Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Facile fabrication of luminescent Tb@HOFs-based films as highly sensitive platform for detecting nicotine and its metabolite cotinine via fluorescence sensing and smartphone

Zhongqian Hu, Bing Yan *

School of Chemical Science and Engineering, Tongji University, Siping Road 1239, Shanghai 200092, China.

* Corresponding author: Email address: byan@tongji.edu.cn (Bing Yan)

1. Experimental Section

1.1. Materials

Except for special instructions, all chemicals were commercially available involved in this work and were used without further purification, which include melamine (MA), benzene-1,3,5-tricarboxylic acid (TMA), nicotine, cotinine, benzene, toluene, ethylbenzene, xylene, benzo[a]pyrene, formaldehyde, crotonaldehyde, catechol, ammonia, hydrazinium hydroxide solution, 1,3-butadiene, lead, cadmium, chromium, dichloromethane, NaCl, KCl, NH_4Cl, $CaCl_2$, $MgCl_2$, Na_2CO_3, NaH_2PO_4, lysozyme, mucin, α-amylase and agarose. $Tb(NO_3)_3 \cdot 6H_2O$ was obtained by dissolving Tb_2O_3quantitatively in 37.5% HNO_3 followed by recrystallization. The aqueous solution with various pH values was prepared by adding different content of HNO_3 and NaOH in deionized water. Human saliva used in this work was purchased from Chang Feng Technology Co., Ltd (Dongguan, China) and the human saliva was diluted by 1:10 ratio with deionized water solution for cotinine test.

1.2. Instruments

The powder X-ray diffraction (PXRD) patterns were recorded on Bruker D8 ADVANCE diffractometer employing Cu Kα radiation (40 mA and 40 kV) with a 2θ range from 5° to 45° at room temperature. Scanning electron microscope (SEM) images were performed on a Hitachi S-4800 field emission scanning electron microscope operating at 3 kV. Energy dispersive X-ray spectroscopy (EDX) were obtained by the scanning electron microscope operating at 15 kV. Fourier transform infrared (FT-IR) spectra were obtained by a Nexus 912 AO446 infrared spectrum radiometer in the wavenumber range of 4000 - 400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) spectra were noted under the ultrahigh vacuum (< 10^{-6} Pa) at pass energy (93.90 eV) with Axis Ultra DLD spectrometer (Kratos, Japan) by employing an Mg Kα (1253.6 eV) anode. Inductively coupled plasma-optical

emission spectrometer (ICP/OES) was obtained by Agilent ICPOES730. Thermogravimetric (TG) curves were measured on a TA TGA 55 system operating at a heating rate of 10 ºC/min in the range of 25 ºC up to 800 ºC under N_2 atmosphere. The fluorescence spectra were obtained on an Edinburgh FLS920 spectrophotometer employing 450 W xenon lamp as the source of excitation with appropriate cutoff filter. The Commission International de I'Eclairage (CIE) coordinate were calculated by CIE1931 chromaticity coordinate calculation according to the fluorescence emission spectra. The UV-vis absorption spectra were carried on an Agilent 8453 spectrometer. The pH values of aqueous solutions were determined by an INESA PHS-25 pH meter with an E-201F pH composite electrode, which was carefully calibrated by standard buffer solution before testing. The HOMO-LUMO orbital energies were optimized by the B3LYP hybrid density functional and the basis set was 6-31G(d).

1.3. Synthesis of MA-TMA

MA-TMA material was synthesized by MA (melamine) and TMA (benzene-1,3,5-tricarboxylic acid) in deionized water according to the literature with some modification[30]. MA (0.5 mmol, 0.0631 g) and TMA (0.5 mmol, 0.1051 g) were respectively dissolved in deionized water (50 mL), which was heated at 80 ℃ with stirring until completely dissolved. Then, the solutions of MA and TMA were mixed and stirred for 1 h at room temperature. The crude product was collected by centrifugated and washed with deionized water three times. Finally, the pure white powder was dried on a vacuum oven at 50 ℃ for 12 h, which was named as MA-TMA.

2. Supporting Figures and Tables

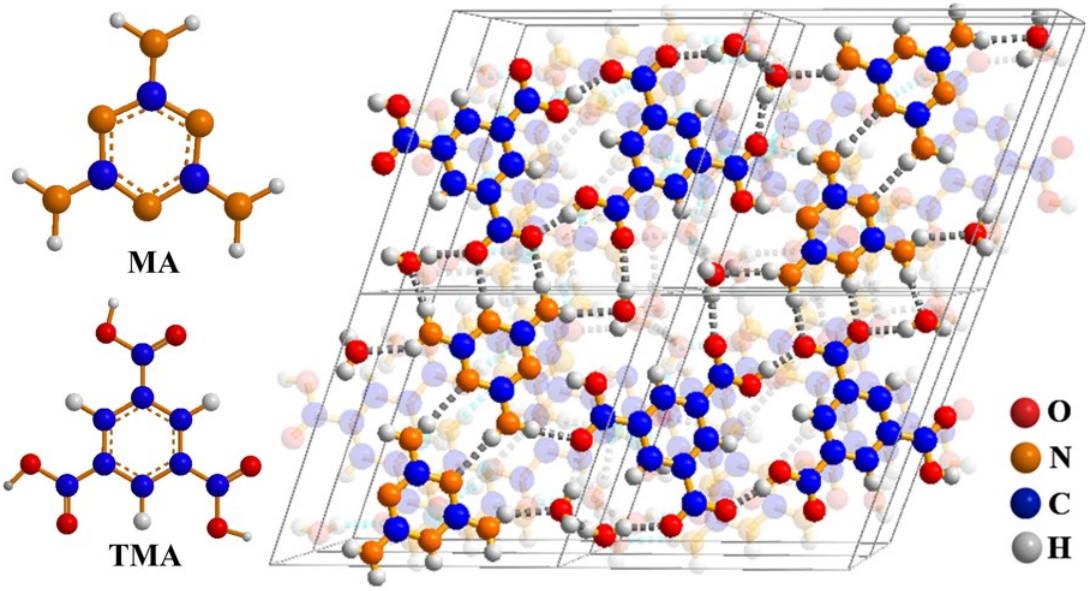


Fig. S1. The structure of MA, TMA and MA-TMA.

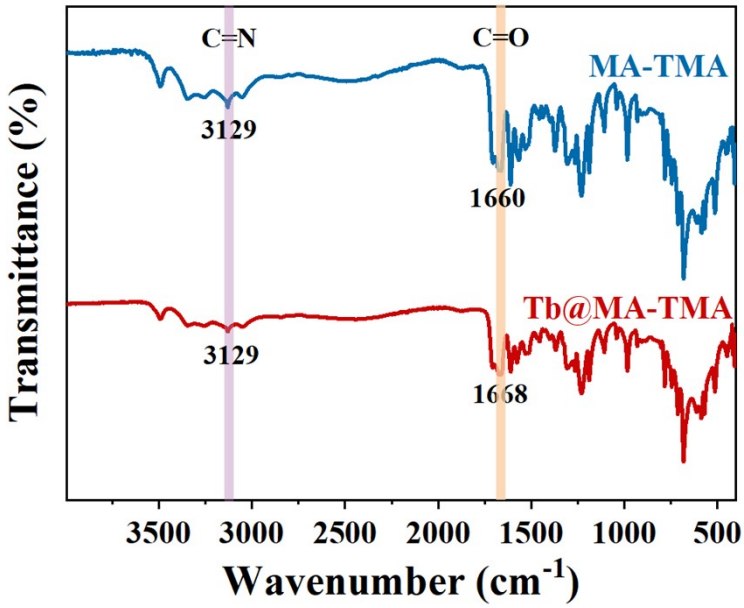
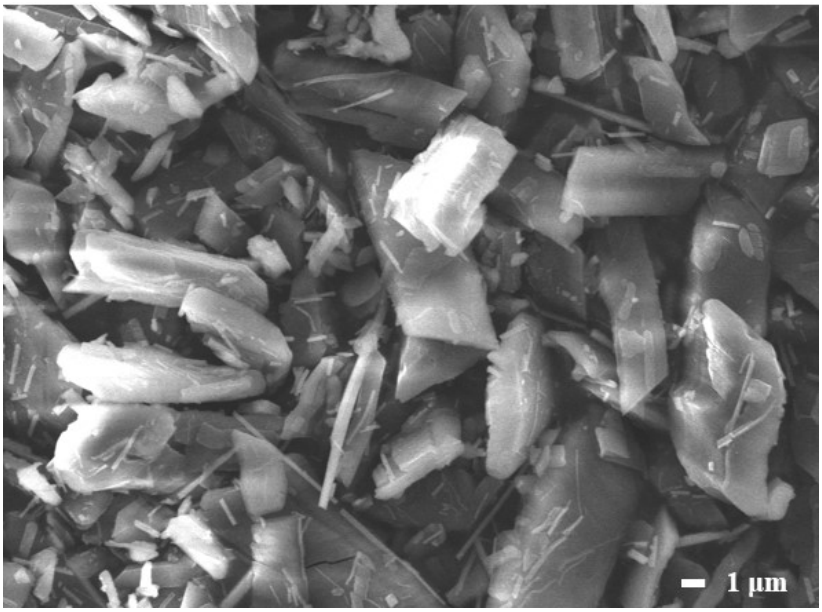


Fig. S2. FT-IR spectra of MA-TMA and Tb@MA-TMA.



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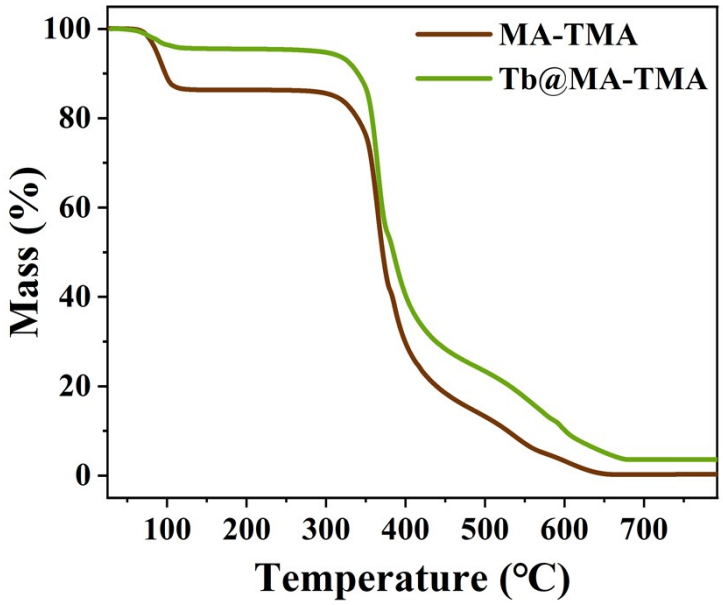
78 **Fig. S3.** SEM images of MA-TMA.



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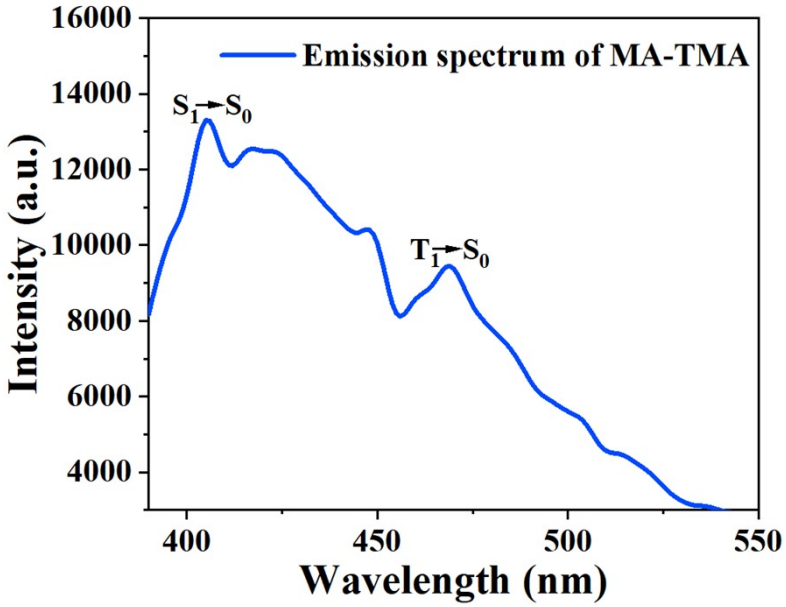
80 **Fig. S4.** TG curves of MA-TMA and Tb@MA-TMA.



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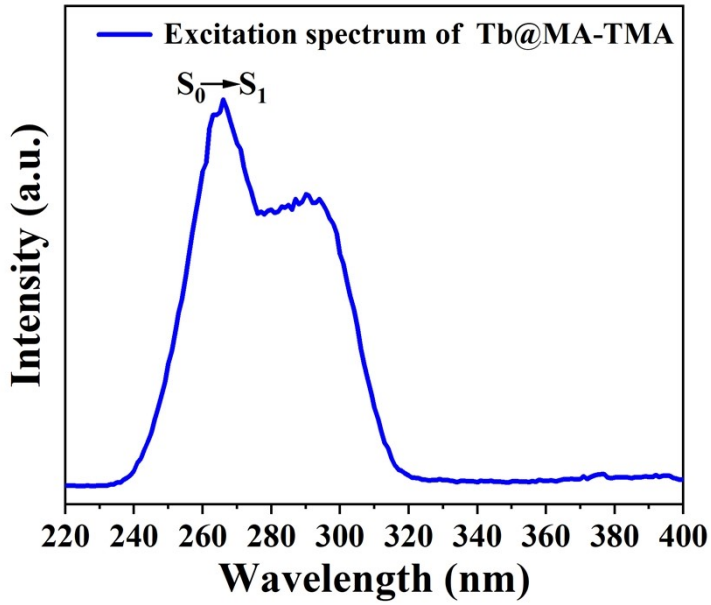
82 **Fig. S5.** Emission spectrum of MA-TMA (λ_{ex} = 302 nm).



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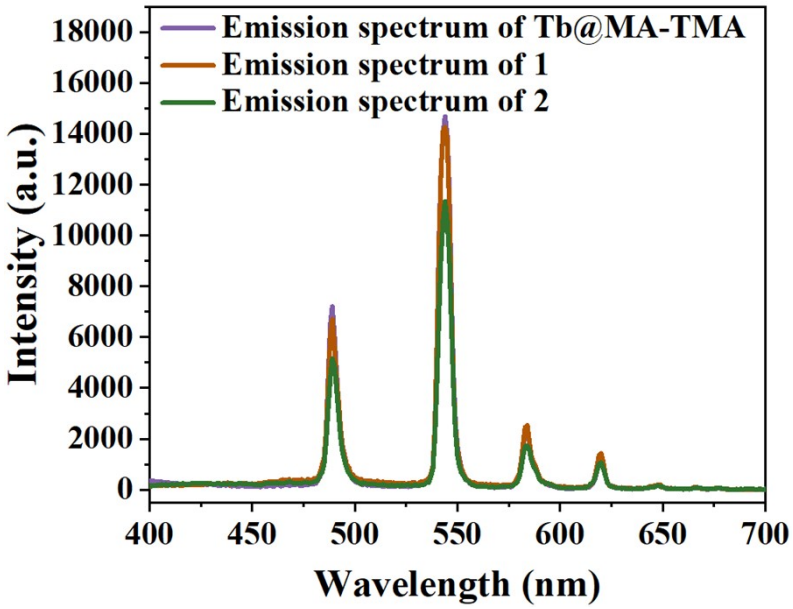
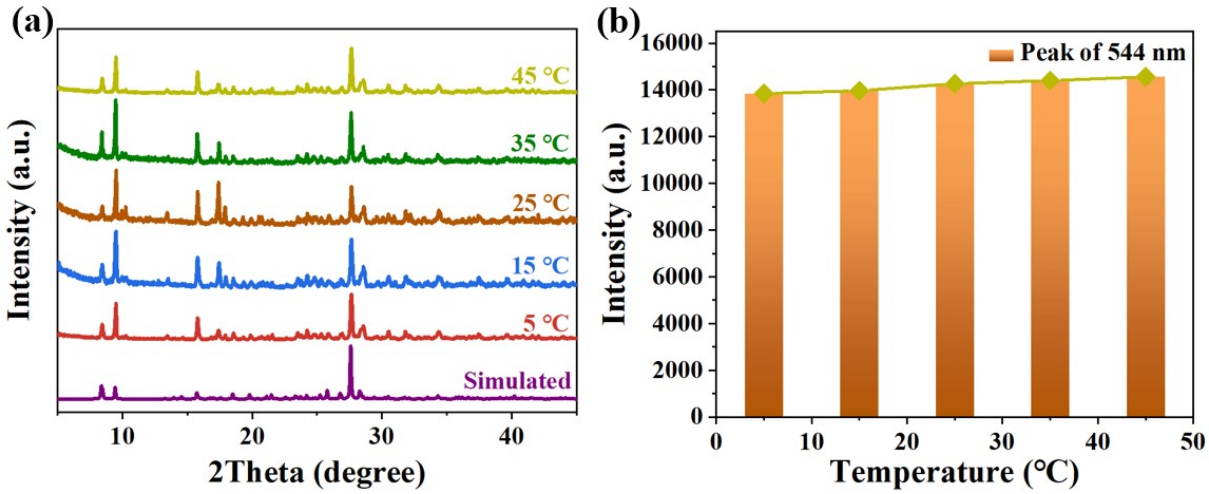
84 **Fig. S6.** Excitation spectra of Tb@MA-TMA, **1** and **2** (λ_{em} = 544 nm).



85

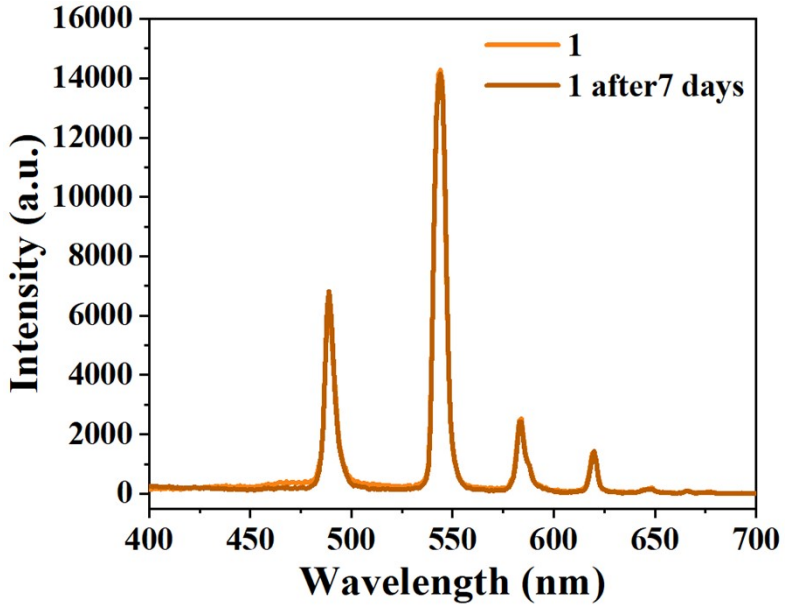
86 **Fig. S7.** Emission spectra of Tb@MA-TMA, **1** and **2** (λ_{ex} = 268 nm).



87

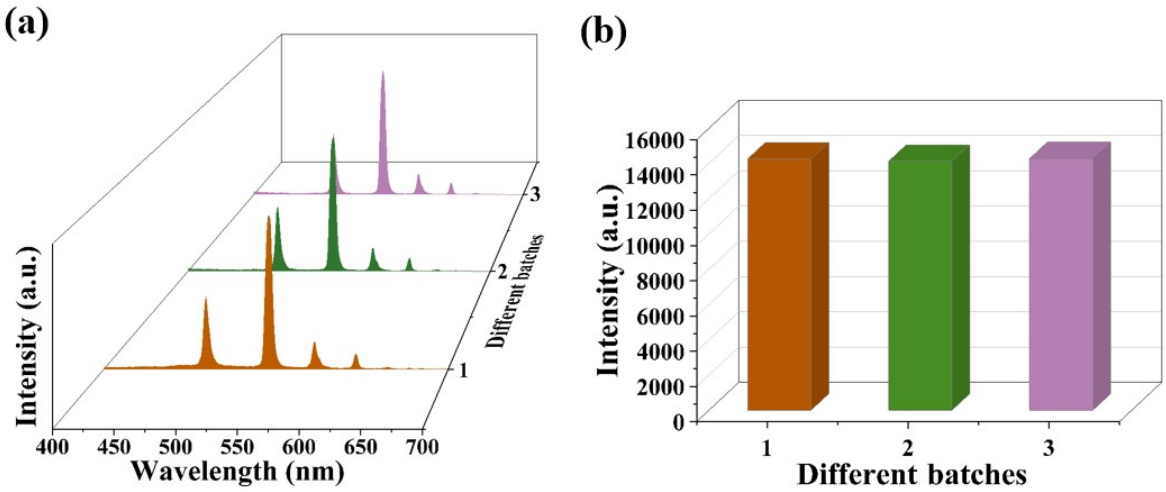
88 **Fig. S8.** (a, b) PXRD patterns and emission intensity of **1** at 544 nm in different temperatures after

89 48 h.



90

91 **Fig. S9.** Emission spectra of **1** before and after 7 days in the air at room temperature (λ_{ex} = 268 nm).



92

93 **Fig. S10.** (a, b) Emission spectra and emission intensity at 544 nm of **1** at different batches (λ_{ex} = 268

94 nm).

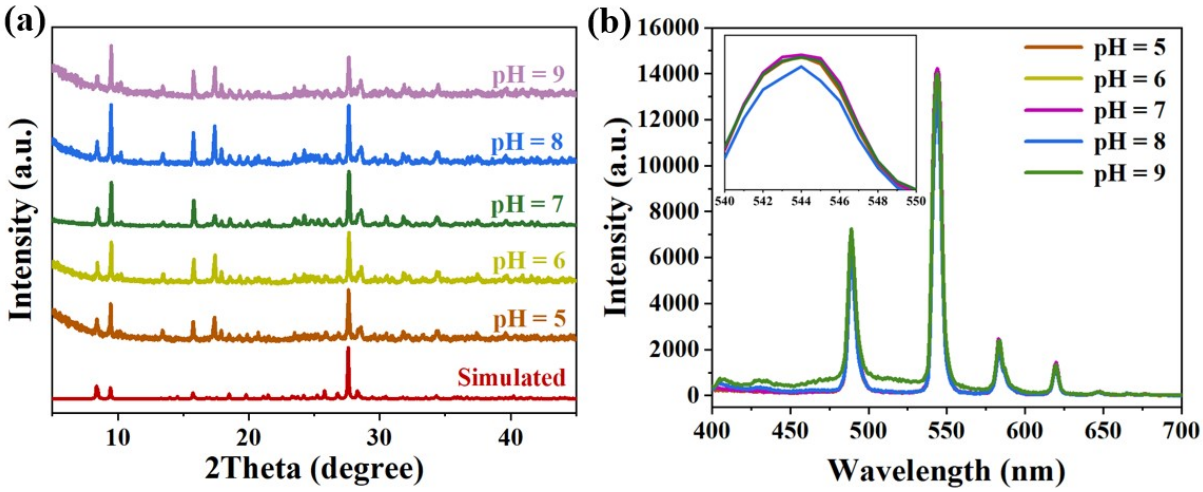


Fig. S11. (a, b) PXRD patterns and emission spectra of **2** in pH range of 5 – 9 (λ_{ex} = 268 nm).

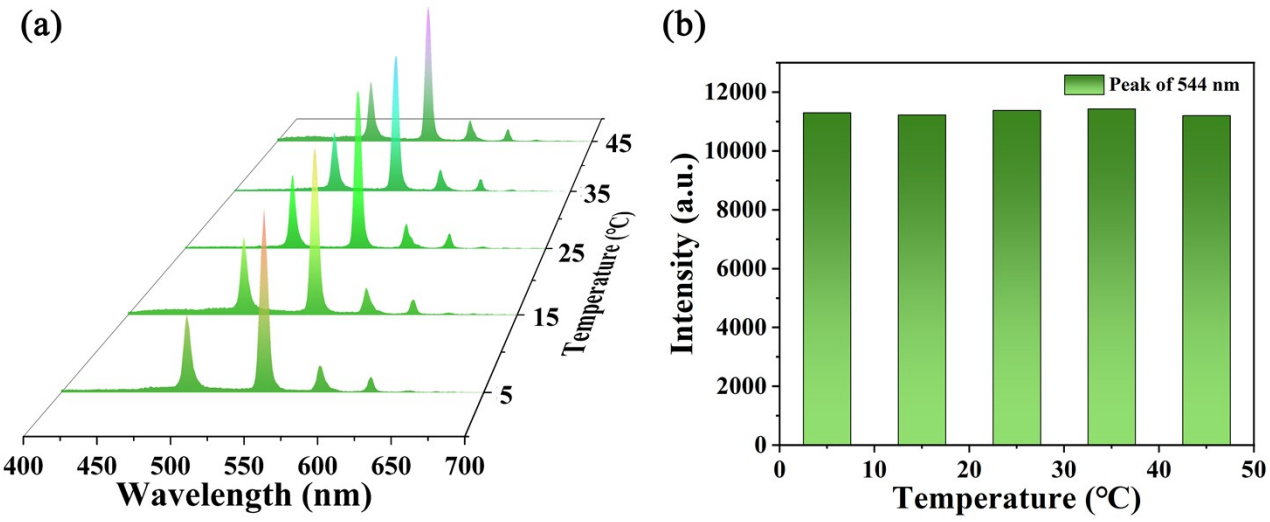
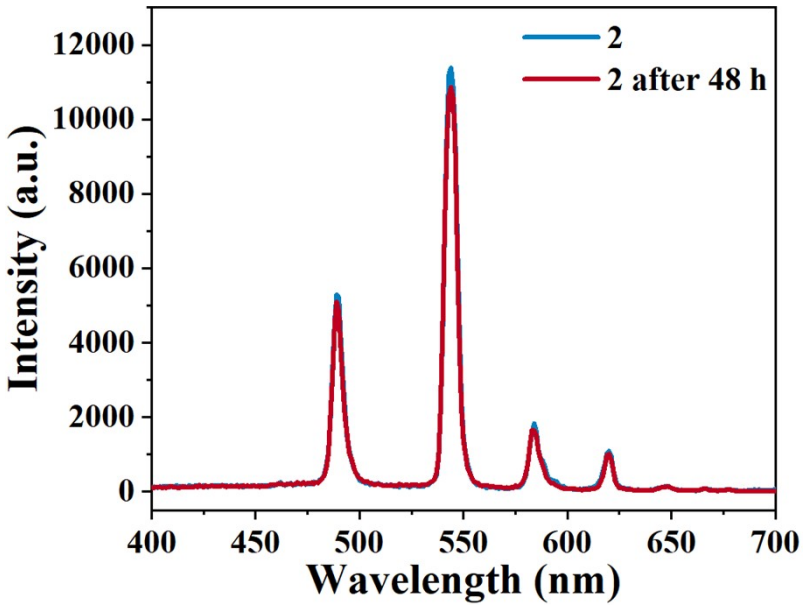


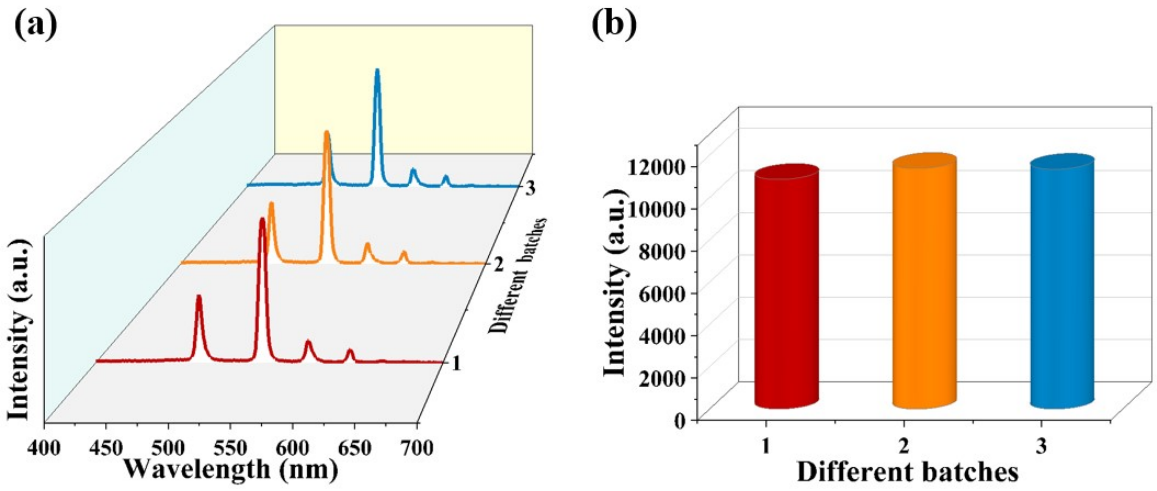
Fig. 12. (a, b) Emission spectra and emission intensity at 544 nm of **2** at different temperatures after 48 h. (λ_{ex} = 268 nm).



100

101 **Fig. S13.** Emission spectra of **2** before and after 48 h in aqueous solution at room temperature (λ_{ex} =

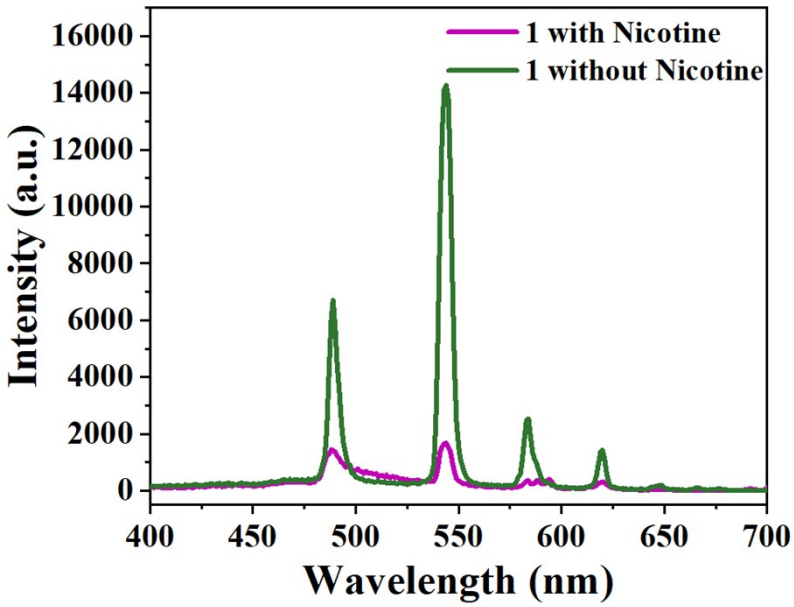
102 268 nm).



103

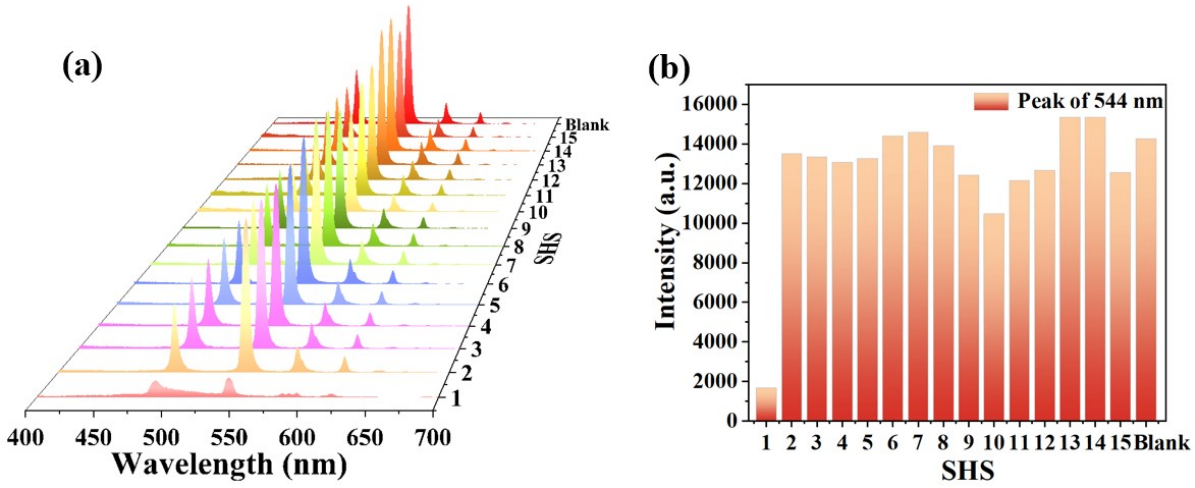
104 **Fig. S14.** (a, b) Emission spectra and emission intensity at 544 nm of **2** at different batches (λ_{ex} = 268

105 nm).



106

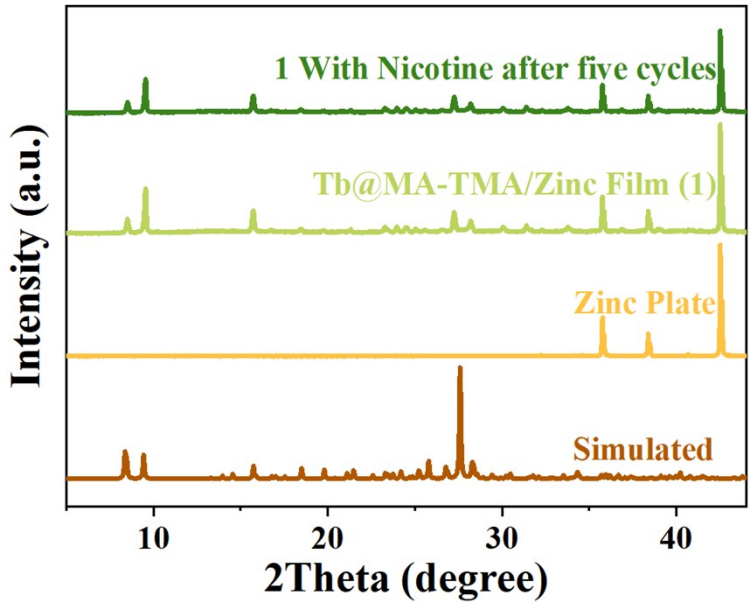
107 **Fig. S15.** Emission spectra of **1** with and without nicotine (λ_{ex} = 268 nm).



108

109 **Fig. S16.** (a, b) Emission spectra and emission intensity at 544 nm of **1** exposed in different gas

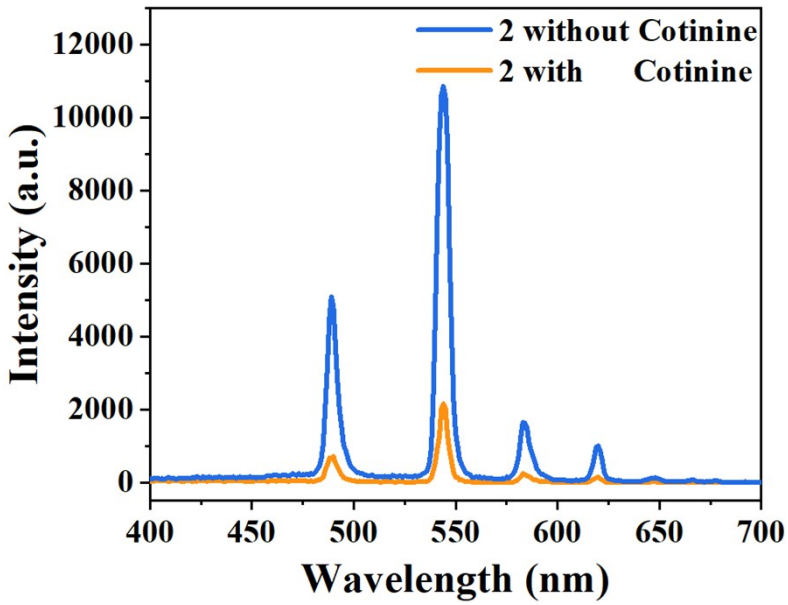
110 atmospheres of SHS (λ_{ex} = 268 nm).



111

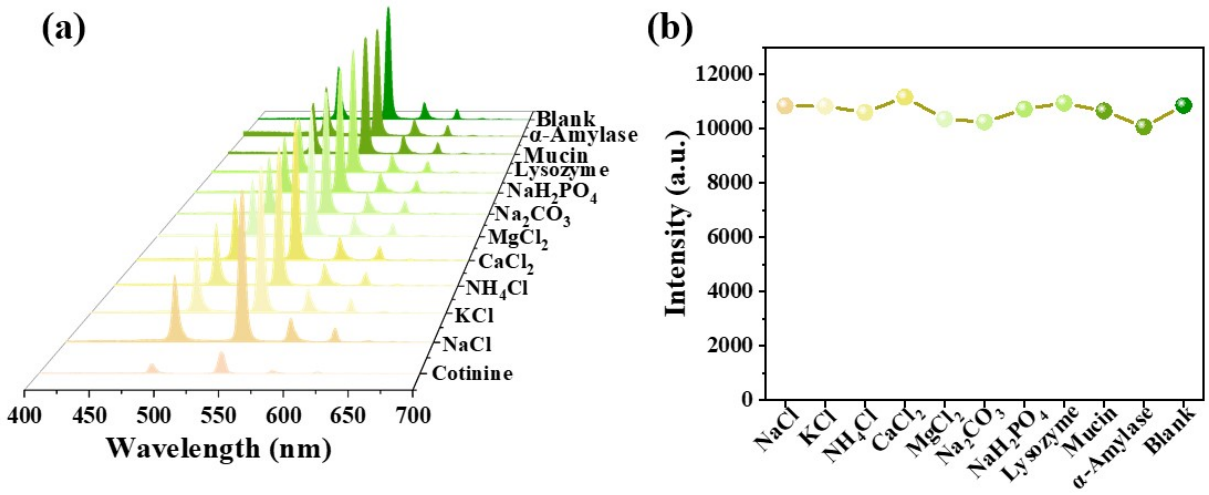
112 **Fig. S17.** PXRD patterns of Zinc Plate, Tb@MA-TMA/Zinc Film (**1**) and **1** with nicotine after five

113 cycles.



114

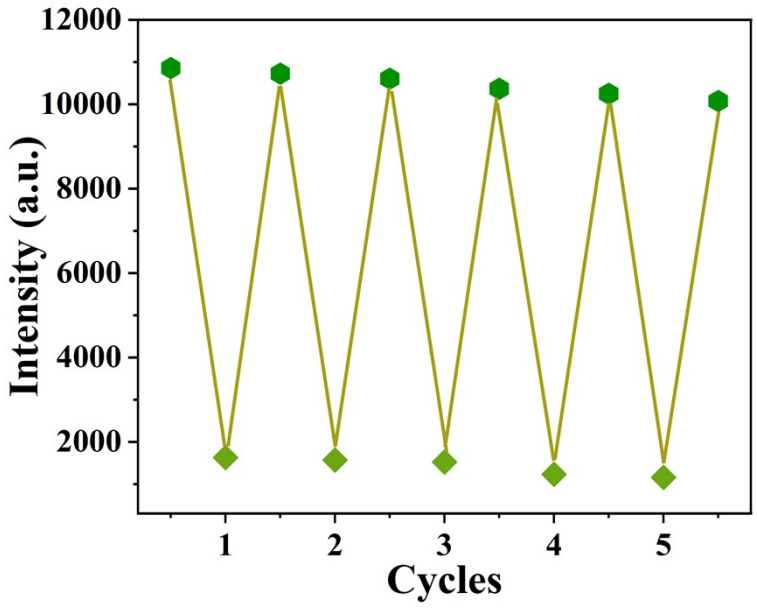
115 **Fig. S18.** Emission spectra of **2** with and without cotinine (λ_{ex} = 268 nm).



116

117 **Fig. S19.** (a, b) Emission spectra and emission intensity at 544 nm of **2** in various components of

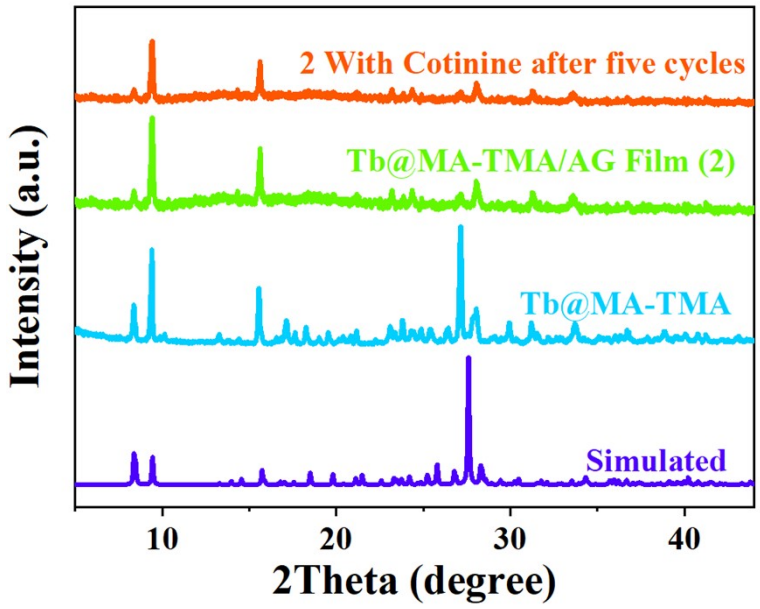
118 saliva (λ_{ex} = 268 nm).



119

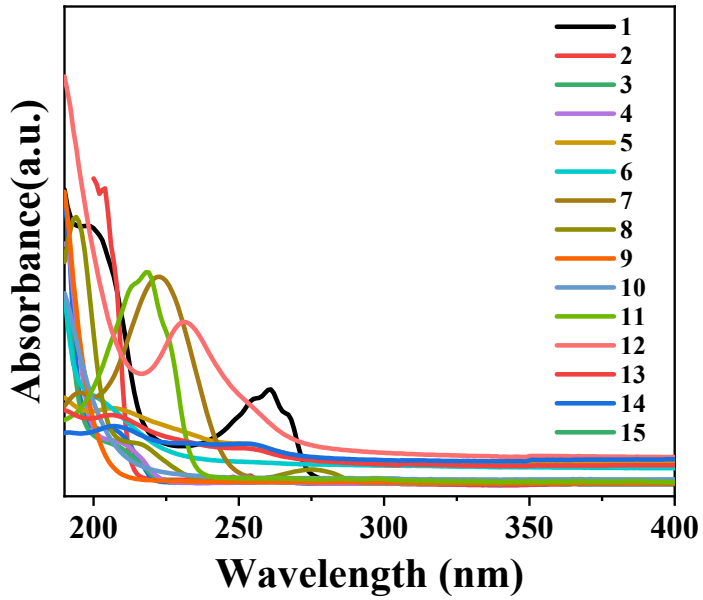
120 **Fig. S20.** Emission intensity of **2** at 544 nm in five cycles for cotinine in aqueous solution (λ_{ex} = 268

121 nm).



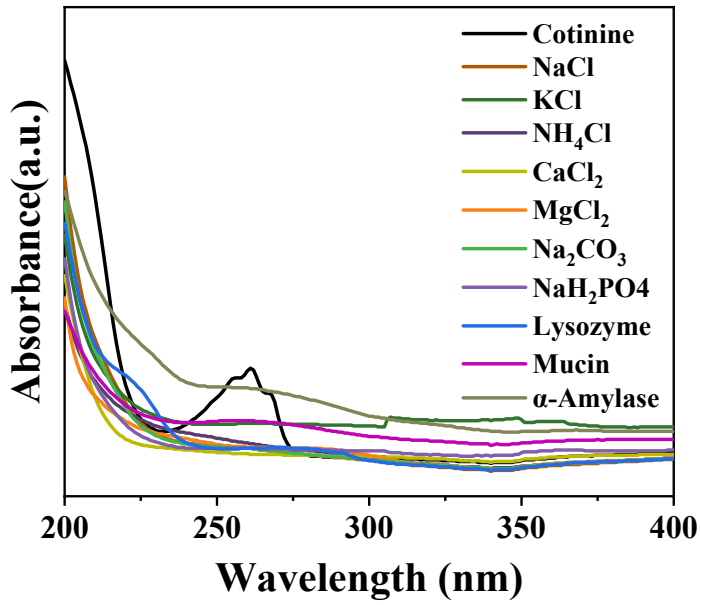
122

123 **Fig. S21.** PXRD patterns of Tb@MA-TMA/AG Film (**2**) and **2** with cotinine after five cycles.



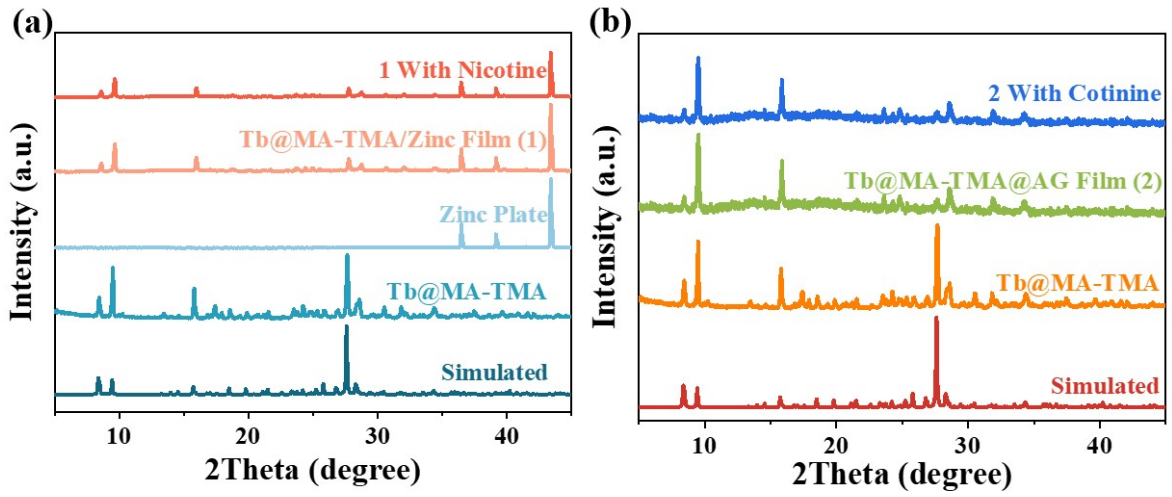
124

125 **Fig. S22.** UV absorption spectra of nicotine and other 14 components of SHS.



126

127 **Fig. S23.** UV absorption spectra of cotinine and other chemicals in saliva.



128

129 **Fig. S24.** (a) PXRD patterns of Tb@MA-TMA/Zinc Film (**1**) and **1** with nicotine. (b) PXRD patterns

130 of Tb@MA-TMA/AG Film (**2**) and **2** with cotinine.

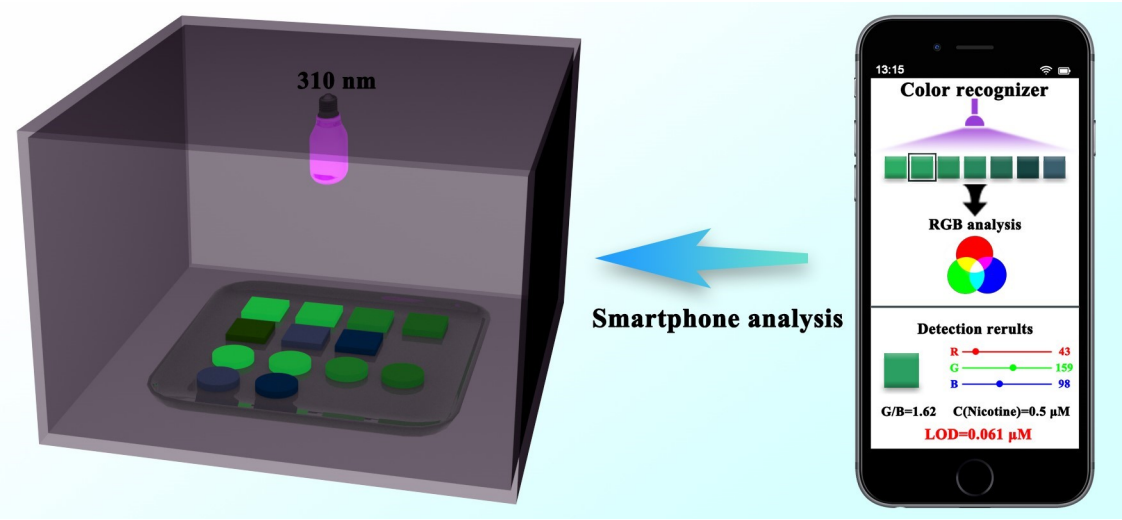


Fig. S25. The 3D views of homemade sensor platform with smartphone.

Table S1. ICP analysis of Tb element.

Sample	m_0 (g)	V_0 (mL)	Test elements	C_0 (mg/L)	f	C_x (mg/kg)	W (%)
Tb@MA-TMA	0.0433	25	Tb	5.97664	10	34507.16	3.45

In Table S1, m_0, V_0, C_0, f, C_x and W is sample mass, constant volume, concentration of elements in the test solution, dilution multiple, sample element content and mass content of test element.

Table S2. Summary of emission transitions and experimental energy gaps of MA-TMA and Tb^{3+} ions.

	Transitions	**Wavelength (nm)**	**Energy gap (eV)**
MA-TMA	$S_1 \rightarrow S_0$	405	3.06
	$T_1 \rightarrow S_0$	469	2.64
	$^5D_4 \rightarrow {}^7F_6$	489	2.54
Tb^{3+}	$^5D_4 \rightarrow {}^7F_5$	544	2.28
	$^5D_4 \rightarrow {}^7F_4$	584	2.12

$^5D_4 \rightarrow {}^7F_3$	620	2.00

Energy = 1240/λ (eV)

Table S3. Physical and chemical parameters of SHS.

Analytes	ρ (g/cm^3), 20 °C	M (g/mol)
nicotine (1)	1.01	162.23
benzene (2)	0.879	78.11
toluene (3)	0.879	78.11
ethylbenzene (4)	0.867	106.17
xylene (5)	0.86	106.17
benzo[a]pyrene (6)	1.286	252.31
formaldehyde (7)	0.815	30.03
crotonaldehyde (8)	0.853	70.09
catechol (9)	0.867	1.371
ammonia (10)	0.91	17.03
hydrazinium hydroxide solution (11)	1.032	32.05
1,3-butadiene (12)	0.62	54.09
lead (13)	11.34	207.20
cadmium (14)	8.65	112.41
chromium (15)	7.19	52.00

Table S4. HOMO and LUMO orbital energies calculated at B3LYP/6-31G* level.

	HOMO (eV)	LUMO (eV)	Band Gap (eV)
benzene-1,3,5-tricarboxylic acid	-7.859	-2.186	5.673
melamine	-6.518	0.248	6.766
nicotine	-0.209	-0.027	0.182
cotinine	-0.243	-0.032	0.211

Table S5. The results of recovery experiments by smartphone (n = 3).

Samples	No.	Spiked (μM)	Found (μM)	Recovery (%)	RSD (%)
nicotine	1	1	1.02	102	2.53
	2	10	9.56	95.60	2.87
	3	100	97.72	97.72	3.86
cotinine	1	10	9.51	95.10	2.95
	2	100	96.12	96.12	2.65
	3	1000	988.76	98.88	2.31

30 X. L. Zhang and X. M. Chen, Cryst. Growth. Des., 2005, 5, 617 – 622.