Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

A novel bicoumarin-based multifunctional fluorescent probe for naked-eye sensing of amines/ammonia

Ensheng Zhang, [a,b] Xiufang Hou, [b] Hua Yang, [b] Yong Zou,[c] Ping Ju*[a]

[a] (*College of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, Shandong, 273165, China*)

[b] (*Laboratory of New Energy & New Functional Materials, College of Chemistry and Chemical Engineering, Yan'an University, Yan'an, Shaanxi, 716000, China*)

[c](*School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou, 510006, P. R. China*)

Email: xiangjianhuan110@163.com

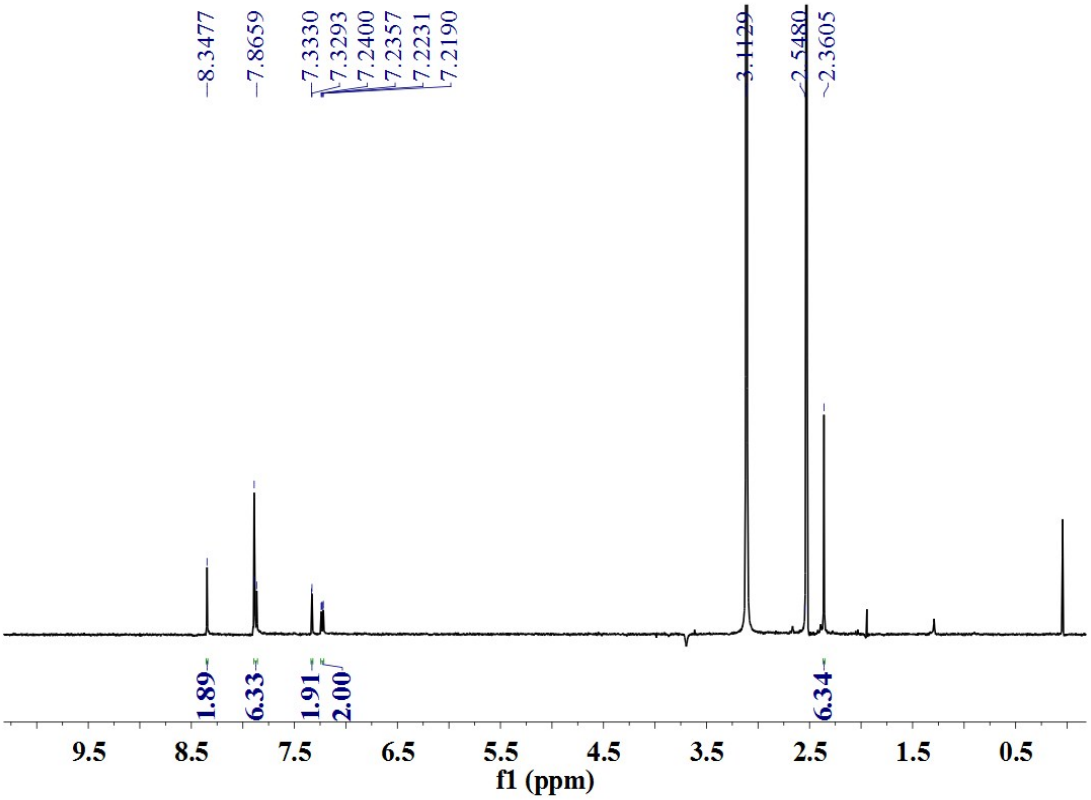


Fig. S1 [1]HNMR of ***apbis-c*** in DMSO-d_6 (500 MHz)

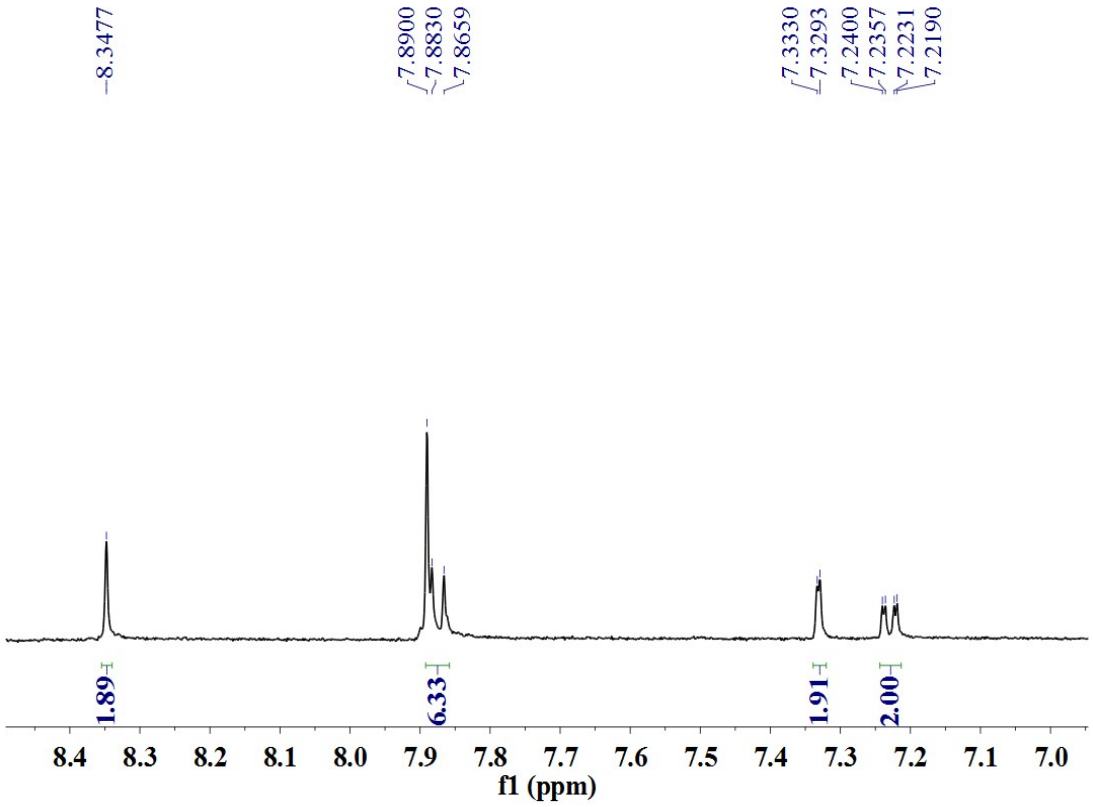


Fig. S2 [1]HNMR of ***apbis-c*** in DMSO-d_6 (500 MHz)

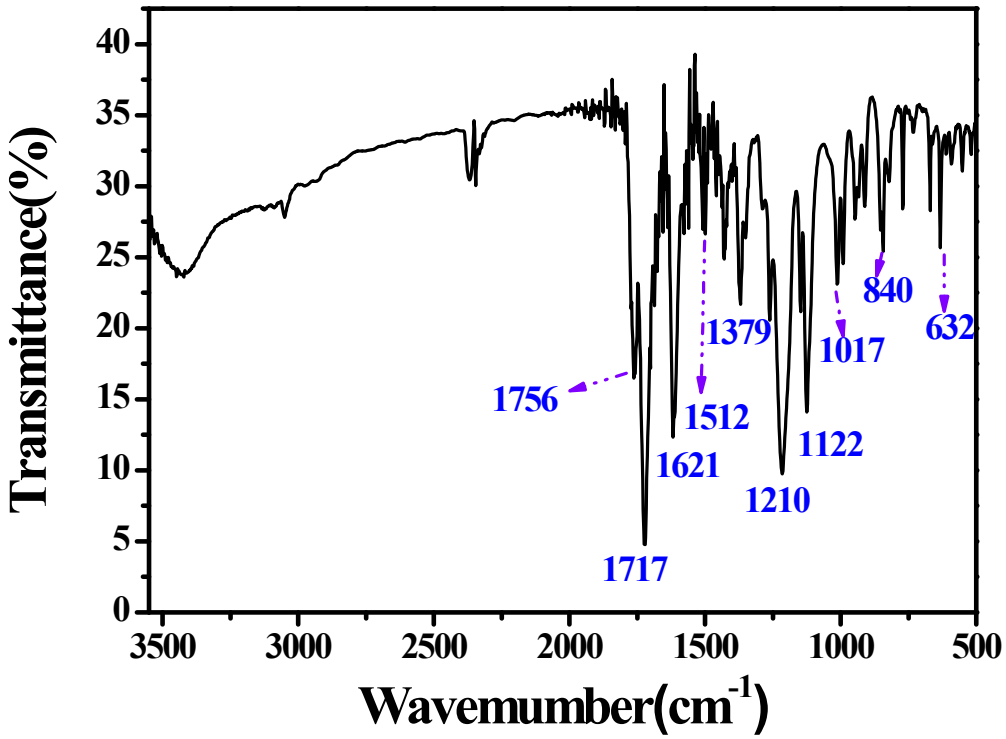


Fig. S3 FT-IR spectrum of ***apbis-c***

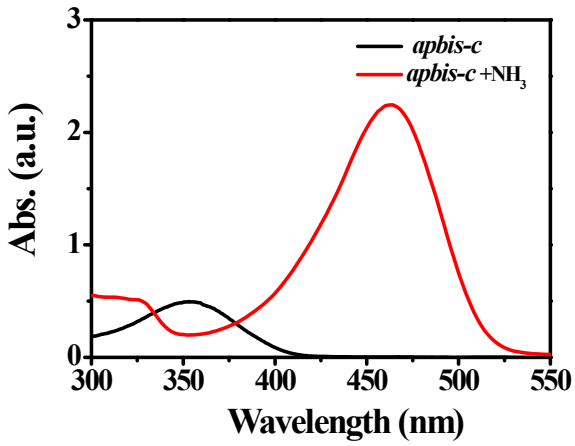


Fig. S4 UV-vis absorption spectra of ***apbis-c*** (50 μM) in the presence or absence of ammonia (200 μM) in DMSO.

pH effect

In order to find a suitable pH for the sensing property study, the effect of pH on the fluorescent intensity of this probe has been investigated. As shown in Fig. S5, fluorescent intensities of ***apbis-c*** in the mixture solvents of THF and water were recorded with gradually changing the pH values. Apparently, no obvious intensity change was observed in a wide range of pH from 2.0 to 10.0.

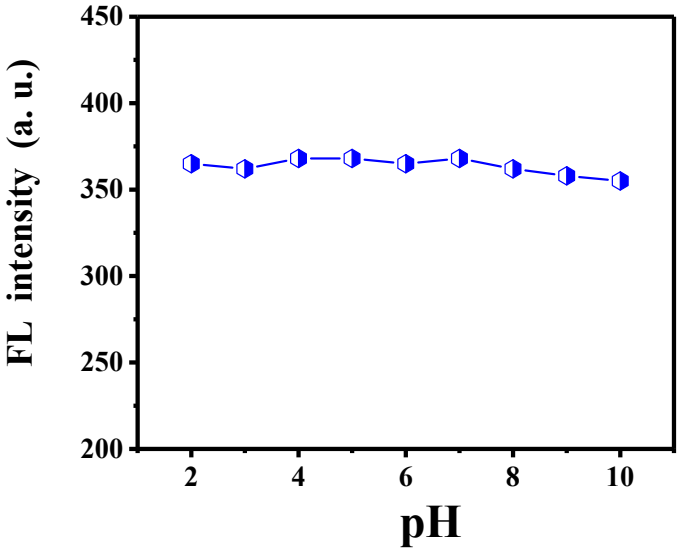


Fig. S5 Fluorescent intensity of ***apbis-c*** (50 μM) at various pH values (λ_{ex} = 356 nm, λ_{em} = 445 nm).

Response time study

In order to investigate the response time, fluorescent intensities centered at 445 nm of the sensor were recorded every ten seconds after exposure to excess ammonia vapor. Plot of fluorescent intensities *versus* the exposure time was displayed in Fig. S6. Interestingly, fast fluorescent quenching was observed in less than ten seconds. As shown in Fig. S6, the fluorescent intensity of the sensor changed from 778 to 30 in ten seconds. And no obvious fluorescent intensity change was observed with the increasing of exposure time (Fig. S6).

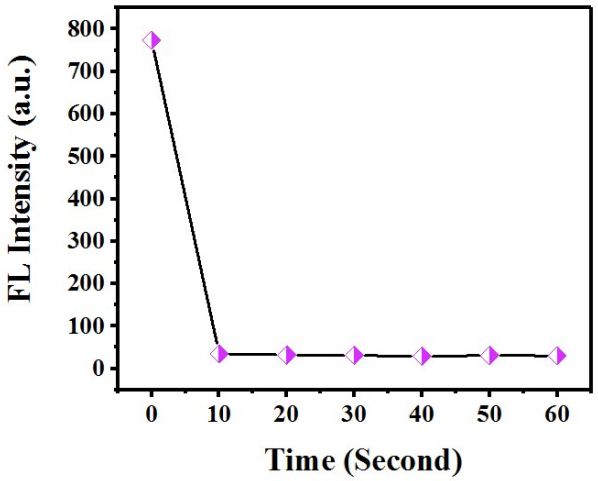


Fig. S6 Plot of fluorescent intensities centered at 445 nm *versus* the exposure time after exposure to excess ammonia vapor.

Calculated LOD

In order to reveal the potential sensitivity of ***apbis-c***, the theoretical LOD (or called the calculated LOD) was calculated by using $3\sigma/k$ (Linear calibration curve between F/F_0 and ammonia vapor concentration is displayed in Fig. S7; σ is the standard deviation of blank measurements; k is the slope between F/F_0 versus ammonia vapor concentration) according to the previous reports. (*ACS Sens.*, 2016, **1**, 179-184; *Chem. Eur. J.,* 2017, **23**, 14911-14917; *Chem. Commun.*, 2019, **55**, 9789-9792; *Talanta,* 2018, **178**, 522-529, et al.) The calculated LOD of ***apbis-c*** for ammonia vapor is 0.71 ppm (Table 1S, entry 11).

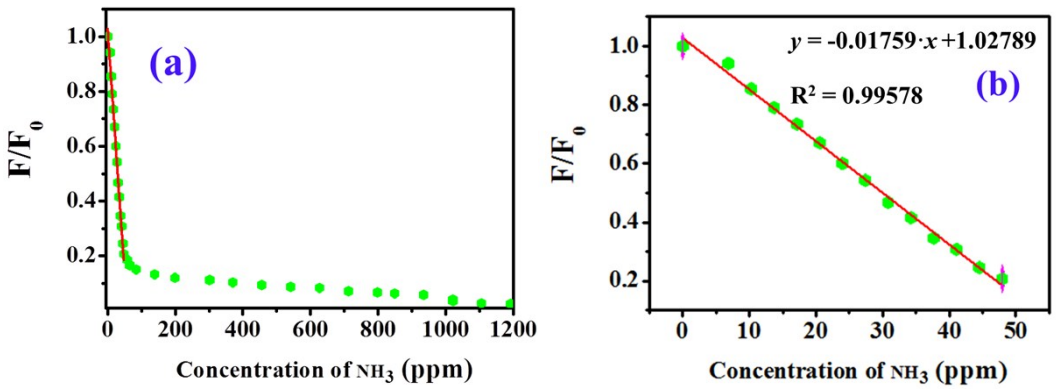


Fig. S7 (a) Plot of the F/F_0 versus the concentration of ammonia vapor (F_0 is the fluorescent intensity in the absence of ammonia vapor and F is the fluorescent intensity in the presence of ammonia vapor); **(b)** The enlarged view of linear calibration curve between F/F_0 (y) and ammonia vapor concentration (x) from 0 ppm to 48 ppm (The inset shows the linear regression equation).

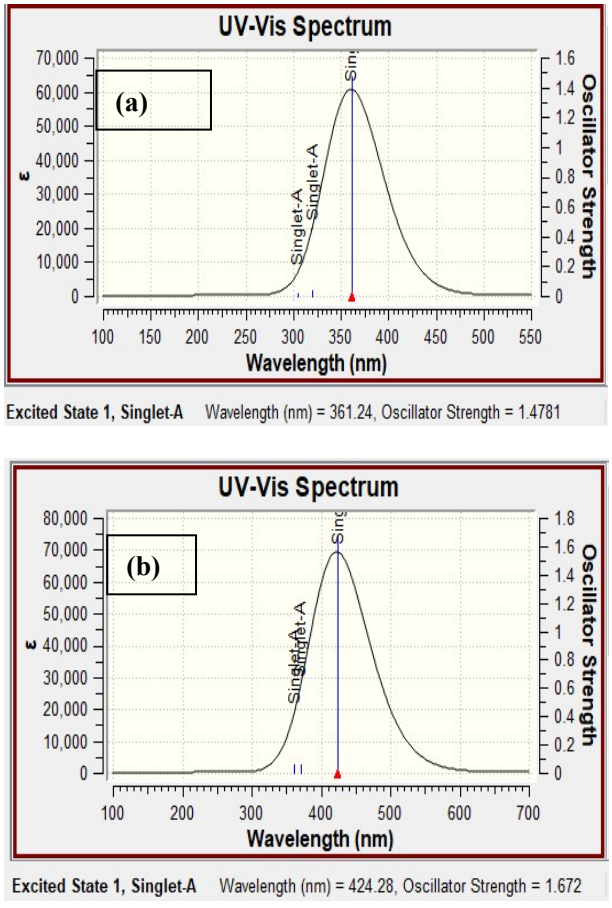


Fig. S8 The calculated UV-vis absorption spectra of ***apbis-c*** (**a**) and ***apbis-c***+8NH_3 (**b**) in DMSO.

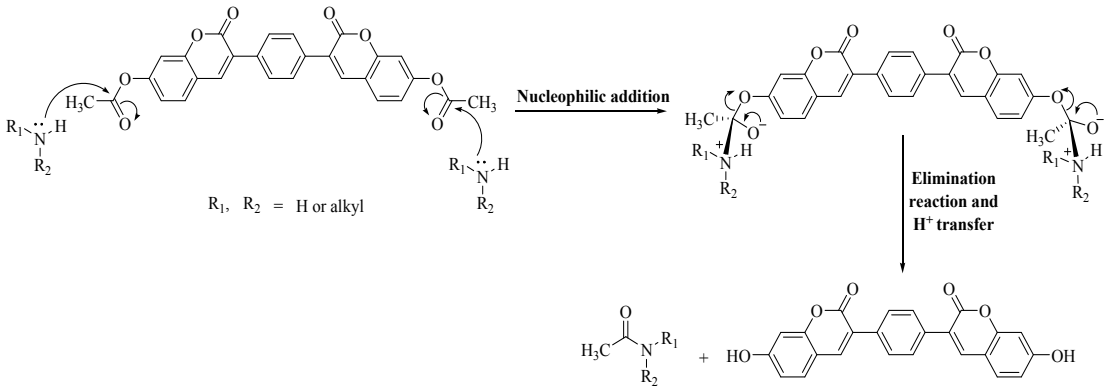
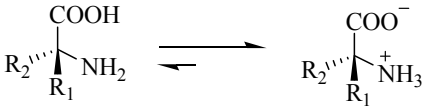
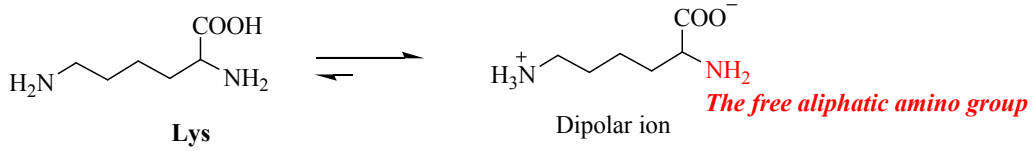


Fig. S9 Reaction mechanism of the ammonolysis process.



General molecular formula of the eighteen genetically encoded amino acids except Arg/Lys



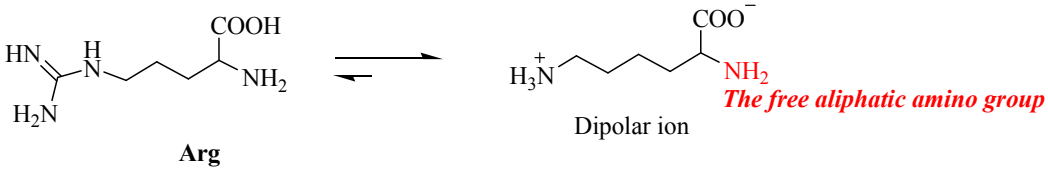


Fig. S10 Dipolar ion form or zwitterion structure of twenty genetically encoded amino acids

Table S1 The comparison of ***apbis-c*** with other probe for ammonia vapor sensing

	Sensing materials	**Response time**	**Experimental LOD**	**Theoretical LOD**	**Ref.**
1	Fluorescent probe (AIE)	5 minutes	10 ppm	8.4 ppm	1
2	Fluorescent Polymer	Real-time	Not Revealed	Not Revealed	2
3	Fluorescent and Colorimetric probe (AIE)	5 minutes	10 ppm	0.69 ppm	3
4	Fluorescent thin-films sensor based on fcu-MOF	1000 seconds	1 ppm	0.1 ppm	4
5	Fluorescent CdSe/SiO2 core-shell nanoparticles	6.1 seconds	10 ppm	1.2 ppm	5

6	FRET based method fluorescent probe	1 minute	6.83 ppm	Not Revealed	6
7	Fluorescent and colorimetric probe (carbon dots)	10 seconds	Not Revealed	3.0 ppm	7
8	Colorimetric probe (**Naked Eye**)	3 minutes	13 ppm	3.3 ppm	8
9	Fluorescent probe (AIE twain probe)	40 seconds	Not Revealed	1.64 Mm (2.61 Pa)	9
10	Fluorescent probe (AIE+TICT)	5 minutes	35 mM (44 Pa)	Not Revealed	10
11	Fluorescent and colorimetric probe (**Naked-eye** probe, ICT)	Less than 10 seconds	6.85 ppm	0.71 ppm	This work

References:

1 M. Gao, S. W. Li, Y. H. Lin, Y. Geng, X. Ling, L. C. Wang, A. J. Qin, B. Z. Tang, *ACS Sens.*, 2016, **1**, 179-184.

2 I. A. Adams , P. A. Rupar, *Macromol. Rapid Commun.,* 2015, **36**, 1336-1340.

3 P. Alam, N. L. C. Leung, H. F. Su, Z. J. Qiu, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Chem. Eur. J.,* 2017, **23**, 14911-14917.

4 A. H. Assen, O. Yassine, O. Shekhah, M. Eddaoudi, K. N. Salama, *ACS Sens.*, 2017, **2**, 1294-1301.

5 T. W. Sung, Y. L. Lo, *Sensor. Actuat. B-Chem.,* 2013, **188**, 702-708.

6 Q. Chang, J. Sipior, J. R. Lakowicz, G. Rao, *Anal. Biochem.,*1995, **232**, 92-97.

7 M. Ganiga, J. Cyriac, *Sensor. Actuat. B-Chem.,* 2016, **255**, 522-528.

8 K. Pan, C. D. Ji, L. J. Ma, M. Z. Yin, W. T. Yang, *Chem.-Asian. J.*, 2016, **11**, 2316-2321.

9 P. J. Shi, J. F. Wang, Y. D. Zhao, Y. Duan, L. Shi, Y. Hou, J. D. Hou, W. J. Li, T. Y. Han, *Talanta,* 2018, **178**, 522-529.

10 T. Y. Han, W. Wei, J. Yuan, Y. Duan, Y. P. Li, L. Y. Hu, Y. P. Dong, *Talanta*, 2016, **150**, 104-112.