Supporting Information

Design and synthesis of molecule with aggregation-induced emission effect and its application in detection of arsenite in groundwater

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Contents

Section A. Materials and method

Section B. Synthesis of 1 and 2

Section C. Spike and recovery test of As³⁺ in real water samples

Section D. Test of fluorescence quantum yield

Section E. Supplementary spectra data

Section F. ¹H and ¹³C NMR spectra and MS spectra

Section A. Materials and method

All chemicals and solvents purchased from Aladdin were used without further purification. Ultrapure water (18.25 M Ω cm) was used throughout all the experiments.

The structures of the products synthesized in this paper were identified by ¹H-NMR spectra, ¹³C-NMR, Mass spectra and Elemental Analysis. ¹H and¹³C NMR spectra were measured in *d*₆-DMSO with a Bruker Avance 400 MHz NMR spectrometer. Mass spectra were recorded on an APEXII-electrospray ionization (ESI) instrument. Elemental Analysis were recorded on an Elementar Vario EL cube. Fluorescence signals were recorded on a HITACHI F-7000 with excitation and emission slits width of 5 nm. UV–vis spectra studies were carried out on a Perkin Elmer Lambda 35 spectrophotometer. Particle size distribution analysis was determined by an ALV-5000 dynamic laser light scattering (DLS). The absolute fluorescence quantum yield was measured by Edinburgh Ins FLS920.

Section B. Synthesis of intermediate 1 and 2

Synthesis of intermediates 1



Scheme S1 Synthesis of intermediates 1

First, a mixture of dioxane (20 mL) and aqueous 2 M K_2CO_3 (5 mL) was repeatedly degassed by evacuation and purging with argon gas and into it, 3,5dibromobenzaldehyde (0.53 g, 2 mmol) and the appropriate (9-phenylcarbazol-3yl)boronic acid (1.29 g, 4.5 mmol) along with 2.5 mol % Pd(PPh_3)₄ (60 mg) were added. Then the mixture was refluxed in an argon atmosphere for 16 h under the complete exclusion of light. Finally, the reaction was quenched with the addition of 30 mL 10% HCl aqueous and organic layer was extracted with dichloromethane. The extracted organic layer was washed consecutively with water and brine before being dried over MgSO₄. After drying under reduced pressure, the reaction afforded pale solid of intermediate **1** and then the **1** was purified by silica gel column chromatography using ethyl acetate/hexanes as the eluent. The obtained product was used in the next step without any further purification.

¹H NMR (400MHz, *d*₆-DMSO) δ (ppm): 9.32 (s, 1H), 7.84 (d, 4H), 7.70-7.60 (m, 10H), 7.57-7.48 (m, 8H), 7.42-7.25 (m, 5H).

¹³C NMR (400MHz, d₆-DMSO) δ (ppm): 183.73, 140.61, 137.33, 130.63, 128.12, 127.16, 126.69, 123.14, 120.97, 120.48, and 116.30.

ESI-MS (m/z): calcd for C₄₃H₂₈N₂O [M]⁺, 588.12; found, 588.1.

Elemental analysis: calcd for C₄₃H₂₈N₂O: C, 87.73; H, 4.79; N, .76. Found: C, 87.55; H, 4.84; N, 4.82.

Synthesis of probe 2



Scheme S2 Synthesis of probe 2

A mixture of intermediate 1 (588 mg, 1 mmol) and cysteine (182 mg, 1.5mmol) and a few drops of glacial acetic acid were refluxed in methanol (30 mL) overnight. After reaction, amount of cold distilled water was added into the mixture and give a precipitate. The pale yellow precipitate was collected by filtration and washed several time with cold methanol and distilled water (295 mg, 42%).

¹H NMR (400MHz, *d*₆-DMSO) δ (ppm): 9.82 (s, 1H), 8.23-8.16 (m, 4H), 8.01-7.88 (m, 2H), 7.67-7.48 (m, 10H), 7.41-7.23 (m, 12H), 4.1 (t, 1H), 3.11-2.94 (m, 2H). ¹³C NMR (400MHz, *d*₆-DMSO) δ (ppm): 167.49, 158.31, 140.61, 137.33, 130.63, 128.12, 127.16, 126.63, 123.18, 120.97, 114.03, 111.97, 110.03, 66.43, and 26.14.

ESI-MS (m/z): calcd for C₄₆H₃₃N₃O₂S [M]⁺, 691.2; found, 691.1.

Elemental analysis: calcd for C₄₆H₃₃N₃O₂S: C, 79.86; H, 4.81; N, 6.07; S, 4.63. Found: C, 79.77; H, 4.84; N, 6.11; S, 4.62.

Section C. Spike and recovery test of As³⁺ in real water samples

The recovery test of As^{3+} was conducted in real water samples, including ultrapure water, tap water, Yangtze River water and Jianghan Plain groundwater. All real water samples were first filtered by filter paper (D = 0.45 µM) and then boiled for 5 min to remove any impurities. After the pretreatment, the real water samples were spiked with different amount of As^{3+} (10 ppb, 100 ppb and 500 ppb), each concentration was done in triplicate and the average was used as the final result.

In detail, 2 mL of **2** solution (water/THF, 7/3; pH=7.1) was first dispersed into a spectrophotometer quartz cuvette, then 100 μ L of the real water samples spiked with different concentrations of As³⁺ was introduced. In this process, the total concentration of As³⁺ in the cuvette was kept at 10 ppb, 100 ppb and 500 ppb, respectively. The fluorescence spectra of **2** from 380 nm to 640 nm were recorded after 2 minutes, and all measurements were performed at least in triplicate at ambient conditions.

Section D. Test of fluorescence quantum yield

The relative fluorescence quantum yield (FQY) of compound **1** and **2** in solution and aggregate state were measured using an anthracene ($\Phi_r = 0.27$) as standard.¹ The FQY of **1** and **2** in solution state was tested in water/THF mixtures (v/v, 7:3). The FQY of **2** in aggregate state was studied in the presence of 240 ppb of As³⁺ in water/THF mixtures (v/v, 7:3). Because the compound **1** cannot form the aggregate state, thus the FQY of **1** is not measured in this test. The fluorescence spectra of the samples were recorded with the excitation wavelength of 330 nm and the relative fluorescence was determined by weighing the area beneath the corrected fluorescence emission spectrum. The absorbance was recorded in water/THF mixtures. Finally, the FQY was calculated as a follow equation:²

$$\frac{F_s}{\Phi_s = \Phi_r} \times \frac{A_r}{A_s}$$
Where Φ_s and Φ_r are the FQY of

the sample and the reference respectively, A_s and A_r represent the absorbance of the sample and the reference at 330 nm, respectively. F_s and F_r are the areas of emission (calculated by Origin 8.5) for sample and reference, respectively.

The absolute FQY of 1 and 2 in solid state was measured by Edinburgh Ins FLS920 (using the integrating sphere, the error is within $\pm 3\%$).



Section E. Supplementary spectra data

Fig. S1 The absorption and emission of 1 and 2 in solution and aggregate state.



Fig. S2 The fluorescence intensity changes of 2 (10 μ M) with the different water content in THF-water mixtures.



Fig.S3 Dimensional fluorescence of the **2** with the addition of 100 ppb of As^{3+} in THF-water mixtures (v/v, 3/7). Form the figure we can know that the excitation wavelength is 330 nm, emission wavelength is 455 nm.



Fig. S4 The plot of $[(I-I_0)/I_0]$ at 460 nm in THF-water mixtures (v/v, 3/7) *vs.* the concentration of As³⁺ (0-240 ppb).



Fig. S5 The selectivity and anti-interference of 2. The red bars represent the fluorescence responses of 2 (10 μ M) to various anions under the same conditions. The gray bars represent the fluorescence of above solution upon subsequent addition of 200 ppb of As³⁺. All experiments were carried out in water/THF mixture (v/v, 7/3; pH =7.1).



Fig. S6 Absorption spectra of 2 (10 μ M) in THF-water mixtures (v/v, 3/7) in the presence of different amount of As³⁺ (from 0 to 240 ppb)



Fig. S7 Job's plot of 2 with As^{3+} in water/THF mixtures (v/v, 7/3; PBS, 10mM; pH=7.1). The Job's analysis was carried out to determine the binding stoichiometry of the 2-As³⁺ complex by keeping the sum of the concentration of As^{3+} and 2 at 10 μ M. The emission intensity at 455 nm versus the mole fraction of As^{3+} was measured.

Compound	State	${f \Phi}_F{}^{[a]}$	$\lambda_{em}(nm)^{[b]}$	$\mathbf{E}_{m,int}^{[c]}$
1	solution	0.007	437	101
	solid		425	1052
2	solution	0.024	455	195
	aggregate	0.381	464	1201
	solid		434	1635

Table S1 The spectroscopic data of compound 1 and 2

[a]: Φ_F is the fluorescence quantum yield. [b]: λ_{em} is the maximum emission peak. [c]: FL is the emission intensity at λ_{em} .

method	LOD(ppb)	reference
Schiff base system	4.10	13
L-cysteine capped CdS quantum dots	0.75	2^{4}
Functionalized gold nanoparticles	2.58-2.84	35
Cationic polymers and aptamers probe	5.30	46
Functionalized silver nanoparticles	0.76	57
Surface-enhanced raman spectroscopy	1.00	68
Glutathione-capped CdTe quantum dots	1.50	7 ⁹
Nano-sized arsenic-imprinted polymer	37.50	810
gold cluster-based fluorescent sensor	4.01	9 ¹¹
Pulsed Laser-Induced Desorption	1.87	1012
IC-HG-AFS	1.00-3.00	1113
Cys-AIE sensor	1.32	This work

Table S2 Comparison of the LOD for the detection of As^{3+} .

Table S3. Recovery test of As^{3+} in real water samples.

Spiked	DI water		Тар	Tap-water		Yangtze River water		Jianghan Plain groundwater	
concentration/ppb	Found/ppb	Recovery/%	Found/ppb	Recovery/%	Found/ppb	Recovery/%	Found/ppb	Recovery/%	
10	9.64	96.4±4.5	10.28	102.8±5.2	9.15	91.5±5.3	8.89	88.9±5.9	
100	97.2	97.6±4.1	92.77	92.7±4.4	90.21	90.2±4.7	89.91	89.4±5.6	
500	465.5	92.8±3.1	461.21	92.2±3.6	457.85	91.4±3.9	442.57	88.4±4.1	









Fig. S9 The 13 C NMR spectrum of 1 in d_6 -DMSO



Fig. S10 The ¹H NMR spectrum of 2 in d_6 -DMSO



Fig. S11 The ¹³C NMR spectrum of 2 in d_6 -DMSO



Fig. S12 ESI-Mass spectrum of 1



Fig. S13 ESI-Mass spectrum of 2



Fig. S14 ESI-Mass spectrum of $As(2)_3$

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