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Convenient and highly effective fluorescence sensing for Hg^{2+} in aqueous solution and thin film

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ABSTRACT

A quinolinocyclodextrin, that is, MQAS-β-cyclodextrin (MQAS = *N*-(2-methyl-8-amino- quinolyl)-*p*-aminobenzene sulfonamide) was synthesized. Further experiments showed that it could form very stable stoichiometric 2:1 complex with Zn^{2+} in water. Significantly, the resultant quinolinocyclodextrin/Zn^{2+} complex showed the specific fluorescence response to Hg^{2+} over other metal ions, which could be readily distinguished in either aqueous solution or the PVA-based thin film. This finding would enable Zn·**3**$_2$ complex as a convenient and highly efficient fluorescence sensor for the detection of Hg^{2+}.

1. Introduction

Mercury is a highly toxic and widespread global pollutant, which could easily pass through biological membranes such as skin, respiratory, and gastrointestinal tissues.[1] Accumulation of mercury in human body is reported able to cause many serious adverse health effects, such as damages in liver, kidney, immune system, nervous system and other organs.[2] This alarming situation makes a lot of efforts greatly contributing to detecting the distribution and content of mercury and preventing its pollution. Towards this goal, a variety of methods have been developed to monitor mercury contamination in water, food, soil, and so on. Among the various methods to monitor mercury ions under the toxicological and environmental conditions, fluorescence chemosensors are widely regarded as one of the most effective ways. So far, a number of fluorescence Hg^{2+} sensors, such as small molecules,[3] gold nanoparticles,[4] DNAzymes,[5] protein,[6] oligonucleotide[7] and polymers,[8] have been reported. However, most of these sensors suffer from the poor water solubility and the non-specific interference from Cu^{2+}, Ni^{2+} and other competing metal ions. Recently, we reported that several quinolino-modified β-cyclodextrins could be used as fluorescence Zn^{2+} probes, showing the satisfactory water solubility and the good sensing ability to Zn^{2+}.[9] In this work, we synthesized another quinolinocyclodextrin, that is, MQAS-β-CD (**3**, MQAS = *N*-(2-methyl-8-amino-quinolyl)-*p*-aminobenzene sulfonamide), and found that it could form very stable stoichiometric 2:1 complex with Zn^{2+} in water. Significantly, the resultant Zn·**3**$_2$ complex exhibited the specific fluorescence response to Hg^{2+}, which could be readily distinguished in either aqueous solution or the PVA-based thin film. This finding would enable Zn·**3**$_2$ complex as a convenient and highly efficient fluorescence sensor for the detection of Hg^{2+}.

2. Results and discussion

The coordination behavior of **3** with Zn^{2+} was investigated by the UV–vis titration at 298 K in aqueous solution. Figure 1a illustrates the typical UV–vis curves of **3** with the gradual addition of Zn^{2+}. As can be seen in Figure 1a, a new absorption peak appeared at 352 nm in the UV–vis spectrum of **3**, and its intensity gradually increased with the stepwise addition of Zn^{2+}. This absorption was expected to correspond to the formation of a five-membered chelate ring between two nitrogen atoms in MQAS unit of **3** and Zn^{2+}, which extended the conjugated system and thus resulted in the appearance of the new absorption in the long wavelength region. In the control experiment, the UV–vis spectrum of Zn^{2+} within the appropriate concentration range displayed no appreciable absorption between 200 and 450 nm under comparable experimental conditions. These indicated that the Zn^{2+} was coordinated to **3**. Moreover, the molar ratio method using the UV–vis spectrometry gave the coordination stoichiometry between **3** and Zn^{2+}. As seen in Figure 1b, the curve of $\Delta A_{\mathbf{3}/Zn^{2+}}$ ($\Delta A_{\mathbf{3}+Zn^{2+}} = A_{\mathbf{3}+Zn^{2+}} - A_{\mathbf{3}}$, $A_{\mathbf{3}}$ was defined as the absorption intensity of **3** at 352 nm) versus Zn^{2+}/**3** molar ratio showed an inflexion point at a molar ratio of 0.5, which corresponded to a 2:1 coordination stoichiometry between **3** and Zn^{2+}. Based on these observations, we deduced the

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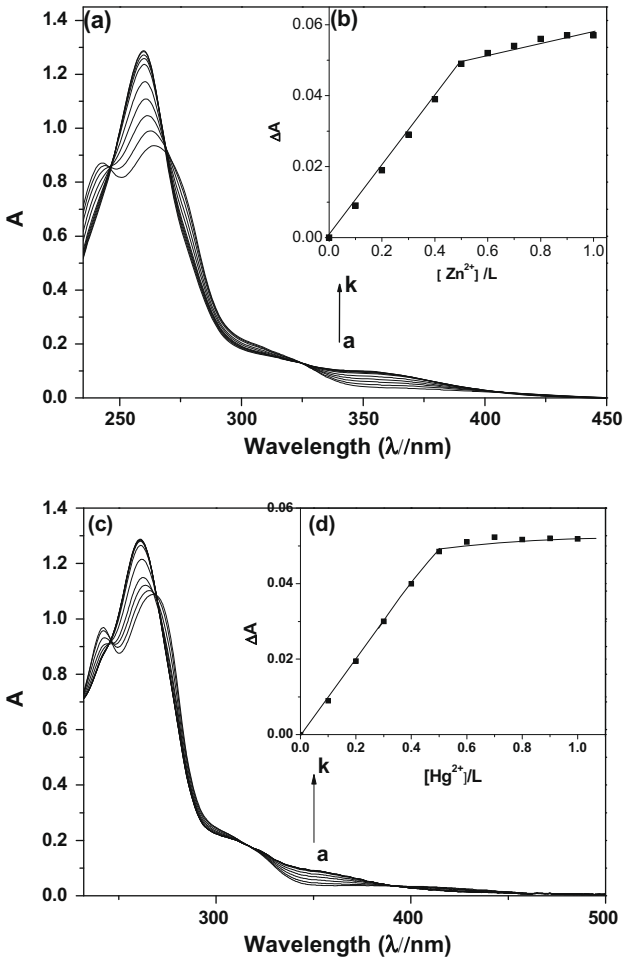


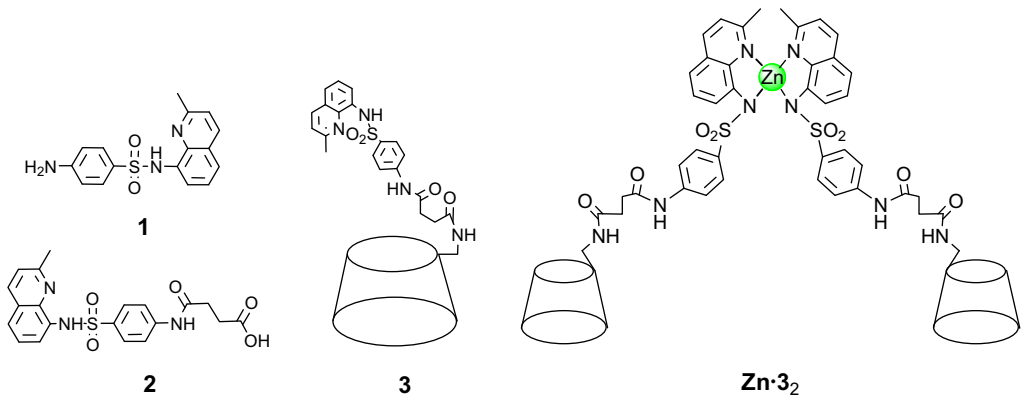
Figure 1. (a) UV–vis spectra of **3** upon the addition of Zn^{2+} in buffer solution (pH 7.2, I = 0.1 M $NaNO_3$) at 25 °C. ([**3**] = 40 μM, [Zn^{2+}] = 0–40 μM from a to k); (b) the absorption changes of **3** at 352 nm upon the addition of Zn^{2+}; (c) UV–vis spectra of **3** upon the addition of Hg^{2+} in buffer solution (pH 7.2, I = 0.1 M $NaNO_3$) at 25 °C. ([**3**] = 40 μM, [Hg^{2+}] = 0–40 μM from a to k); (d) the absorption changes of **3** at 352 nm upon the addition of Hg^{2+}.

possible coordination mode of Zn·$\mathbf{3}_2$ as shown in Scheme 1. Moreover, the binding ability of **3** to Zn^{2+} was quantitatively determined by a competitive binding method[9a] using fluorescence titration, and the apparent stability constant (log K, $K = [Zn{\cdot}\mathbf{3}_2]/[Zn^{2+}][\mathbf{3}]^2$) of Zn·$\mathbf{3}_2$ complex was observed to be equal to 12.4. It should be noted that, when the Zn^{2+}/**3** molar ratio exceeded 0.5, the absorbance still changed with the increase of Zn^{2+} concentration up to 1:1 Zn^{2+}/**3** molar ratio. Through a simple calculation based on the apparent stability constant of Zn·$\mathbf{3}_2$ complex and the concentrations of Zn^{2+} and **3**, there should existed 5.5% free **3** in solution at a molar ratio of 0.5. With the increase of Zn^{2+} concentration up to 1:1, 4.2% free **3** would further convert to Zn·$\mathbf{3}_2$ complex, which consequently resulted in the further increase of the absorbance upon the addition of Zn^{2+} between 0.5 and 1 Zn^{2+}/**3** molar ratio. Considering the concentrations of **3** and Zn^{2+} employed in our experiments, this strong binding ability of **3** to Zn^{2+} indicated that most of **3** was converted to Zn·$\mathbf{3}_2$ in a 2:1 **3**/Zn^{2+} mixture. Therefore, Zn·$\mathbf{3}_2$ could be prepared in situ by mixing **3** and $Zn(OAc)_2$ with a molar ratio of 2:1 in our experiments. Like many reported sulfonamidoquinoline/Zn^{2+} complexes,[10] Zn·$\mathbf{3}_2$ exhibited a satisfactory fluorescence emission (quantum yield 0.312), giving an emission maximum at 500 nm.

Significantly, Zn·$\mathbf{3}_2$ showed the good fluorescence sensing ability to Hg^{2+}. As can be seen in Figure 2, the fluorescence intensity of Zn·$\mathbf{3}_2$ complex at 500 nm gradually decreased with the stepwise addition of Hg^{2+}. After 1 equiv of Hg^{2+} was added, ca. 50% of the emission intensity of Zn·$\mathbf{3}_2$ complex was quenched, and this value would further increase to 88% when adding 4 equiv of Hg^{2+}. A possible reason for the quenched fluorescence may be the competition of Hg^{2+} and Zn^{2+} in coordinating with **3**. Using the same methods, the stoichiometry and the apparent stability constant (log K', $K' = [Hg{\cdot}\mathbf{3}_2]/[Hg^{2+}][\mathbf{3}]^2$) for the coordination of **3** with Hg^{2+} were measured to be 2:1 and 13.3, respectively. On the other hand, the apparent stability constants (log K, $K = [M{\cdot}\mathbf{3}_2]/[M^{2+}][\mathbf{3}]^2$) of other metal ions, such as Cu^{2+}, Ni^{2+}, Cd^{2+}, Cr^{2+}, etc, with **3** were determined to be less than 10. This indicated that, with the addition of Hg^{2+} to Zn·$\mathbf{3}_2$, a part of Zn·$\mathbf{3}_2$ would convert to fluorescent inert Hg·$\mathbf{3}_2$, which consequently resulted in the quenched fluorescence. In addition, the detection limit ($3\sigma/K$) of this probe for Hg^{2+} was determined to be 3.0×10^{-7} mol L^{-1}.

It is noteworthy that Zn·$\mathbf{3}_2$ maintained its good fluorescence sensing ability to Hg^{2+} over a wide pH range. As can be seen in Figure 3, Zn·$\mathbf{3}_2$ barely fluoresced at a pH value below 4 either with or without Hg^{2+}, which may be due to the competition of H^+ at low pH values leading to a weak coordination ability of metal ion with **3**.[9a] However, when the pH value increased to the 5–10 range, Zn·$\mathbf{3}_2$ showed the satisfactory fluorescence sensing ability to Hg^{2+} with the $F_{Zn{\cdot}\mathbf{3}_2+Hg^{2+}}/F_{Zn{\cdot}\mathbf{3}_2}$ value varied in a range of 0.15–0.74. This available pH scope of Zn·$\mathbf{3}_2$ for Hg^{2+} was practicable to the drinking water, food and soil.

As an effective Hg^{2+} sensor, Zn·$\mathbf{3}_2$ exhibited good fluorescence sensing selectivity to Hg^{2+}. Figure 4 illustrates the fluorescence intensities of Zn·$\mathbf{3}_2$ at 500 nm in the presence of various metal ions, especially possible competing ions when Zn·$\mathbf{3}_2$ was used as one



Scheme 1. The chemical structures of **1**, **2**, **3** and Zn·$\mathbf{3}_2$.

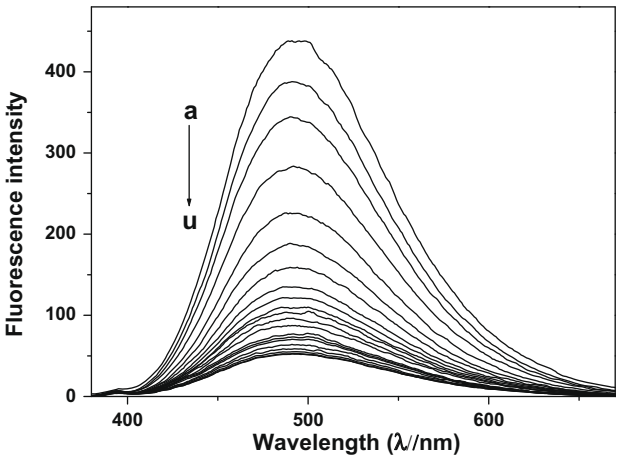


Figure 2. Fluorescence spectral changes of Zn·**3**$_2$ (10 μM) complex with addition of Hg^{2+} (0–40 μM from a to u) in aqueous buffer solution (pH 7.20) at 298 K (λ_{ex} = 352 nm).

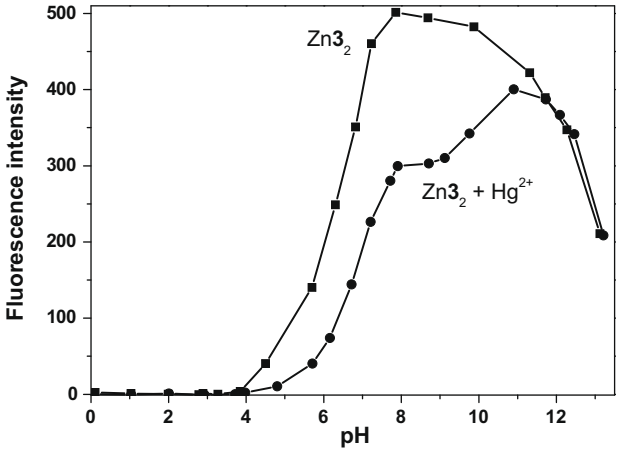


Figure 3. Fluorescence intensities of Zn·**3**$_2$ (10 μM) in the absence and presence of Hg^{2+} (10 μM) at various pH values in aqueous solution at 298 K (λ_{ex} = 352 nm, λ_{em} = 500 nm).

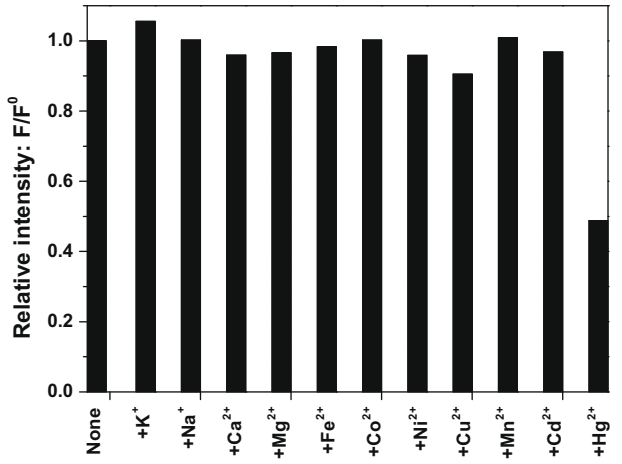


Figure 4. Fluorescence intensities of Zn·**3**$_2$ (10 μM) in the presence of various metal ions. ([K^+] = [Na^+] = [Ca^{2+}] = [Mg^{2+}] = 5 mM, [Fe^{2+}] = [Co^{2+}] = [Ni^{2+}] = [Cu^{2+}] = [Mn^{2+}] = [Cd^{2+}] = [Hg^{2+}] = 10 μM). All data were obtained in aqueous buffer solution (pH 7.2) at 298 K (λ_{ex} = 352 nm, λ_{em} = 500 nm) and normalized with respect to the emission intensity of free Zn·**3**$_2$ (F_0).

Hg^{2+} sensor in the environment. As can be seen in Figure 4, the fluorescence intensity of Zn·**3**$_2$ only showed slight changes ($1.06 > F/F_0 > 0.95$) in the presence of a large excess of (500 equiv) of alkali metal ions (Na^+, K^+) and alkali earth metal ions (Ca^{2+}, Mg^{2+}) or the equivalent amount of transition metal ions (Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, Cd^{2+}), and these changes in no case approached the corresponding quenching effect observed for Hg^{2+} (F/F_0 = 0.5), which unambiguously demonstrated the high sensing selectivity of Zn·**3**$_2$ to Hg^{2+} over other ions.

Besides in water, Zn·**3**$_2$ also exhibited the good fluorescence sensing ability to Hg^{2+} in organic thin film, which could be readily distinguished under the UV light. Herein, the organic thin film was prepared by casting the aqueous poly(vinyl alcohol) (PVA) solution of Zn·**3**$_2$ on glass slips and then dried in air. As can be seen in Figure 5, the fluorescence intensity of Zn·**3**$_2$—contained film obviously quenched when Hg^{2+} was dripped on, but quite slightly or hardly responded to other metal ions, such as Cu^{2+}, Ni^{2+}, Cr^{2+}, which was basically consistent with the sensing selectivity of Zn·**3**$_2$ in water. In the control experiment, Zn/**2** or Zn/**1** system, which was poorly soluble in water, was found to difficult to achieve a homogeneous dispersion in the PVA film.

In conclusion, we successfully prepare a water soluble quinolin-ocyclodextrin/Zn^{2+} complex in situ as a fluorescence sensor for Hg^{2+}. This sensor system presents the obvious fluorescence responses, which can be readily monitored by both eyes and fluorescence spectroscopy, to Hg^{2+} in either water solution or organic thin film, and this fluorescence sensing was not obviously affected by a variety of cations. Considering its satisfactory water solubility, convenience in Hg^{2+}-detection, and high sensing specificity for Hg^{2+} over other competing cations, this complex is expected to have potential application to meet the detection requirements of an Hg^{2+} assay in environmental fields.

3. Experimental

3.1. Materials

All chemicals used were reagent grade unless noted. 2-Methyl-8-amino-quinoline was obtained from J & K Chemical LTD. Acetanilide,

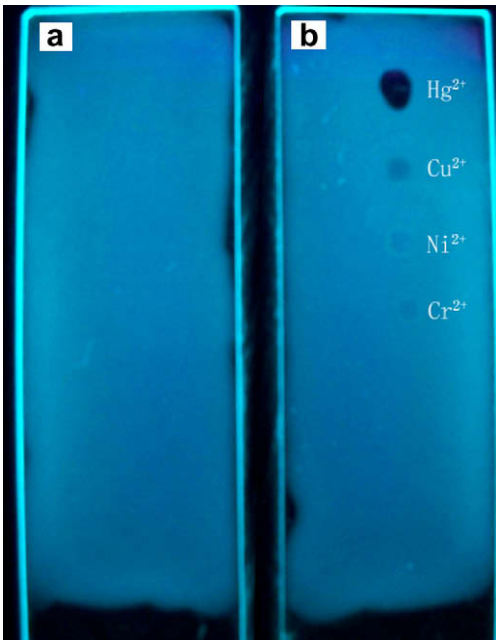


Figure 5. Images of Zn·**3**$_2$—contained PVA film in the absence (a) and (b) presence of metal ions under the low intensity UV light (λ = 360 nm).

sulfurochloridic acid, and succinic anhydrides were all obtained from Aldrich. Poly(vinyl alcohol) (PVA, $M_w = (7.79 \pm 0.2) \times 10^4$) was provided by the Chemical & Engineering Department of Tianjin University and used as a polymer matrices. β-Cyclodextrin (β-CD) of reagent grade was recrystallized twice from water and dried in vacuo at 95 °C for 24 h prior to use. *N*,*N*-Dimethyl-formamide (DMF) was dried over CaH_2 for 2–3 days and then distilled under reduced pressure prior to use. Pyridine was dried over CaH_2 for 2–3 days and then distilled prior to use. 6-Amino-β-CD was prepared according to the procedure described in the literature.[11] 4-Acetamidobenzene-1-sulfonyl chloride was prepared by the reaction of acetanilide with HSO_3Cl.

3.2. Measurements

Elemental analyses were performed on a Perkin–Elmer-2400C instrument. ^1H NMR spectra were recorded on a Varian Mercury VX300 spectrometer. UV–vis spectra were recorded in a 10 mm quartz cell on a Shimadzu UV-3600 UV–vis-NIR spectrophotometer (SHIMADZU corporation) equipped with a TCC-240 thermoelectrically temperature controlled cell holder to keep the temperature at 298 K. Fluorescence spectra were recorded in a conventional quartz cell (10 × 10 × 45 mm) at 298 K on a JASCO FP-750 fluorescence spectrometer (xenon lamp photosource) equipped with a PTC-348WI temperature controller to keep the temperature at 298 K. The measurement of pH value in water was performed on a PHS-3C pH-meter (Shanghai Rex Instruments Factory). Fluorescence images were performed on a ZF-7B three-used ultraviolet analysis instrument (Shanghai Kanghua Biochemistry instrument Co., LTD) and a Kodak Z885 zoom digital camera (Eastman Kodak Company) for photo collection. Tris-HCl buffer solution (pH 7.2) was used as solvent in all spectral measurements.

3.3. Synthesis

3.3.1. *N*-(2-Methyl-8-amino-quinolyl)-*p*-acetylamidobenzenesulfonamide (MQAAS)

To the solution of 2-methyl-8-amino-quinoline (840 mg, 5.4 mmol) in 3 mL of anhydrate pyridine was added 4-acetamidobenzene-1-sulfonyl chloride (1.42 g, 6 mmol) in potions. The mixture was stirred for 1 h at room temperature, then at 60 °C for 3–4 h. The reaction mixture was poured onto 20 mL of ice. At the same time the glass stick was used to stir the mixture and rub the wall of the glass beaker to produce a brown precipitate. The precipitate was collected by filtration and dried in vacuo to afford the crude product of MQAAS (800 mg, 43% yield) as brown needles. Mp: 200 °C. The crude product was used directly without further purification.

3.3.2. *N*-(2-Methyl-8-amino-quinolyl)-*p*-aminobenzenesulfonamide (1)

To an aqueous solution (15 mL) containing 1.5 mL of conc. hydrochloric acid was added MQAAS (1.5 g, 4.2 mmol). The mixture was stirred at 90 °C for 3–4 h. Then the mixture was neutralized to pH 6–7 with the aqueous solution of NaOH (10%), and then cooled to room temperature. The precipitate was collected by filtration, washed with water, and dried in vacuo to get the crude product as black green crystal. The crude product was recrystallized from EtOH to afford **1** (1.0 g, 76% yield) as a beige crystal. MS (ESI): *m/z* 312.37 ($[M-H]^-$), 485.4 ($[M+NH_2PhSO_3]^-$). ^1H NMR ($CDCl_3$, 300 MHz, TMS, ppm): δ 2.690 (s, 3H, quinoline-CH_3), 3.995 (s, 2H, Ph–NH_2), 6.529 (d, J = 8.7 Hz, 2H, H^3 and H^5 of Ph), 7.294 (d, J = 7.8 Hz, 1H, quinoline), 7.329–7.397 (m, 2H, quinoline), 7.671–7.754 (m, 3H, Ph and quinoline), 7.955 (d, J = 8.4 Hz, 1H, quinoline), 9.218 (s, 1H, SO_2–NH–). Anal. Calcd for $C_{16}H_{15}N_3O_2S$: C, 61.32; H, 4.82; N, 13.41; S, 10.23. Found: C, 61.08; H, 4.90; N, 13.57; S, 10.17.

3.3.3. *N*-MQAS-4-amino-4-oxobutanoic acid (2)

To 200 mL of toluene was added **1** (3.0 g, 9.6 mmol) and succinic anhydrides (9.6 g, 96 mmol). The mixture was stirred at 150 °C for 5 h. After cooled to room temperature, the precipitate was collected by filtration, washed with 100 mL of hot water and dried in vacuo to give a slight yellow solid, which was recrystallized from EtOH twice and dried in vacuo to afford **2** (2.4 g, 61% yield) as a slight green crystal. MS (ESI): *m/z* 412.20 ($[M-H]^-$), 447.98 ($[M+Cl]^-$), 824.92 ($[2M-H]^-$). ^1H NMR (DMSO-d_6, 300 MHz, TMS, ppm): δ 2.504 (s, 4H, –CH_2–CH_2– overlapped with the peak of DMSO), 2.674 (s, 3H, quinoline-CH_3), 7.434 (m, 2H, quinoline), 7.617 (m, 3H, quinoline), 7.837 (d, J = 8.7 Hz, 2H, Ph), 8.212 (d, J = 8.4 Hz, 2H, Ph), 9.603 (s, 1H, Ph–NH–), 10.292 (s, 1H, quinoline-NH–), 12.103 (s, 1H, COOH). Anal. Calcd for $C_{20}H_{19}N_3O_5S{\cdot}0.25H_2O$: C, 56.86; H, 5.73; N, 9.95; S, 7.59. Found: C, 56.90; H, 5.70; N, 10.00; S, 7.60.

3.3.4. MQAS-β-CD (3)

To 20 mL of anhydrate DMF was added **2** (220 mg, 0.53 mmol) and HOBt (81 mg, 0.6 mmol). After the mixture was stirred at 0 °C for 2 h, DCC (124 mg, 0.6 mmol) was added. The mixture was stirred at 0 °C for 3 h, then 6-amino-β-CD (600 mg, 0.53 mmol) was added. The reaction mixture was stirred for 6 h in an ice bath, then at room temperature for 2 days. The precipitate was filtrated off, and the filtrate was poured into 300 mL of acetone and stirred for 3 h. The precipitate was collected by filtration, dried in vacuo, and purified by column chromatography on a Sephadex CM-25 column with 1 M NH_3 aqueous solution (500 mL) as the eluent to give **3** as a brown solid (200 mg, 25% yield). MS (ESI): *m/z* 1527.54 ($[M-H]^-$), 1563.43 ($[M+Cl]^-$). ^1H NMR (D_2O, 300 MHz, TMS, ppm): δ 2.565 (d, J = 8.1 Hz, 2H, –CH_2–), 2.677–2.884 (5H, CO–CH_2 and quinoline-CH_3), 2.888–4.273 (42H, H^2∼H^6 of β-CD), 5.029 (d, J = 16.5 Hz, 7H, H^1 of β-CD), 7.373 (s, 1H, H^7 of quinoline), 7.454–7.642 (4H, H^3, H^5 of Ph and H^3, H^5 of quinoline), 7.775 (d, J = 7.2 Hz, 1H, H^6 of quinoline), 7.919 (d, J = 8.1 Hz, 2H, H^2, H^6 of Ph), 8.406 (d, J = 8.4 Hz, 1H, H^4 of quinoline). Anal. Calcd for $C_{62}H_{88}N_4O_{38}S{\cdot}H_2O$: C, 48.69; H, 5.80; N, 3.66; S, 2.10. Found: C, 48.50; H, 5.90; N, 3.64; S, 2.04.

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