Electronic Supplementary Information

Specific detection and determination of cysteine by a luminescent samarium macrocycle-based fluorescence probe platform

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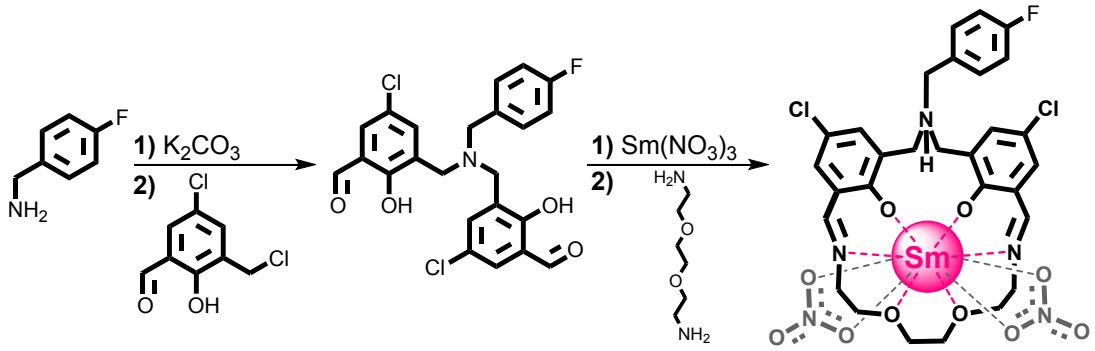
Experimental Section

Materials and Instrumentations

All starting materials under the 99% purity were commercially purchased from the TCI Shanghai Company and directly used without any further purifications.

^{1}H NMR spectrum was recorded on Bruker DPX 400 MHz spectrometer at room temperature, with TMS as internal standard using $CDCl_3$ as deuterated solvent. The electrospray ionization mass spectra (ESI-MS) were measured by a ThermoFisher Scientific LCQ-Fleet mass spectrometer in a scan range of 500-2000 amu. The FT-IR spectra were recorded from 4000 to 400 cm^{-1} on a Nicolet FT-IR 170X spectrophotometer with 1 cm^{-1} resolution. Samples were dried and grinded with KBr to obtain pellet for recording FT-IR. UV-vis spectra were monitored by a Shimadzu UV-3150 double-beam spectrophotometer between a wavelength range of 250–550 nm. Fluorescence measurements in this work were determined from 500 to 750 nm on the HORIBA JOBIN YVON FluoroMax-4 fluorometer equipped with a R928P PMT emission detector in the visible region, and the slits of 5/5 nm.



Scheme S1. Synthesis route of the dialdehyde H_2Q_n and complex **Sm-2$_n$**.

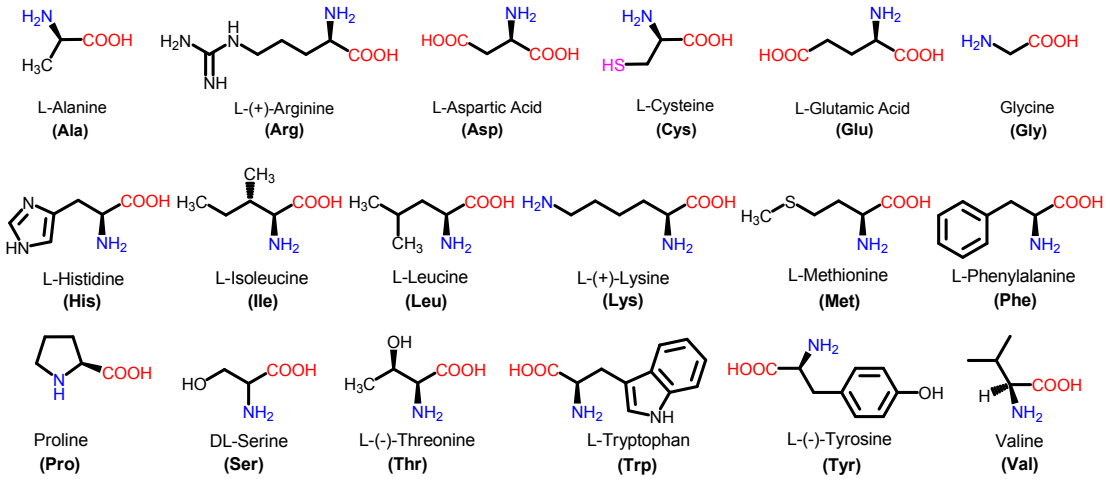
Syntheses of H_2Q_n

The dialdehyde H_2Q_n was synthesized by previous procedures[1] except that 4-fluorobenzylamine (0.313 g, 2.50 mmol) and 5-chloro-3-bromomethyl-2-hydroxybenzaldehyde (1.248 g, 5.00 mmol) was used here, and H_2Q_n was finally obtained in the yield of 68 % (0.785 g) by silica gel column chromatography using ethyl acetate/petroleum ether (*v*/*v* = 1:5) as the eluent. Mp: 185−186 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.40 (s, 2H), 10.01 (s, 2H), 7.51 (s, 2H), 7.43 (s, 2H), 7.33 (s, 2H), 7.06 (s, 2H), 3.74 (s, 4H), 3.70 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 193.17, 163.60, 158.78, 136.47, 132.63, 130.93, 130.92, 127.32, 124.30, 122.01, 115.68, 58.19, 53.26. Main FT-IR absorptions (KBr pellets, cm^{-1}): 2924 (w), 2851 (w), 1660 (s, -CH=O), 1602(m), 1458 (s), 1239 (m), 1017(w), 744 (w)，680(w). UV-vis spectrum, λ/nm (ε/L·mol^{-1}·cm^{-1}) in CH_3OH: 342 (9550).

Syntheses of Sm-2$_n$ [$Sm(HL2_n)(NO_3)_2$]

Upon reported template synthesis method[1] with $Sm(NO_3)_3·6H_2O$ (0.045 g, 0.10 mmol) as the template reagent, the targeted yellow-green product **Sm-2$_n$** could be finally obtained by use of dialdehyde H_2Q_n (0.046 g, 0.10 mmol) and diamine 1,2-bis(2-aminoethoxy)ethane (0.015 g, 0.10 mmol). Yield: 70 %, (0.059 g). ESI-MS (positive mode, m/z): 1033.42 {**Sm-2$_n$**+5CH_3OH+Na}$^+$ and 981.50 {**Sm-2$_n$**+3CH_3OH+2H_2O}$^+$. Main FT-IR absorptions (KBr pellets, cm^{-1}): 2907 (w), 1638 (s, CH=N), 1385 (s, N=O), 1290 (m), 1064 (m), 774 (m). UV-vis spectrum, λ/nm (ε/L·mol^{-1}·cm^{-1}) in CH_3OH: 359 (13758). After the slow evaporation in air at room temperature for six days, yellow-green single crystals

of complex **Sm-2$_n$** in prismatic shape were grown from its mixture of CH_3CN/CH_3OH (v/v = 1:4).



Scheme S2. The structures of used amino acids.

Cysteine sensing experiments

Complex **Sm-2$_n$** was firstly dispersed in MeOH (0.5 mM), and 0.6 ml of prepared **Sm-2$_n$** suspension was transferred to volumetric flasks, followed by the addition of 0.5 ml of amino acids (50 mM) and specific volumes of MeOH using a precise pipette to maintain the total volume of mixtures at 10 mL. At the same time, under the same volume (0.6 ml) of **Sm-2$_n$** (0.5 mM), different volumes of Cys (50 mM) and MeOH were added into volumetric flasks for titration experiments. Shake treatments were applied to these mixtures to keep uniform dispersion for latter spectral measurements. The final concentration of **Sm-2$_n$** in all samples remained at 30 μM.

Crystal structure determination and refinement

The single-crystal sample of complex **Sm-2$_n$** was covered with glue and mounted on glass fiber for data collection. Crystallographic data were collected at 293(2) K on a Bruker SMART 1K CCD diffractometer, using graphite mono-chromated Mo$K\alpha$ radiation (λ = 0.71073 Å). Absorption corrections were performed to all data and the structure was solved by direct method and refined by full-matrix least-squares method on F_{obs}^2 by using the SHELXTL-PC software package.[2] All non-H atoms were anisotropically refined and all hydrogen atoms were inserted in the calculated

positions assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. A summary of the crystal data, experimental details and refinement results for **Sm-2$_n$** was listed in Table S1. Selected bond lengths and bond angles of **Sm-2$_n$** were tabulated in Table S2, and hydrogen-bonding parameters were shown in Table S3. CCDC nos. 2012636 for disalicylaldehyde **Sm-2$_n$** contains the supplementary crystallographic data in this work. This datum could be acquired free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: [+44]1223-336-033; or deposit @ccdc.cam.ac.uk).

References

1 K. Zhang, M.-L. Lin, C.-C. Feng, P.-P. Nie, Z.-R. Yang, T.-T. Chen, L.-F. Zhang, S. Ma, Y.-J. Shen, Z.-Y. Lu, *Polyhedron* 2019, **173**, 114133.

2 G. M. Sheldrick, SHELXTL (Version 6.10). Software Reference Manual; Madison, Wisconsin (USA): Bruker AXS, Inc.: 2000.

Tables

Table S1. Crystal data and structural refinements for complex **Sm-2$_n$**.

Complex	**Sm-2$_n$**
Empirical formula	$C_{29}H_{29}Cl_2FN_5O_{10}Sm$
Formula weight	847.82
Temperature / K	293
Wavelength / Å	0.71073
Crystal Size (mm)	0.15×0.21×0.26
Crystal system	Triclinic
Space group	$P\bar{1}$
a / Å	19.968(6)
b / Å	8.587(3)
c / Å	19.820(6)
α / °	90
β / °	92.046(9)
γ / °	90
V / Å^3	3396.3(2)
Z / D_{calcd} (g / cm^3)	4 / 1.658
F(000)	1692
μ / mm^{-1}	1.953
h_{min} / h_{max}	–26 / 25
k_{min} / k_{max}	–10 / 11
l_{min} / l_{max}	–25 / 25
Data / parameters	7713 / 433
R_1, wR_2 [$I > 2\sigma(I)$][a]	R_1 = 0.0894, wR_2 = 0.1914
R_1, wR_2 (all data)[a]	R_1 = 0.1194, wR_2 = 0.2050
S	1.09
Max/min $\Delta\rho$/e Å^{-3}	4.13 / –2.26

[a] $R_1 = \Sigma||Fo|-|Fc|| / \Sigma|Fo|$, $wR_2 = [\Sigma[w(Fo^2-Fc^2)^2] / \Sigma w(Fo^2)^2]^{1/2}$

Table S2. Selected bond distances (Å) and angles (°) in complex **Sm-2$_n$**.

Bond distances		Bond angles	
Sm-2$_n$			
Sm1–O1	2.343(6)	O1–Sm1–O2	113.5(2)
Sm1–O2	2.649(7)	O1–Sm1–O3	139.5(3)
Sm1–O3	2.688(8)	O1–Sm1–O4	69.0(2)

Sm1–O4	2.338(8)	O1–Sm1–O5	92.5(3)
Sm1–O5	2.588(8)	O1–Sm1–O6	134.0(2)
Sm1–O6	2.531(8)	O1–Sm1–O8	73.7(3)
Sm1–O8	2.621(11)	O1–Sm1–O9	68.9(3)
Sm1–O9	2.627(12)	O1–Sm1–N2	68.1(2)
Sm1–N2	2.646(8)	O1–Sm1–N3	134.8(3)
Sm1–N3	2.693(10)	O2–Sm1–O3	60.0(2)
		O2–Sm1–O4	177.5(2)
		O2–Sm1–O5	110.1(3)
		O2–Sm1–O6	68.5(2)
		O2–Sm1–O8	108.4(3)
		O2–Sm1–O9	67.8(3)
		O2–Sm1–N2	62.3(2)
		O2–Sm1–N3	111.4(3)
		O3–Sm1–O4	118.4(3)
		O3–Sm1–O5	127.9(3)
		O3–Sm1–O6	83.6(3)
		O3–Sm1–O8	71.9(3)
		O3–Sm1–O9	72.5(3)
		O3–Sm1–N2	122.3(3)
		O3–Sm1–N3	63.6(3)
		O4–Sm1–O5	69.1(3)
		O4–Sm1–O6	109.6(2)
		O4–Sm1–O8	72.4(3)
		O4–Sm1–O9	114.0(3)
		O4–Sm1–N2	119.1(3)
		O4–Sm1–N3	66.2(3)
		O5–Sm1–O6	49.7(3)
		O5–Sm1–O8	141.5(3)
		O5–Sm1–O9	156.7(4)
		O5–Sm1–N2	71.8(3)
		O5–Sm1–N3	77.4(3)
		O6–Sm1–O8	152.0(3)
		O6–Sm1–O9	136.2(3)
		O6–Sm1–N2	74.6(2)
		O6–Sm1–N3	69.5(3)
		O8–Sm1–O9	48.3(4)

		O8–Sm1–N2	130.1(3)
		O8–Sm1–N3	87.3(4)
		O9–Sm1–N2	87.8(3)
		O9–Sm1–N3	125.6(3)
		N2–Sm1–N3	142.6(3)

Table S3. Intramolecular hydrogen bonding parameters (Å, °) in complex **Sm-2$_n$**.

D–H···A	D–H	H···A	D···A	∠DHA
Sm-2$_n$				
N1–H1···O1	0.98	2.10	2.858(10)	133
N1–H1···O4	0.98	1.82	2.615(11)	136

Table S4. Bond distances ($d_{Sm,j}$), bond valences ($v_{Sm,j}$) and total lanthanide atom valence (V_{Sm}) in the crystal structure of complex **Sm-2$_n$**.

Compound	Atom	Donor type	$d_{Sm,j}$/Å	$v_{Sm,j}$	V_{Sm}
Sm1	O1	$HL2_n^-$	2.343	0.464	2.803
	O2	$HL2_n^-$	2.649	0.203	
	O3	$HL2_n^-$	2.688	0.183	
	O4	$HL2_n^-$	2.338	0.470	
	O5	NO_3^-	2.588	0.239	
	O6	NO_3^-	2.531	0.279	
	O8	NO_3^-	2.621	0.219	
	O9	NO_3^-	2.627	0.215	
	N2	$HL2_n^-$	2.646	0.282	
	N3	$HL2_n^-$	2.693	0.249	

Figures

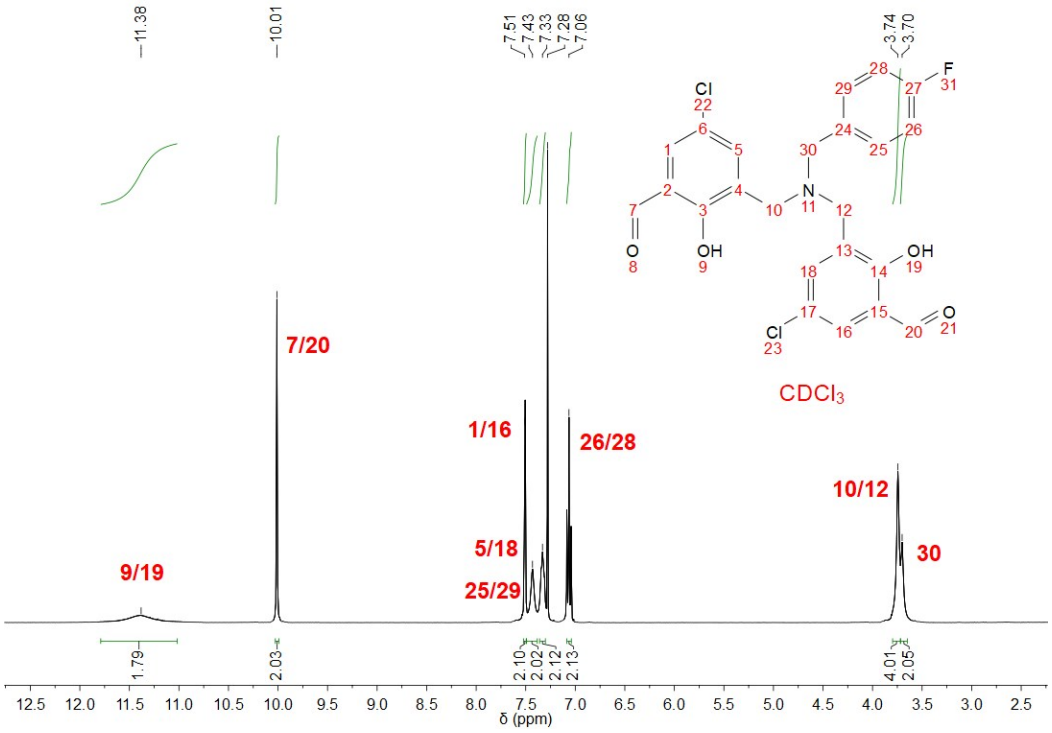


Fig. S1. ^{1}H NMR spectrum of dialdehyde H_2Q_n in $CDCl_3$.

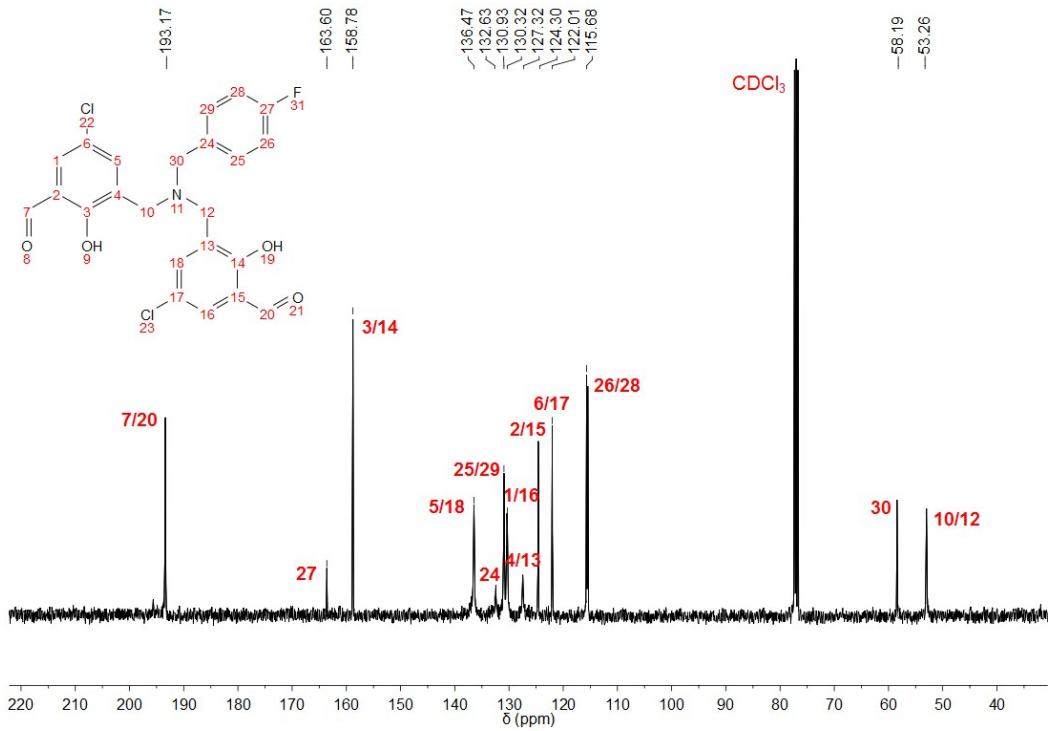


Fig. S2. ^{13}C NMR spectrum of dialdehyde H_2Q_n in $CDCl_3$.

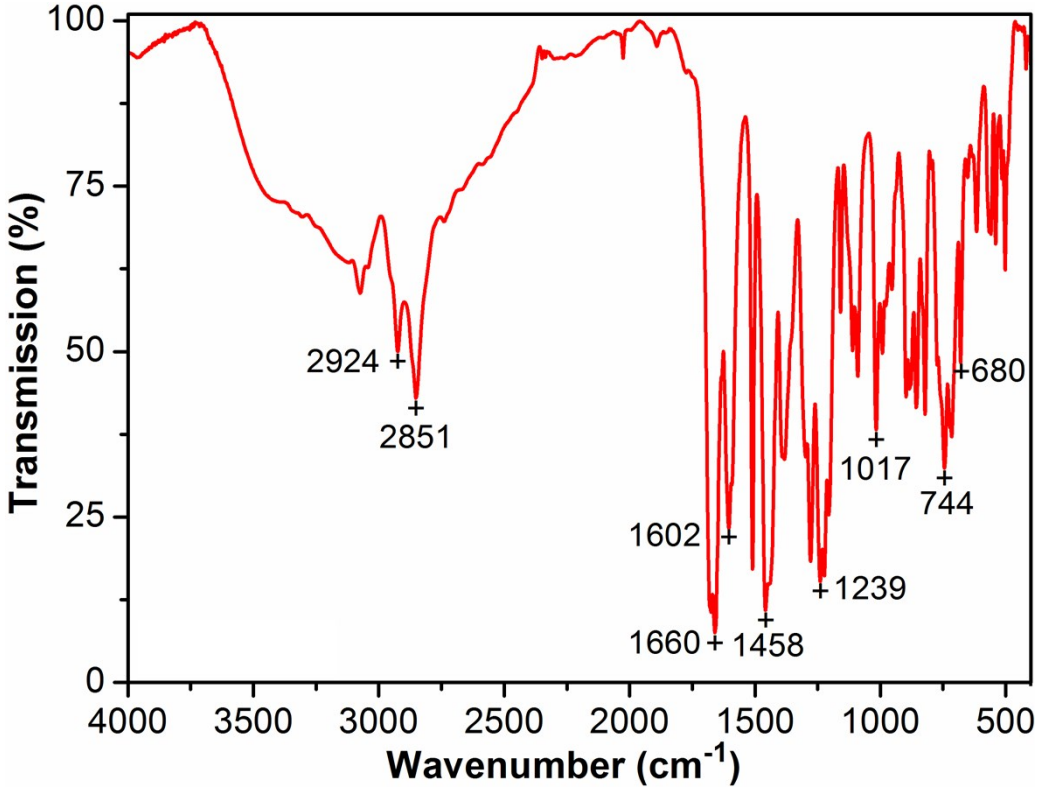


Fig. S3. FT-IR spectrum of dialdehyde H_2Q_n.

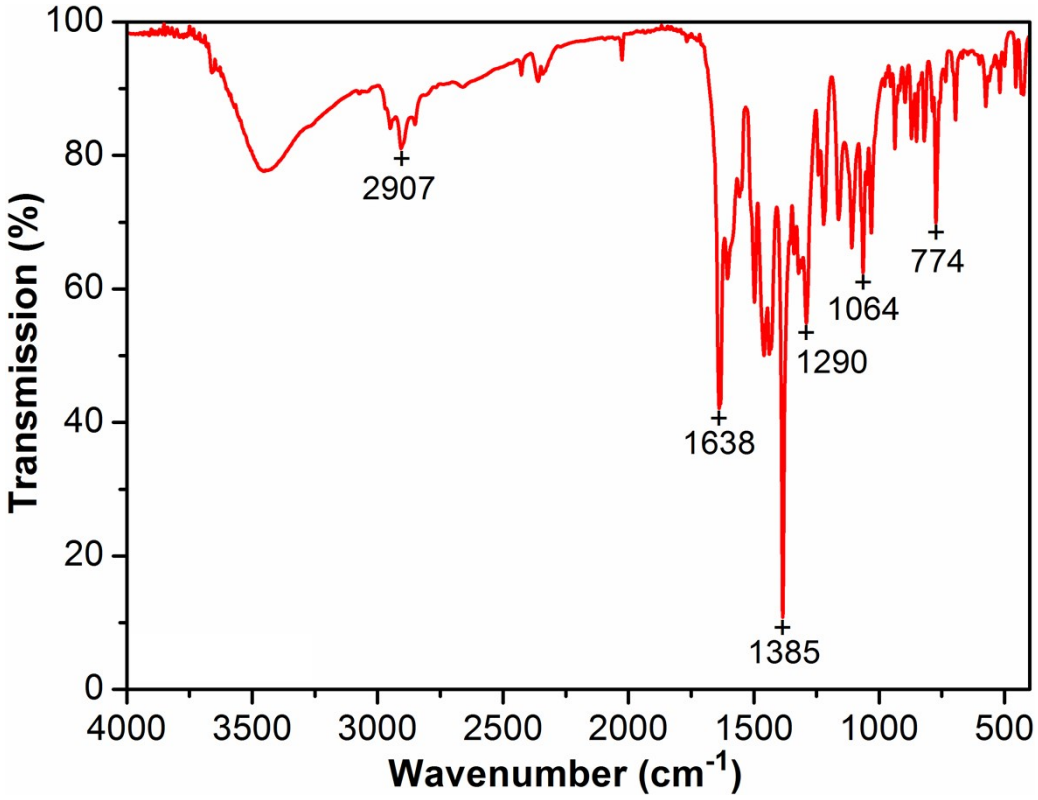


Fig. S4. FT-IR spectrum of macrocyclic Sm(III) complex **Sm-2$_n$**.

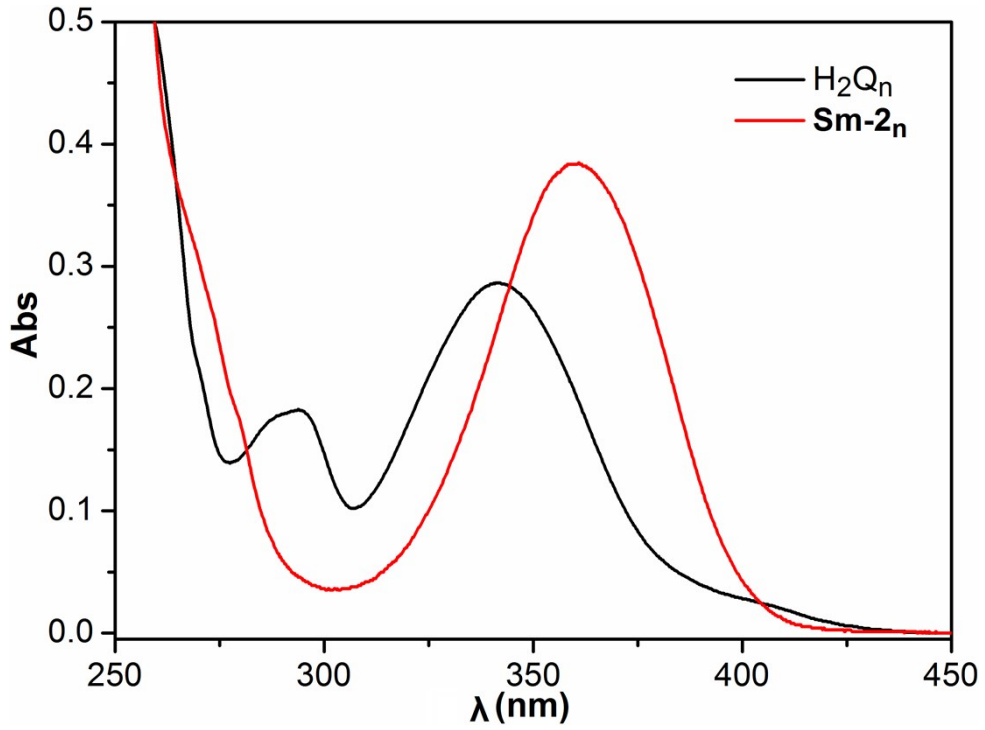


Fig. S5. UV-vis spectra of dialdehyde H_2Q_n (30 μM) and macrocyclic Sm(III) complex **Sm-2$_n$** (30 μM) in CH_3OH.

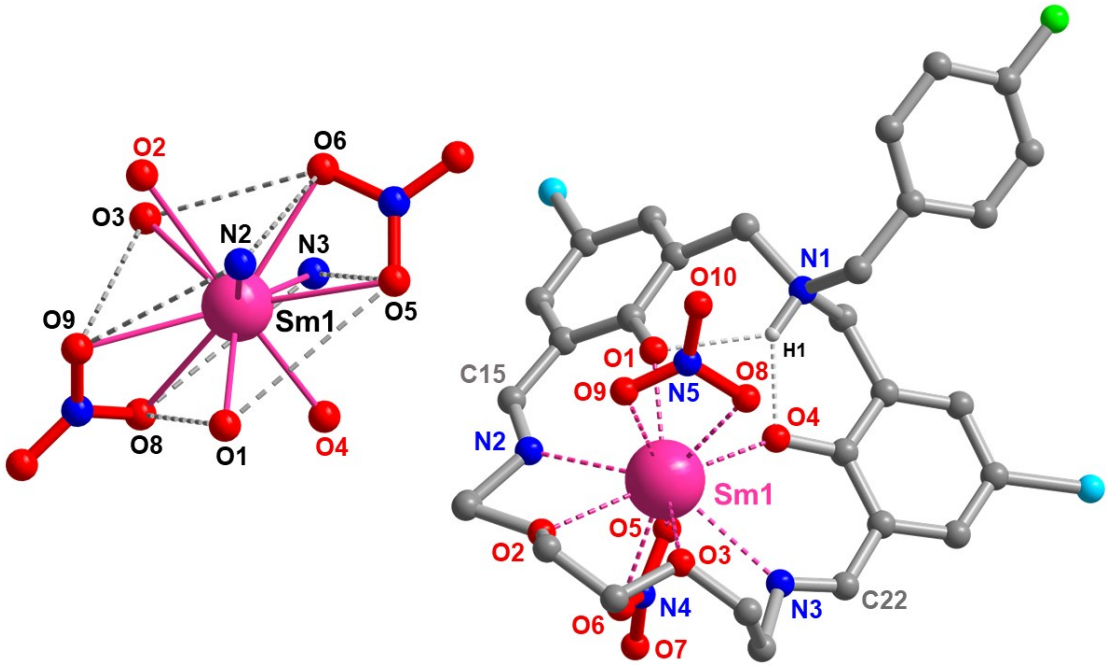


Fig. S6. X-ray crystal structure of complex **Sm-2$_n$**: white: hydrogen, gray: carbon, red: oxygen, blue: nitrogen, cyan: chlorine, green: fluorine, pink: samarium. For clarity, only the amide hydrogen (H1) related to hydrogen bonding interactions was kept. Insert: Description of distorted bicapped square antiprism coordination geometry of central Sm(III).

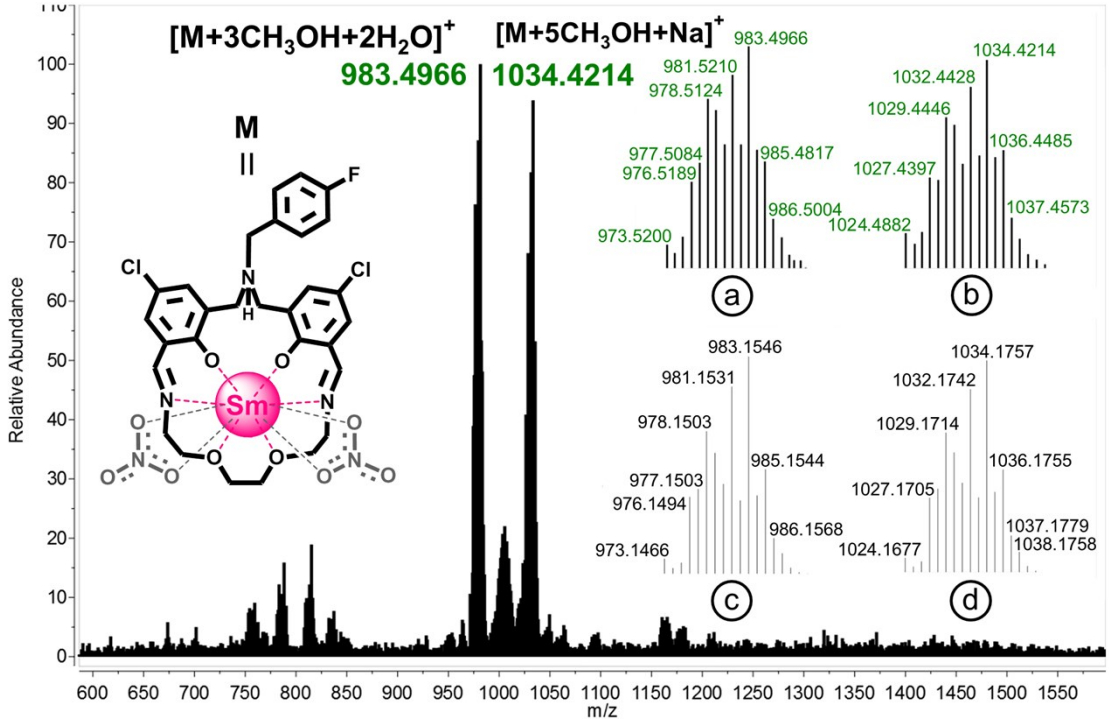


Fig. S7. ESI-MS (positive) of macrocyclic Sm(III) complex **Sm-2$_n$** together with the inserted experimental (**a** and **b**) and simulative (**c** and **d**, calculation for $[C_{32}H_{45}Cl_2FN_5O_{15}Sm]$ and $[C_{34}H_{49}Cl_2FN_5O_{15}NaSm]$, respectively) peaks of isotopic distribution corresponding to the peaks at m/z = 983.4966 and 1034.4214.

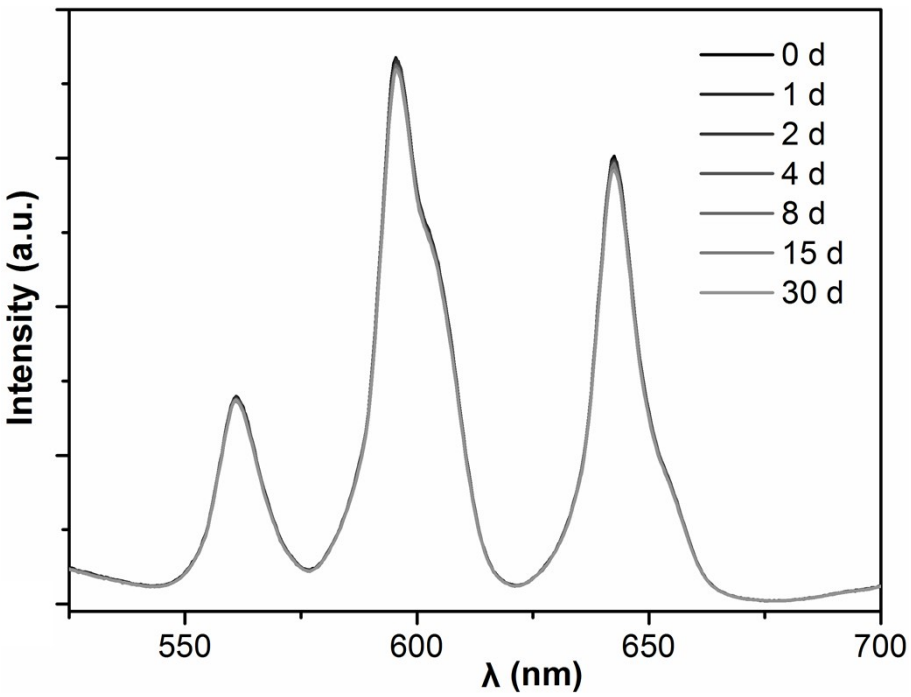


Fig. S8. Emission spectra of Sm(III) complex **Sm-2$_n$** (λ_{ex} = 359 nm, 30 μM) in air over multiple time points, recorded in H_2O-CH_3OH (*v*/*v*, 1:19) at 298 K.

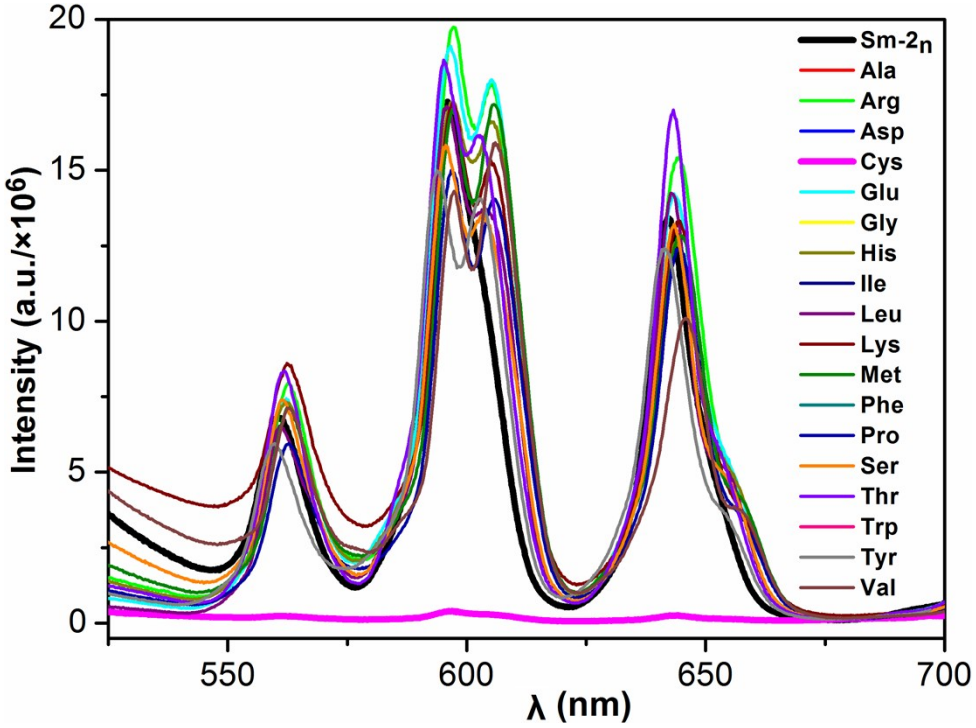


Fig. S9. Fluorescence spectra (λ_{ex} = 359 nm) of complex **Sm-2$_n$** (30 μM) before and after the addition of various amino acids (2.5 mM) in 5% H_2O/CH_3OH (*v*/*v*) at 298 K.

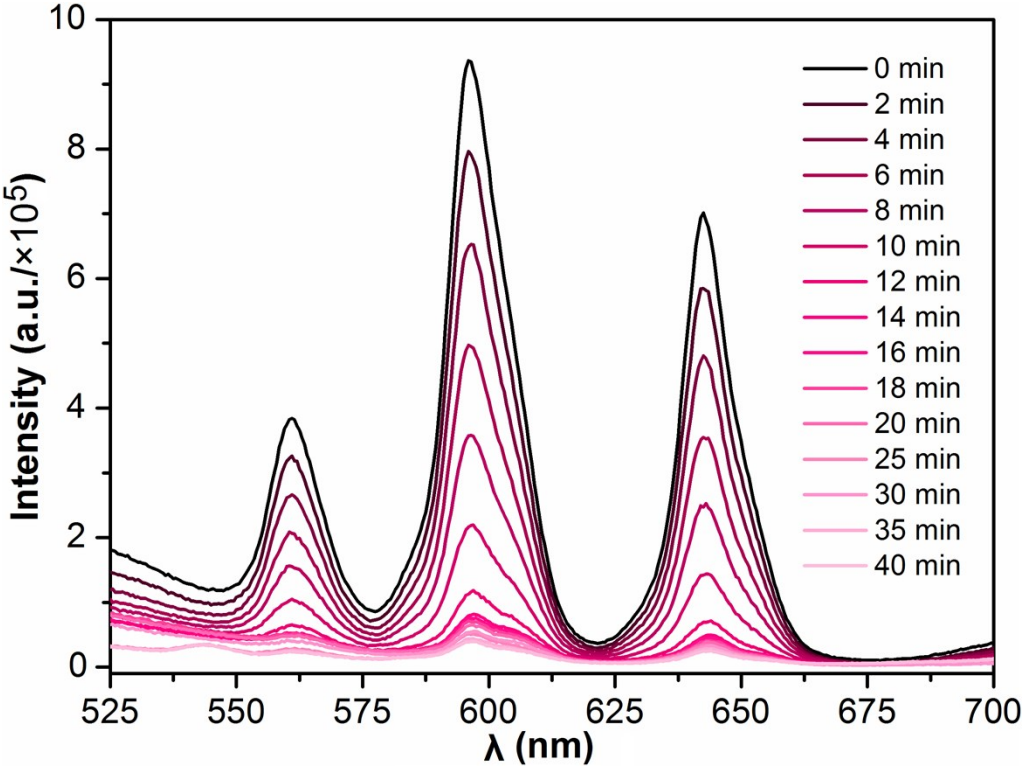


Fig. S10. The time-dependent fluorescence spectra (λ_{ex} = 359 nm) of complex **Sm-2$_n$** (15 μM) mixed with Cys (1.25 mM) in 5% H_2O/CH_3OH (*v*/*v*) at 298 K.

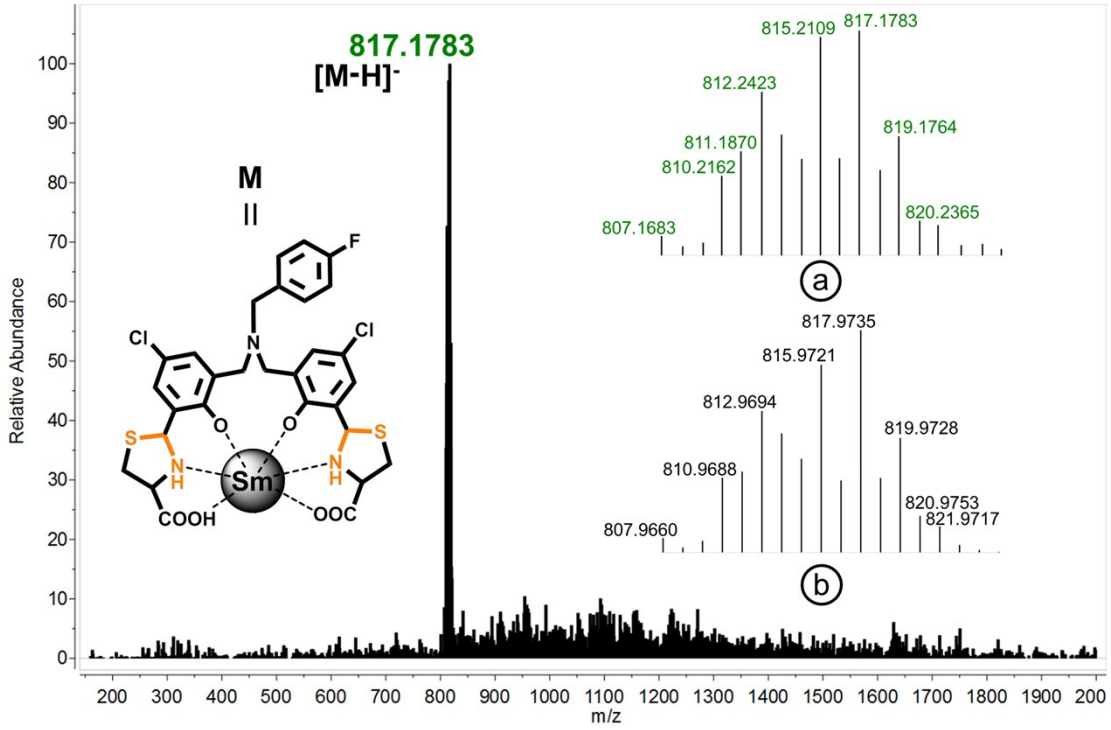


Fig. S11. ESI-MS (negative) of probe complex **Sm-2$_n$** mixed with excessive Cys together with the inserted experimental (**a**) and simulative (**b**, calculation for [$C_{29}H_{24}Cl_2FN_3O_6S_2Sm$]) peaks of isotopic distribution corresponding to the peak at m/z = 817.1783.

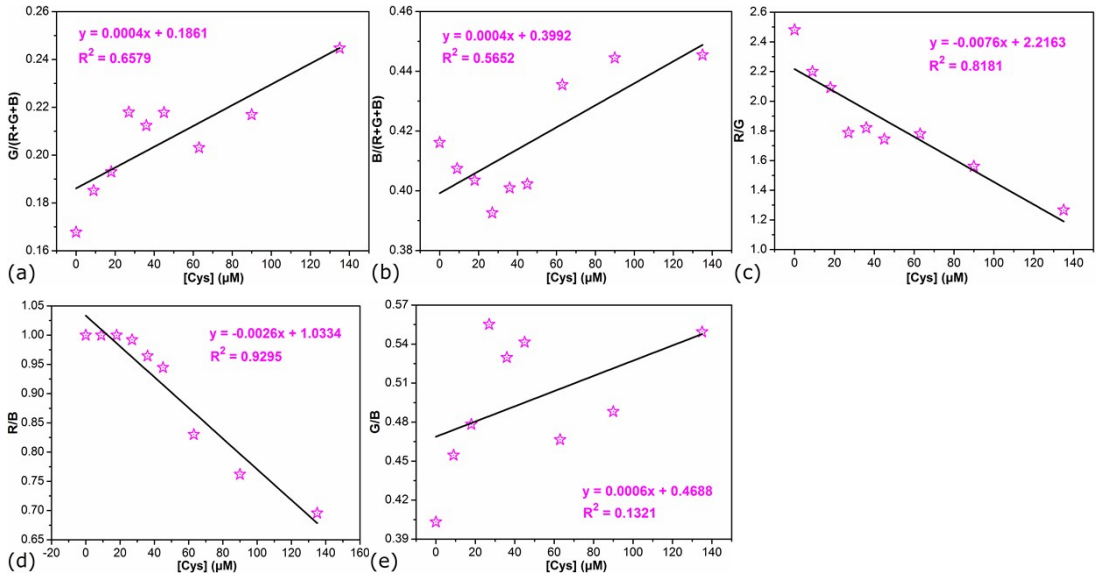


Fig. S12. The ratio of G/(R+G+B) (**a**), G/(R+G+B) (**b**), R/G (**c**), R/B (**d**), and G/B (**e**) versus [Cys] in various Cys solutions (0–0.135 mM).

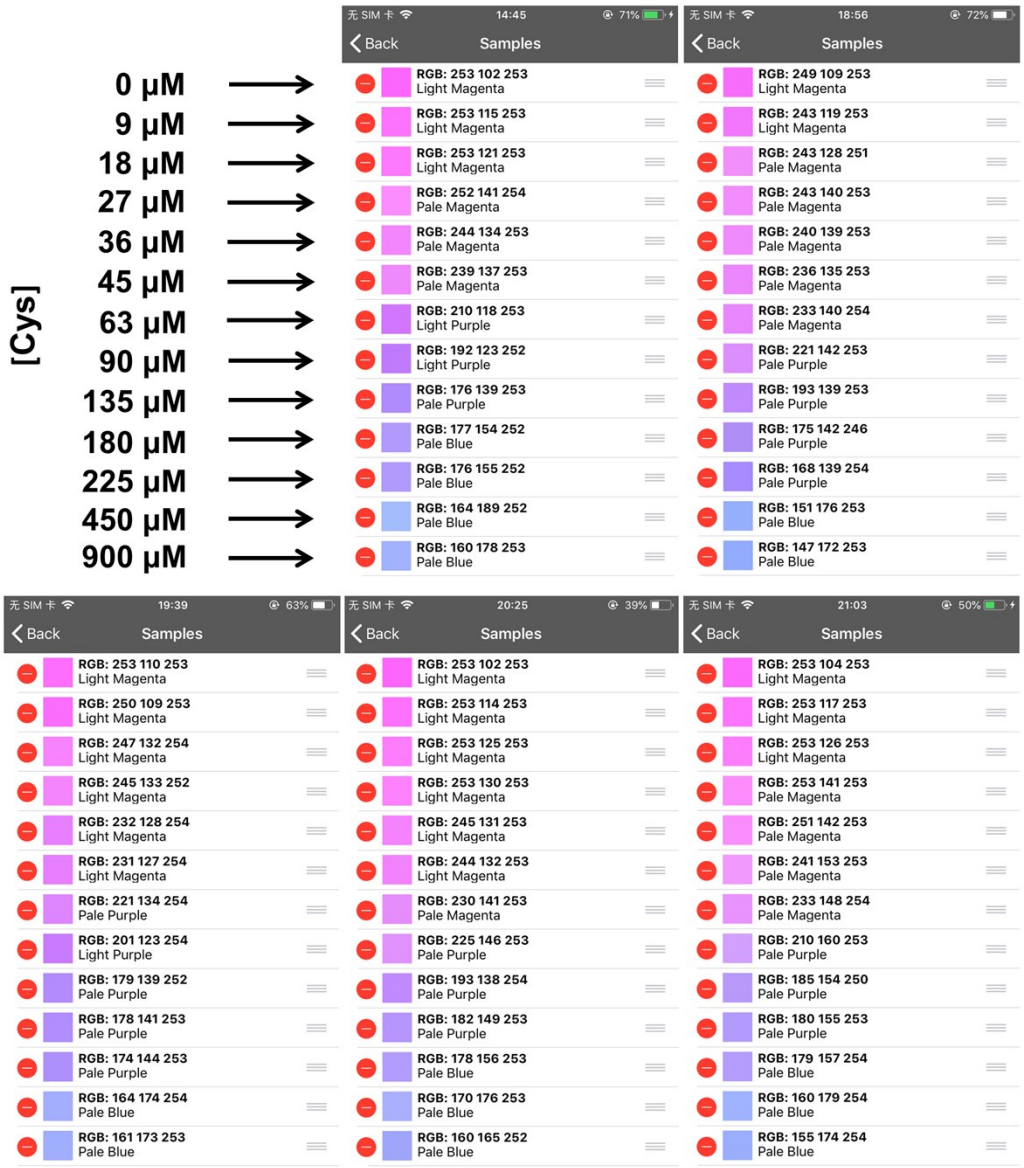


Fig. S13. The RGB values of smartphone-based analysis for detecting Cys in the release capsule by probe **Sm-2$_n$** impregnated test paper strips with five repetitions.