Electronic Supplementary Information (ESI)

for

Rapid detection of hydrazine in almost wholly water solution and in living cells with a new colorimetric and fluorescent turn-on probe

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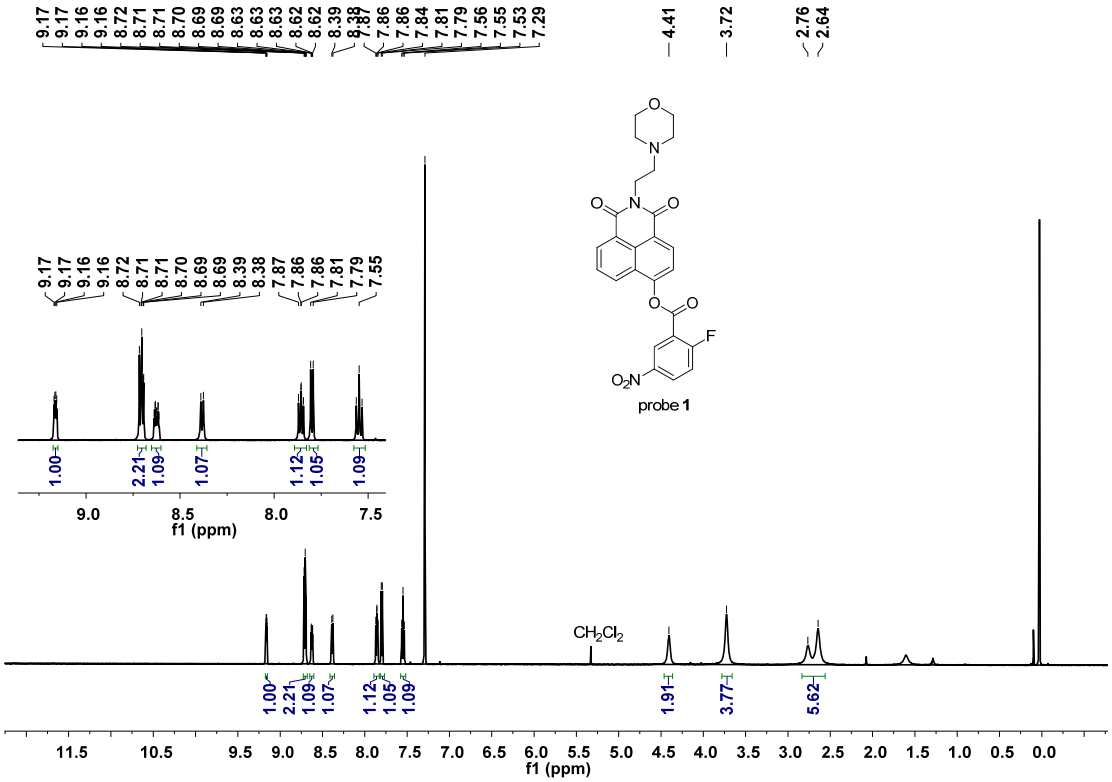
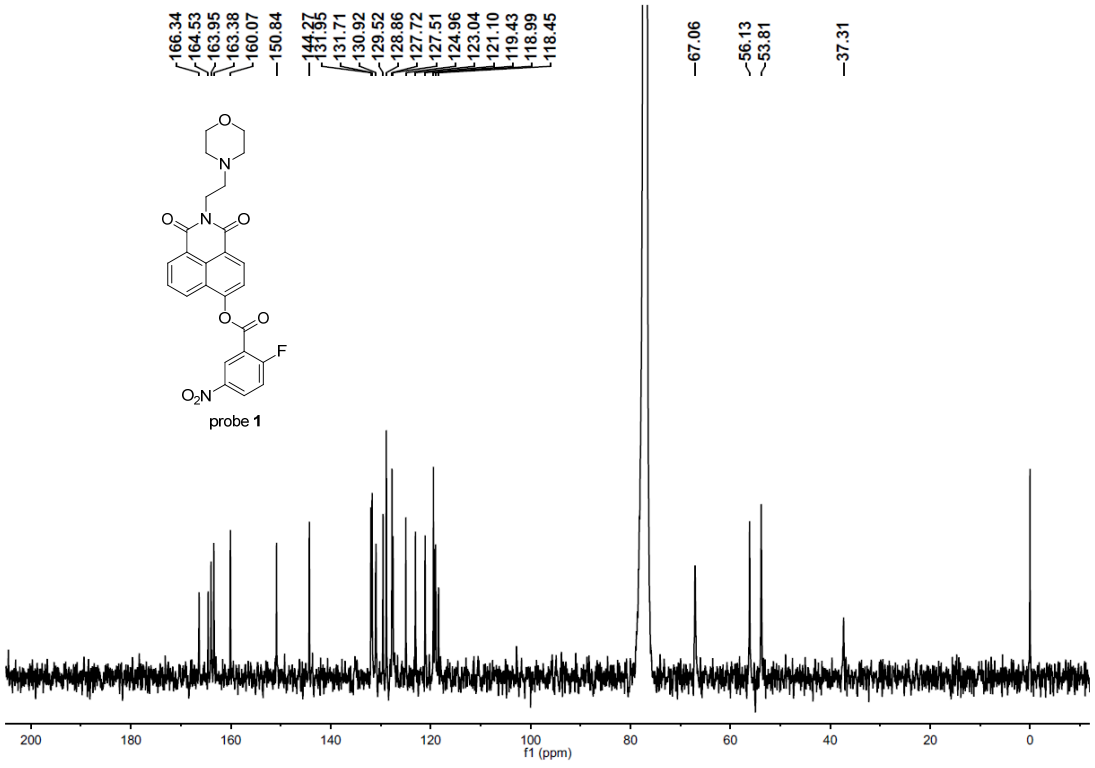
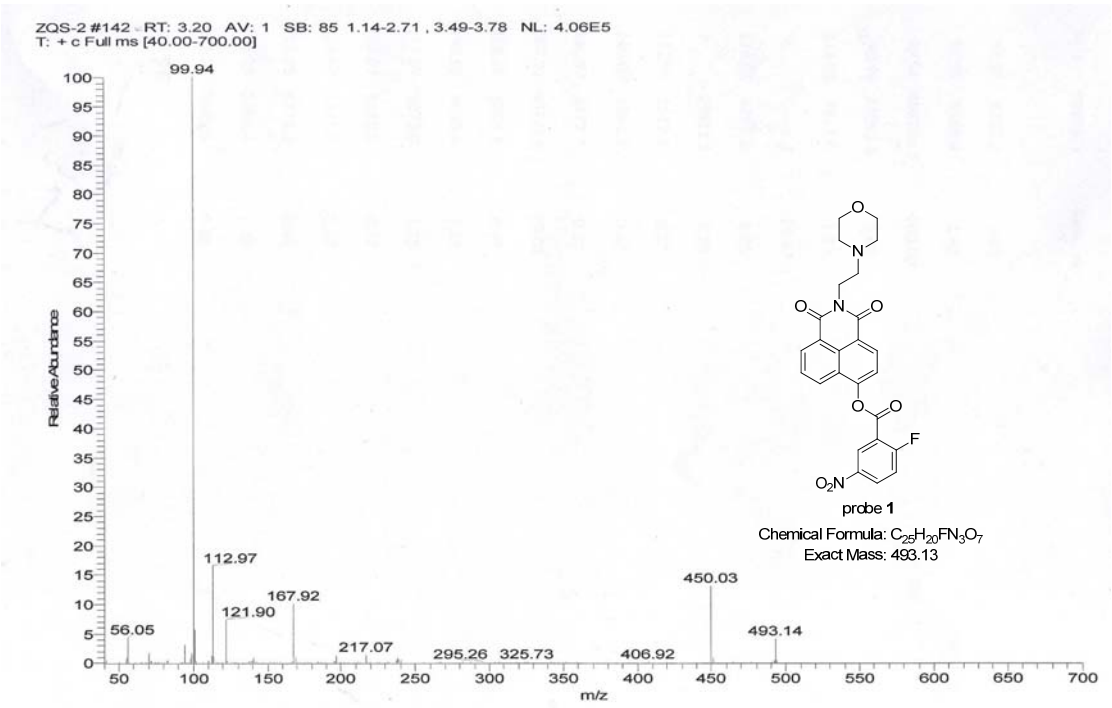
1. Structure characterizations of probe 1



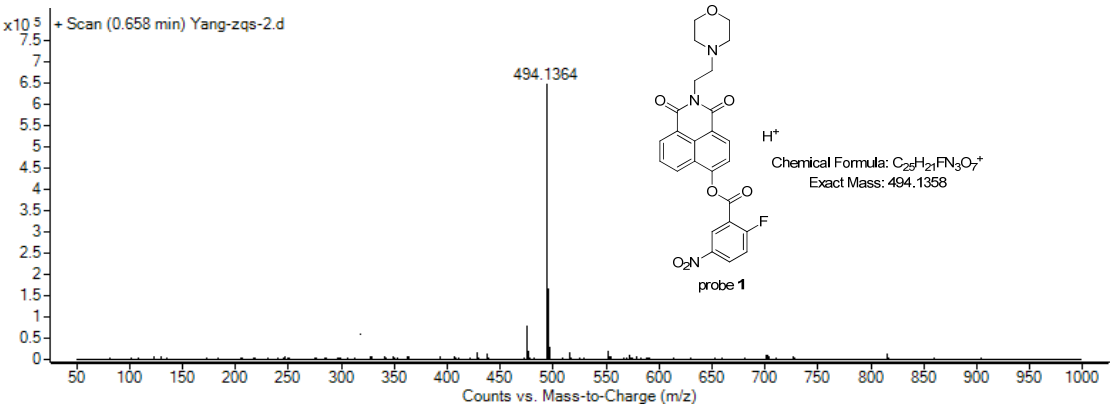
^{1}H-NMR spectrum of probe **1** in $CDCl_3$



^{13}C-NMR spectrum of probe **1** in $CDCl_3$



MS (EI) spectrum of probe **1**



HR-MS spectrum of probe **1**

2. Additional spectra and data

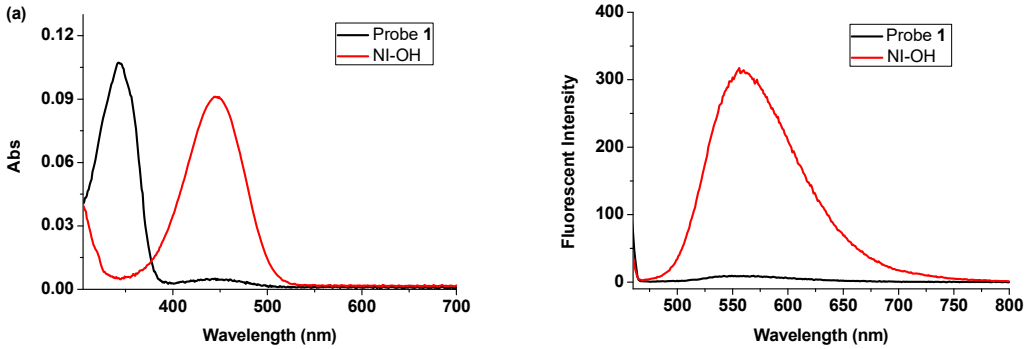


Fig. S1. (a) UV-Vis and (b) fluorescence spectra of probe **1** (10 μM) and **NI-OH** (10 μM) in PBS buffer (10 mM, pH 7.4) with 2% CH_3CN at 37 °C. For fluorescence, λ_{ex} = 450 nm, slit width: d_{ex} = 5 nm, d_{em} = 10 nm.

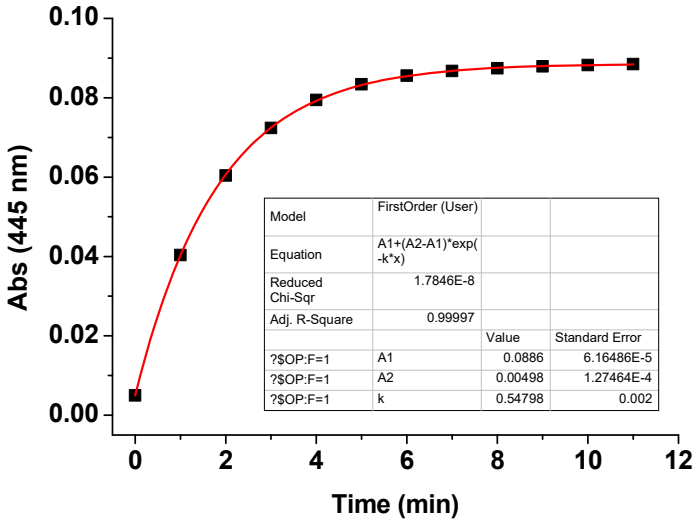


Fig. S2. Kinetic curve of probe **1** (10 μM) with hydrazine (50 μM) in PBS buffer (10 mM, pH 7.4) with 2% CH_3CN at 37 °C. The reaction was monitored by absorbance change at 445 nm and the data were fitted by a first-order reaction scheme as shown in the figure.

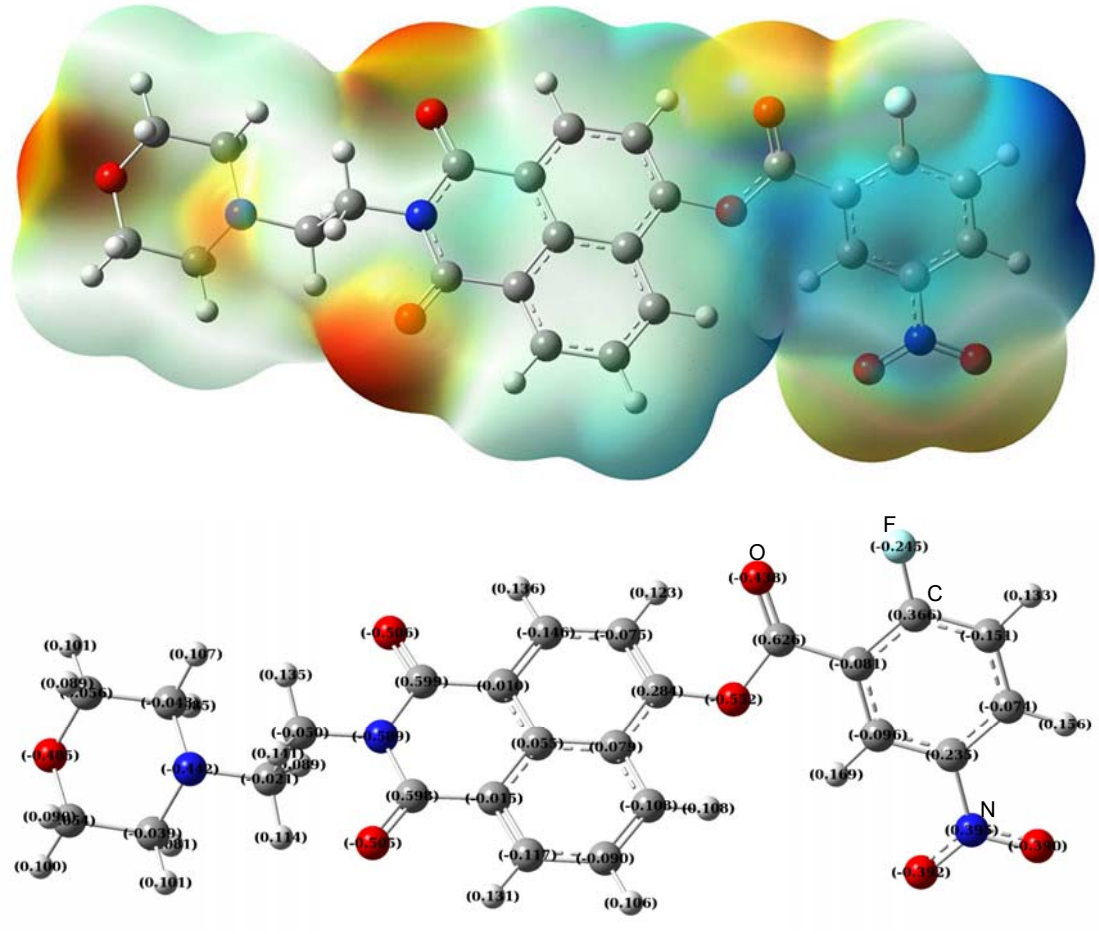


Fig. S3. Calculated charge distribution map of probe **1** by DFT (density functional theory).

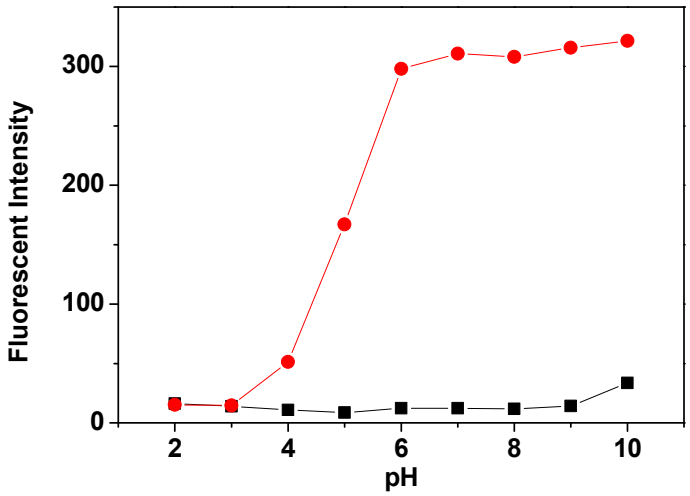


Fig. S4. The fluorescent responses of probe **1** (10 μM, black) and probe **1** with hydrazine (50 μM, red) at 558 nm under different pHs. All experiment was performed in PBS buffer (10 mM) with with 2% CH_3CN at 37 °C and each spectrum was obtained 10 min after mixing. λ_{ex} = 450 nm, slit width: d_{ex} = 5 nm, d_{em} = 10 nm.

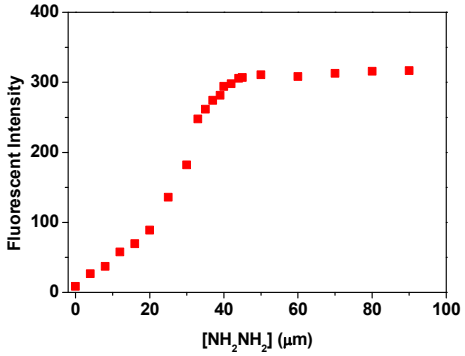


Fig. S5. Fluorescence responses of probe **1** (10 μM) at 558 nm upon addition of hydrazine (0-90 μM) in PBS buffer (10 mM, pH 7.4) with 2% CH_3CN (v/v) at 37 °C. Final concentration of hydrazine: 0, 4, 8, 12, 16, 20, 25, 30, 33, 35, 37, 39, 40, 42, 44, 45, 50, 60, 70, 80 and 90 μM.

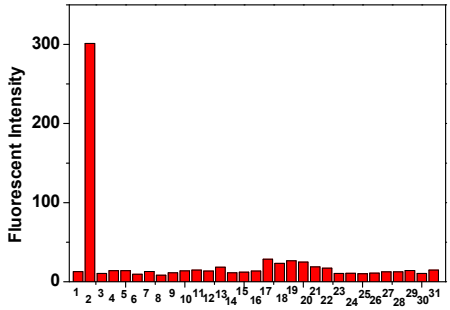


Fig. S6. Fluorescence intensity changes of probe **1** (10 μM) at 558 nm toward 100 μM (except: hydrazine 50 μM) of various analytes including: 1. none, 2. hydrazine, 3. Cys, 4. Hcy, 5. GSH, 6.NaF, 7. NaCl, 8. NaBr, 9. NaI, 10. $Na_2S_2O_7$, 11. Na_2SO_3, 12. Na_2CO_3, 13. NaHS, 14. $NaNO_3$, 15. NaSCN, 16. NaAc, 17. $NH_3{\cdot}H_2O$, 18. $NH_2OH{\cdot}HCl$, 19. $H_2NCH_2CH_2NH_2$, 20. $HOCH_2CH_2NH_2$, 21. $C_6H_5NH_2$, 22. $C_6H_5CH_2NH_2$, 23. NaClO, 24. H_2O_2, 25. $NaNO_2$, 26. $^tBuOO^{\bullet}$, 27. $^{\bullet}OH$, 28. NaN_3, 29. Na_3PO_4, 30. Na_2SO_4, 31. Na_2S. All experiments were performed in PBS buffer (10 mM, pH 7.4) with 2% CH_3CN at 37 °C, and each spectrum was obtained 10 min after addition of an analyte. λ_{ex} = 450 nm, slit width: d_{ex} = 5 nm, d_{em} = 10 nm.

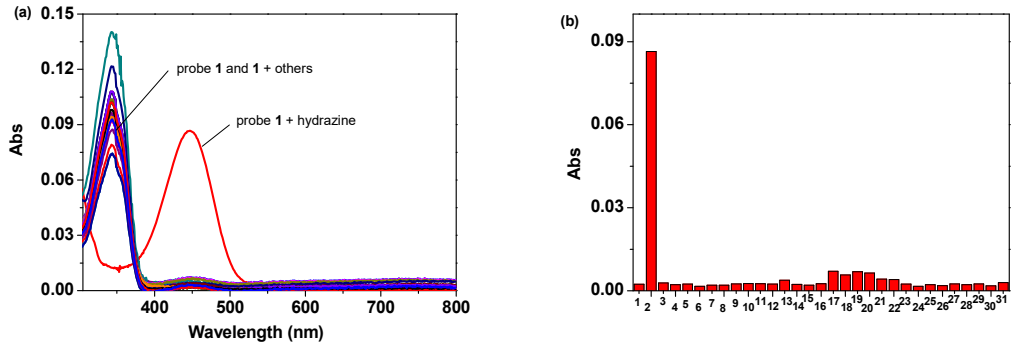


Fig. S7. (a) Absorption spectra changes of probe **1** (10 μM) toward various analytes (100 μM, except hydrazine 50 μM). (b) Absorbance intensity changes of probe **1** (10 μM) at 445 nm toward 100 μM of various analytes including: 1. none, 2. Hydrazine (50 μM), 3. Cys, 4. Hcy, 5. GSH,

6.NaF, 7. NaCl, 8. NaBr, 9. NaI, 10. $Na_2S_2O_7$, 11. Na_2SO_3, 12. Na_2CO_3, 13. NaHS, 14. $NaNO_3$, 15. NaSCN, 16. NaAc, 17. $NH_3 \cdot H_2O$, 18. $NH_2OH \cdot HCl$, 19. $H_2NCH_2CH_2NH_2$, 20. $HOCH_2CH_2NH_2$, 21. $C_6H_5NH_2$, 22. $C_6H_5CH_2NH_2$, 23. NaClO, 24. H_2O_2, 25. $NaNO_2$, 26. $^tBuOO^\bullet$, 27. $^\bullet OH$, 28. NaN_3, 29. Na_3PO_4, 30. Na_2SO_4, 31. Na_2S. All experiments were performed in PBS buffer (10 mM, pH 7.4) with 2% CH_3CN at 37 °C, and each spectrum was obtained 10 min after addition of an analyte.

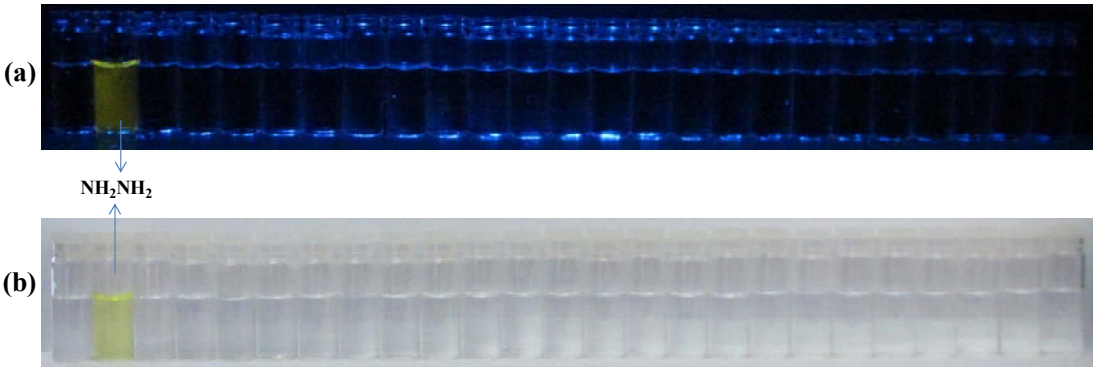


Fig. S8. (a) Emission color changes and (b) color changes of probe **1** (10 μM) upon addition of 100 μM (except hydrazine 50 μM) of different analytes in PBS buffer (10 mM, pH 7.4,) with 2% CH_3CN (v/v) at room temperature. Each vial from left to right: blank, hydrazine, Cys, Hcy, GSH, NaF, NaCl, NaBr, NaI, $Na_2S_2O_7$, Na_2SO_3, NaAc, NaHS, NaSCN, $NH_3 \cdot H_2O$, $NH_2OH \cdot HCl$, $H_2NCH_2CH_2NH_2$, $HOCH_2CH_2NH_2$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$, NaClO, H_2O_2, $NaNO_2$, $^tBuOO^\bullet$ and $^\bullet OH$). The fluorescent color changes were observed under a potable 365 nm UV lamp. Visual color changes were observed under ambient light.

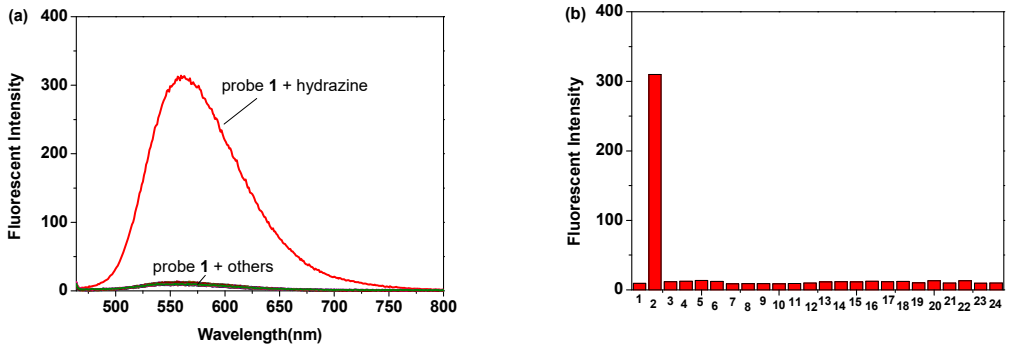


Fig. S9. (a) Fluorescence spectra changes of probe **1** (10 μM) toward various analytes (100 μM, except hydrazine, 50 μM). (b) Fluorescence intensity changes of probe **1** (10 μM) at 558 nm toward 100 μM (except: hydrazine 50 μM) of various analytes including: 1. none, 2. hydrazine, 3. K^+, 4. Ca^{2+}, 5. Na^+, 6. Mg^{2+}, 7. Zn^{2+}, 8. Cu^{2+}, 9. Trp, 10. Phe, 11. Gln, 12. Ala, 13. Leu, 14. Thr, 15. Ser, 16. Asp, 17. Ile, 18. Met, 19. Lys, 20. Gly, 21. Arg, 22. Tyr, 23. Pyr, 24. His. All experiments were performed in PBS buffer (10 mM, pH 7.4) with 2% CH_3CN at 37 °C, and each spectrum was obtained 10 min after addition of an analyte. λ_{ex} = 450 nm, slit width: d_{ex} = 5 nm, d_{em} = 10 nm.

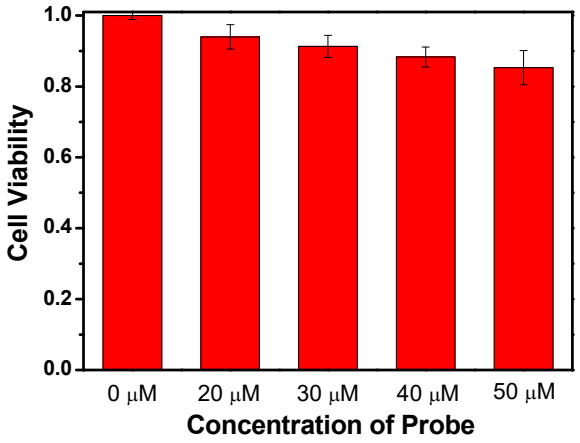
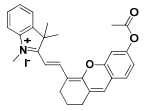
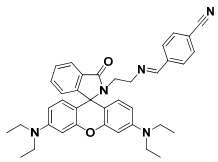
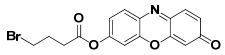
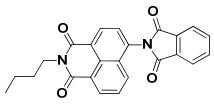
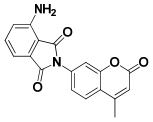
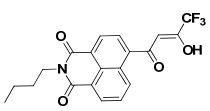
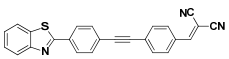
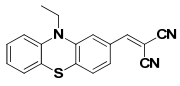
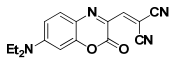
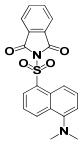
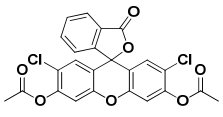
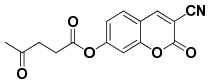
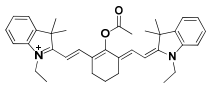
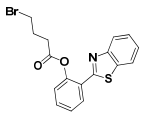
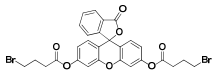
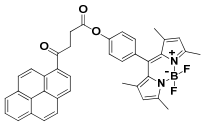
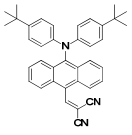
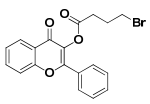
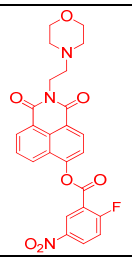


Fig. S10. Percentage of viable HeLa cells after treatment with indicated concentrations of probe after 24 hours. The cell viability was observed via MTT assay.

3. Table S1. Comparison of some representative fluorescent hydrazine probes

Probes	Detection system	Range of linear correlation / μM	LOD	Time / min	Ref.
	DMSO-HEPES buffer (1:4, v/v)	0-50	0.17 μM (5.4 ppb).	10	Anal. Chem. 2015, 87, 9101
	CH_3CN-HEPES buffer (9:1, v/v)	1-150	58 nM	--	Anal. Chim. Acta 2015,893,84
	CH_3CN-HEPES buffer (1:9, v/v)	10-200	2 μM	60	Biosens. Bioelectron. 2014,58,282
	H_2O-DMSO (4:6, v/v)	1-50	0.3 ppb	2	Chem. Commun., 2014, 50, 1485
	H_2O-DMSO (3:7, v/v)	0.1-1.0	3.2 ppb	0.5	Anal. Chem., 2014, 86, 4611
	H_2O-CH_3CN (1:9, v/v)	0-5	3.2 ppb	60	Chem. Sci. 2013, 4, 4121
	H_2O-THF (1:1, v/v)	0.06-0.12	0.11 ppb	3	Dyes Pigm. 2013, 99, 966
	Tris.HCl buffer-DMF (3/7, v/v)	5-20	12.191 nM	--	J. Mater. Chem. B, 2014, 2, 1846

	DMSO-acetate buffer (9:1, v/v)	0.5-3.5	13.4 ppb	20	Chem. Commun., 2012,48, 8117
	DMSO-HEPES buffer (9:1, v/v)	0-5	6.01 ppb	60	J. Mater. Chem. B, 2014,2, 7344
	DMSO- Tris buffer solution (1 : 1, v/v)	0-25	2.9 ppb	10	Org. Biomol. Chem. 2013, 11, 2961
	DMSO- acetate buffer (7:3, v/v)	0-14	2.46 μM	15	Org. Lett., 2011,13,5260
	DMSO-acetate buffer (9:1, v/v)	10.0-80.0	0.81 ppb	40	Org. Lett., 2013, 15, 4022
	CH_3CN-HEPES buffer (2:3, v/v)	1-9.5	2.2 ppb	15	Org. Lett., 2013, 15, 5412
	$CH_3OH–H_2O$ (1 : 1, v/v,)	2-39	38.81nM	15	RSC Adv., 2014, 4, 14210
	DMSO-HEPES buffer (7:3, v/v)	0-10	1.87 μM	--	RSC Adv., 2015, 5, 58228
	CH_3CN	0-5.5	0.2 μM (7 ppb) in CH_3CN	--	Sens. Actuators, B 2014,199,93
	DMSO-PBS buffer (9:1, v/v)	0-50	0.15 μM (4.8 ppb)	30	Sens. Actuators, B 2015,216,141
	PBS buffer (2% CH_3CN, v/v)	0-20	0.10 μM (~3 ppb)	10	This work