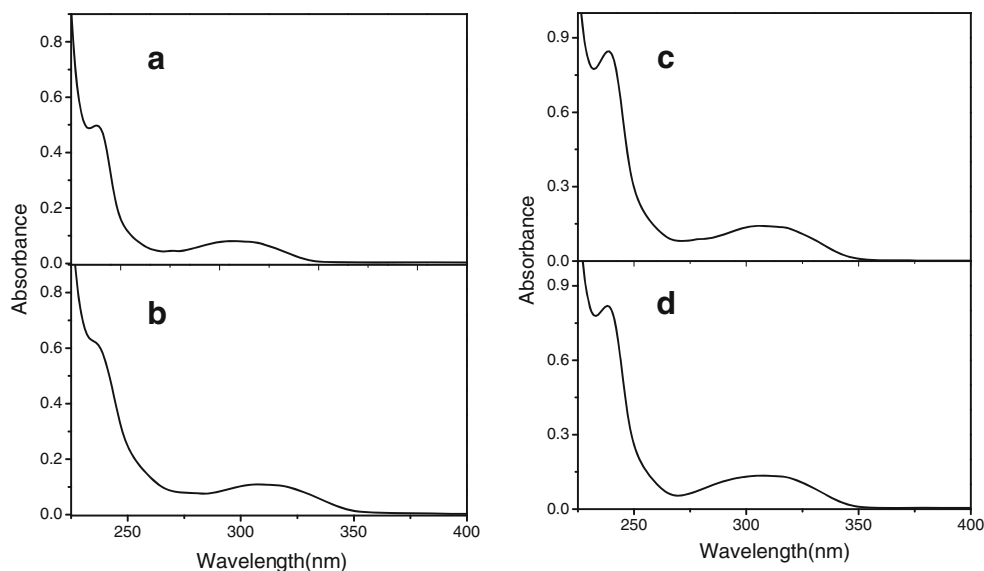
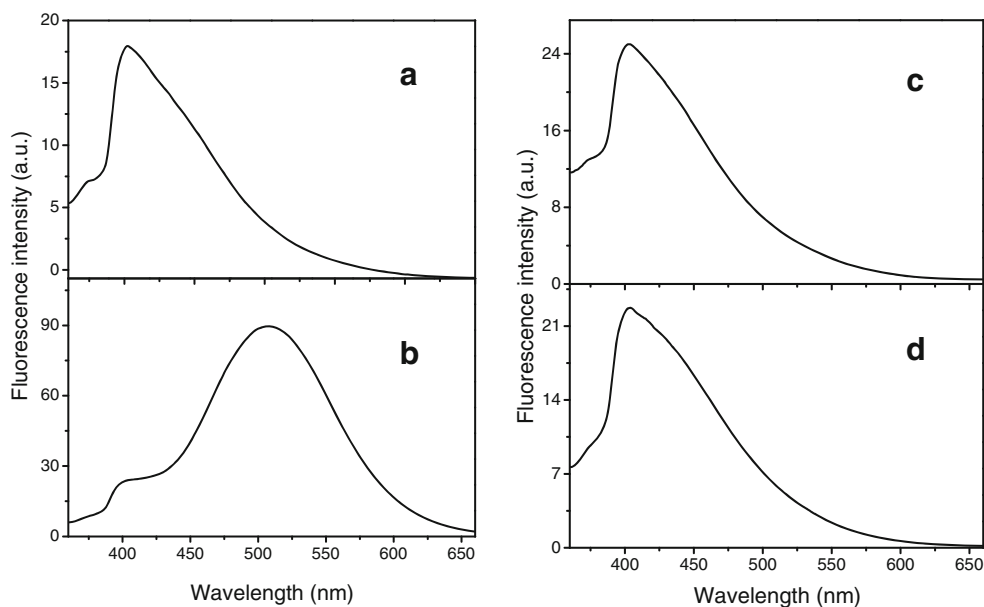


Fig. 2 Fluorescence spectra of sensors (10 μ M). **a** MQ **b** *o*-DQ **c** *m*-DQ **d** *p*-DQ (methanol/water=9:1, v/v, 0.01 M HEPES, pH=8.3, λ_{ex} =350 nm)



products were purified by column chromatography using CH_2Cl_2 as eluant.

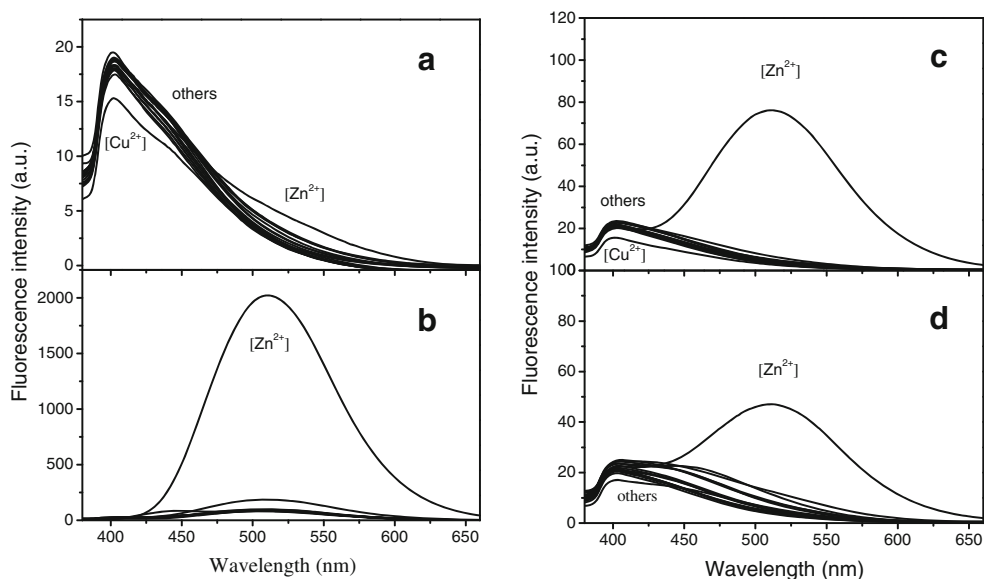
Phendiol 0.045 g (0.41 mmol), potassium carbonate (4.0 eq.) and 2-chloro-*N*-(quinol-8-yl)acetamide (2.2 eq.) were mixed in anhydrous DMF (5 mL), the resulting mixture was kept stirring under N_2 atmosphere at 100 $^\circ\text{C}$ for 1 h. Then it was diluted by water and extracted with CH_2Cl_2 . The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The crude products were purified by column chromatography using dichloromethane/ethyl acetate (20:1, v/v) as eluant.

Yields and spectral details of target sensors are given below.

MQ, 0.109 g, yield 72.7 %, mp: 107.5–108.6 $^\circ\text{C}$. ^1H NMR (600 MHz, CDCl_3): δ 10.98 (s, 1H), 8.87 (dd, $J=4.2, 1.7$ Hz, 1H), 8.82 (dd, $J=5.8, 3.1$ Hz, 1H), 8.18 (dd, $J=8.3, 1.7$ Hz, 1H), 7.59–7.55 (m, 2H), 7.47 (dd, $J=8.2, 4.2$ Hz, 1H), 7.39–7.35 (m, 2H), 7.13 (dt, $J=9.2, 1.7$ Hz, 2H), 7.08–7.04 (m, 1H), 4.76 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ 166.80, 157.42, 148.61, 138.76, 136.19, 133.71, 129.75, 127.97, 127.21, 122.20, 122.19, 121.68, 116.79, 115.13, 68.14. FTIR(cm^{-1}): 3313, 3047, 2921, 1679, 1593, 1548, 1241, 1066. MS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}_2^+$ ($\text{M} + \text{H}^+$) 279.1133, found 279.1301.

o-DQ, 0.130 g, yield 66.5 %, mp: 218.1–219.0 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 600 MHz): δ 11.104 (s, 2H), 8.68 (d, $J=7.2$ Hz, 2H), 8.51 (d, $J=4.2$ Hz, 2H), 7.82 (d, $J=8.4$ Hz,

Fig. 3 Fluorescence spectra of sensors (10 μ M) with different metal ions (10 μ M) including Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cr^{3+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Hg^{2+} , Cd^{2+} , Pb^{2+} , Al^{3+} . **a** MQ **b** *o*-DQ **c** *m*-DQ **d** *p*-DQ (methanol/water=9:1, v/v, 0.01 M HEPES, pH=8.3, λ_{ex} =350 nm)



2H), 7.39 (t, $J=7.8$ Hz, 2H), 7.32 (d, $J=8.4$ Hz, 2H), 7.15–7.7.12 (m, 2H), 7.08–7.04 (m, 4H), 4.94 (s, 4H). ^{13}C NMR (150 MHz, CDCl_3): δ 166.66, 148.26, 147.68, 138.01, 135.43, 133.56, 127.34, 126.69, 122.91, 122.02, 121.32, 116.64, 114.82, 69.16. FTIR(cm^{-1}): 3309, 3051, 2917, 1687, 1601, 1544, 1258, 1053. MS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{23}\text{N}_4\text{O}_4^+$ ($\text{M} + \text{H}^+$) 479.1719, found 479.1873.

m-DQ, 0.133 g, yield 68.3 %, mp: 233.1–233.7 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 11.97 (s, 2H), 8.87 (dd, $J=1.8$ Hz, 1.8 Hz, 2H), 8.82 (q, $J=3.0$ Hz, 2H), 8.19 (dd, $J=0.6$ Hz, 1.2 Hz, 2H), 7.60–7.56 (m, 4H), 7.47 (q, $J=4.2$ Hz, 2H), 7.32 (t, $J=8.4$ Hz, 1H), 6.97 (t, $J=2.4$ Hz, 1H), 6.80 (dd, $J=2.4$ Hz, 2.4 Hz, 2H), 4.81 (s, 4H). ^{13}C NMR (150 MHz, CDCl_3): δ 166.49, 158.73, 148.64, 138.68, 136.25, 133.63, 130.59, 127.98, 127.21, 122.26, 121.71, 116.86, 108.64, 103.39, 68.99. FTIR(cm^{-1}): 3321, 3047, 2908, 1691, 1610, 1548, 1184, 1066. MS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{23}\text{N}_4\text{O}_4^+$ ($\text{M} + \text{H}^+$) 479.1719, found 479.1923.

p-DQ, 0.124 g, yield 63.7 %, mp: 231.4–232.4 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 10.95 (s, 2H), 8.85 (dd, $J=1.8$ Hz, 1.8 Hz, 2H), 8.82 (q, $J=3.0$ Hz, 2H), 8.18 (dd, $J=1.8$ Hz, 1.2 Hz, 2H), 7.58–7.56 (m, 4H), 7.47 (q, $J=1.8$ Hz, 2H), 7.13 (s, 4H), 4.81 (s, 4H). ^{13}C NMR (150 MHz, CDCl_3): δ 166.85, 152.75, 148.62, 138.75, 136.27, 133.70, 128.01, 127.25, 122.25, 121.71, 116.85, 116.49, 68.99. FTIR(cm^{-1}): 3325, 3043, 2908, 1683, 1552, 1507, 1241, 1066. MS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{23}\text{N}_4\text{O}_4^+$ ($\text{M} + \text{H}^+$) 479.1719, found 479.1941.

Results and Discussion

Absorption and Fluorescence Spectra of the Sensors

To investigate the effects of the number and position of substituents, UV and fluorescence spectra of four free sensors

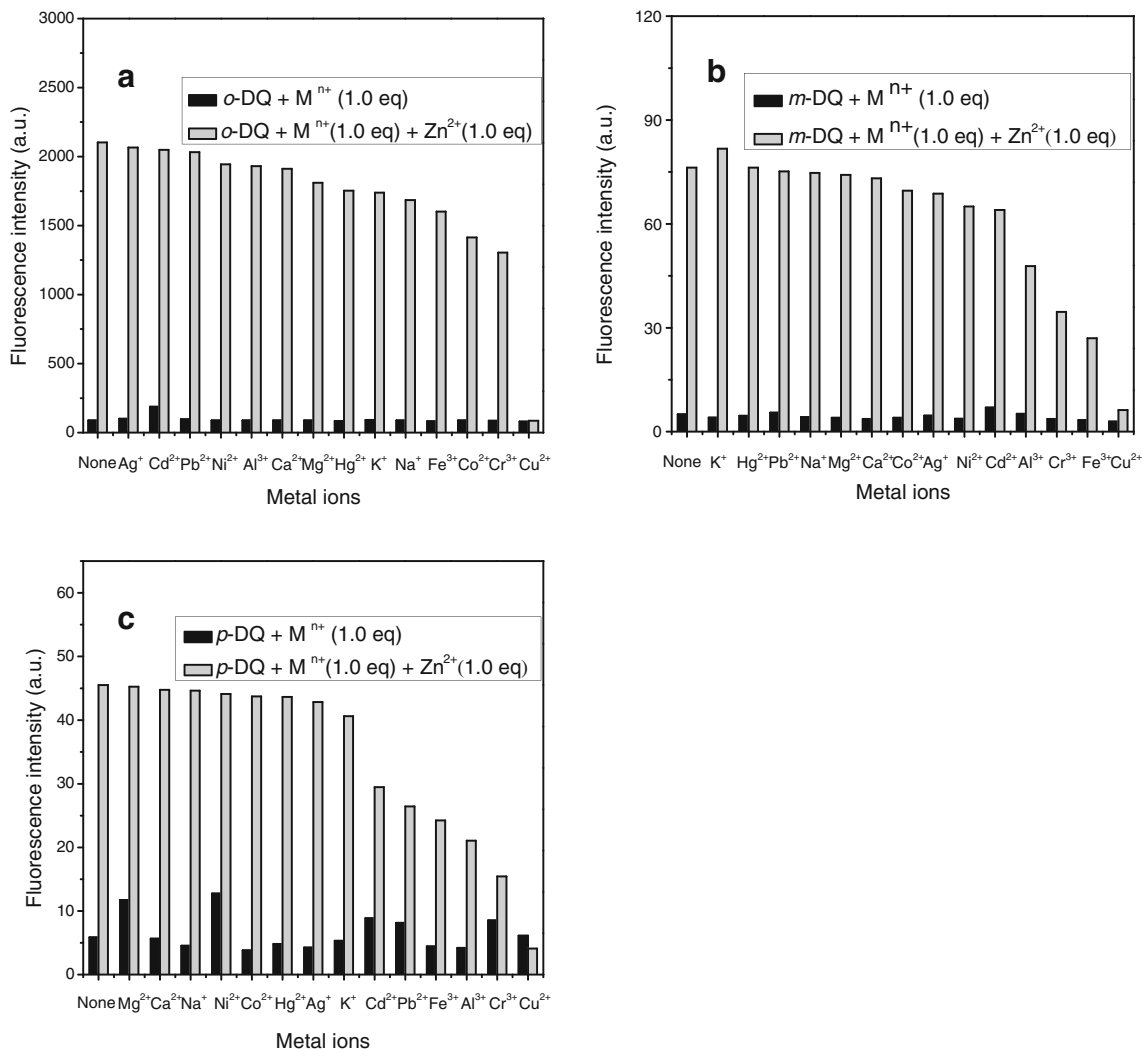


Fig. 4 Fluorescence response of sensors (10 μM) to various tested metal ions (10 μM) (black bar) and to the mixture of 10 μM of tested metal ions with 10 μM Zn^{2+} ion (gray bar). ($\lambda_{\text{ex}}=350$ nm, $\lambda_{\text{em}}=510$ nm) **a** *o*-DQ **b** *m*-DQ **c** *p*-DQ (methanol/water=9:1, v/v, pH=8.3, 0.01 M HEPES)

were obtained. As shown in Fig. 1, the maximum absorption wavelengths of the four compounds were at about 320 nm and the peak shapes were similar. All these suggested that the effects of the number and position of substituents on the conjugated system were not significant. That is to say, the ground electronic states of the four sensors had no obvious distinction.

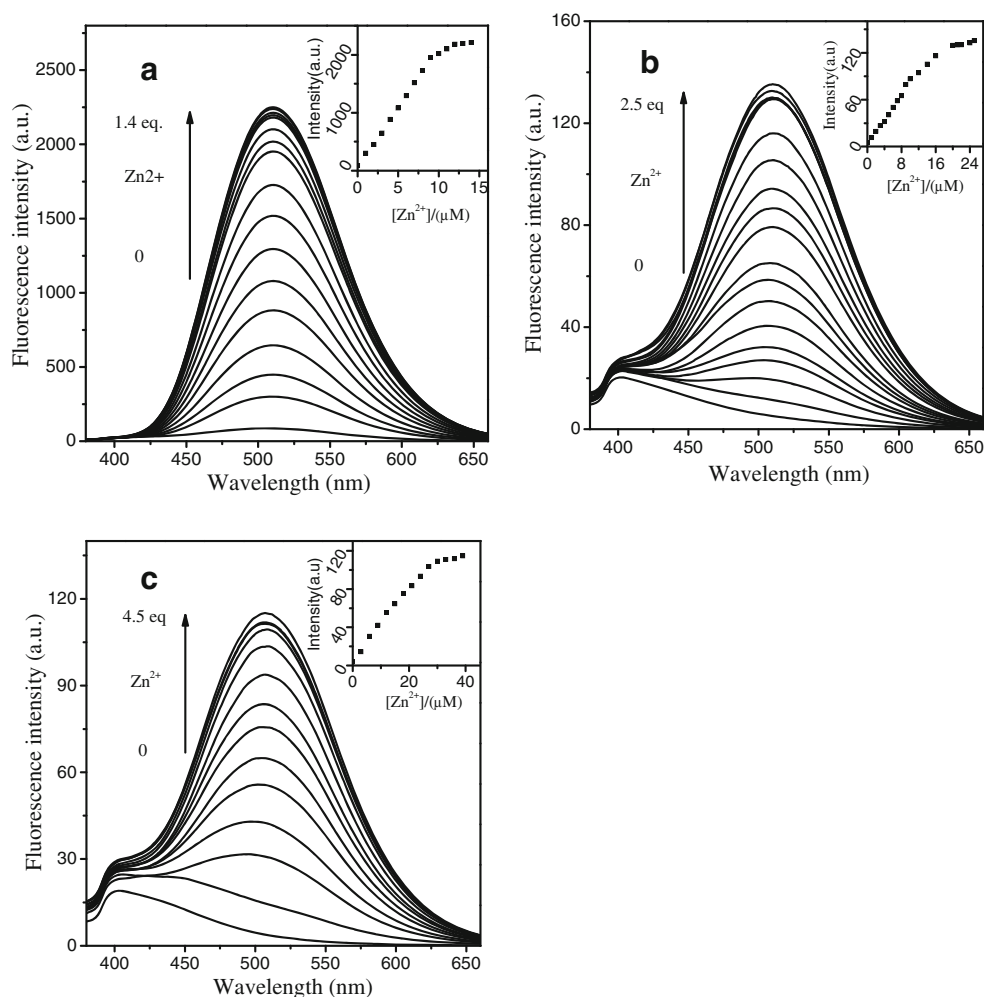
It could be seen from Fig. 2, the three compounds (MQ, *m*-DQ, *p*-DQ) had similar peak shape and maximum emission wavelength around 400 nm, but the maximum emission wavelength of *o*-DQ shifted to 510 nm. The results showed that the excited electronic state of *o*-DQ was different from the others, which resulted from the effects of the number and position of substituents. The phenomenon may be explained as that a certain excited aggregation was formed because of the short distance of two carboxamidoquinoline groups of *o*-DQ, and the excited aggregation was easier to transfer the proton of the amide group to the nitrogen atom of quinoline, which broken the intermolecular hydrogen bonds and strengthened the ICT process [31, 32]. So the fluorescence spectrum of *o*-DQ was different from others.

Metal Ion Selectivity

Fluorescence spectra of four sensors were examined following the treatment with different metal ions (1.0 eq.) in methanol-water HEPES buffer solutions. As shown in Fig. 3, after adding Zn^{2+} , the fluorescence intensity ($I_{510\text{ nm}}$) of *o*-DQ increased 23 times, while that of *m*-DQ and *p*-DQ increased 15 times and 8 times, respectively. The weaker binding capacity with a longer distance of two receptors caused that the fluorescence intensity of the compound became gradually weaker.

As may be seen in Fig. 3, the sensor of monocarboxamidoquinoline did not recognize Zn^{2+} , but the sensors of bicarboxamidoquinoline might identify Zn^{2+} via fluorescence enhancement with a red-shift. This indicated that the chelation process of Zn^{2+} binding was accomplished by the cooperation of two quinolyl groups. The bicarboxamidoquinoline ligand binding to Zn^{2+} raised the rigidity of the original fluorophore and induced chelation-enhanced fluorescence (CHEF) [33–35]. The deprotonation of amide NH by the induction of Zn^{2+} promoted the ICT process, which resulted in a 110 nm red-shift [36].

Fig. 5 Fluorescent spectra of sensors (10 μM) upon the addition of Zn^{2+} . Insert: Fluorescence intensity [$I_{510\text{ nm}}$] as a function of Zn^{2+} concentration. **a** *o*-DQ **b** *m*-DQ **c** *p*-DQ ($\lambda_{\text{ex}} = 350\text{ nm}$, methanol/water=9:1, v/v, pH=8.3, 0.01 M HEPES)



Metal Ion Competition

In order to further test the interference of other common cations on the determination of Zn^{2+} , a competition experiment was carried out. As shown in Fig. 4, with the growing distance of two receptors, the number of metal ions species which could cause fluorescence quenching of sensor / Zn^{2+} complex increased gradually. A possible reason was that the sensor with a longer distance of receptors had a weaker binding capacity and was easily disturbed by other metal ions in recognition process, which was consistent with the reason of the decreasing intensity in Fig. 3.

Bonding Strength and Binding Model

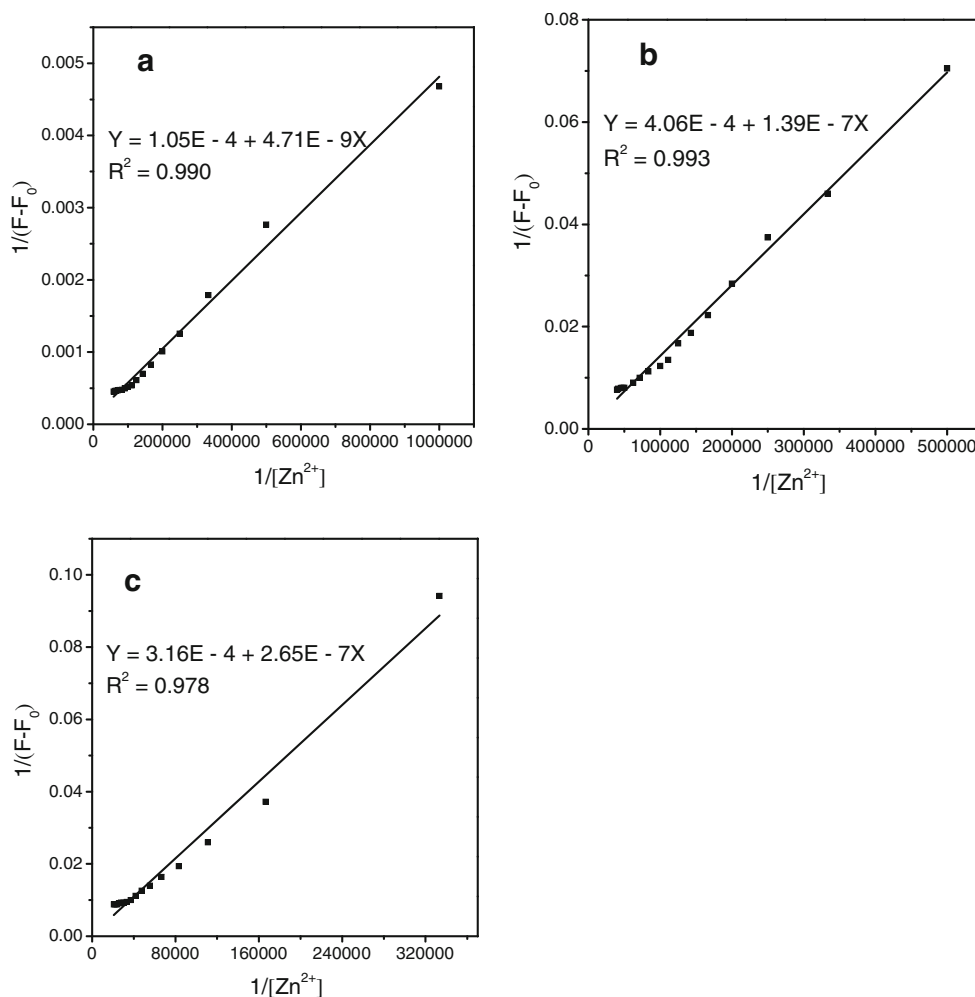
The emission spectra of sensors were examined by fluorescence titrations. As shown in Fig. 5, the saturation emission at 510 nm decreased upon increasing distance of two receptors. This might be due to the decreasing binding capacity resulting from the increasing distance. As seen in the insert picture of

Fig. 5, the maximum fluorescence intensity of *o*-DQ with 1.2 equiv. of Zn^{2+} was retained, the maximum fluorescence intensity of *m*-DQ with 2.0 equiv. of Zn^{2+} was retained, the maximum fluorescence intensity of *p*-DQ with 3.0 equiv. of Zn^{2+} was retained. The increasing changes in saturated complexation of the sensors revealed that the binding capacity decreased with increasing distance of two receptors, which confirmed the supposal of binding capacity above.

To study the binding capacity of the sensors, the binding constants of sensors with Zn^{2+} were determined from fluorescence titration data. As shown in Fig. 6, the binding constants which were obtained using the Benesi–Hildebrand equation [37, 38] were 2.21×10^4 , 2.94×10^3 and $1.19 \times 10^3 \text{ M}^{-1}$ for *o*-DQ, *m*-DQ and *p*-DQ, respectively, which further confirmed the binding capacity decreased with the growing distance of receptors. Those are consistent with the conclusion from the insert picture of Fig. 5.

Based on the results and the 1:1 stoichiometry between sensors and Zn^{2+} derived from the job's plot curves (seen in

Fig. 6 Benesi–Hildebrand plot from fluorescence titration data of sensors (10 μM). **a** *o*-DQ **b** *m*-DQ **c** *p*-DQ ($\lambda_{\text{ex}}=350 \text{ nm}$, $\lambda_{\text{em}}=510 \text{ nm}$, methanol/water=9:1, v/v, pH=8.3, 0.01 M HEPES)



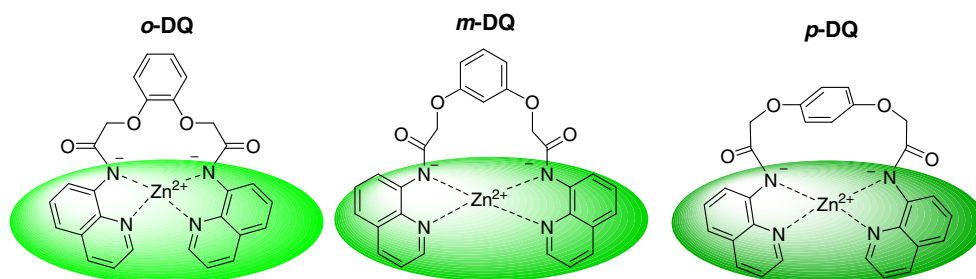
Scheme 2 Probable binding model of sensors with Zn^{2+} 

Fig. S1, supplementary material), the plausible binding model was proposed as Scheme 2.

determine limit with the growing distance of receptors indicated the sensitivity became poor.

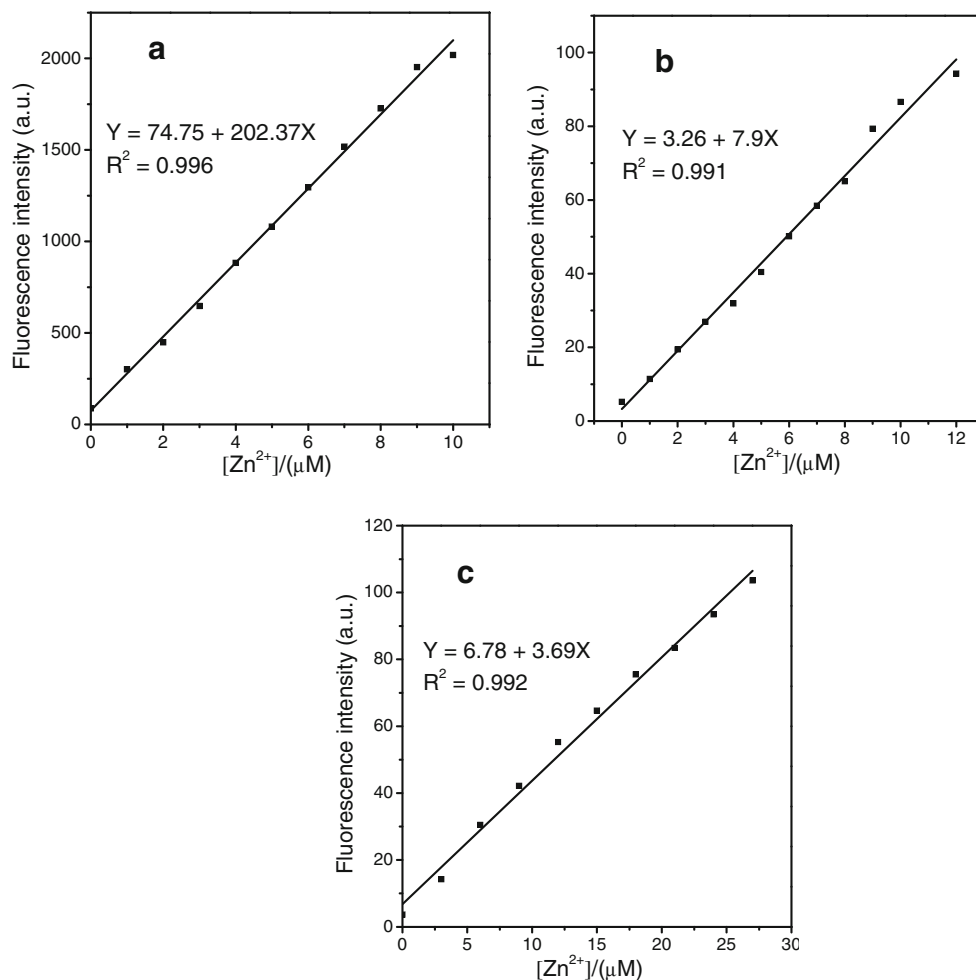
Detection Limit

To study the variation regularity of the sensitivity of sensors, the detection limit of the sensors were obtained from Fig. 7. The determine limit of the *o*-DQ was 5.3×10^{-9} M, the *p*-DQ was 5.6×10^{-8} M, the *m*-DQ was 3.1×10^{-7} M. The increasing

Conclusions

In summary, three sensors based on bicarboxamidoquinoline have been developed which can recognize Zn^{2+} with the different recognition performance. The fluorescent signal strength, the selectivity and sensitivity have been successfully

Fig. 7 Curve of fluorescence intensity at 510 nm of sensors versus increasing concentrations of Zn^{2+} . **a** *o*-DQ **b** *m*-DQ **c** *p*-DQ (λ_{ex} =350 nm, methanol/water=9:1, v/v , pH=8.3, 0.01 M HEPES)



tuned by varying the substituent positions of bicarboxamidoquinoline. As the distance of receptors grew, the fluorescent intensity and the binding constant decreased, and the detection limit increased.

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