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A dual-functional halloysite nanotube-based fluorescent probe for the detection and removal of hypochlorite

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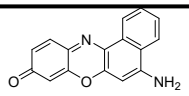
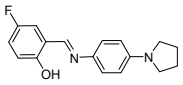
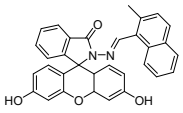
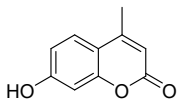
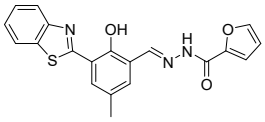
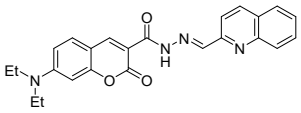
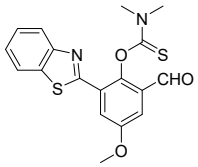
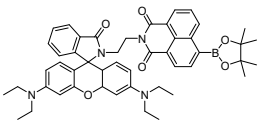
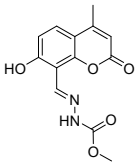
Table S1. The functional comparison of HNTs-probe with some fluorescent probes

Probes	λ_{ex} (nm)	λ_{em} (nm)	Solvent	LOD (nM)	Interference	Separation	Ref.
	580	626	DMSO/H_2O （1/99,v/v）	72	no	no	[20]
	400	470	DMSO/ H_2O, （1/9,v/v）	390	no	no	[21]
	470	525	DMSO/H_2O （1/99,v/v）	9.6	no	no	[22]
	370	450	C_2H_5OH /H_2O, (1:1, v/v)	6.7	no	no	[23]
	440	500	DMSO/H_2O （1/9,v/v）	1.4	Cu^{2+}	no	[24]
	401	460	CH_3CN /H_2O （4/1,v/v）	5.7	no	no	[25]
	460	590	CH_3CN /H_2O （1/99,v/v）	0.14	no	no	[26]
	400	550	DMSO /H_2O （4/1,v/v）	1.36	no	no	[27]
	365	473	DMSO/H_2O （4/1,v/v）	56	no	no	This study
HNTs-probe	366	460	H_2O	8.4	no	yes	This study

S1. Materials and instruments

Halloysite nanotubes (CAS: 1332-58-7) was purchased from HuNan shanlinshiyu Co., Ltd (China). 8-Formyl-7-hydroxy-4-methylcoumarin was synthesized according to previous work. Other reagents (analytically pure) were purchased from market suppliers and used directly without further treatment.

The main instruments include a field emission scanning electron microscope (regulus8100, Hitachi Scientific Instruments Co., LTD, Japan), a thermal gravimetric analyzer (NETZSCH TG209F3, Germany), a Cary Eclipse fluorescence spectrophotometer (Varian, USA), a UV-vis (PerkinElmer Lambda 750 photometer), an NMR spectrum (Bruker Avance III Ascend TM NMR spectrometer, 500 MHz), and a fourier infrared spectrum analyzer (Nicolet iS10).

S2. Synthesis

S2.1 of HNTs-NH_2

The mixture of (3-aminopropyl)triethoxysilane (20 mL), HNTs (3.0 g) and anhydrous Na_2CO_3 (0.10 g) was stirred at 80 °C for 48 h. After centrifugal separation, the residue was washed with water, C_2H_5OH, and THT in turn. A white solid HNTs-NH_2 (1.62 g) was obtained after freeze-drying.

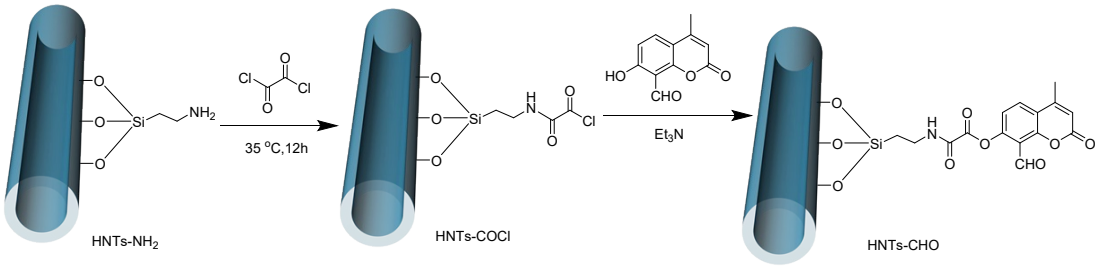
S2.2 Synthesis of HNTs-COCl

HNTs-NH_2 (0.3 g) and triethylamine (0.5 mL, 3.6 mmol) were dispersed in DMSO (6 mL). When oxalyl chloride (0.16 mL, 1.89 mmol) was slowly added drop by drop in an ice bath, the mixture was stirred at room temperature for 16 h. After centrifugation at 8000 rpm for 3 min, the sediment was further washed with ethyl acetate and CH_2Cl_2, successively. A light yellow product HNTs-COCl (0.14 g) was obtained after freeze-drying.

S2.3 Synthesis of HNTs-CHO

Formyl-7-hydroxy-4-methylcoumarin (0.11 g, 0.54 mmol) was dissolved in DMSO (3 mL). After the addition of HNTs-COCl (0.29 g) and triethylamine (1 mL, 7.2 mmol), the mixture was stirred at room temperature for 2 h and at 45 °C for 12 h. When the mixture was cooled, the precipitate was centrifuged at 8000 rpm for 3 min,

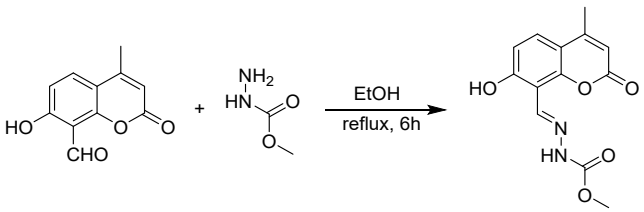
washed with ethyl acetate, CH_3OH, and CH_2Cl_2 in turn. After freeze-drying, a yellow product HNTs-CHO (0.32 g) was obtained.



Scheme S1. Synthetic route of HNTs-CHO.

S2.4 Synthesis of coumarin-based fluorophore

8-Formyl-7-hydroxy-4-methylcoumarin (0.21 g, 1.0 mmol) and methyl hydrazinecarboxylate (0.10 g, 1.1 mmol) were dissolved in EtOH (15 mL). The mixture was stirred and refluxed for 6 h. After suction filtration, a light yellow powder was obtained, yield 69.3%. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 12.38 (s, 1H), 11.70 (s, 1H), 8.71 (s, 1H), 7.71 – 7.69 (d, J = 10 Hz, 1H), 6.95 – 6.94 (d, J = 5 Hz, 1H), 6.25 (s, 1H), 3.75 (s, 3H), 2.41 (s, 3H). HR-MS for $C_{13}H_{12}N_2O_5$ found 276.0756, calculated 276.07.



Scheme S2. Synthetic route of coumarin-based fluorophore.

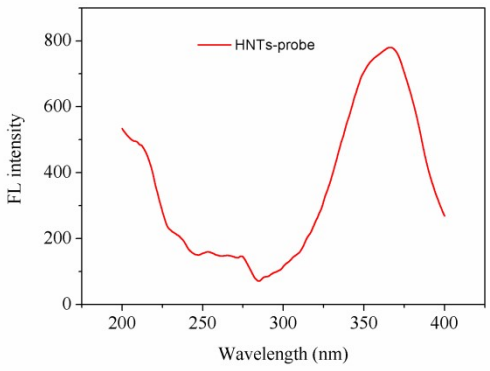


Fig. S1.The excitation wavelength (λ_{ex}) of HNTs-probe when the emission wavelength was set as 460 nm in water.

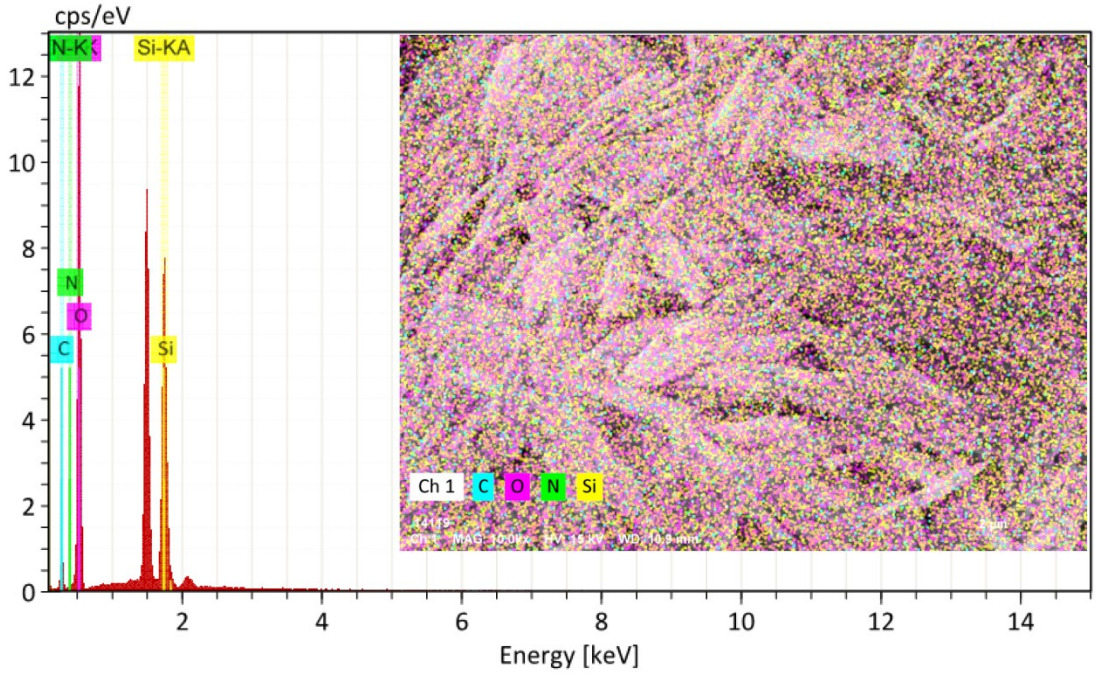


Fig. S2. EDS mapping of HNTs. C: blue color, N: green color, O: pink color.

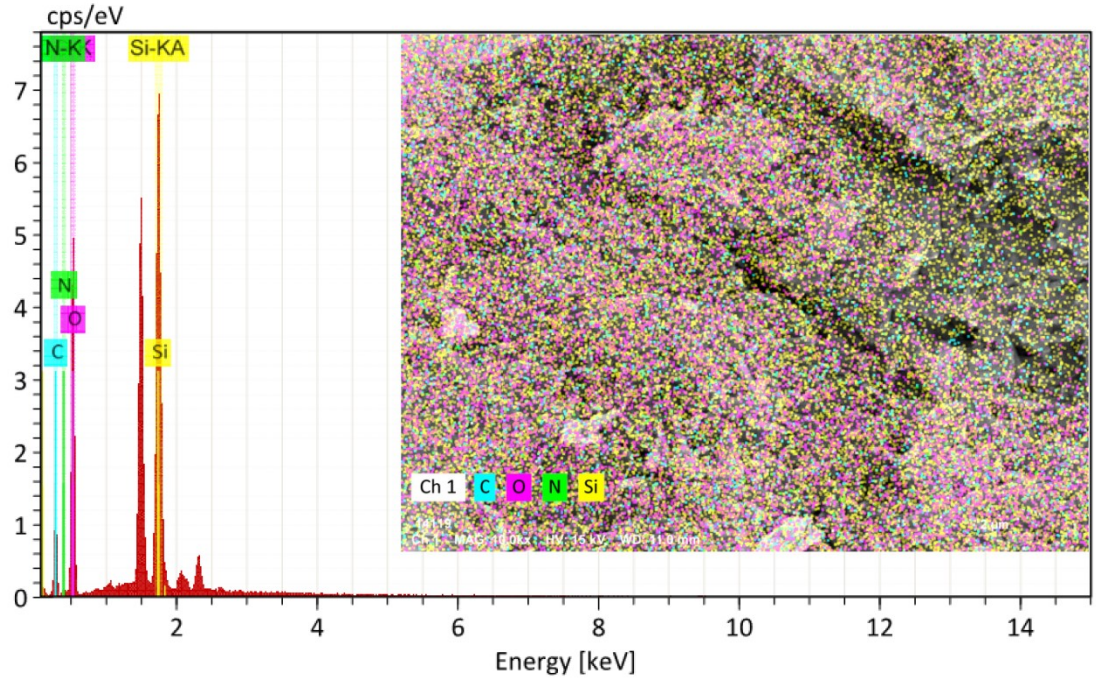


Fig. S3. EDS mapping of HNTs-probe. C: blue color, N: green color, O: pink color.

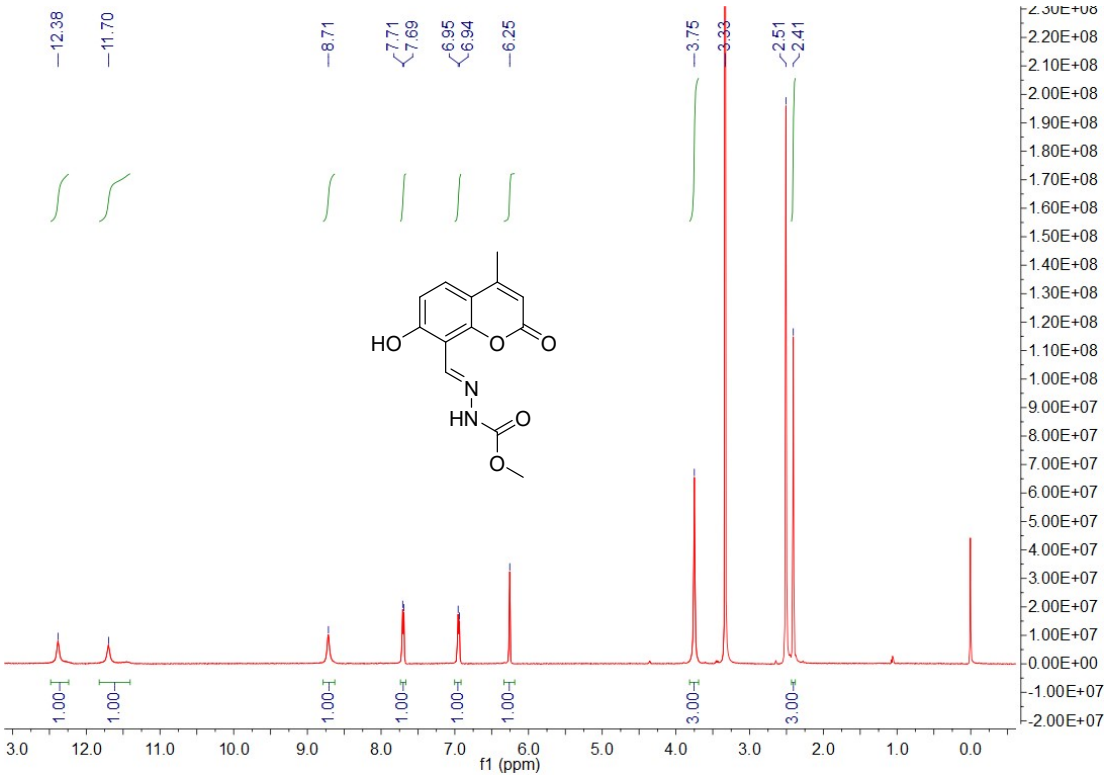


Fig. S4. ^{1}H NMR of coumarin-based fluorophore in DMSO-d_6.

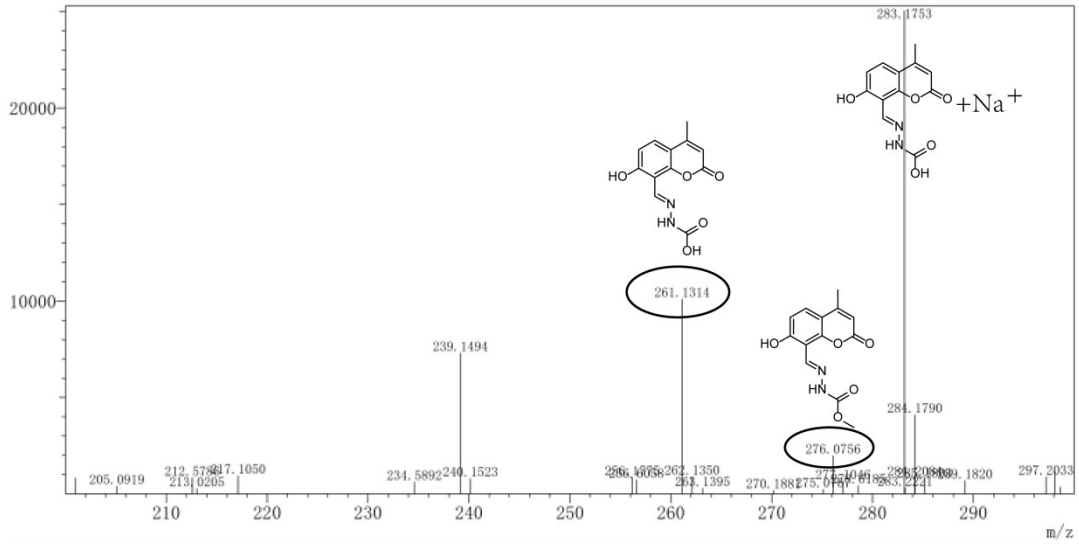


Fig. S5. HR-MS of coumarin-based fluorophore in CH_3CN.

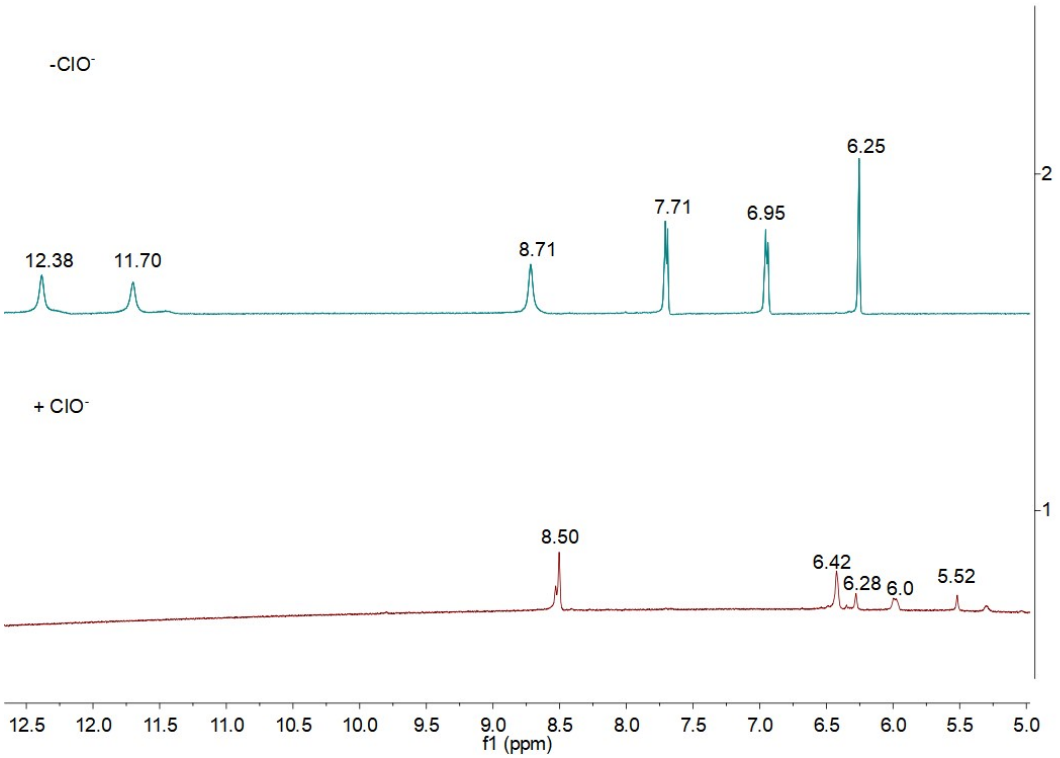


Fig. S6. ^{1}H NMR of coumarin-based fluorophore before and after adding ClO^- in DMSO-d_6.

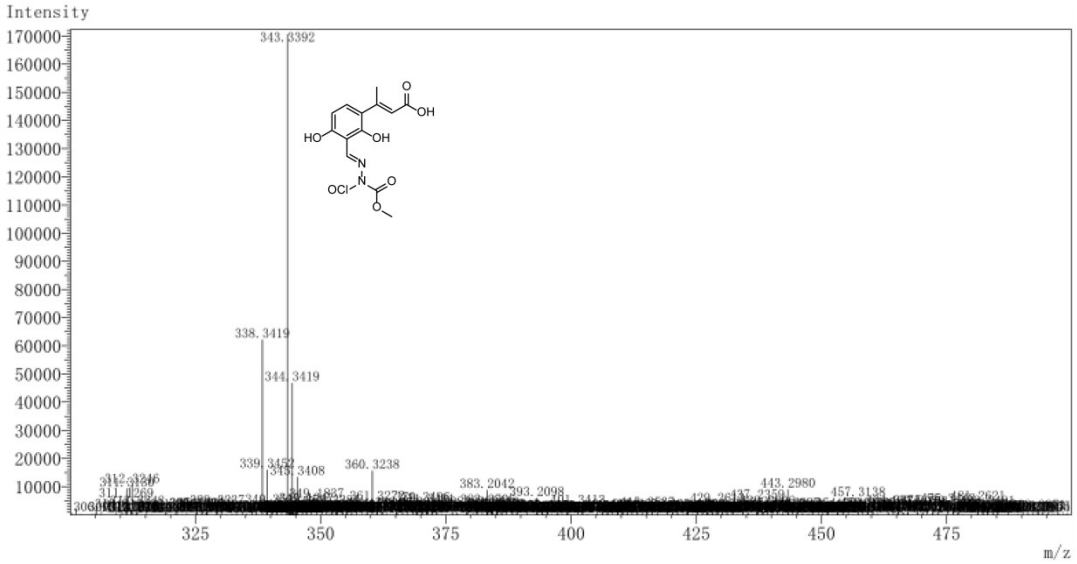
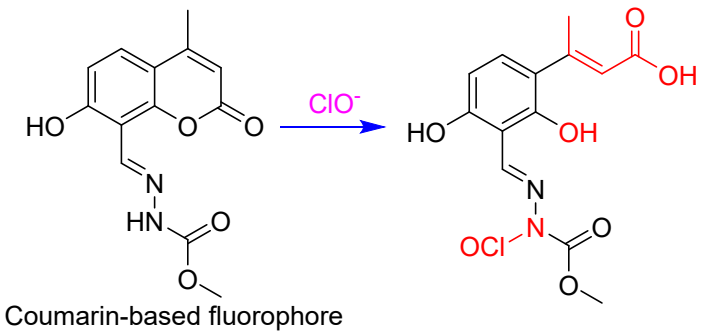


Fig. S7. HR-MS of coumarin-based fluorophore reacted with ClO^- in CH_3CN (Negative ion modes).



Scheme S3. Reaction mechanism between coumarin-based fluorophore with ClO^-.