Supplementary Information

Determination of ammonium in natural water using a quinoline-based *o*-dialdehyde fluorescent reagent with visible excitation wavelength

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(1) Characterization of compound 1 and 2 by gas chromatography - mass spectrometry

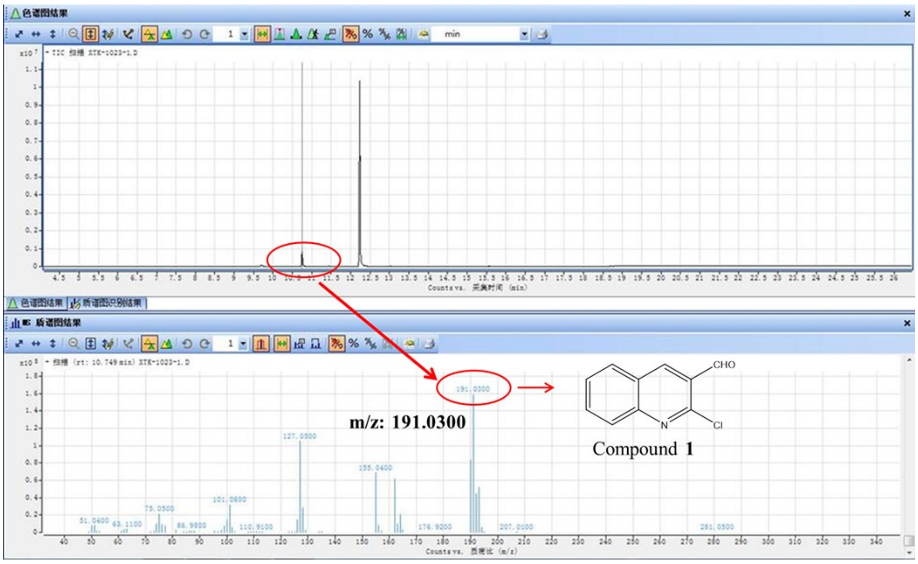

Fig. S1. Separation of Compound 1 by GC - MS

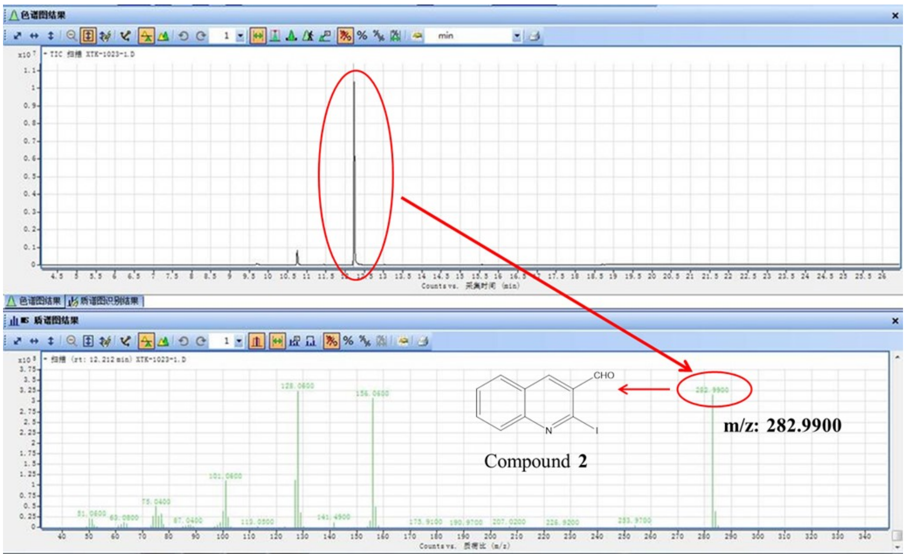

Fig. S2. Separation of Compound 2 by GC - MS

(2) Characterization of compound 3 and 4 and QDA by nuclear magnetic resonance (NMR) spectroscopy

The NMR results are shown below. Fig. S3 shows the NMR spectrum of compound 3.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.20 (s, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.59-7.56 (m, 1H), 6.05 (s, 1H), 4.21 – 4.13 (m, 4H).

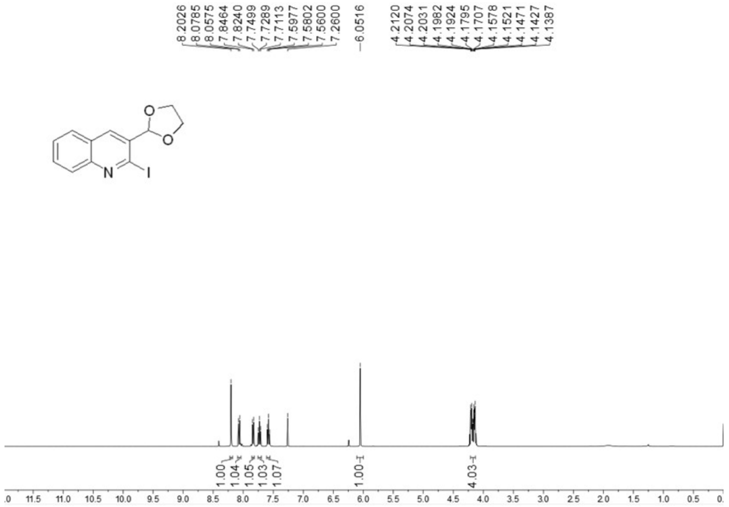

Fig. S3. The NMR spectrum of compound 3

Fig. S4 shows the NMR spectrum of compound 4.

^{1}H NMR (400 MHz, Chloroform-d) δ 10.32 (s, 1H), 8.61 (s, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.859-7.817 (m, 1H), 7.73-7.69 (m, 1H), 6.85 (s, 1H), 4.15 (s, 4H).

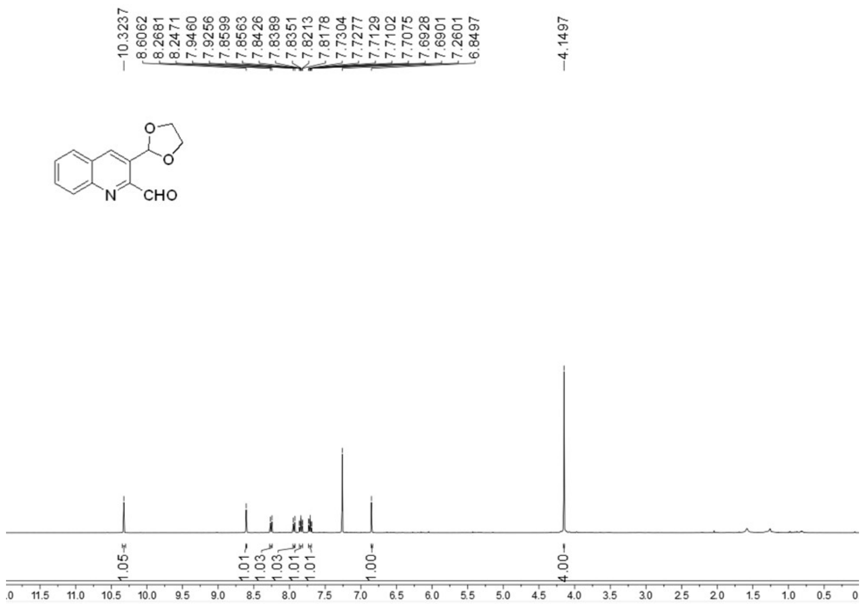

Fig. S4. The NMR spectrum of compound 4

Fig. S5 shows the NMR spectrum of quinoline-2,3-dialdehyde.

[1]H NMR (400 MHz, Chloroform-*d*) δ 10.97 (s, 1H), 10.36 (s, 1H), 8.82 (s, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.98-7.93 (m, 1H), 7.76-7.80 (m, 1H).

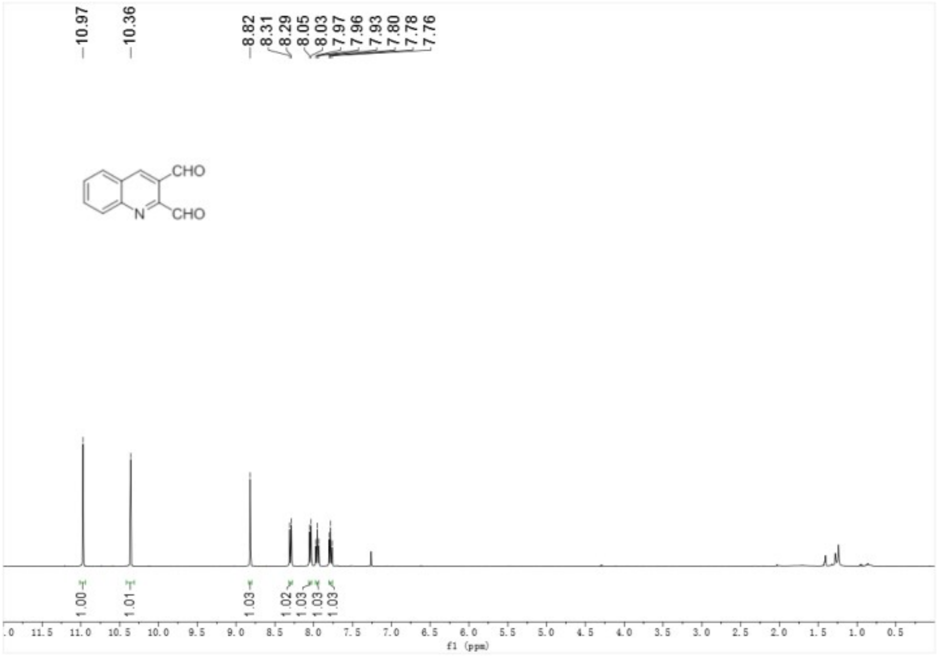

Fig. S5. The NMR spectrum of quinoline-2,3-dialdehyde

(3) Characterization of blank and QDA - NH_4^+ - SO_3^{2-} product by HPLC-MS

HLB SPE cartridge was used to extract the QDA product from water, then the HLB cartridge was eluted with methanol and the eluted fraction was injected into a HPLC-MS. The corresponding HPLC-MS results of blank and product are as following:

Fig. S6. Characterization of blank (QDA - SO_3^{2-}) by HPLC-MS

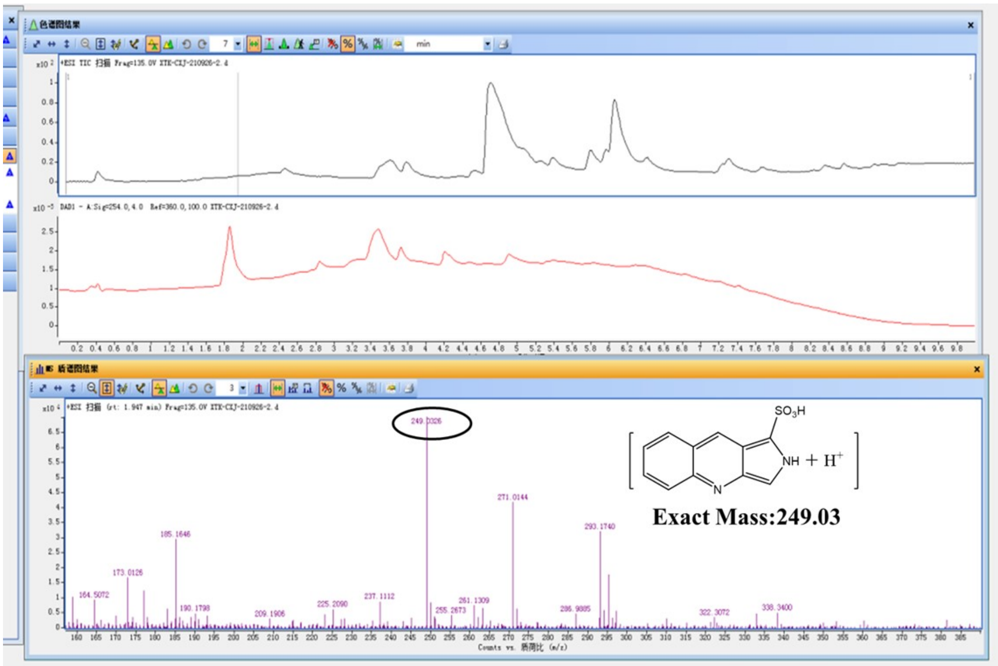

Fig. S7. Characterization of QDA - NH_4^+ - SO_3^{2-} product by HPLC-MS

(4) Excitation and emission spectra of fluorescence products added with different concentrations of QDA

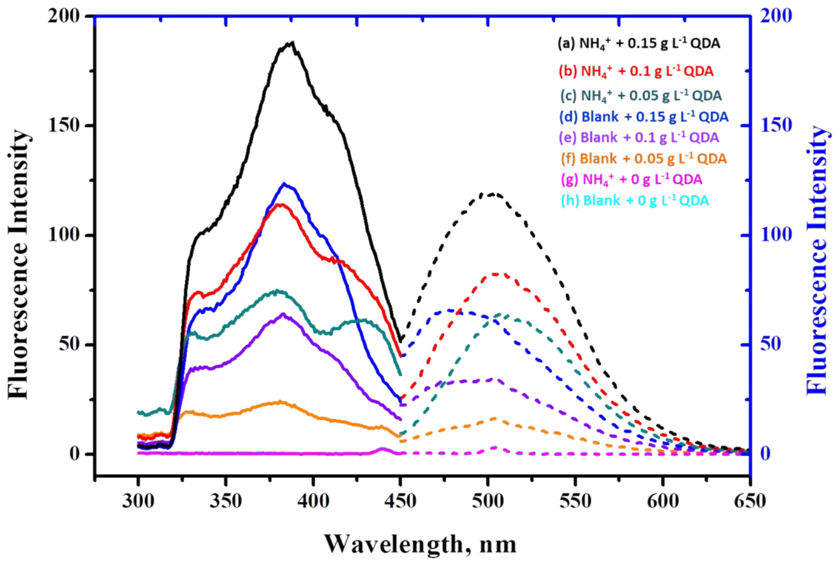

Fig. S8. Excitation (solid line) and emission (dash line) spectra of the fluorescence products with 0/0.05/0.1/0.15 g L^{-1} added to the solution.

NH_4^+ concentration: 1.5 μmol L^{-1}; Na_2SO_3 concentration: 0.0315 g L^{-1}; $Na_2B_4O_7$ buffer concentration: 3.0 g L^{-1}; pH: 9.4. Reaction time: 50 min; Reaction temperature: 50℃

(5) Excitation and emission spectra of fluorescence products added with different concentrations of Na_2SO_3

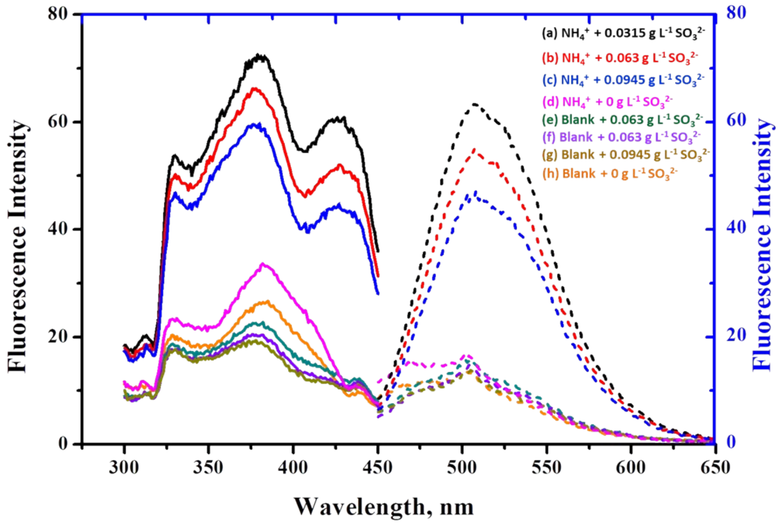

Fig. S9. Excitation (solid line) and emission (dash line) spectra of the fluorescence products with 0/0.0315/0.063/0.0945 g L^{-1} added to the solution.

NH_4^+ concentration: 1.5 μmol L^{-1}; QDA concentration: 0.083 g L^{-1}; $Na_2B_4O_7$ buffer concentration: 3.0 g L^{-1}; pH: 9.4. Reaction time: 50 min; Reaction temperature: 50℃.

(6) Emission spectra of fluorescence products which without calcium ions

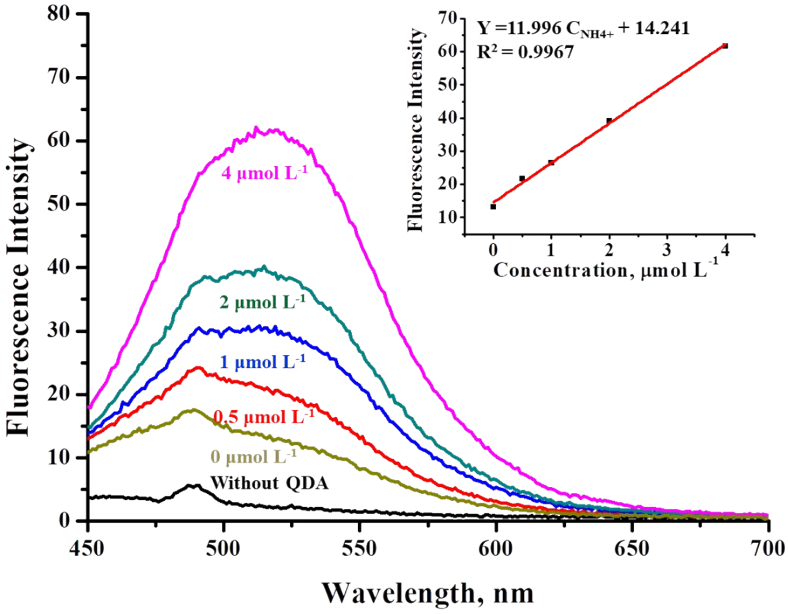

Fig. S10. Emission spectra of the fluorescence products with 0/0.5/1/2/4 μmol L^{-1} NH_4^+. QDA concentration :0.083 g L^{-1}; Na_2SO_3 concentration: 0.0315 g L^{-1}; $Na_2B_4O_7$ buffer concentration: 3.0 g L^{-1}; pH: 9.4. Reaction time: 30 min; Reaction temperature: 40°C.

(7) Effects of inorganic ions on measuring ammonium solution

Table S1 Effects of Inorganic ions on measuring ammonium solution (3 μmol L^{-1}).

Ion	Concentration, μmol L^{-1}	Relative sensitivity to ammonium, %
NH_4^+	3	100.0 ± 2.5
Sr^{2+}	60	101.2 ± 0.8
	120	102.4 ± 0.5
Ni^{2+}	0.5	106.1 ± 1.4
	1.5	104.2 ± 0.3
Ba^{2+}	3	103.2 ± 0.5
	6	104.0 ± 0.1
Zn^{2+}	0.5	106.1 ± 4.0
	1.5	100.5 ± 1.2
Cd^{2+}	3	101.4 ± 0.2
	6	101.1 ± 0.5
Co^{2+}	0.5	103.8 ± 1.1
	1.5	82.1 ± 3.7
Mg^{2+}	100	103.6 ± 0.2
	2000	109.0 ± 0.4
	4000	114.5 ± 1.0
K^+	50	98.1 ± 0.2
	100	98.6 ± 0.3
	200	100.4 ± 0.5
Fe^{3+}	30	101.2 ± 0.3
Na^+	30	101.9 ± 0.4
HPO_4^{2-}	30	101.3 ± 0.2
NO_3^-	30	99.6 ± 0.8

(8) Calibration curves of different times

Table S2 Calibration curves of different times

Serial number	Calibration curve	R^2
1	FI=(31.012 ± 0.77) C_{NH4^+} + (13.879 ± 2.79)	0.995
2	FI=(34.233 ± 0.37) C_{NH4^+} + (11.409 ± 0.31)	0.9997
3	FI=(30.671 ± 0.37) C_{NH4^+} + (10.984 ± 1.26)	0.9994
4	FI=(29.89 ± 4.18) C_{NH4^+} + (16.52 ± 1.24)	0.9931
5	FI=(31.501 ± 0.88) C_{NH4^+} + (23.704 ± 2.22)	0.9977
6	FI=(32.072 ± 1.24) C_{NH4^+} + (16.996 ± 3.13)	0.9955
7	FI=(29.611 ± 0.10) C_{NH4^+} +(34.742 ± 4.60)	0.9944