Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Tetranitrile-anthracene as Probe for Fluorescent Detection of Viscosity in Fluid Drinks via Aggregation-induced Emission

Lingfeng Xu, Ling Ni, Fang Zeng*, Shuizhu Wu*

State Key Laboratory of Luminescent Materials & Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, College of Materials Science & Engineering, South China University of Technology, Guangzhou 510640, China

*Corresponding author. E-mail: mcfzeng@scut.edu.cn.

E-mail: shzhwu@scut.edu.cn

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Materials and instruments

2-Bromoanthracene-9,10-dione, tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$), 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)benzeneamine, anhydrous sodium sulphate (Na_2SO_4), potassium carbonate, pectin, xanthan gum, sodium carboxymethyl cellulosepectin, pyridine, malononitrile, tetrahydrofuran (THF), dichloromethane (DCM), dimethylsulfoxide (DMSO), ethyl acetate, acetonitrile, ethanol, methanol, N,N-dimethylformamide (DMF), and dioxane, glycerol were purchased from Aladdin Regents (Shanghai) Co., Ltd. Various inorganic salts ($CaCl_2$, $MgSO_4$, NaCl, etc.), and common food additives (disodium hydrogen phosphate, trisodium citrate dehydrate) were obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Glutathione (GSH), cysteine (Cys), homocysteine (Hcy) and other amino acids were purchased from Sigma-Aldrich (Merck Life Sciences Co., Ltd., Shanghai, China). And phosphate-buffered saline (PBS) was brought from Gibco (Life Technologies, ThermoFisher Scientific Corp., Shanghai, China). The other reagents used in this work were of analytical grade and used as received. The column chromatography for purification was performed through silica gel (300-400 mesh). The water was triple distilled prior to use.

Nuclear magnetic resonance (NMR) spectra were performed on a Bruker (Germany) AVANCE III HD 600 Superconducting Fourier Transform Nuclear Magnetic Resonance Spectrometry. Mass spectra of synthesized compounds were analyzed by mass spectrometer (Esquire HCT PLUS, Bruker, Germany) in electrospray ionization (ESI) mode and the matrix-assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF-MS, Autoflex III smartbean, Bruker, Germany). Fluorescence spectra were measured by the Hitachi F-4600 fluorescence spectrophotometer (Hitachi High-Tech Science, Japan). UV-vis spectra were recorded on a Hitachi U-3010 UV-vis spectrophotometer (Hitachi High-Tech Science, Japan). The viscosity determination test was operated on the rotating viscometers (DV2T, Brookfield, AMETEK Corp., USA).

Synthesis procedure

Synthesis of the 2-(4-(bis(4-methoxyphenyl)amino)phenyl)anthracene-9,10-dione (Compound 1)

A solution of 2-bromoanthracene-9,10-dione (28.6 mg, 0.1 mmol) dissolved in the THF, was added dropwise to the 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzenamine (43.1 mg, 0.1 mmol) solution in THF to form a mixture. Afterwards, the potassium carbonate aqueous solution (2 M) was added into the above solution, and the mixture was stirred under room temperature for half an hour, and then heated up to 68 °C, refluxed under nitrogen atmosphere overnight. During the heating process, a solution of $Pd(PPh_3)_4$ (1.2 mg, 0.001 mmol) was injected into the reaction system through the syringe slowly. Afterwards, the organic solvent was evaporated through the vacuum-rotary evaporation. Then the mixture was poured into the saturated salt water and extracted with DCM three times. Before being further concentrated via vaccum-rotary evaporation, the organic phase was dried via anhydrous Na_2SO_4. The crude product was purified through the column chromatography with silica gel using the DCM/methanol (10:1, v/v) to obtain Compound 1 as a dark red solid powder (40.9 mg, 80% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.33 (d, J = 1.9 Hz, 1H), 8.23-8.19 (m, 3H), 8.13 (dd, J = 8.2, 2.0 Hz, 1H), 7.97-7.91 (m, 2H), 7.68 (d, J = 8.9 Hz, 2H), 7.12 (d, J = 8.9 Hz, 4H), 6.96 (d, J = 9.0 Hz, 4H), 6.85 (d, J = 8.8 Hz, 2H), 3.77 (s, 6H). HR-MS (ESI): calcd for $C_{34}H_{25}NO_4$ ($[M+H]^+$) 511.1786, found 511.1775.

Synthesis of the 2,2'-(2-(4-(bis(4-methoxyphenyl)amino)phenyl)anthracene-9,10-diylidene)di-malononitrile (the probe TPAEQ)

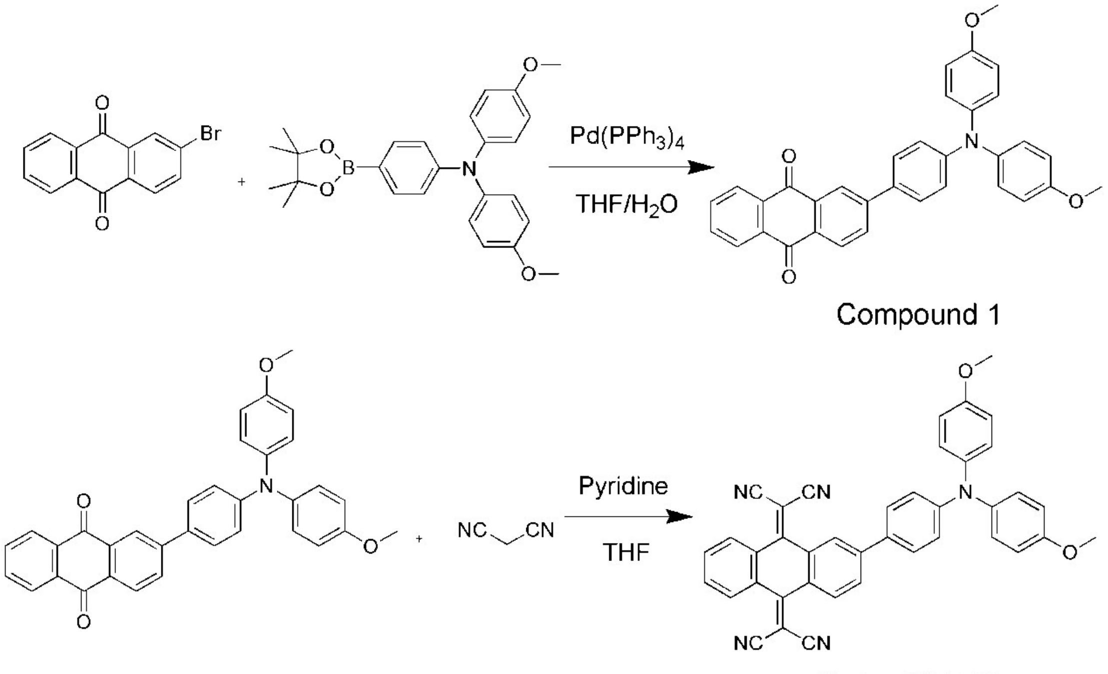
A solution of Compound 1 (51.1 mg, 0.1 mmol) dissolved in the THF was added in a 50 mL flask, then the malonitrile (19.8 mg, 0.3 mmol) solution in THF (5 mL) was added. After the mixture was stirred at room temperature for half an hour, then the solution was heated up to 68 °C. During the heating process, the pyridine (23.7 mg, 0.3 mmol) in the THF (5 mL) solution was added dropwise via the springe into the mixture. Then the mixture was refluxed at 68 °C overnight under nitrogen atmosphere. Afterwards, the solvent was removed through vacuum-rotary evaporation, and the obtained crude product was further purified by silica gel chromatography with dichloromethane/ethyl acetate (1:1, v/v) to give a blackish green solid as the probe TPAEQ (45.6 mg, 75% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, J = 1.6 Hz, 1H), 8.29-8.23 (m, 3H), 7.85 (dd, J = 8.3, 1.7 Hz, 1H), 7.76-7.69 (m, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 8.9 Hz, 4H), 6.98 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.9 Hz, 4H), 3.82 (s, 6H). HR-MS (ESI): calcd for $C_{40}H_{25}N_5O_2$ ($[M+H]^+$) 608.2088, found 608.2275. MALDI-TOF-MS: calcd for $C_{40}H_{25}N_5O_2$ 608.2088, found 608.275.

The Förster–Hoffmann equation

The relationship between the fluorescence intensity of the probe TPAEQ and the viscosity can be determined by the Förster–Hoffmann equation as following [1,2]:

$$\log I = \mathrm{C} + \mathrm{x} \log \eta \qquad (1)$$

where η represents the viscosity, I represents the fluorescence intensity of the probe TPAEQ at 759 nm, and C is a constant, where x represents the sensitivity of the fluorescent probe towards the viscosity.



Scheme S1. Illustration of the synthetic route for the probe TPAEQ.

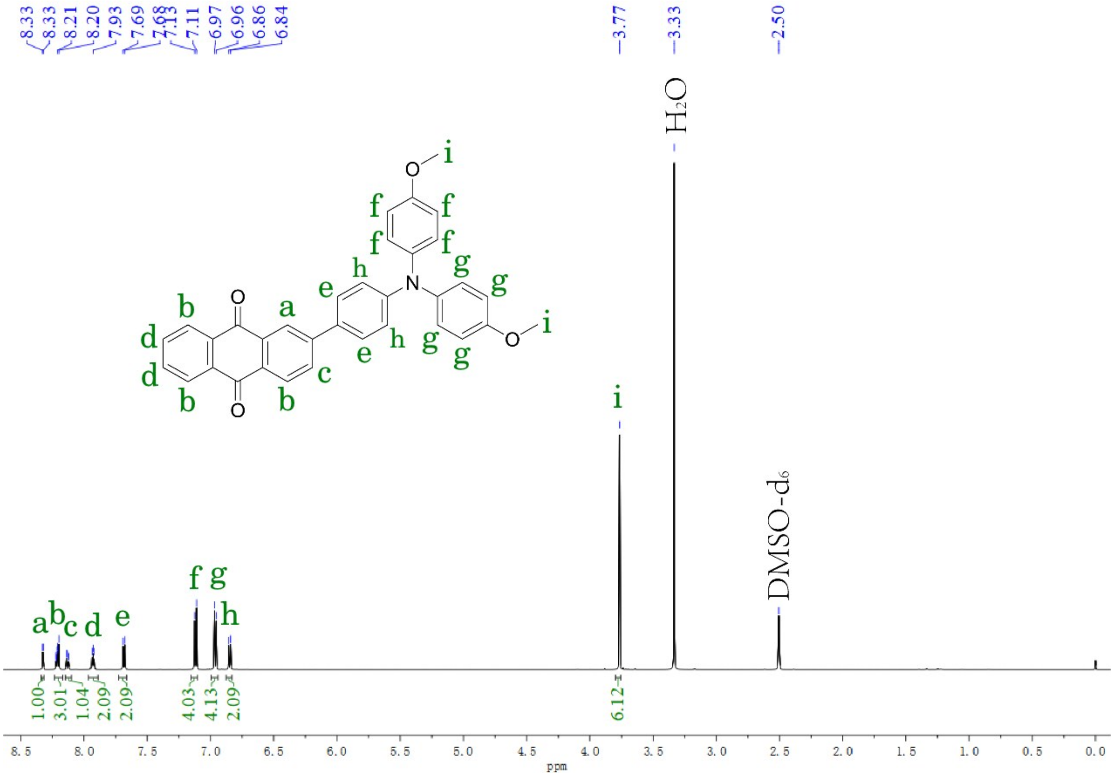


Fig. S1 ^{1}H NMR spectrum of Compound 1 in DMSO-d$_6$.

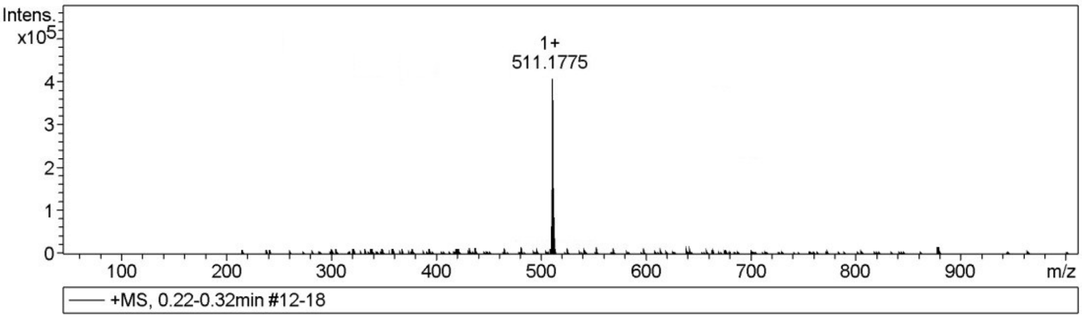


Fig. S2 HR-MS Spectrum of Compound 1 (m/z 511.1775 [M+H]$^+$).

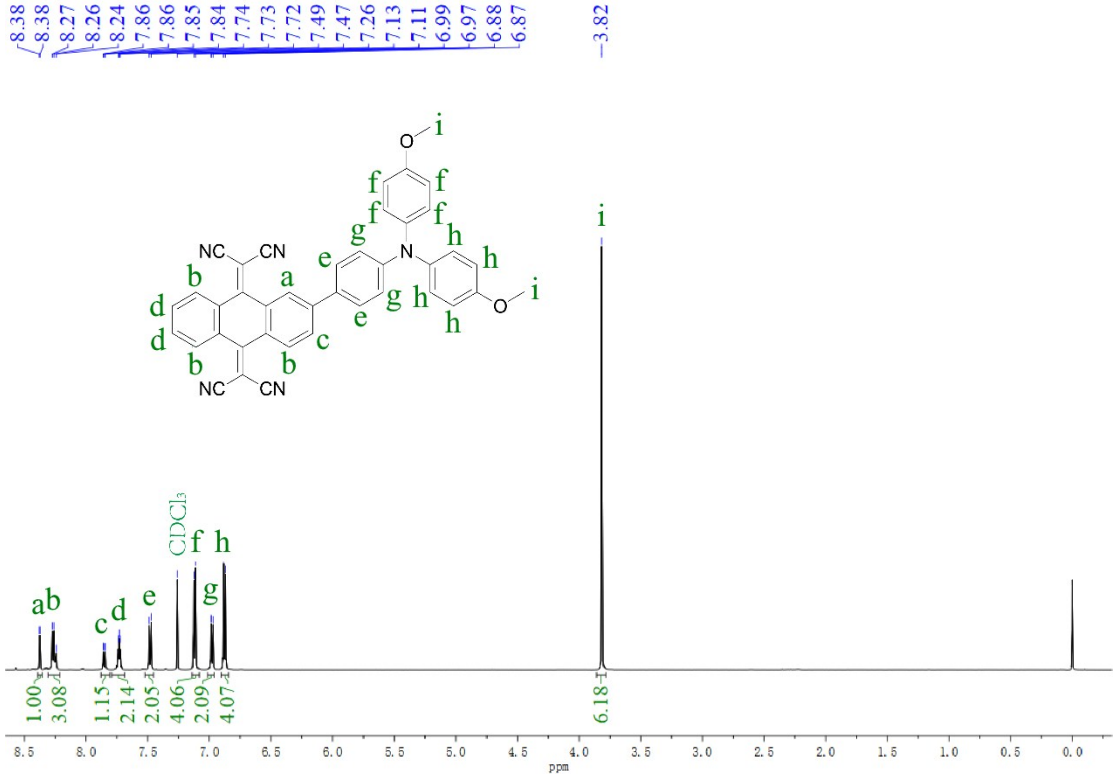


Fig. S3 ^{1}H NMR spectrum of the Probe TPAEQ in $CDCl_3$.

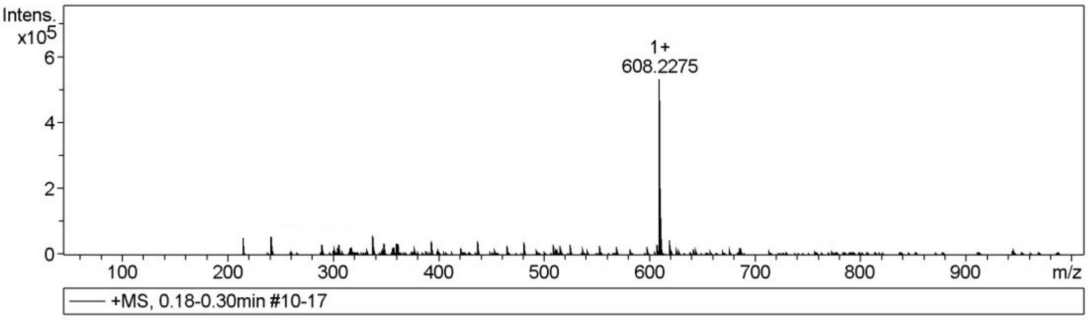


Fig. S4 HR-MS Spectrum of the probe TPAEQ (m/z 608.2275 $[M+H]^+$).

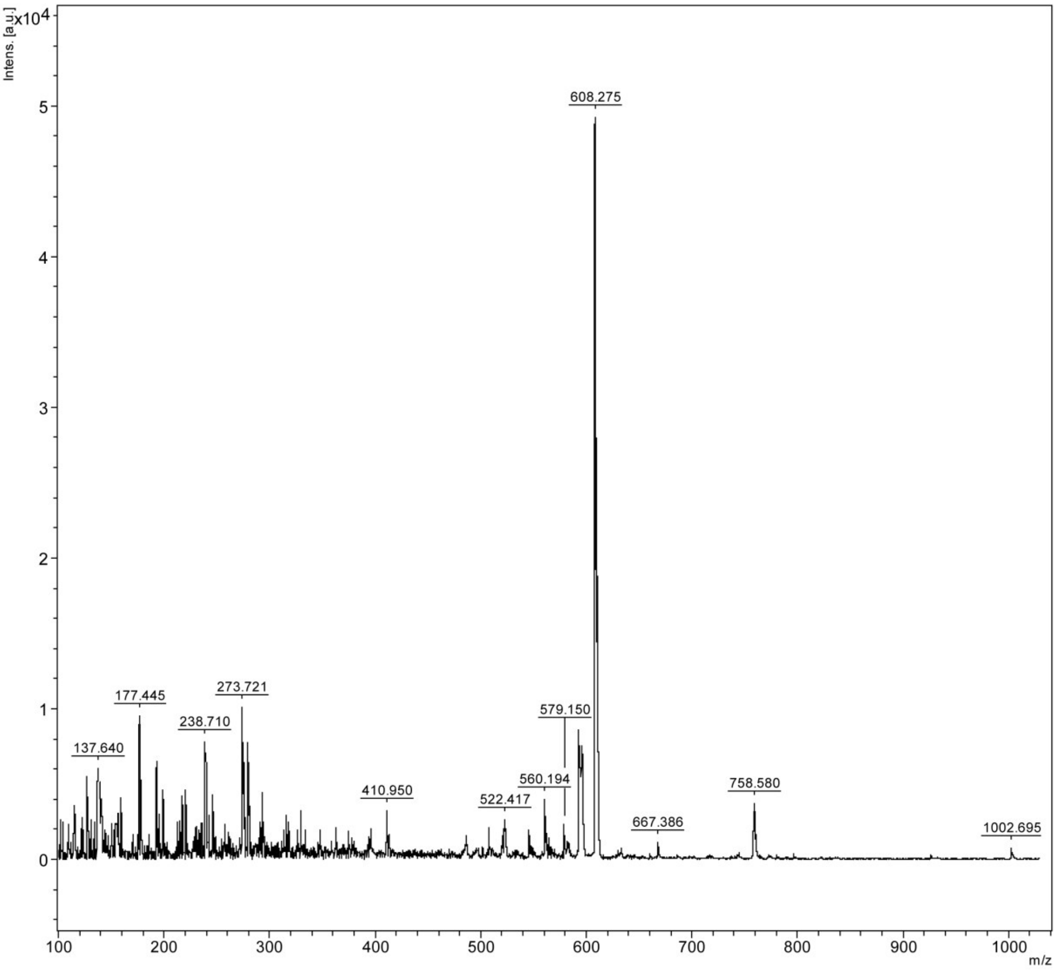


Fig. S5 MALDI-TOF mass spectrum of the probe TPAEQ.

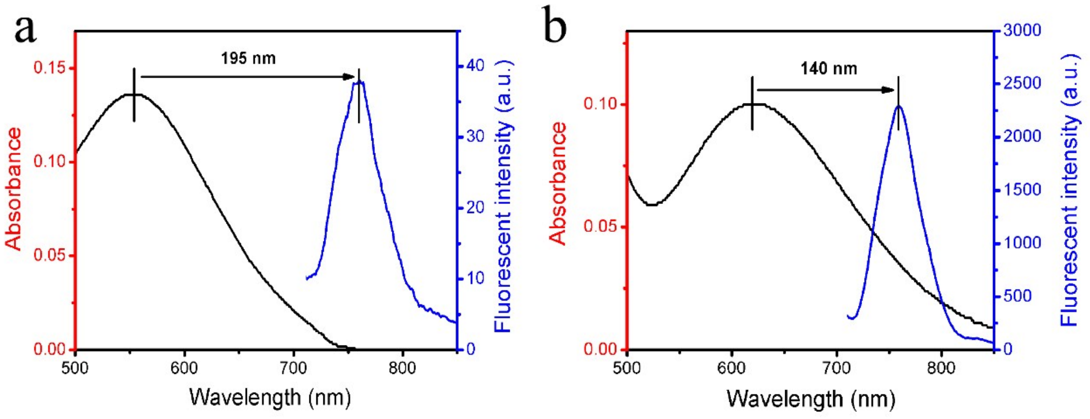


Fig. S6 (a) Absorption spectrum (black curve) and fluorescent spectrum (blue curve) of the probe TPAEQ in water (containing 1% DMSO). (b) Absorption spectrum (black curve) and fluorescent spectrum (blue curve) of the probe TPAEQ in glycerol (containing 1% DMSO).

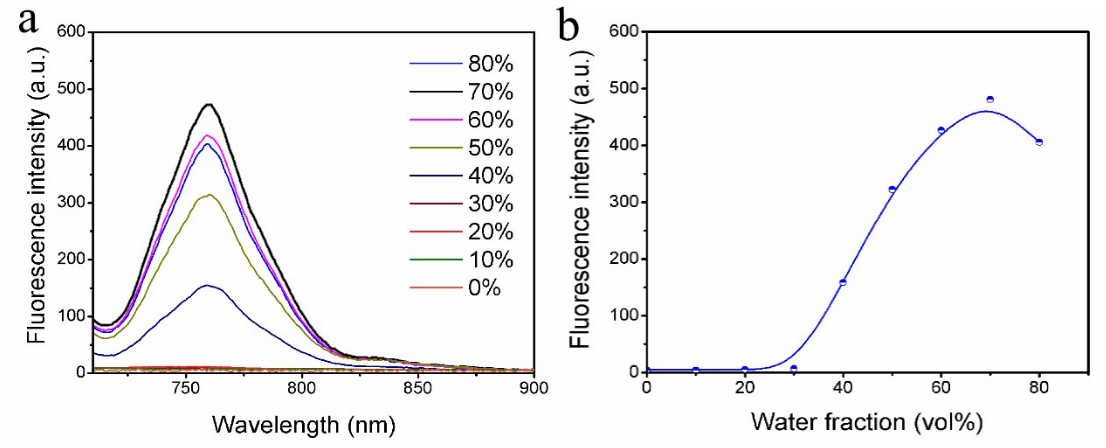


Fig. S7 (a) Fluorescence spectrum of the probe TPAEQ (10 μM) in THF/water mixture with different volume ratios of water (0%, 10%, 20%, 30%, 40%, 50%, 60%, 70% and 80%). (b) Fluorescence intensity at 759 nm with different volume ratios of water, λ_{ex}= 650 nm.

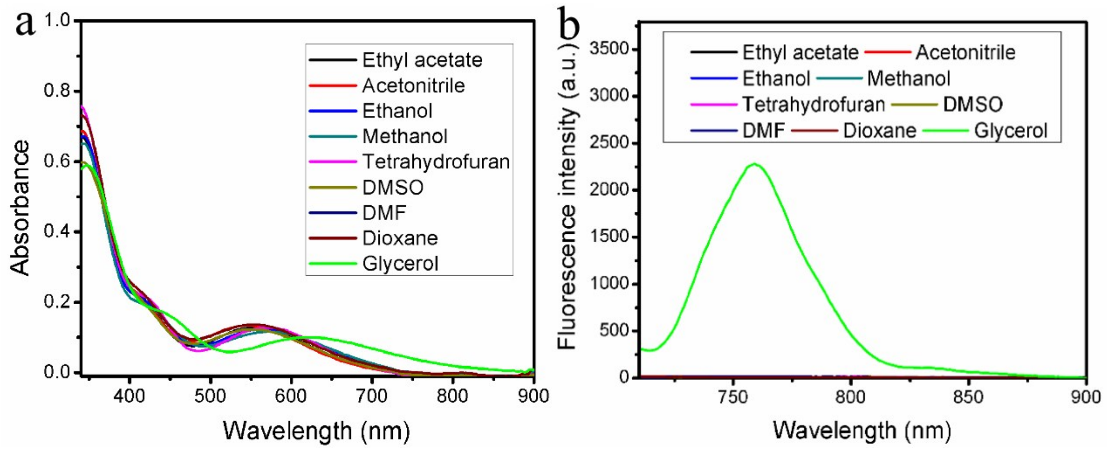


Fig. S8 (a) The absorption spectra of the probe TPAEQ (10 μM) in various solvents, λ_{ex}=650 nm. (b) The fluorescent spectra of the probe TPAEQ (10 μM) in various solvents, λ_{ex}=650 nm. The solvents included ethyl acetate, acetonitrile, ethanol, methanol, tetrahydrofuran, DMSO, DMF, dioxane and glycerol.

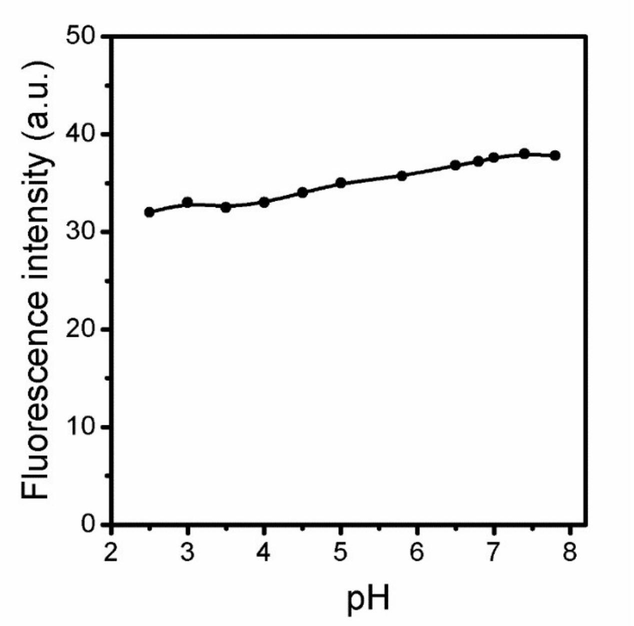


Fig. S9 Fluorescence emission intensity of TPAEQ (10 μM) at 759 nm under various pH values (in buffer solutions containing 1% DMSO), λ_{ex}=650 nm.

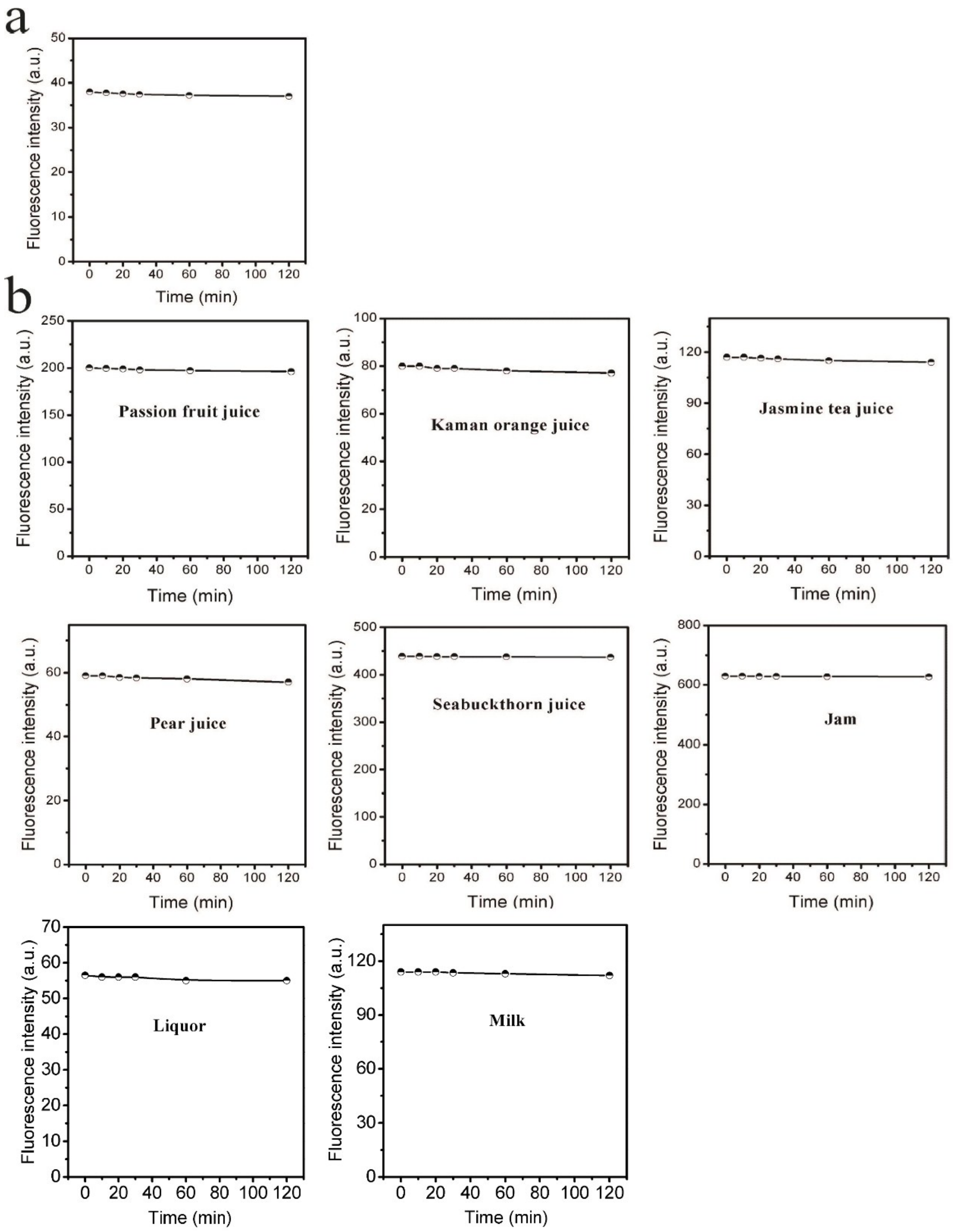


Fig. S10 Photostability analysis of the probe TPAEQ in (a) water (containing 1% DMSO) and (b) eight kinds of fresh fluid drinks (containing 1% DMSO). All the samples were tested under continuous light irradiation with 365 nm UV lamp.

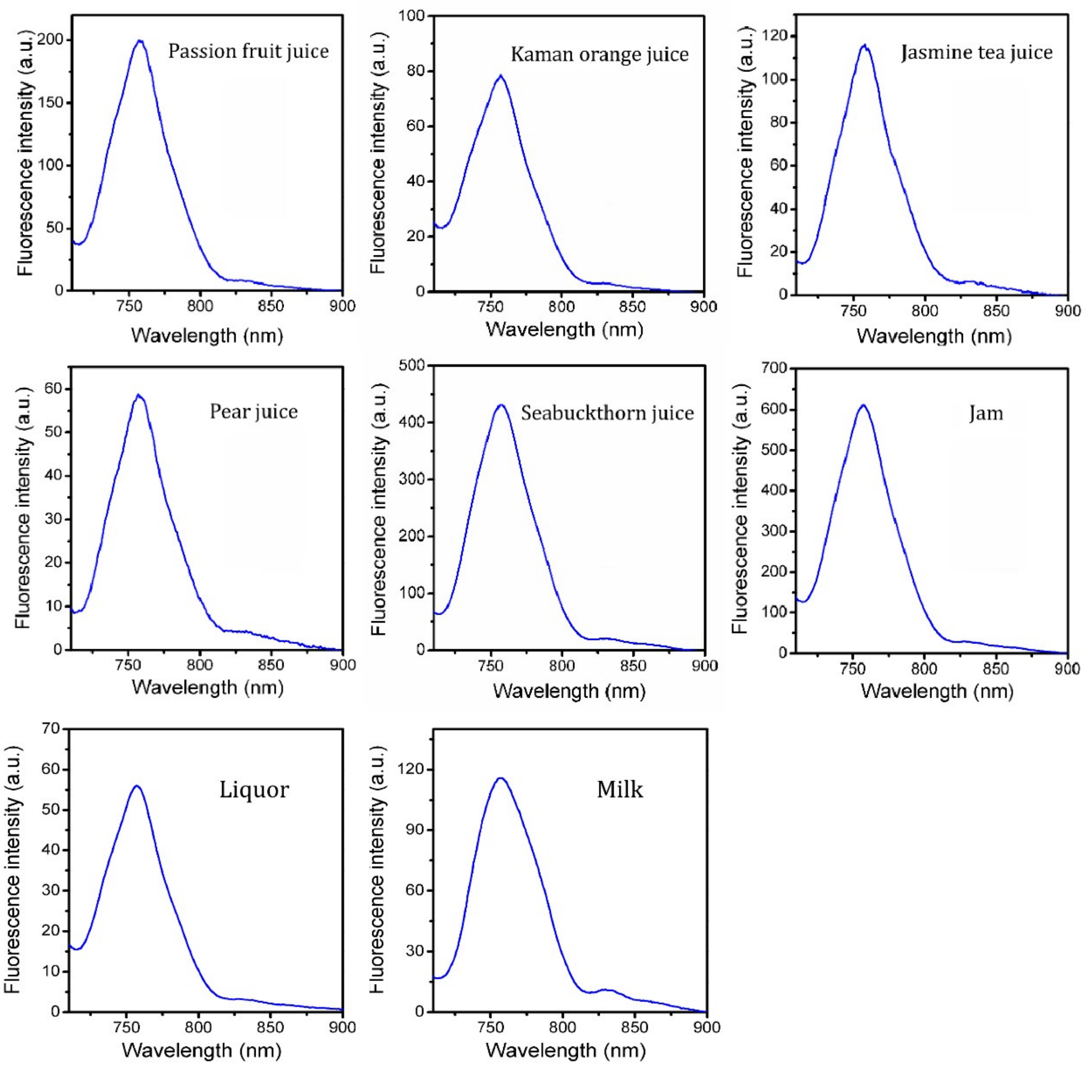


Fig. S11 Fluorescence emission spectra of the probe TPAEQ (10 μM, containing 1% DMSO) in eight kinds of common fluid beverages, including the passion fruit juice, Kaman orange juice, jasmine tea juice, pear juice, seabuckthorn juice, jam, liquor and milk.

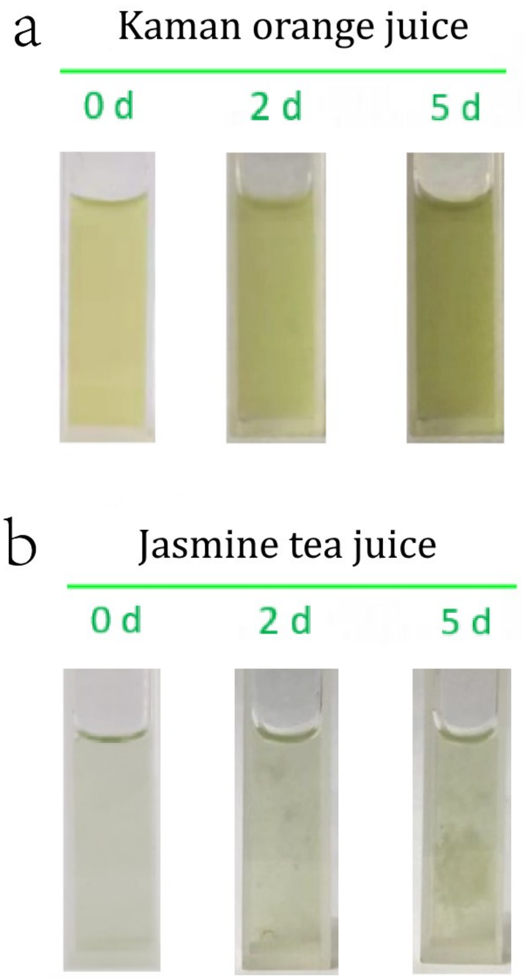


Fig. S12 (a) Photos of Kaman orange juice that was placed under the ambient temperature (25 °C) exposed to air for different time (0-5 days). (b) Photos of jasmine tea juice that was placed under the ambient temperature (25 °C) exposed to air for different time (0-5 days).

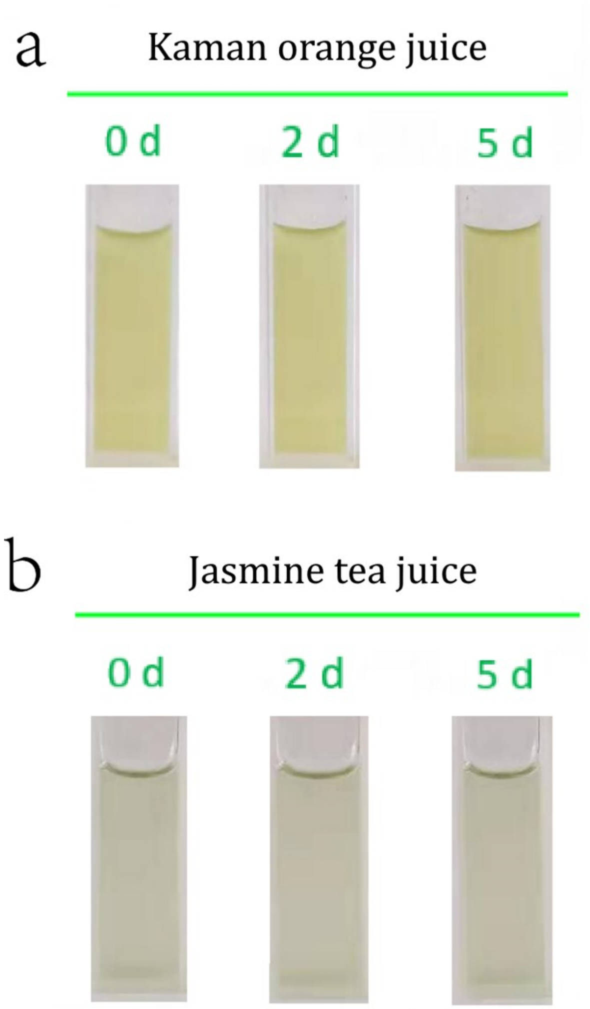
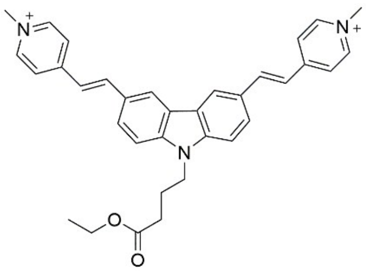
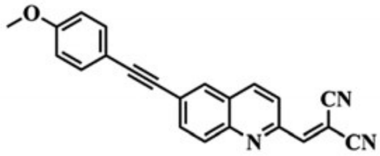
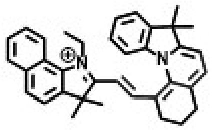
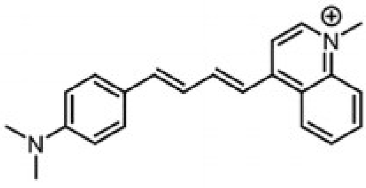
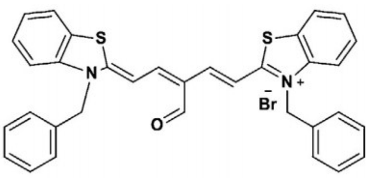
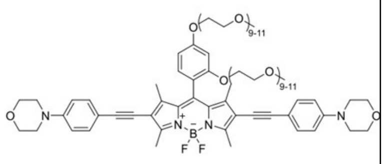
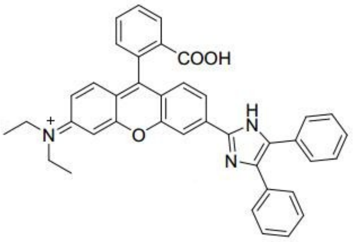
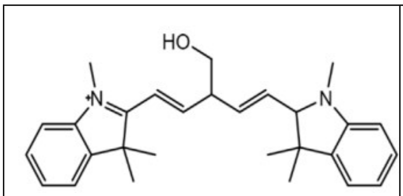
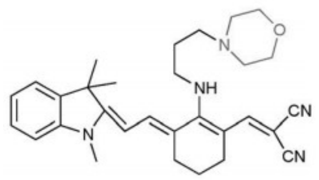
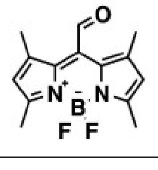
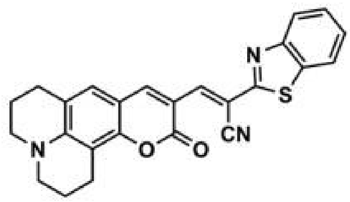
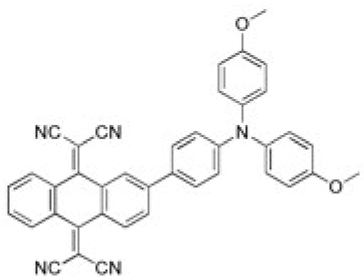


Fig. S13 Photos of Kaman orange juice that was placed under the fresh-keeping layer in the refrigerator (4 °C) for different time (0-5 days). (h) Photos of jasmine tea juice that was placed under the fresh-keeping layer in the refrigerator (4 °C) for different time (0-5 days).

Table S1. Comparison of the literature-reported representative fluorescent probes for viscosity detection and this probe.

Chemical structure of probe	λ_{ab}^{*}	λ_{em}^{**}	Stokes shift***	Application fields	Reference
	470 nm	550 nm	80 nm	Biological system, living cells imaging.	3
	400 nm	470 nm	70 nm	Biological system, living cells imaging.	4
	610 nm	710 nm	100 nm	Biological system, living cells imaging.	5
	500 nm	625 nm	125 nm	Biological system, living cells imaging.	6
	600 nm	658 nm	58 nm	Biological system, living cells imaging.	7
	560 nm	580 nm	20 nm	Biological system, living cells imaging.	8
	573 nm	650 nm	77 nm	Biological system, living cells imaging, inflammatory mice imaging.	9

	550 nm	570 nm	20 nm	Biological system, living cells imaging.	10
	580 nm	620 nm	40 nm	Biological system, living cells imaging.	11
	480 nm	538 nm	58 nm	Biological system, living cells imaging.	12
	570 nm	640 nm	70 nm	Biological system, living cells imaging, inflammatory mice imaging.	13
	619 nm	759 nm	140 nm	Fluid drinks, food safety analysis.	This work.

[*] Absorption peak. The absorption was measured in the glycerol (99%, v/v) solution containing 1% DMSO.

[**] Emission peak. The fluorescence emission was measured in the glycerol (99%, v/v) solution containing 1% DMSO.

[***] The stokes shift herein was obtained from the absorption and emission measured in the glycerol (99%, v/v) solution containing 1% DMSO.

Table S2. Photo-physical properties of the probe TPAEQ in different solvents with different polarities.

Solvents	Dielectric constant (ε)	η^* (cP)	Absorption λ_{ab} (nm)	Emission λ_{em} (nm)
Ethyl acetate	7.3	0.43	555	/**
Acetonitrile	37.5	0.37	550	/
Ethanol	24.9	1.2	566	/
Methanol	32.6	0.6	578	/
THF	7.4	0.5	572	/
DMSO	46.8	2.1	558	/
DMF	36.7	0.8	567	/
Dioxane	2.2	1.5	553	/
Glycerol	45.8	956.0	619	759

* Viscosity of the solvent.

** Non-emissive.

Table S3. The probe TPAEQ for determining the added amount of food thickeners in fluid drinks via detecting viscosity.

Beverage type	Thickener	Determined amount* (mass percentage)	Commercially commonly-used amount (mass percentage)
Passion fruit juice	Xanthan gum	0.074%	0.01%-0.3%
Kaman orange juice	Sodium carboxymethyl cellulose	0.367%	0.01%-0.5%
Jasmine tea juice	Xanthan gum	0.022%	0.01%-0.3%
Pear juice	Sodium carboxymethyl cellulose	0.077%	0.01%-0.5%
Seabuckthorn juice	Xanthan gum	0.952%	0.1%-2%
Jam	Pectin	1.081%	1%-5%

*The mass percentage of determined amount was calculated from the measured fluorescent intensities with the fitting curves (Fig. 3d-3f).

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