RSC Advances

Supplementary Information

A natural extract caffeic acid as an activatable molecular probe for viscosity detection in liquid system

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Experimental section

1 Materials and apparatus

Tetrahydrofuran (THF), toluene, dimethylsulfoxide (DMSO), N, N-dimethylformamide (DMF), methanol, ethyl acetate (EA), glycerol and various metal salts were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. 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.

Nuclear magnetic resonance (NMR) spectra were obtained with Bruker AVANCE III HD 600 NMR Spectrometer. High resolution mass spectra (HR-MS) were performed through Aglient 7250 & JEOL-JMS-T100LP AccuTOF mass spectrometer. 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).

2 The Förster–Hoffmann equation

Förster–Hoffmann equation:

$$\log I = C + x \log \eta \quad (1)$$

where η represents the viscosity, I represents the fluorescence intensity of the natural molecular probe CaC at 400 nm, C is a constant, and x represents the sensitivity of the natural molecular probe CaC toward viscosity.

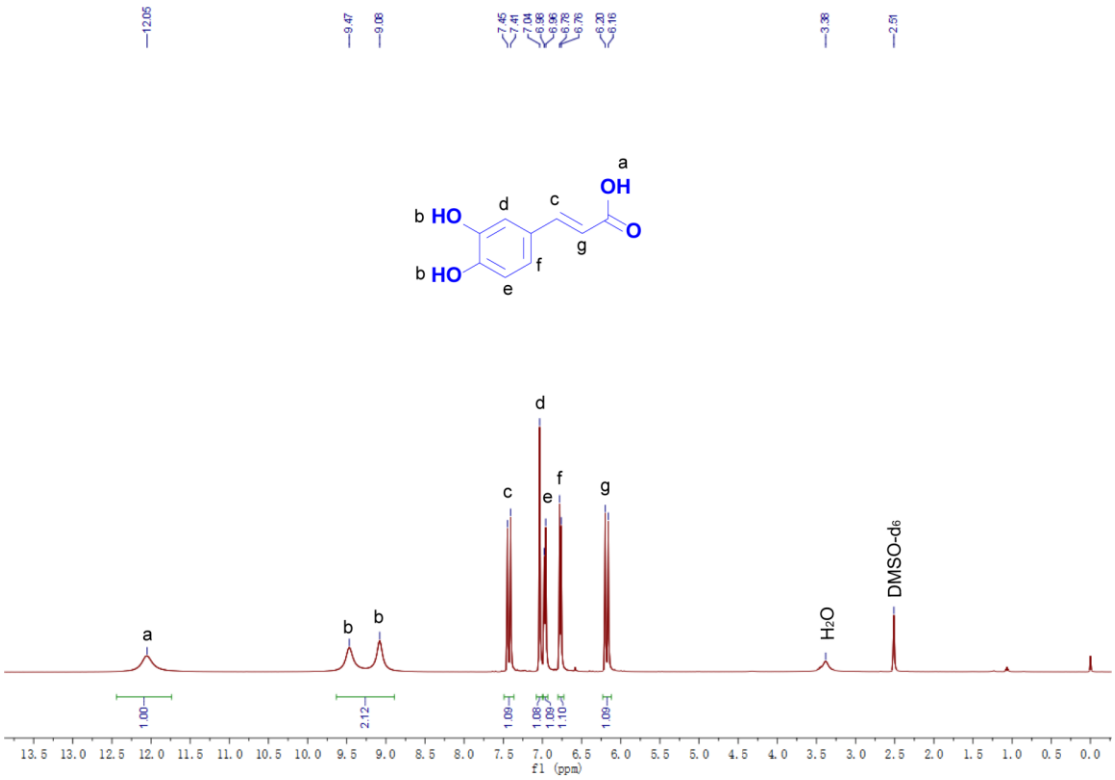


Figure S1 ^{1}H NMR spectrum of the extracted molecular probe caffeic acid (CaC).

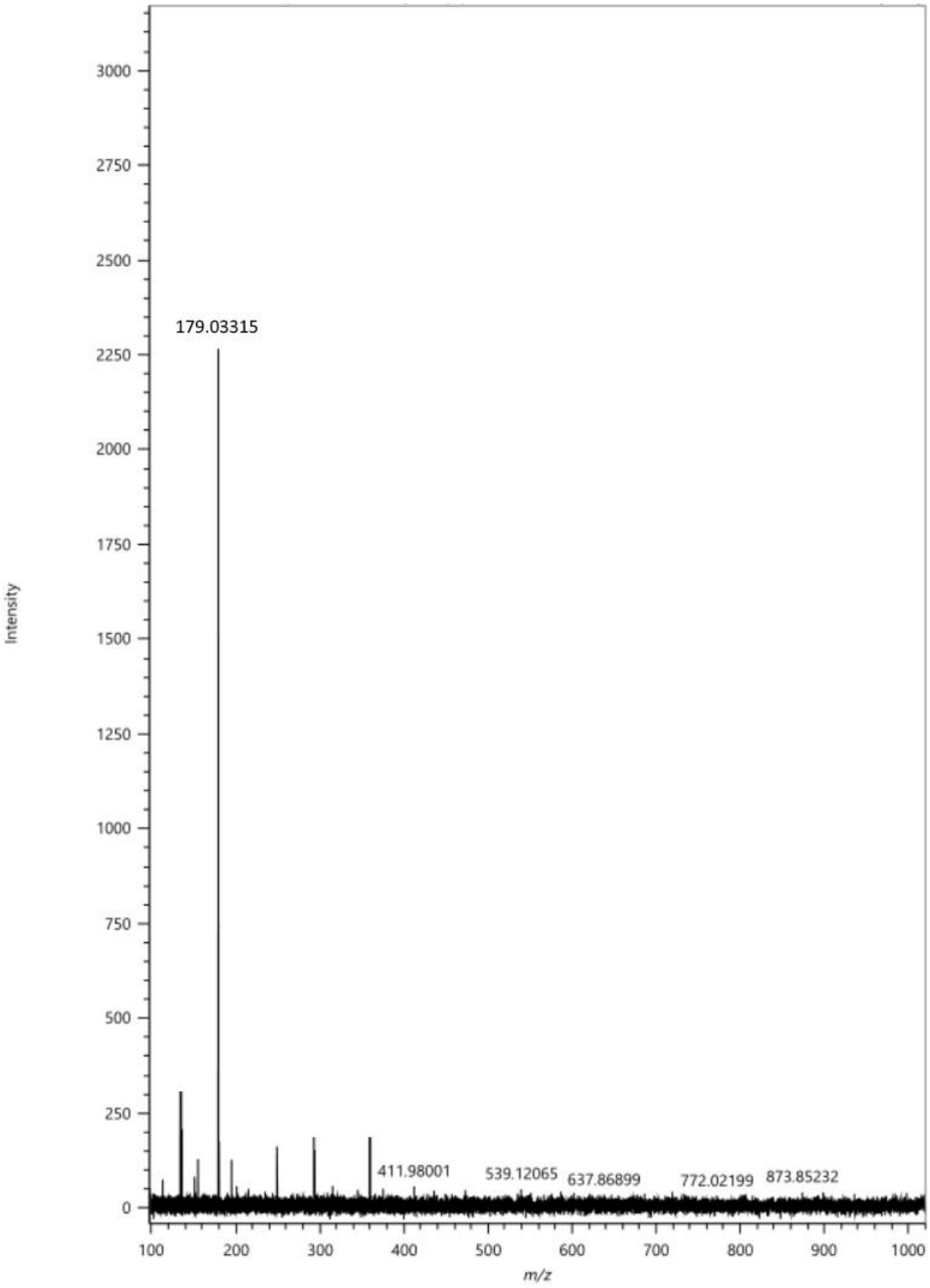


Figure S2 HR mass spectrum of the extracted molecular probe caffeic acid (CaC). MS (ESI): m/z 179.03315 $[M-H]^+$.

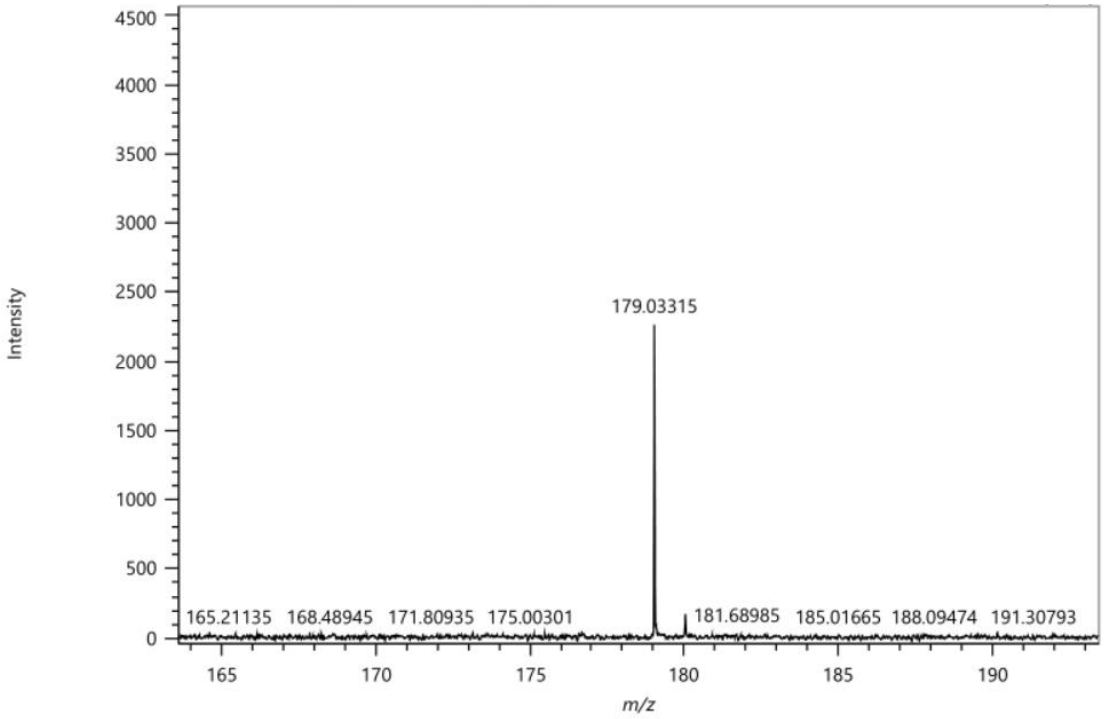


Figure S3 Partial enlargement of the spectrum on the caffeic acid (CaC) $[M-H]^+$.

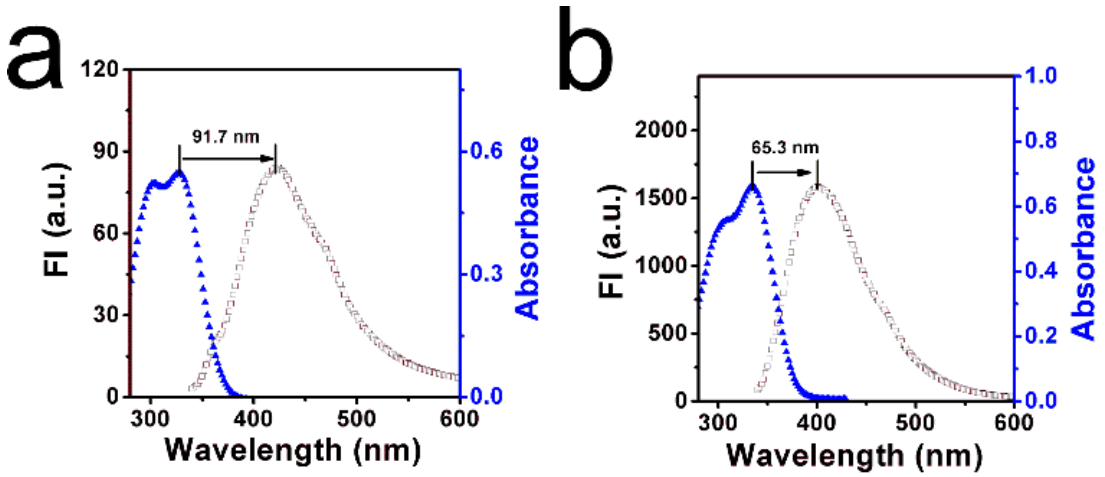


Figure S4 (a) Recorded absorption and emission spectra of CaC in water. (b) Recorded absorption and emission spectra of CaC in glycerol.

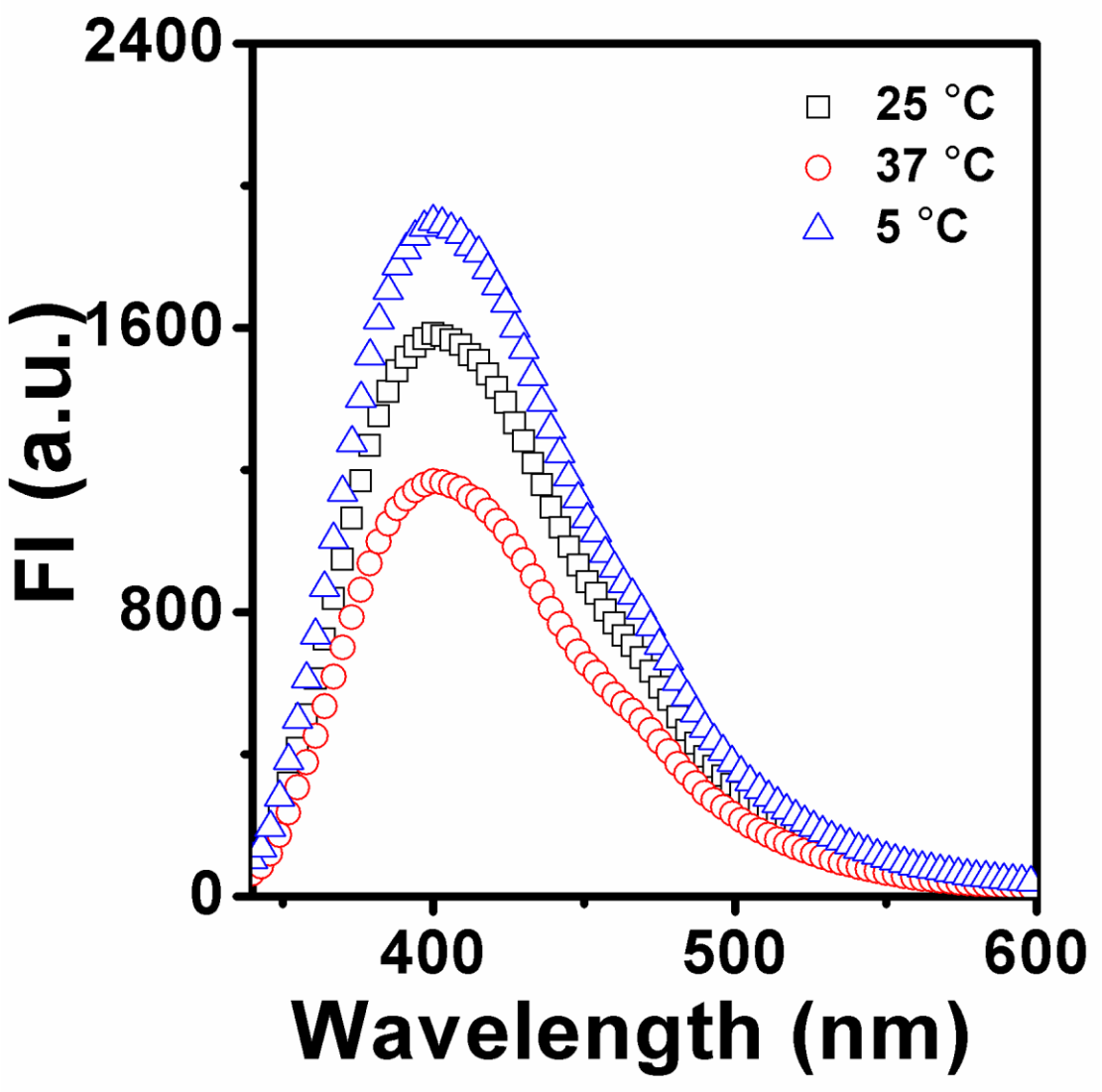


Figure S5 Fluorescence spectra of the natural molecular tool CaC (10 μM) in glycerol under different temperature, including the ambient temperature (25 °C), higher storage temperature (37 °C), and lower-maintenance temperature (5 °C).

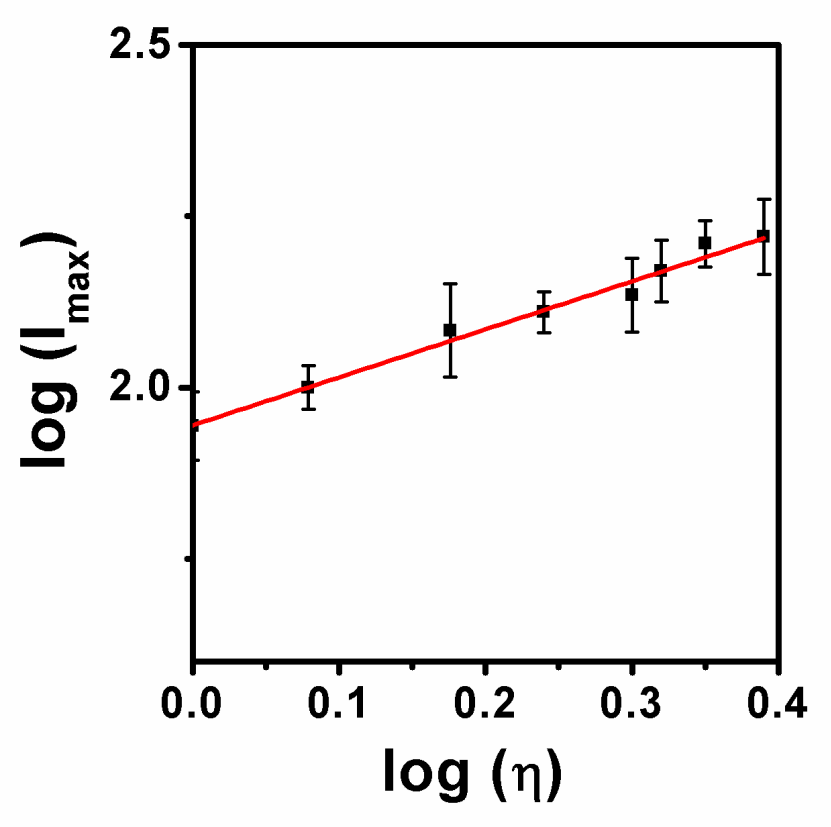


Figure S6 Detection limit of the natural molecular probe caffeic acid (CaC).

The calibration curve was first obtained from the plot of log (I_{max}) 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_{max}) of natural molecular probe CaC.

log (I_{max}) = 1.940 + 0.701 × log (η) (R^2 = 0.991)

log (LOD) = 3 × 0.031/0.701 = 0.132

LOD =10^0.132 =1.355 cP

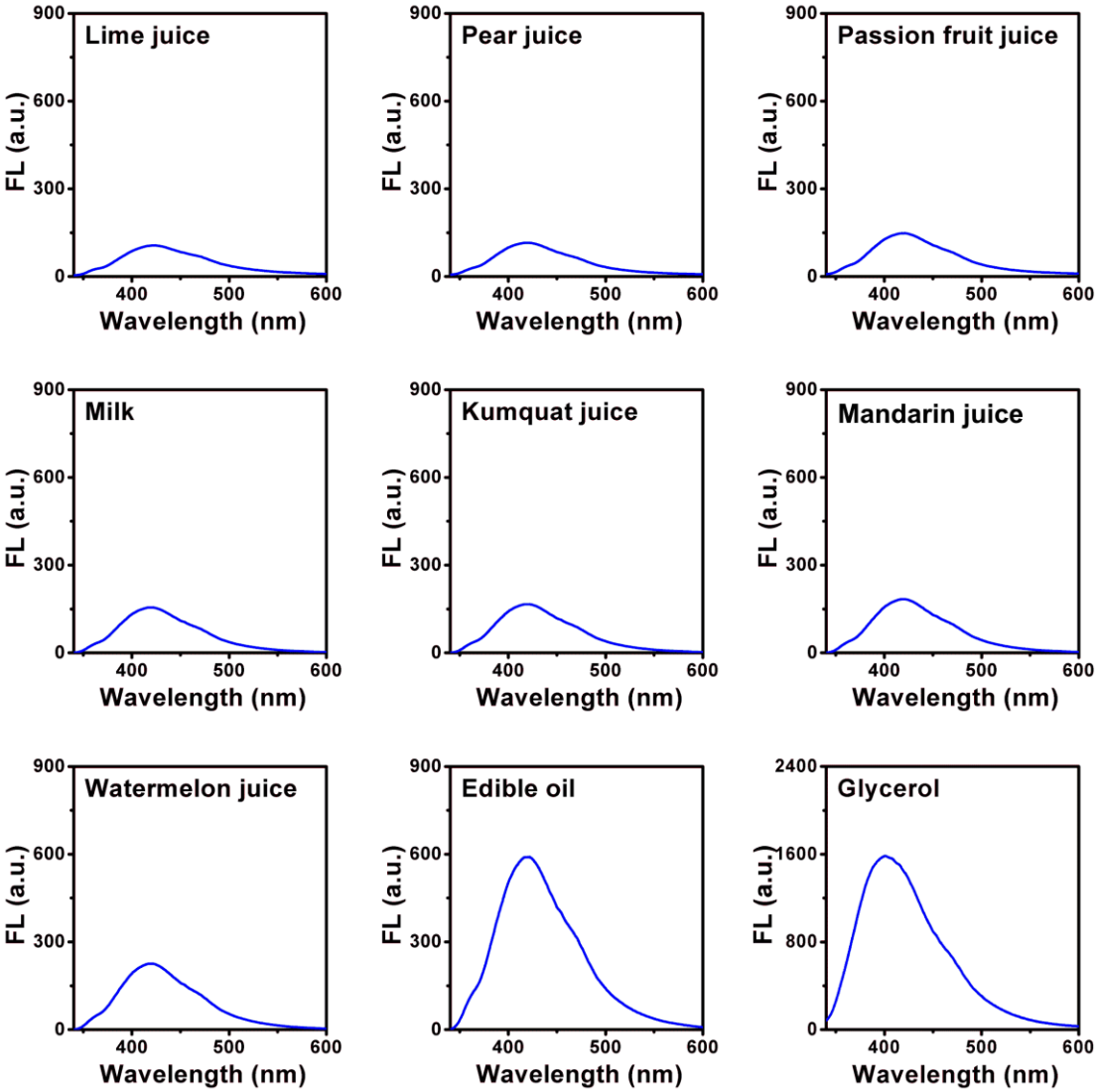


Figure S7 Fluorescence spectra of the natural molecular tool CaC (10 μM) in nine kinds of common liquids, including the lime juice, pear juice, passion fruit juice, milk, kumquat juice, mandarin juice, watermelon juice, edible oil and glycerol, λ_{ex}=320 nm.

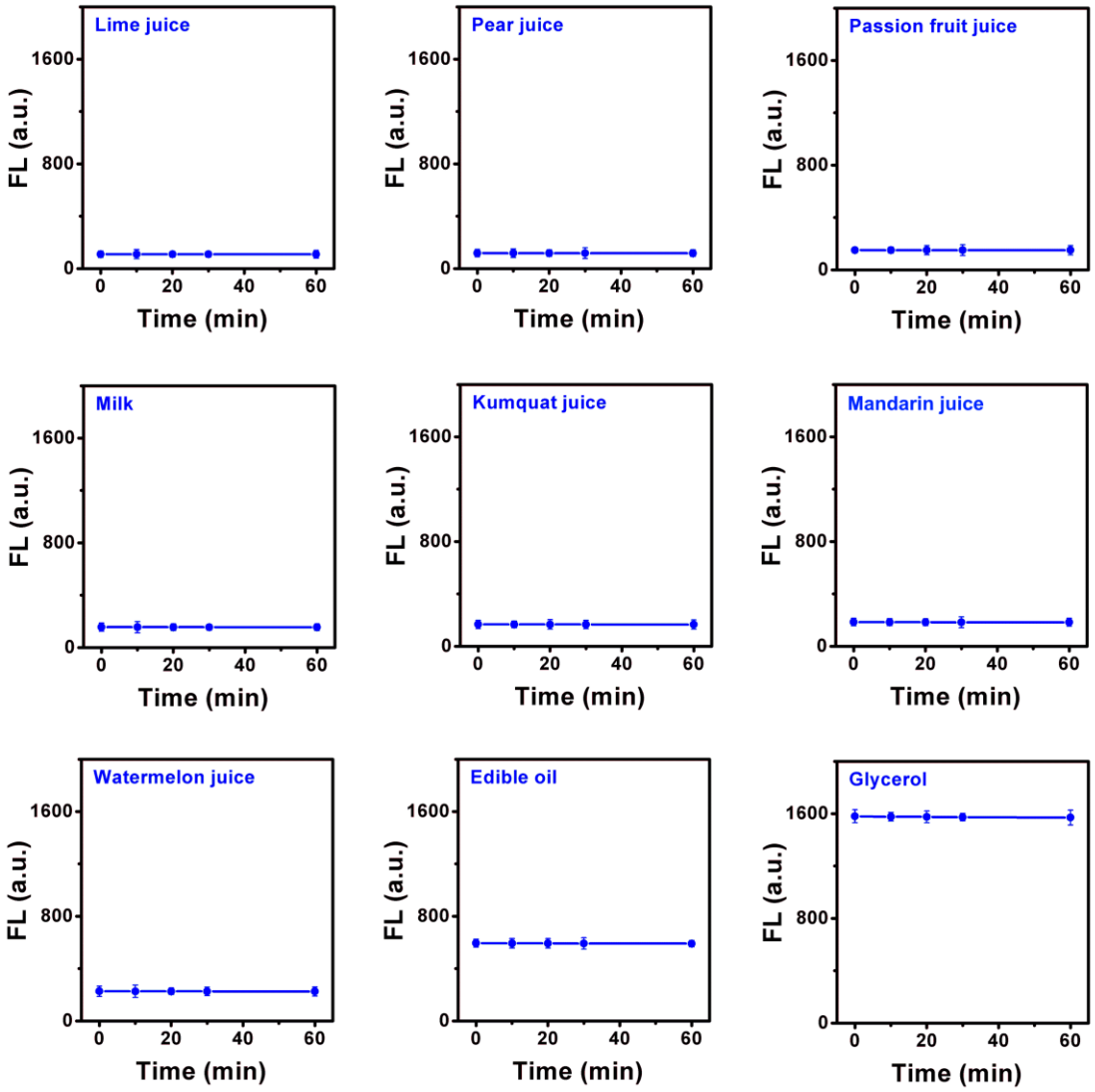


Figure S8 Photo-stability analysis of the natural molecular tool CaC in the glycerol and other eight kinds of common liquids. All upon samples were tested under continuous light irradiation with 320 nm UV lamp.

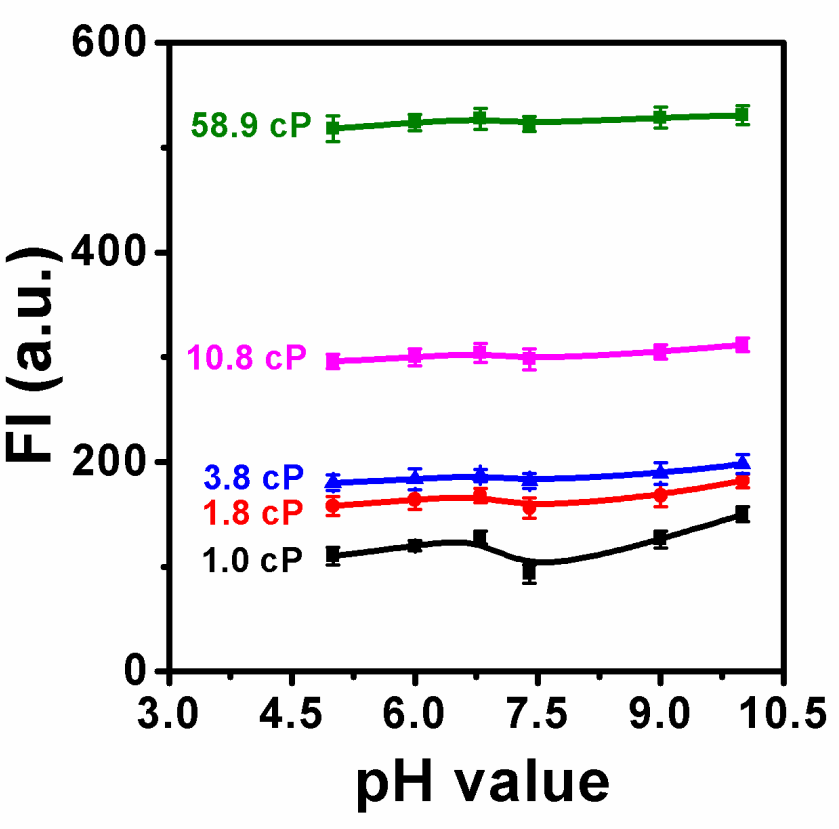


Figure S9 Fluorescence intensity of CaC (10 μM) in different mixed solvents with various volumes of glycerol (from 1.0 cP to 58.9 cP) at common pH range (5~10).

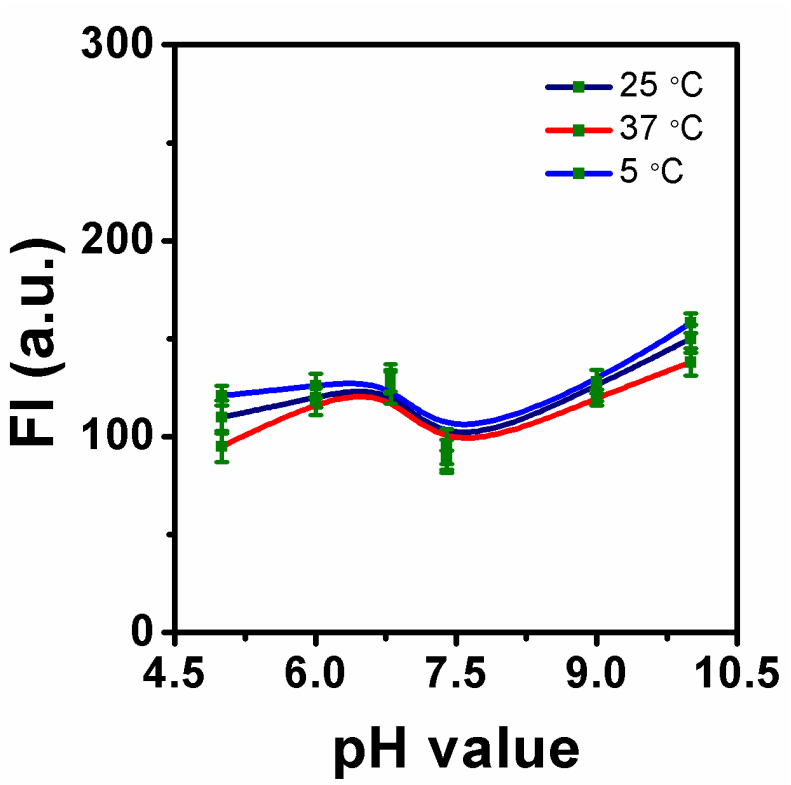


Figure S10 Fluorescence emission intensity of the natural molecular tool CaC (10 μM) during the common pH range in the distilled viscosity water under typical temperatures, λ_{ex}=320 nm.

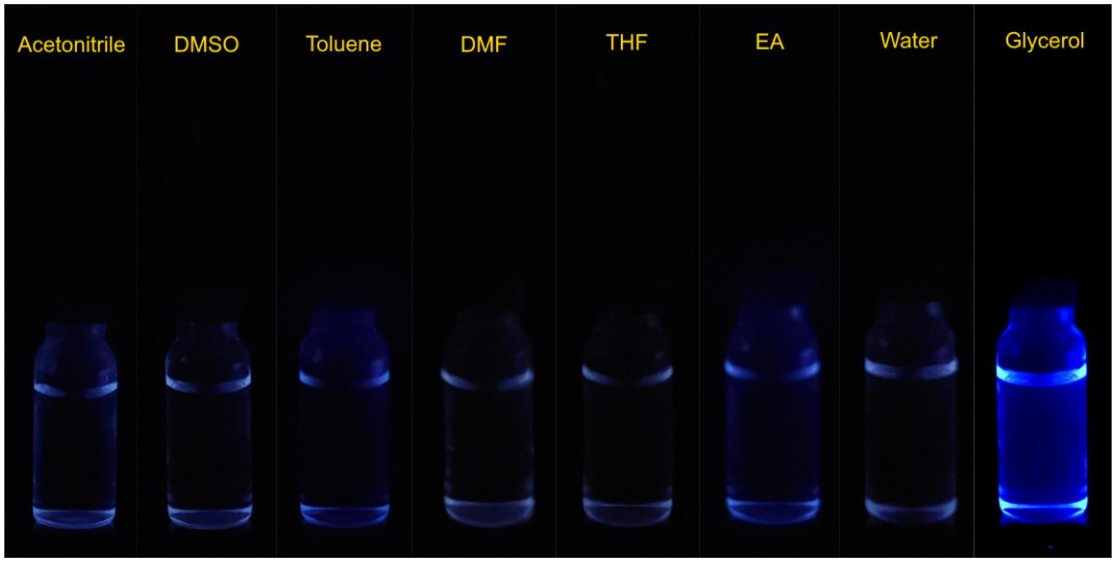


Figure S11 Visualized images of CaC under various solvents.

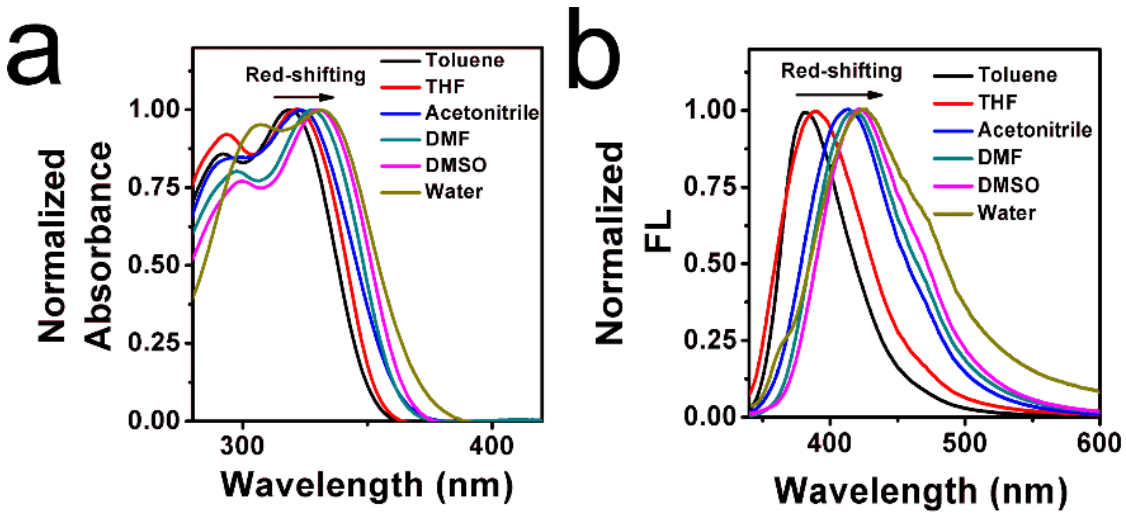


Figure S12 (a) Normalized absorption spectra of CaC in the toluene, THF, acetonitrile, DMF, DMSO, and water. (b) Normalized fluorescence spectra of molecular probe CaC in the six kinds of representative solvents.

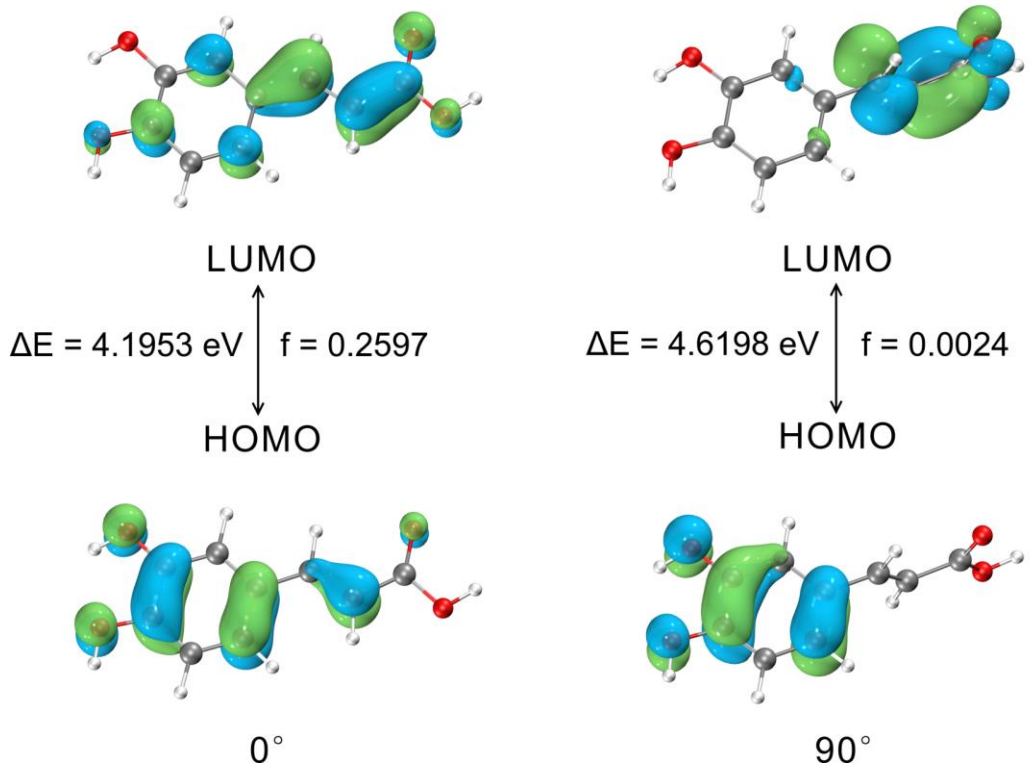


Figure S13 Optimized molecular structure and calculated molecular orbital energy levels of the LUMOs and HOMOs of CaC based on B3LYP/6-31G basis set.

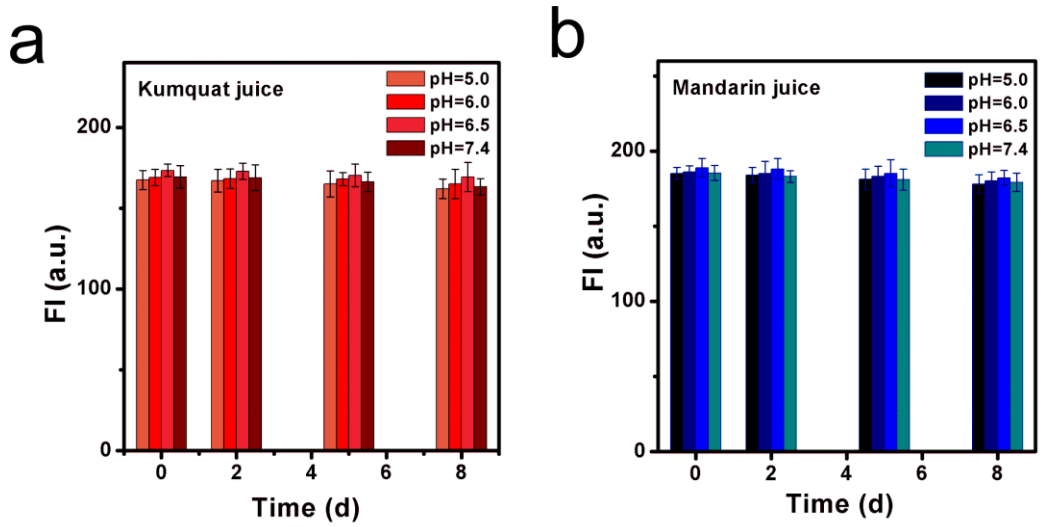
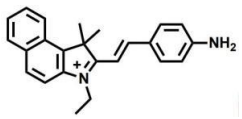
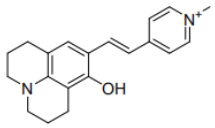
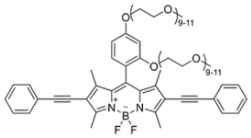
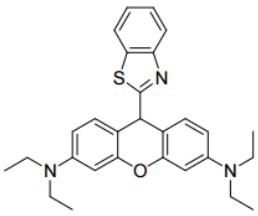
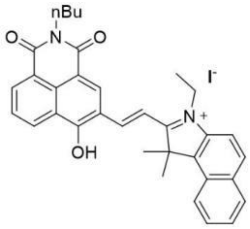
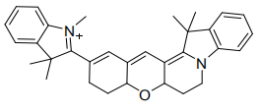
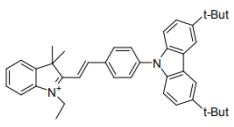
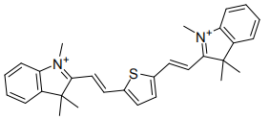
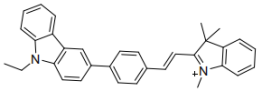
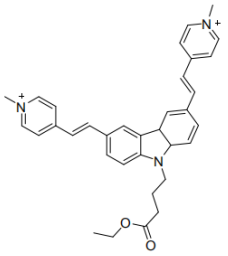
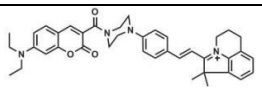
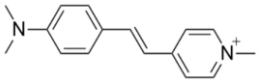
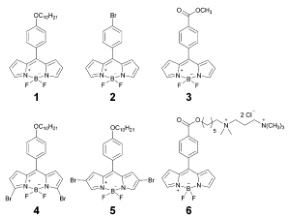
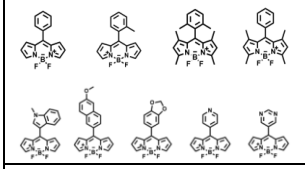
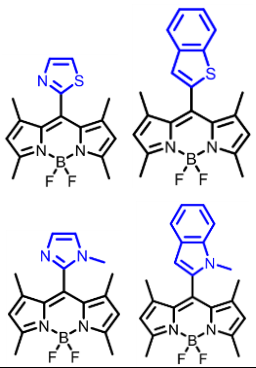
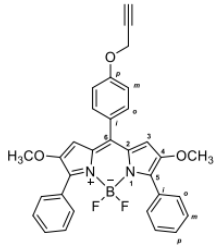
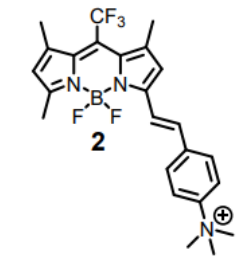
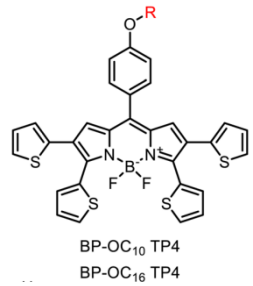
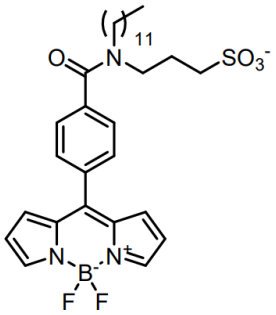
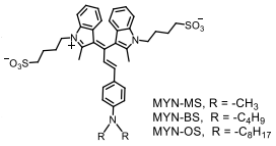
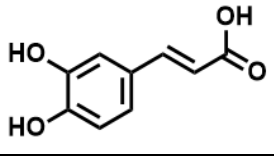


Figure S14 Fluorescence intensity of CaC (10 μM) stored under the same viscous media as (a) kumquat juice and (b) mandarin juice of various pH values (pH = 5.0, 6.0, 6.5, 7.4) for 8 days.

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

Probe	Sources	Sensitivity coefficient	Stokes shift*	Application	Reference
	Chemical synthesis	0.58	72 nm	Biological system, living cells.	[1]
	Chemical synthesis	/	90 nm	Biological system, living cells.	[2]
	Chemical synthesis	0.26	20 nm	Biological system, living cells.	[3]
	Chemical synthesis	0.41	35 nm	Biological system, living cells, in vivo.	[4]
	Chemical synthesis	0.45	55 nm	Biological system, living cells.	[5]
	Chemical synthesis	0.38	20 nm	Biological system, living cells, rat slice.	[6]
	Chemical synthesis	0.43	83 nm	Biological system, living cells.	[7]
	Chemical synthesis	0.59	70 nm	Biological system, living cell.	[8]

	Chemical synthesis	0.52	90 nm	Biological system, living cell, zebra fish, mice.	[9]
	Chemical synthesis	0.53	90 nm	Biological system, living cell.	[10]
	Chemical synthesis	0.46	60 nm	Biological system, living cell.	[11]
	Chemical synthesis	0.45	148 nm	Polymer solutions	[12]
	Chemical synthesis	0.25	20 nm	Cellular imaging	[13]
	Chemical synthesis	0.20	20 nm	Protein aggregation indication	[14]
	Chemical synthesis	0.32	20 nm	Organelle imaging	[15]
	Chemical synthesis	0.41	50 nm	DNA Labelling	[16]

	Chemical synthesis	0.39	30 nm	Mitochondria imaging.	[17]
	Chemical synthesis	/	75 nm	Living cells imaging.	[18]
	Chemical synthesis	0.28	20 nm	Plasma membrane imaging.	[19]
	Chemical synthesis	0.56	40 nm	Cell membrane imaging.	[20]
	Natural product	0.43	65 nm	Liquid system, 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 probe **CaC**.

Liquids	Fluorescence intensity
Lime juice	109.50
Pear juice	117.60
Passion fruit juice	150.66
Milk	156.10
Kumquat juice	167.42
Mandarin juice	184.50
Watermelon juice	226.98
Edible oil	594.30
Glycerol	1587.80

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

Liquids	Viscosity (cP)	Calculated (cP)
Lime juice	1.18	1.46
Pear juice	1.78	2.10
Passion fruit juice	2.36	2.82
Milk	2.79	3.06
Kumquat juice	3.32	3.56
Mandarin juice	4.51	4.62
Watermelon juice	7.48	7.52
Edible oil	68.00	67.88
Glycerol	956.00	962.30

Table S4. Photo-physical properties of the molecular probe **CaC** in different solvents.

Solvents	Dielectric constant (ε)	η (cP)	Absorption λ_{ab} (nm)	Emission λ_{em} (nm)
Glycerol	45.8	956.0	335.5	400.8
Water	78.5	1.0	331.8	423.5
Toluene	2.4	0.6	319.4	381.8
DMSO	46.8	2.1	330.8	422.2
THF	7.4	0.5	322.8	388.9
Acetonitrile	37.5	0.4	323.7	412.2
DMF	36.7	0.8	327.8	417.3
EA	6.1	0.4	321.8	387.6

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.

12 A. Y. Jee, E. Bae, and M. Lee, *J. Chem. Phys.*, 2010, **133**, 014507.

13 A. Vyšniauskas, I. López-Duarte, N. Duchemin, T. -T. Vu, Y. Wu, E. M. Budynina, Y. A. Volkova, E. P. Cabrera, D. E. Ramírez-Ornelas, and M. K. Kuimova, *Phys. Chem. Chem. Phys.*, 2017, **19**, 25252-25259

14 B. Shen, K. H. Jung, S. Ye, C. A. Hoelzel, C. H. Wolstenholme, H. Huang, Y. Liu, X. Zhang, *Aggregate*, 2023, **4**, e301.

15 W. Shi, X. Yan, J. Yang, Y. Wei, Y. Huo, C. Su, J. Yan, D. Han, L. Niu, *Anal. Chem.*, 2023, **95**, 9646–9653.

16 M. Kuba, R. Pohl, T. Kraus, M. Hocek, *Bioconjugate Chem.*, 2023, **34**, 1, 133–139.

17 W. Shi, J. Yang, Y. Wei, X. Li, X. Yan, Y. Wang, H. Leng, L. Zheng, J. Yan, *Chem. Commun.*, 2022, **58**, 1930-1933.

18 R. Žvirblis, K. Maleckaitė, J. Dodonova-Vaitkūnienė, D. Jurgutis, R. Žilėnaitė, V. Karabanovas, S. Tumkevičius, A. Vyšniauskas, *J. Mater. Chem. B*, 2023, **11**, 3919-3928.

19 A. Polita, M. Stancikaitė, R. Žvirblis, K. Maleckaitė, J. Dodonova-Vaitkūnienė, S. Tumkevičius, A. P. Shivabalan, G. Valinčius, *RSC Adv.*, 2023, **13**, 19257-19264.

20 Y. Liu, X. Li, W. Shi, H. Ma, *Chem. Commun.*, 2022, **58**, 12815-12818.