Analytical Methods

Supplementary Information

Green extract rosemary acid as a viscosity-sensitive molecular sensor in the liquid system

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Experimental Section

Materials and methods

Potassium carbonate, tetrahydrofuran (THF), toluene, dimethylsulfoxide (DMSO), tetrahydrofuran (THF), N,N-dimethylformamide (DMF), ethanol, ethyl acetate (EA), glycerol and various metal salts such as the sodium chloride, sodium nitrate, and so on, were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Common food additives including the glucose, D-mannitol, acesulfame, sorbitol, sodium carboxymethyl cellulose (SCC), pectin (Pec), xanthan gum (XG), trisodium citrate dehydrate (TCD), vitamin C (VC), sodium benzoate (SB) and beet molasses (BM) were obtained from Energy-chemical technology (Anhui) Co., Ltd. All the chemical reagents used in this work were of analytical grade and used as received. Triple distilled water was used in the experiments.

Fluorescence spectra were measured by a Hitachi F-7000 fluorescence spectrophotometer. Absorption spectra were recorded on a Hitachi U-3010 UV-vis spectrophotometer. The viscosity determination test was performed on a rotating viscometer (DV2T, Brookfield, AMETEK Corp., USA).

The Förster–Hoffmann equation

Förster–Hoffmann equation:

$$\log I = C + x \log \eta \tag{1}$$

where η represents the viscosity, I represents the fluorescence intensity of the natural molecular sensor **RA** at 421 nm, C is a constant, and x represents the sensitivity of the natural molecular sensor **RA** toward viscosity.

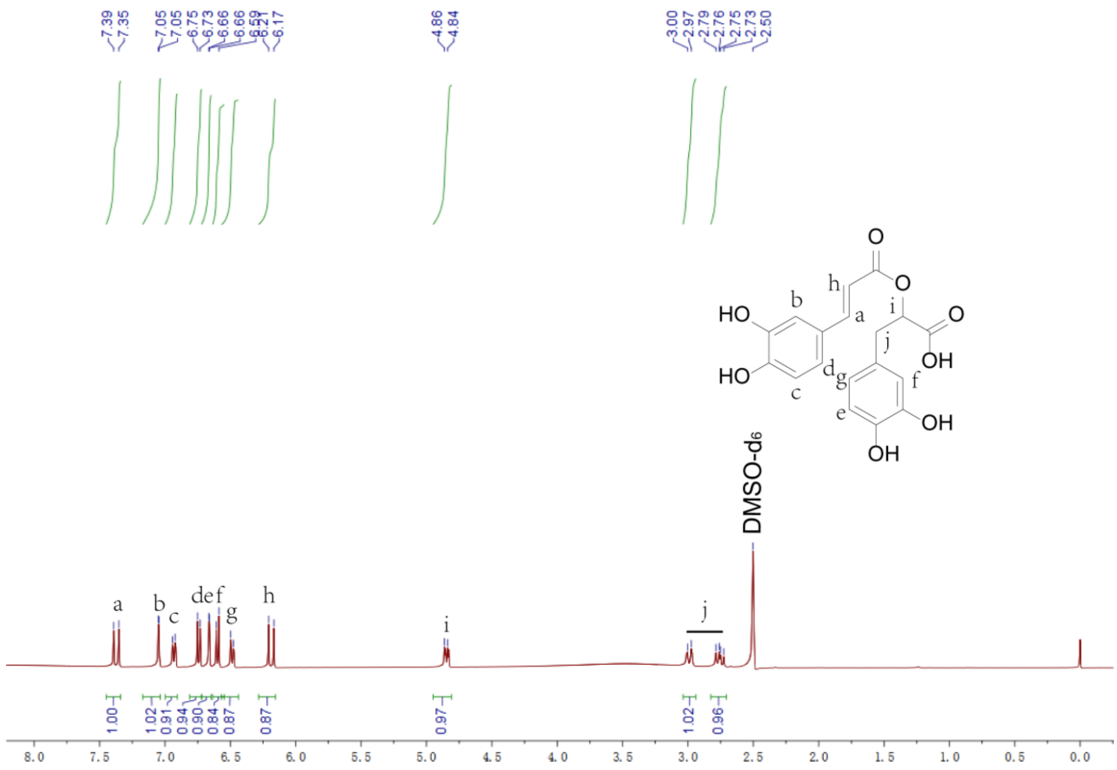


Figure S1 [1]H-NMR spectrum of the extracted molecular sensor rosmarinic acid.

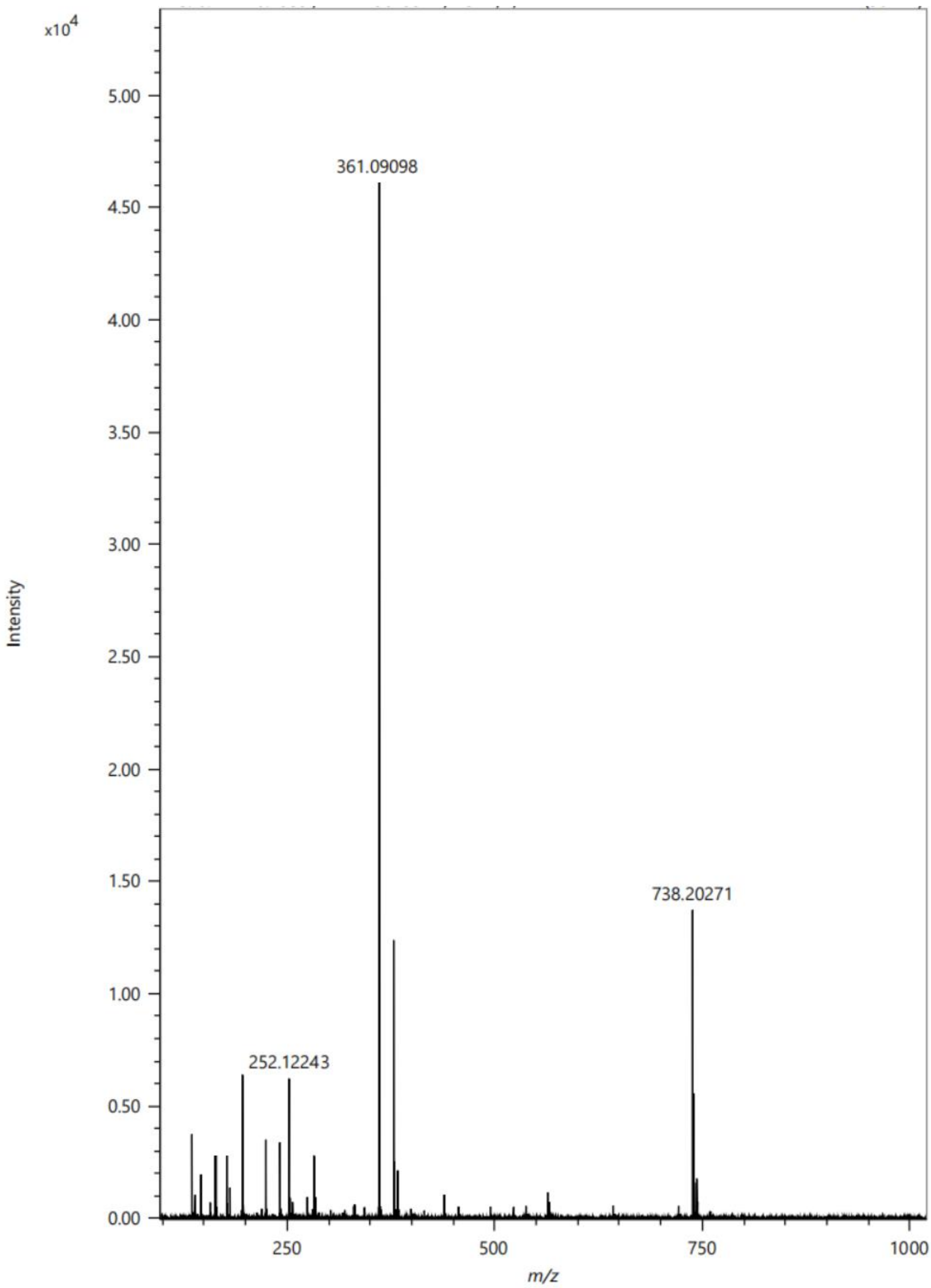


Figure S2 HR mass spectrum of the extracted molecular sensor rosmarinic acid. MS (ESI): m/z 361.09098 $[M+H]^+$.

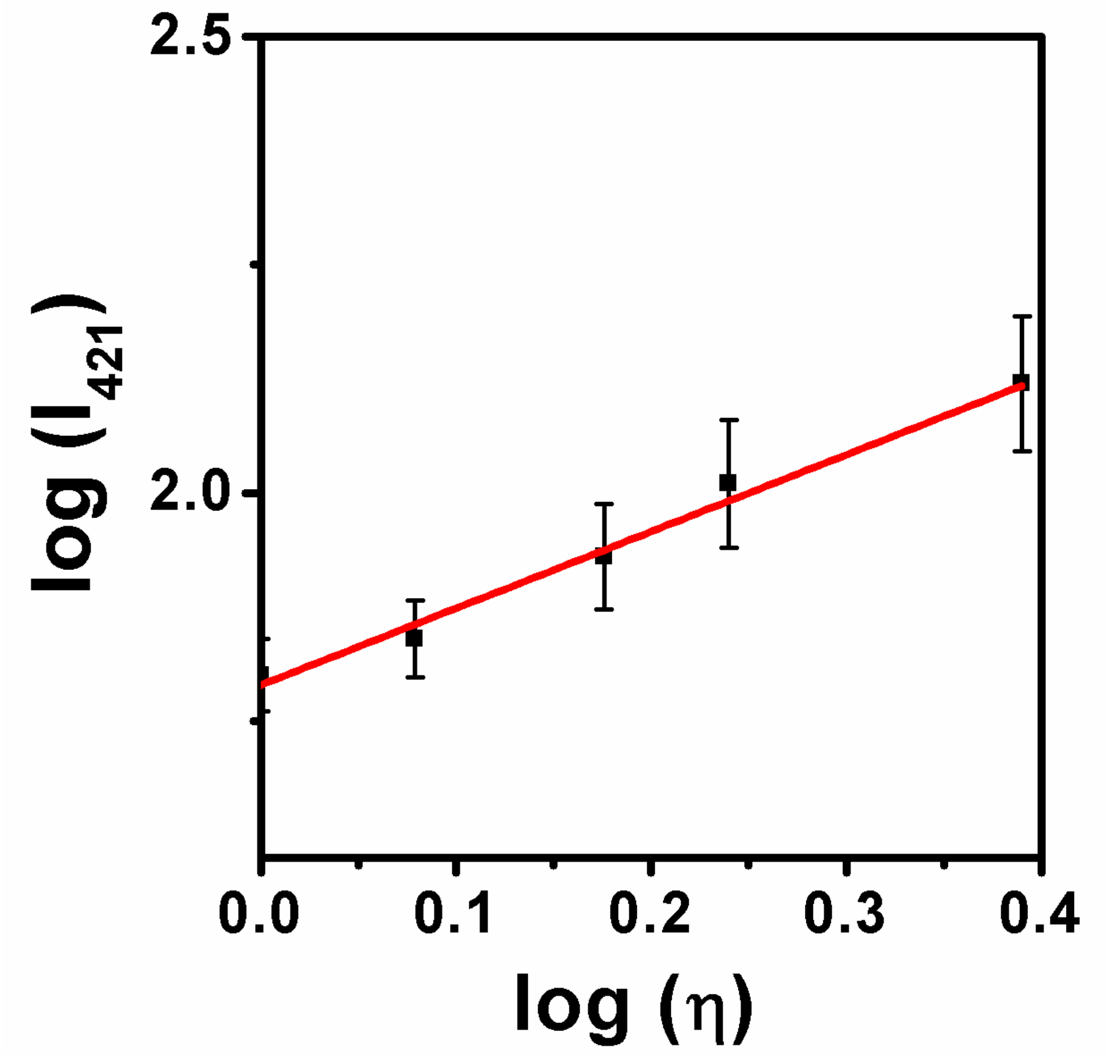


Figure S3 Detection limit of the natural molecular sensor rosmarinic acid (RA).

The calibration curve was first obtained from the plot of log (I_{421}) as a function of log (η). Then the regression curve equation was obtained for the lower viscosity part.

The detection limit = 3 × *S.D.*/*k*

Where *k* is the slope of the curve equation, and *S.D.* represents the standard deviation for the log (I_{421}) of natural molecular sensor RA.

log (I_{421}) = 1.789 + 0.842 × log (η) (R^2 = 0.990)

log (LOD) = 3 × 0.032/0.842 = 0.114

LOD =10^0.114 =1.301 cP

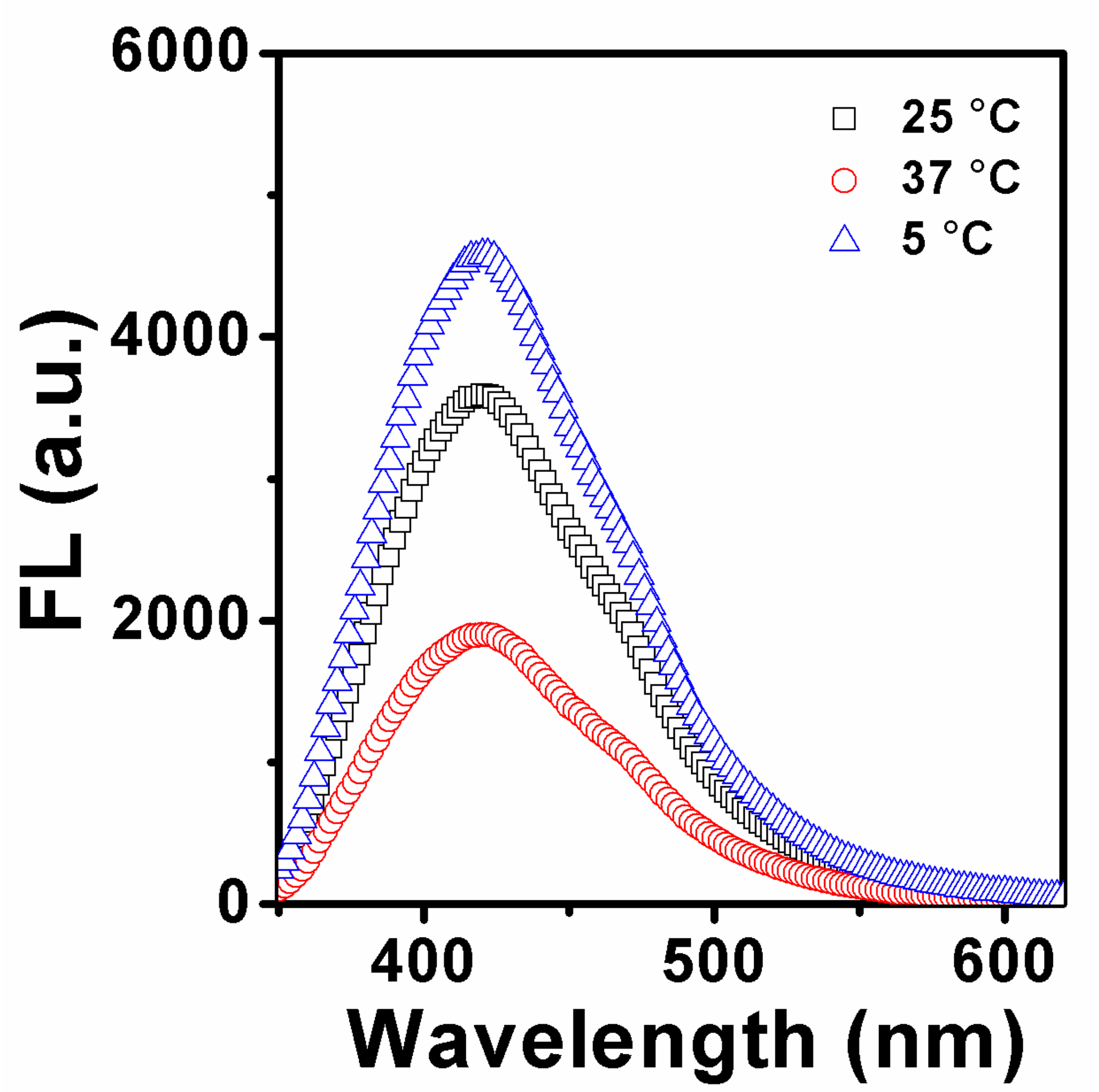


Figure S4 Fluorescence spectra of the natural molecular sensor **RA** (10 μM) in glycerol under different temperature, including the ambient temperature (25 °C), higher storage temperature (37 °C), and lower storage temperature (5 °C).

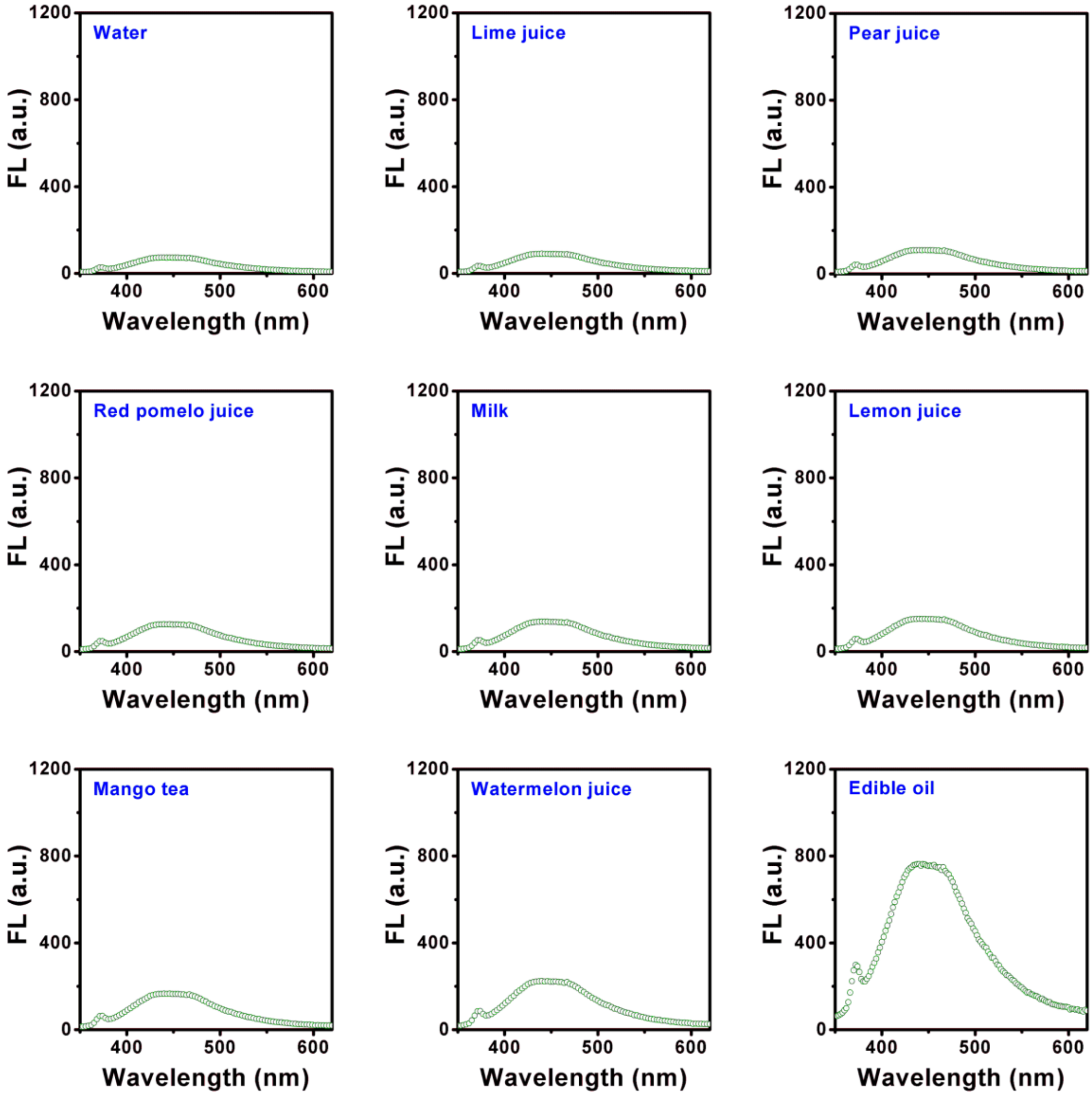


Figure S5 Fluorescence spectra of the natural molecular sensor **RA** (10 μM, containing 1% DMSO) in nine kinds of common liquid food, including the water, lime juice, pear juice, red pomelo juice, milk, lemon juice, mango tea, watermelon juice and edible oil, λ_{ex}=330 nm.

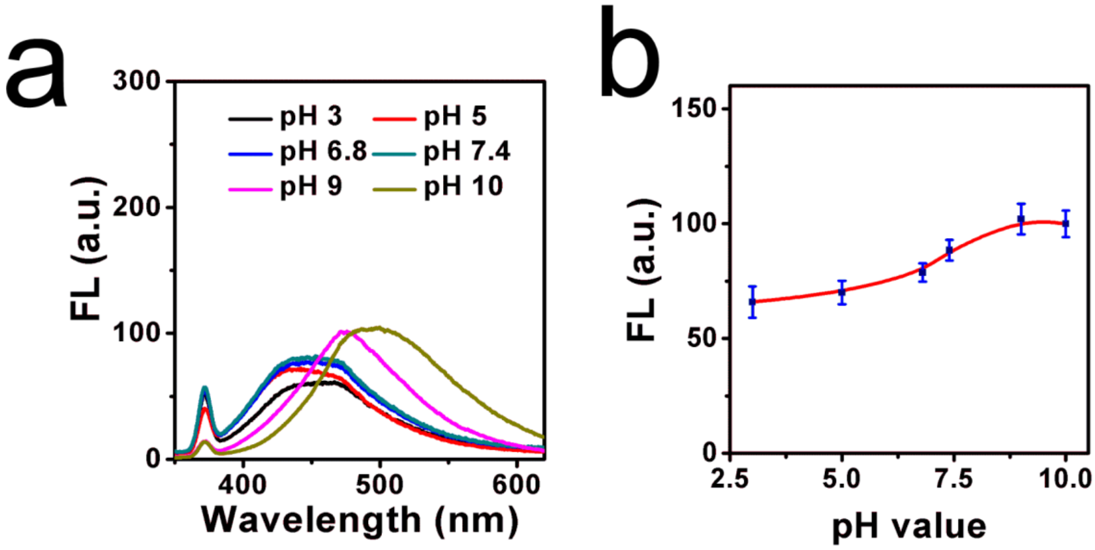


Figure S6 Fluorescence emission intensity of the natural molecular sensor **RA** (10 μM) under various pH values (containing 1% DMSO) in low viscosity water, λ_{ex}=330 nm.

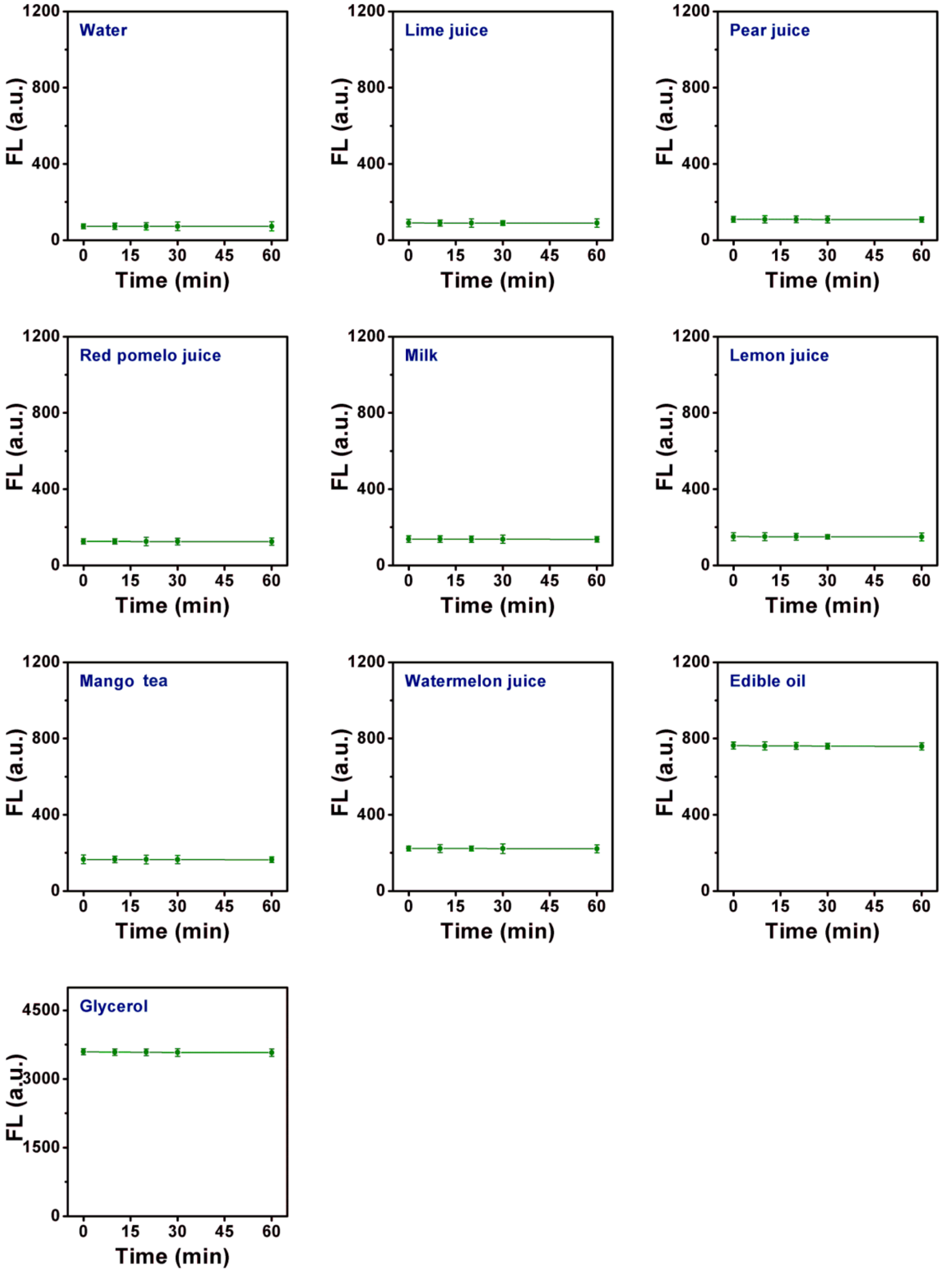


Figure S7 Photo-stability analysis of the natural molecular sensor **RA** in water, glycerol and other eight kinds of common liquids (containing 1% DMSO). All upon samples were tested under continuous light irradiation with 330 nm UV lamp.

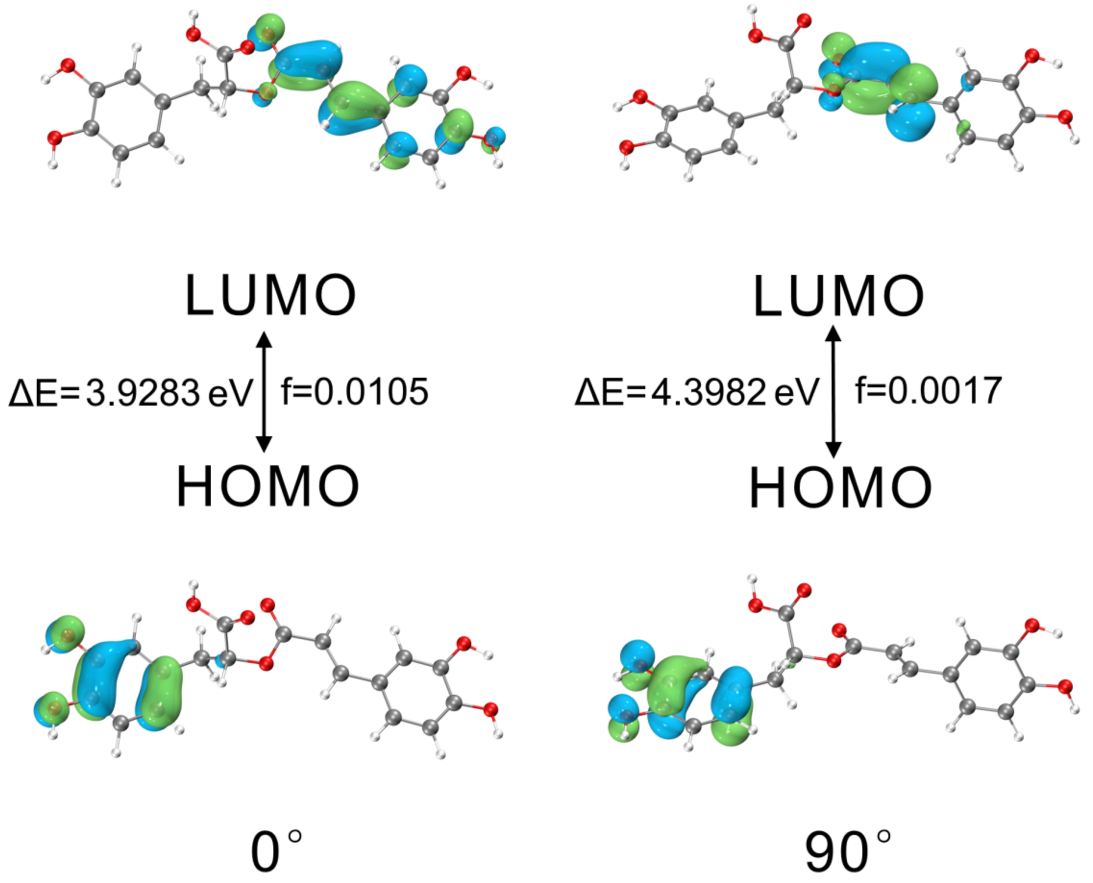
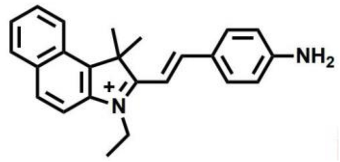
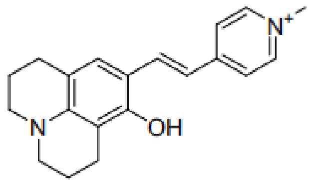
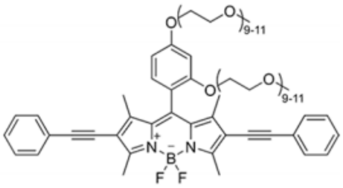
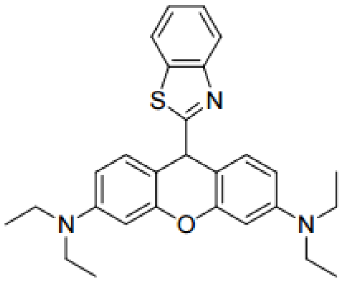
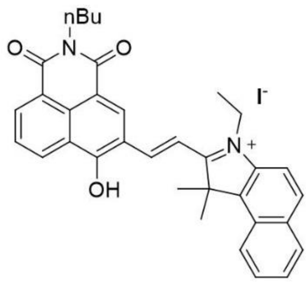
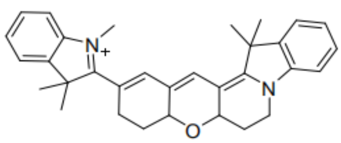
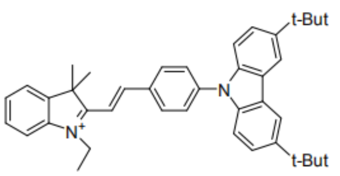
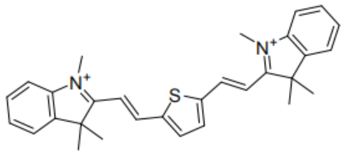
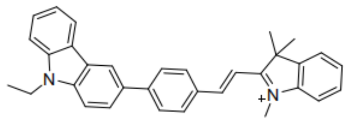
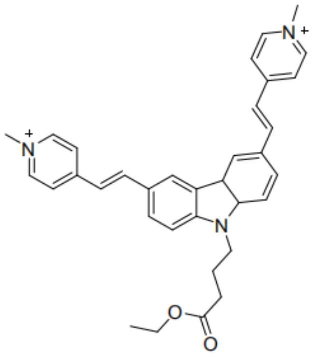
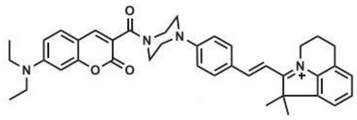
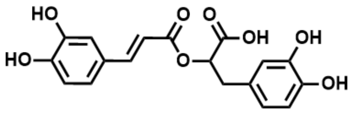


Figure S8 Optimized molecular structure and calculated molecular orbital energy levels of the LUMOs and HOMOs of **RA** based on B3LYP/6-31G basis set.

Table S1. Comparison of the representative fluorescence-based dyes for viscosity detection reported in recent years.

Probe	Sources	Stokes shift*	Application	Reference
	Artificial synthesis	72 nm	Biological system, living cells.	[1]
	Artificial synthesis	90 nm	Biological system, living cells.	[2]
	Artificial synthesis	20 nm	Biological system, living cells.	[3]
	Artificial synthesis	35 nm	Biological system, living cells, in vivo.	[4]
	Artificial synthesis	55 nm	Biological system, living cells.	[5]
	Artificial synthesis	20 nm	Biological system, living cells, rat slice.	[6]
	Artificial synthesis	83 nm	Biological system, living cells.	[7]

	Artificial synthesis	70 nm	Biological system, living cell.	[8]
	Artificial synthesis	90 nm	Biological system, living cell, zebra fish, mice.	[9]
	Artificial synthesis	90 nm	Biological system, living cell.	[10]
	Artificial synthesis	60 nm	Biological system, living cell.	[11]
	Natural product	88.0 nm	Liquid food, food spoilage analysis.	This work

* The stokes shift herein was obtained from the absorption and emission measured in the glycerol.

Table S2. Fluorescence intensity of commercial liquids with the molecular sensor **RA**.

Liquids	Fluorescence intensity
Water	63.10
Lime juice	93.22
Pear juice	113.50
Red pomelo juice	124.50
Milk	142.30
Lemon juice	149.50
Mango tea	170.60
Watermelon juice	230.80
Edible oil	758.60

Table S3. Viscosity values of the liquids determined by viscometer and fluorescent spectrometer.

Liquids	Viscosity (cP)	Calculated (cP)
Water	1.00	1.02
Lime juice	1.42	1.47
Pear juice	2.10	2.06
Red pomelo juice	2.44	2.49
Milk	3.01	3.03
Lemon juice	3.50	3.54
Mango tea	4.28	4.34
Watermelon juice	7.52	7.45
Edible oil	68.10	68.22

Table S4. Photo-physical properties of the molecular sensor RA in different solvents.

Solvents	Dielectric constant (ε)	η (cP)	Absorption λ_{ab} (nm)	Emission λ_{em} (nm)
Glycerol	45.8	956.0	333.8	421.8
Water	78.5	1.0	330.5	454.3
Toluene	2.4	0.6	324.5	377.8
DMSO	46.8	2.1	329.9	421.6
THF	7.4	0.5	327.9	412.1
Ethanol	24.9	1.2	328.8	415.4
DMF	36.7	0.8	329.4	418.1
EA	6.1	0.4	327.3	394.9

References

1 B. Chen, C. Li, J. Zhang, J. Kan, T. Jiang, J. Zhou and H. Ma, *Chem. Commun.*, 2019, **55**, 7410–7413.

2 G. Zhang, Y. Sun, X. He, W. Zhang, M. Tian, R. Feng, R. Zhang, X. Li, L. Guo, X. Yu and S. Zhang, *Anal. Chem.*, 2015, **87**, 12088–12095.

3 L.-L. Li, K. Li, M.-Y. Li, L. Shi, Y.-H. Liu, H. Zhang, S.-L. Pan, N. Wang, Q. Zhou and X.-Q. Yu, *Anal. Chem.*, 2018, **90**, 5873–5878.

4 M. Ren, L. Wang, X. Lv, J. Liu, H. Chen, J. Wang and W. Guo, *J. Mater. Chem. B*, 2019, **7**, 6181–6186.

5 L. Zhu, M. Fu, B. Yin, L. Wang, Y. Chen and Q. Zhu, *Dye. Pigment.*, 2020, **172**, 107859.

6 S. J. Park, B. K. Shin, H. W. Lee, J. M. Song, J. T. Je and H. M. Kim, *Dye. Pigment.*, 2020, **174**, 108080.

7 K. Zhou, M. Ren, B. Deng and W. Lin, *New J. Chem.*, 2017, **41**, 11507–11511.

8 Y. Baek, S. J. Park, X. Zhou, G. Kim, H. M. Kim and J. Yoon, *Biosens. Bioelectron.*, 2016, **86**, 885–891.

9 J. Yin, M. Peng and W. Lin, *Anal. Chem.*, 2019, **91**, 8415–8421.

10 Z. Zou, Q. Yan, S. Ai, P. Qi, H. Yang, Y. Zhang, Z. Qing, L. Zhang, F. Feng and R. Yang, *Anal. Chem.*, 2019, **91**, 8574–8581.

11 L. He, Y. Yang and W. Lin, *Anal. Chem.*, 2019, **91**, 15220–15228.