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A solothiocarbonyl quinacridone with long chains used as a fluorescent tool for rapid detection of Hg^{2+} in hydrophobic naphtha samples

Supplementary data

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Experimental Details

Materials, Instruments and Methods

Materials. Quinacridone was obtained from Changzheng Chemical Co. Ltd (Shangyu, Zhejiang, China) Lawesson's reagent was purchased from J&K (Beijing, China). All metal salts and solvents were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Toluene was pretreated with CaH_2 and fractional distilled before use. The HPLC grade n-hexane was used without further purification. All other chemicals were obtained from qualified reagent suppliers with analytical reagent grade.

Instruments. A Vortex shaker (Vortex QL-861) provided the high rate mode was obtained from Qilinbeier Co. Ltd. in Jiangsu, China. The constant temperature shaking incubator (XHZ-032) was obtained from Chemstar instrument Co. Ltd. in Shanghai, China. Fluorescence spectra were recorded by a Fluorescence spectrometer (Edinburgh FS-5) with Xenon lamp (450 W) and 10-mm quartz cells at the slits of 1/1 nm. The background correction and the excitation and emission correction were selected. The absorption spectra were measured on a UV-visible spectrophotometer (Cary 300). The NMR spectra were determined by 400 MHz using a Bruck NMR instruments. All ^1H NMR chemical shifts were reported relative to TMS (= 0.0 ppm), and all ^{13}C NMR chemical shifts were reported relative to $CHCl_3$ (= 77 ppm).

Methods. The stock solution of **STQA16** was prepared at 1.0 mM in toluene. Solutions of all metal ions (0.01 M) were prepared with deioned water. For absorption and emission spectra, different concentrations of mercury ion were added to the test solution with 10 μM of **STQA16**. The excited wavelength was chose at 485 nm in all emission spectra and the emission wavelength was set at 570 nm in the excitation spectrum in Figure S3.

Synthesis of STQA16

1. Synthesis of 5,12-dihexadecylquinolino[2,3-b]acridine-7,14-dione (QA16)

5,12-Dihydroquino[2,3-b]acridine-7,14-dione (4.68 g, 15 mmol) and tetrabutyl-ammonium bromide (TBAB) (966 mg, 3 mmol) were dissolved in 100 mL DMSO, and while stirring vigorously, 50% NaOH (20 mL) and bromohexadecane (18.3 g, 60 mmol) were added slowly. The resulting mixture was heated to 70 ^oC for 24 h. The reaction was quenched with water (30 mL) and filtered. The organic layer from the filtrate was separated, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography eluting with petroleum ether and methylene chloride (1/1, v/v) yielding the product as red solids (3.15 g, 27.6%). ^1H NMR ($CDCl_3$, 400 MHz), δ (TMS, ppm): 0.90 (t, *J* = 6.53 Hz, 6 H) 1.28 (br. s., 40 H) 1.49 (br. s., 4 H) 1.58 - 1.68 (m, 4 H) 1.75 (br. s., 4 H) 2.03 (br. s., 4 H) 4.48 - 4.59 (m, 4 H) 7.25 - 7.34 (m, 2 H) 7.53 (d, *J* = 8.78 Hz, 2 H) 7.77 (t, *J* = 7.53 Hz, 2 H) 8.59 (d, *J* = 7.78 Hz, 2 H) 8.78 (s, 2 H)

2. 5,12-dihexadecyl-14-thioxo-12,14-dihydroquinolino[2,3-b]acridin-7(5H)-one (STQA16) and 5,12-dihexadecylquinolino[2,3-b]acridine-7,14(5H,12H)-dithione (DTQA16)

QA16 (130 mg, 0.17 mmol) and Lawesson's reagent (81 mg, 0.20 mmol) were dissolved in toluene (25 mL) in a 100 mL round-bottom flask. Then the reaction mixture was warmed to reflux and stirred for 60 min under Ar protection. The mixture was concentrated under vacuum, purified by silica gel column chromatography with methylene dichloride/petroleum ether (1:1, v/v) to give DTQA16 as a dark green solid (40 mg, 29%) and STQA16 as a purple solid (74 mg, 56%).

Character of STQA16

^{1}H NMR ($CDCl_3$, 400 MHz), δ ppm 0.90 (t, *J* = 6.53 Hz, 6 H) 1.28 (br. s., 40 H) 1.49 (br. s., 4 H) 1.64 (br. s., 4 H) 1.72 (br. s., 4 H) 2.03 - 2.15 (m, 4 H) 4.57 (t, *J* = 7.78 Hz, 2 H) 4.65 (t, *J* = 8.03 Hz, 2 H) 7.32 - 7.39 (m, 2H) 8.59 (dd, *J* = 8.03, 1.51 Hz, 1 H) 8.88 (s, 1 H) 9.21 (dd, *J* = 8.41, 1.38 Hz, 1 H) 9.50 (s, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ ppm 22.53, 32.11, 32.35, 44.25, 47.45, 110.48, 110.68, 111.45, 111.64, 118.04, 121.72, 122.73, 126.64, 128.00, 133.82, 136.73, 137.68, 139.14, 142.17, 167.75, 171.53. HRMS (ESI) Calcd. for $C_{52}H_{77}N_2OS$ ($[M+H]^+$) m/z: 777.5757, found: 777.5762.

Character of DTQA16

^{1}H NMR ($CDCl_3$, 400 MHz), δ ppm 0.90 (t, *J* = 6.40 Hz, 6 H) 1.25 - 1.34 (m, 40 H) 1.53 - 1.61 (m, 8 H) 1.69 (dt, *J* = 14.56, 7.28 Hz, 4 H) 2.03 -2.12 (m, 4 H) 4.53 - 4.65 (m, 4 H) 7.21 - 7.27 (m, 2 H) 7.53 (d, *J* = 8.78 Hz, 2 H) 7.69 - 7.78 (m, 2 H) 9.08 (dd, *J* = 8.41, 1.13 Hz, 2 H) 9.39 (s, 2 H)

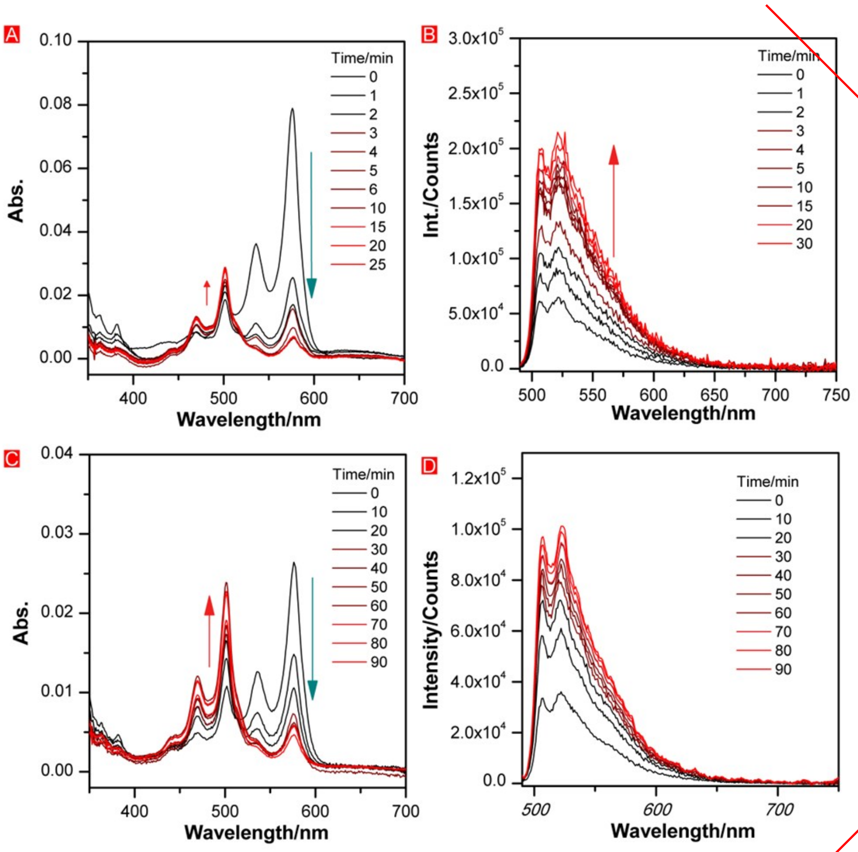


Fig. S1 Kinetic experiments of STQA16 with 10 eq. of Hg^{2+} under a Vortex shaker (A, B) and a constant temperature shaking incubator (C, D). (A,C) monitoring by UV-vis spectra; (B,D) monitoring by emission spectra.

Comment [Y. Qu]: We supplemented the experiments of both absorbance and fluorescence ranged a longer time region.

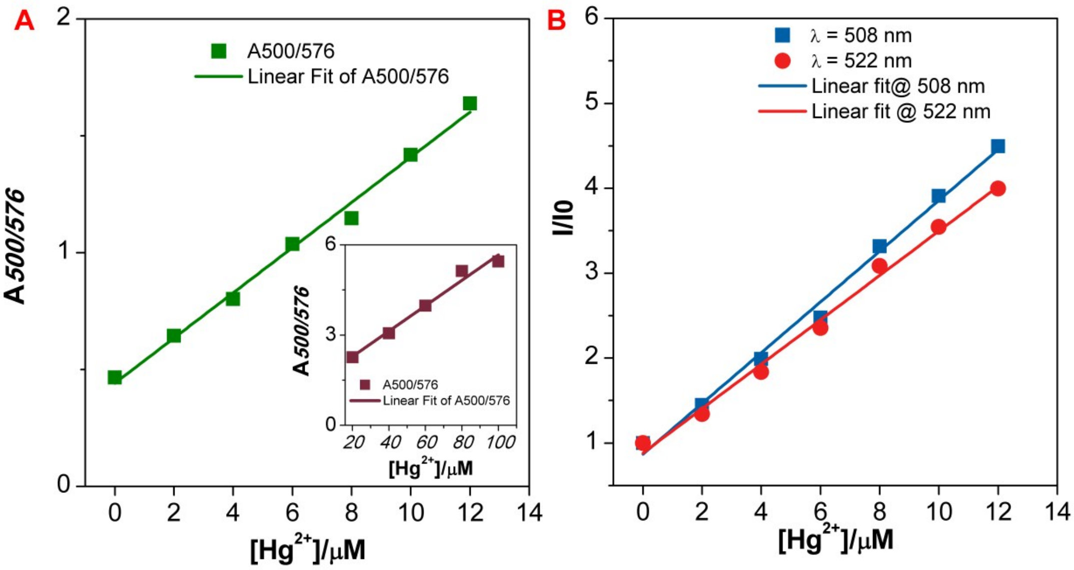


Fig. S2 DL value detection experiment in real naphtha sample. (A) Correction between the absorbance ratio of $A_{500/576}$ and $[Hg^{2+}]$; (B) correction between the emission enhancement factor (I/I_0) at both 508 nm and 522 nm and $[Hg^{2+}]$.

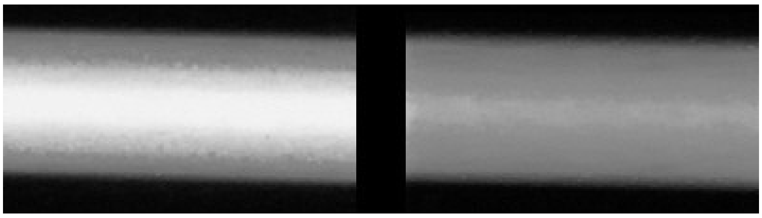


Fig. S3 Image sampling processing from the fluorescent images of STQA16 with (left) and without (right) 10 eq. of Hg^{2+}.

The digital processing of these images was operated by a origin software (Ver. 8.0).

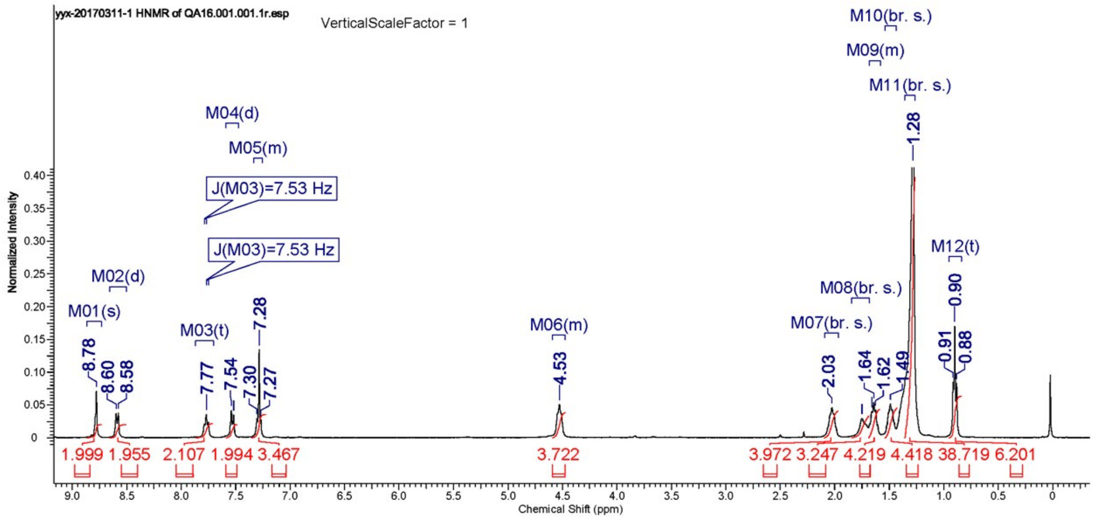


Fig. S4 The emission and excitation spectra of the toluene solution of **QA16**

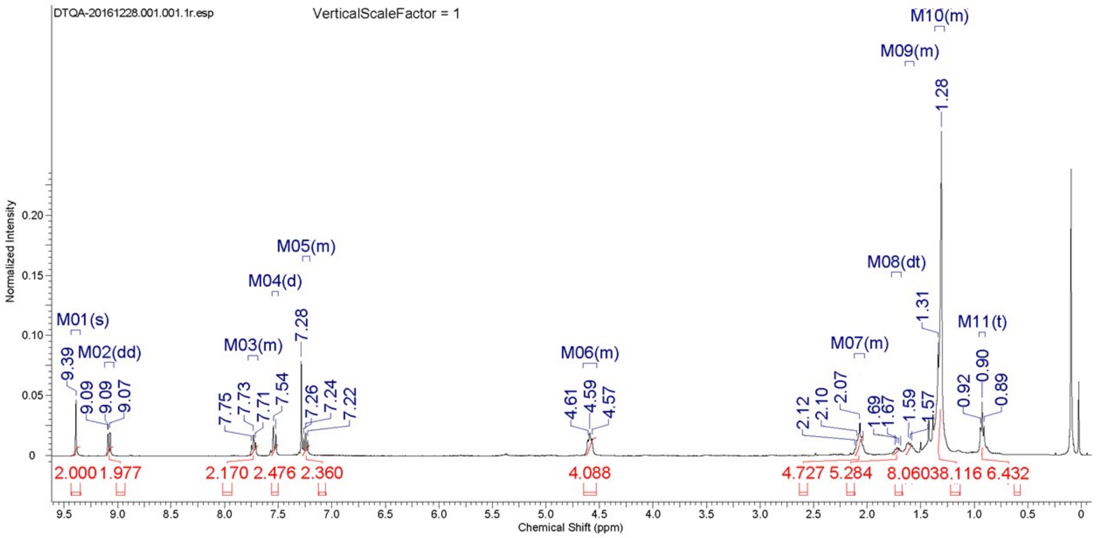


Fig. S5 The emission and excitation spectra of the toluene solution of **DTQA16**

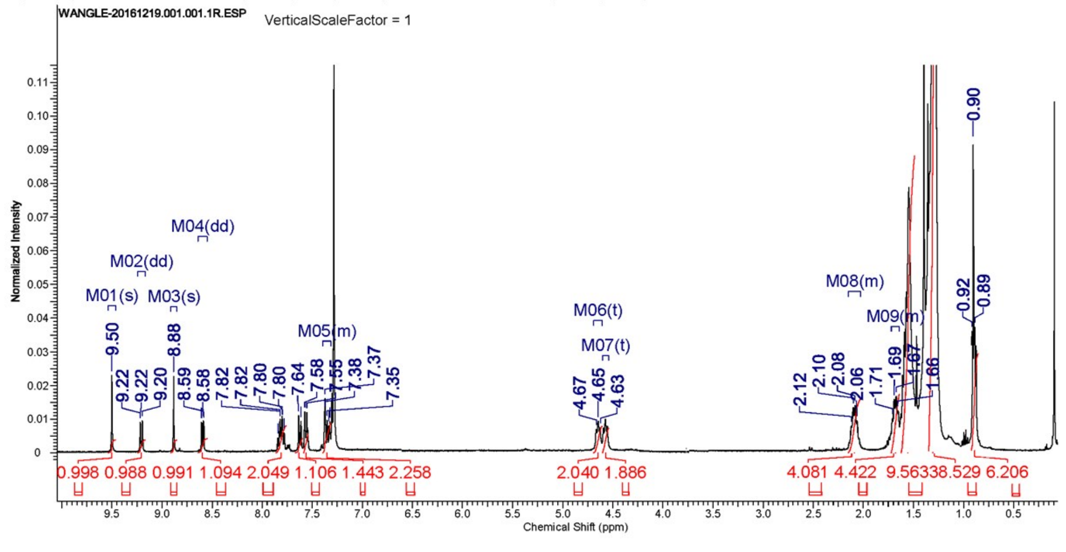


Fig. S6 The emission and excitation spectra of the toluene solution of **STQA16**

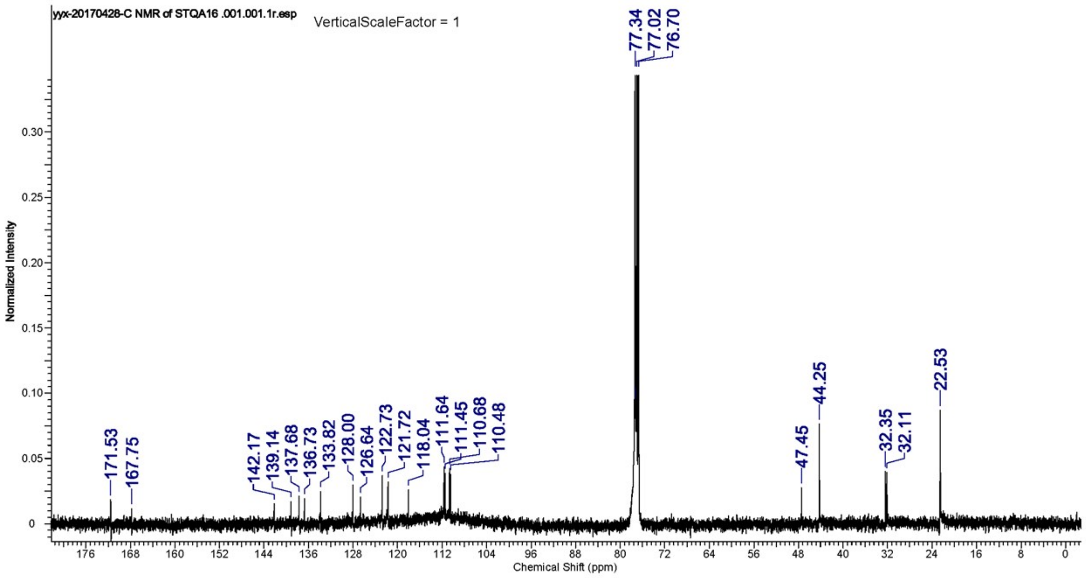
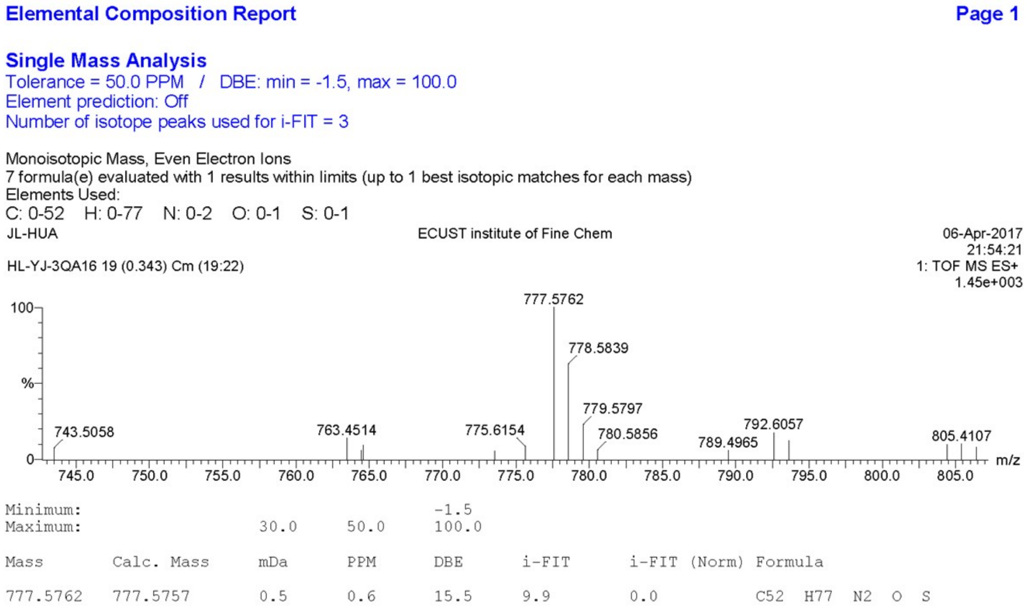


Fig. S7 The emission and excitation spectra of the toluene solution of **STQA16**



Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-52 H: 0-77 N: 0-2 O: 0-1 S: 0-1

JL-HUA ECUST institute of Fine Chem 06-Apr-2017
21:54:21
HL-YJ-3QA16 19 (0.343) Cm (19:22) 1: TOF MS ES+
1.45e+003

```
Minimum:                                    -1.5
Maximum:                   30.0      50.0    100.0

Mass       Calc. Mass      mDa       PPM     DBE      i-FIT      i-FIT (Norm) Formula

777.5762   777.5757        0.5       0.6     15.5     9.9        0.0          C52  H77  N2  O  S
```

Fig. S8 The emission and excitation spectra of the toluene solution of **STQA16**