Supplementary Information

The excellent colorimetric and "turn off" fluorescent probe for tetrahydrofuran based on a luminescent macrocyclic samarium (III) complex

Zhuo-Ran Yang, Cheng-Cheng Feng, Peng-Peng Nie, Ting-Ting Chen, Lin-Feng Zhang, Shuang Ma, Yin-Jing Shen, Ze-Ying Lu, Meng-Lu Lin and Kun Zhang*
Department of Chemistry, Zhejiang Sci-Tech University, Xiasha Higher Education District, Hangzhou 310018, P. R. China

Tables

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

Complex	**Sm-2$_e$**
Empirical formula	$C_{30}H_{31}Cl_2FN_5O_{10}Sm$
Formula weight	861.85
Temperature / K	291(2)
Wavelength / Å	0.71073
Crystal Size (mm)	0.26×0.21×0.14
Crystal system	Monoclinic
Space group	*P*21/n
a / Å	13.122(2)
b / Å	13.632(2)
c / Å	20.773(2)
α / °	90
β / °	96.846(3)
γ / °	90
V / Å^3	3689.2(5)
Z / D_{calcd} (g / cm^3)	4 / 1.552
F(000)	1724
μ / mm^{-1}	1.799
h_{min} / h_{max}	–16 / 16
k_{min} / k_{max}	–17 / 17
l_{min} / l_{max}	–26 / 25
Data / parameters	7511 / 413
R_1, wR_2 $[I > 2\sigma(I)]^a$	R_1 = 0.0760 wR_2 = 0.1834

R_1, wR_2 (all data)[a]	R_1 = 0.1066 wR_2 = 0.1993
S	1.03
Max/min $\Delta\rho$/e Å^{-3}	1.20 / –2.09

[a] $R_1 = \Sigma||Fo|-|Fc|| / \Sigma|Fo|$, w$R_2 = [\Sigma[w(Fo^2-Fc^2)^2] / \Sigma w(Fo^2)^2]^{1/2}$

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

Bond distances		Bond angles	
Sm-2$_e$			
Sm1–O1	2.362(7)	O1–Sm1–O2	101.8(3)
Sm1–O2	2.661(7)	O1–Sm1–O3	144.7(3)
Sm1–O3	2.602(7)	O1–Sm1–O4	69.4(2)
Sm1–O4	2.320(7)	O1–Sm1–O5	86.2(2)
Sm1–O5	2.594(6)	O1–Sm1–O6	71.1(2)
Sm1–O6	2.561(7)	O1–Sm1–O8	95.8(2)
Sm1–O8	2.576(6)	O1–Sm1–O9	133.5(2)
Sm1–O9	2.547(7)	O1–Sm1–N2	68.7(2)
Sm1–N2	2.601(8)	O1–Sm1–N3	137.7(2)
Sm1–N3	2.641(8)	O2–Sm1–O3	59.0(2)
		O2–Sm1–O4	170.6(3)
		O2–Sm1–O5	106.6(3)
		O2–Sm1–O6	65.0(3)
		O2–Sm1–O8	115.9(2)
		O2–Sm1–O9	75.8(3)
		O2–Sm1–N2	60.3(3)
		O2–Sm1–N3	118.9(3)
		O3–Sm1–O4	126.3(2)
		O3–Sm1–O5	73.6(3)
		O3–Sm1–O6	73.8(3)
		O3–Sm1–O8	118.9(3)
		O3–Sm1–O9	74.1(3)
		O3–Sm1–N2	114.9(2)
		O3–Sm1–N3	63.0(2)
		O4–Sm1–O5	70.1(2)
		O4–Sm1–O6	107.8(2)
		O4–Sm1–O8	69.6(2)
		O4–Sm1–O9	112.6(2)

		O4–Sm1–N2	117.4(2)
		O4–Sm1–N3	69.1(2)
		O5–Sm1–O6	49.4(2)
		O5–Sm1–O8	135.9(2)
		O5–Sm1–O9	139.7(2)
		O5–Sm1–N2	146.6(2)
		O5–Sm1–N3	72.4(2)
		O6–Sm1–O8	166.4(2)
		O6–Sm1–O9	138.2(3)
		O6–Sm1–N2	100.1(2)
		O6–Sm1–N3	115.0(2)
		O8–Sm1–O9	49.5(2)
		O8–Sm1–N2	70.7(2)
		O8–Sm1–N3	77.2(2)
		O9–Sm1–N2	70.5(2)
		O9–Sm1–N3	71.8(2)
		N2–Sm1–N3	140.9(3)

Symmetry codes: [a], 2–*x, –y,* 1–*z*; [b], 1–*x,* 1–*y, –z*; [c], *x, –y, z*.

Table S3 Hydrogen bonding parameters (Å, °) in complex **Sm-2**$_e$.

D–H···A	D–H	H···A	D···A	∠DHA	Symmetry
Sm-2$_e$					
N1–H1···O1	1.00	2.08	2.850(12)	132	
N1–H1···O4	1.00	1.82	2.643(11)	137	

Figures

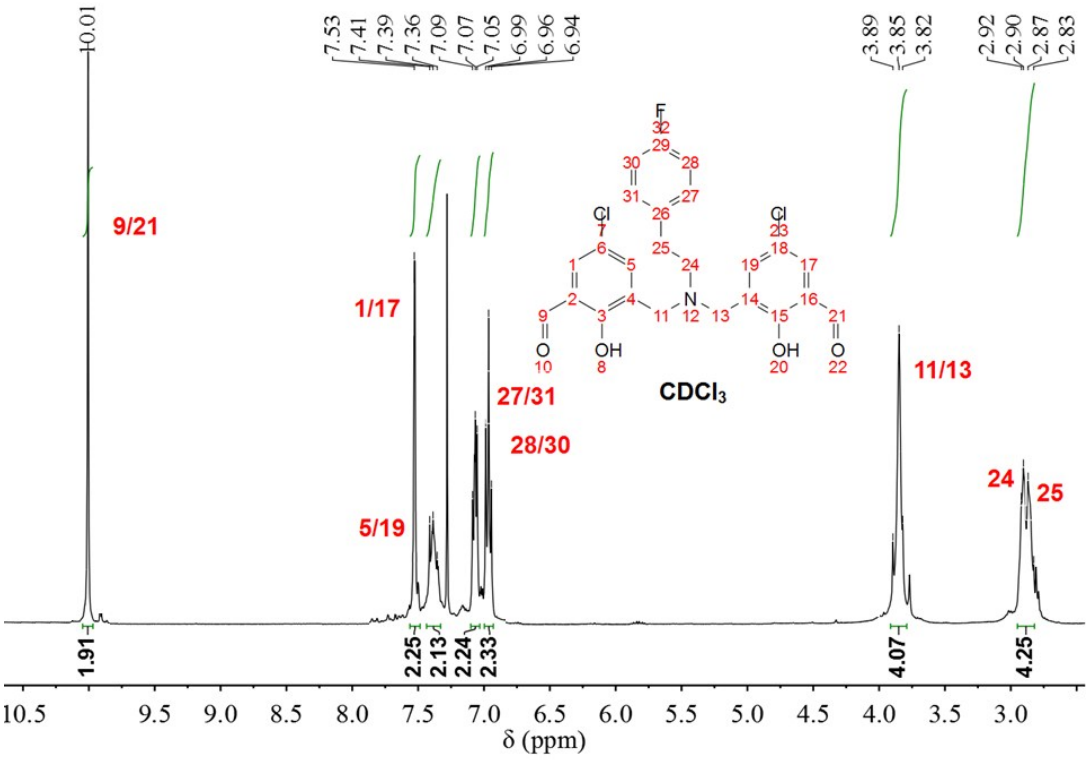


Fig. S1 ^{1}H NMR spectrum of compound H_2Q_e in $CDCl_3$.

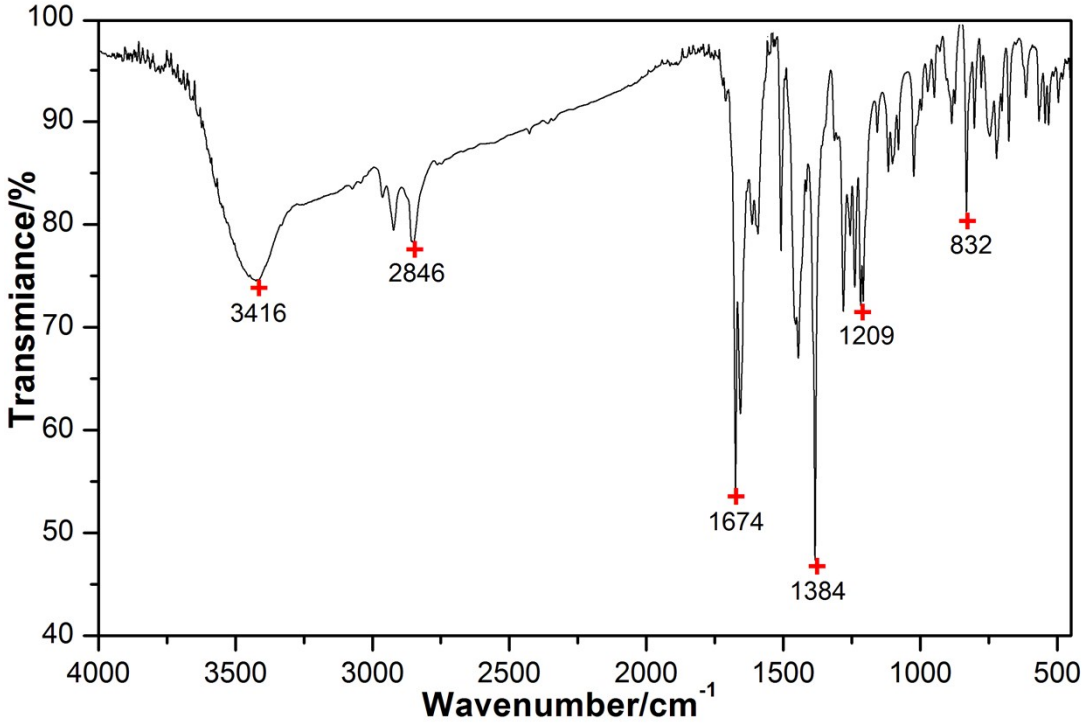


Fig. S2 FT-IR spectrum of dialdehyde H_2Q_e.

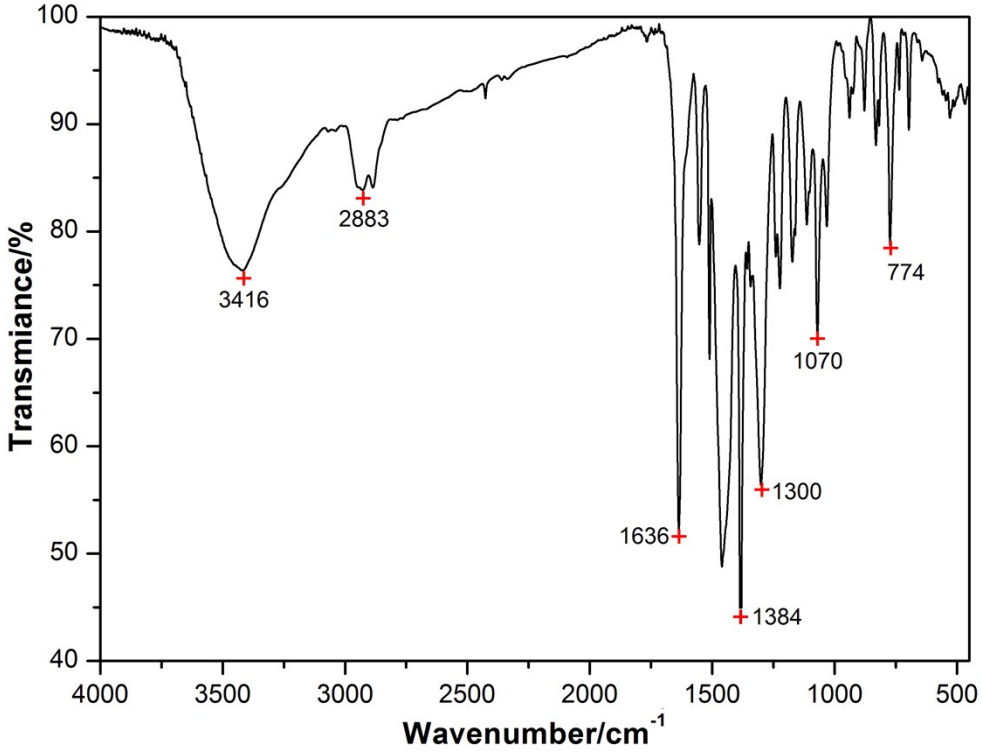


Fig. S3 FT-IR spectrum of complex **Sm-2$_e$**.

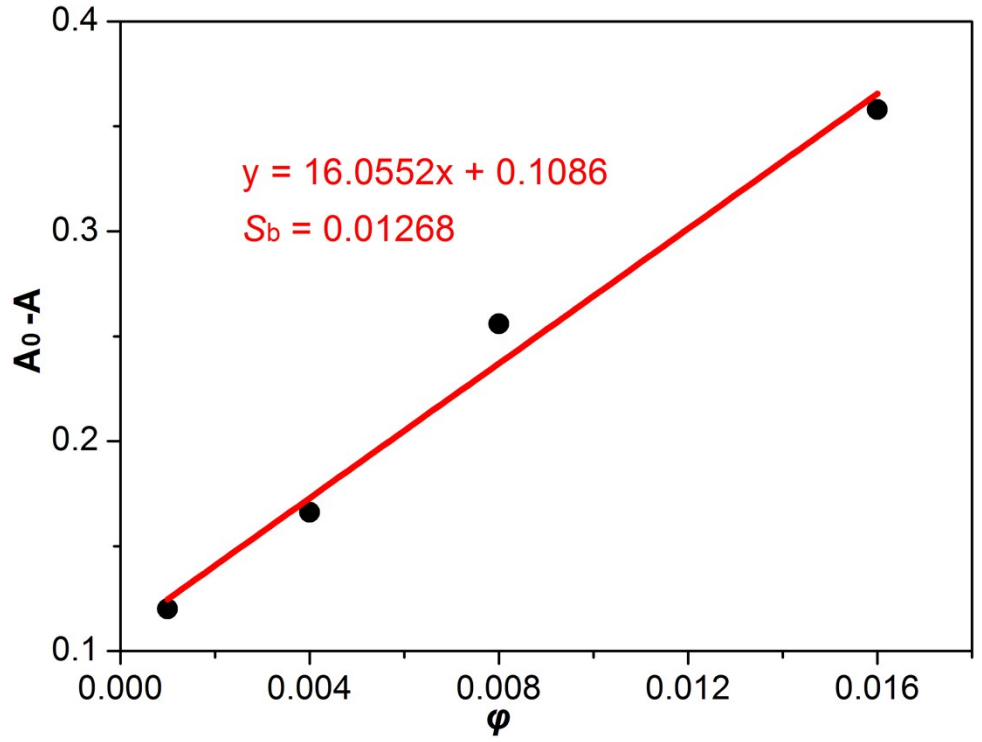
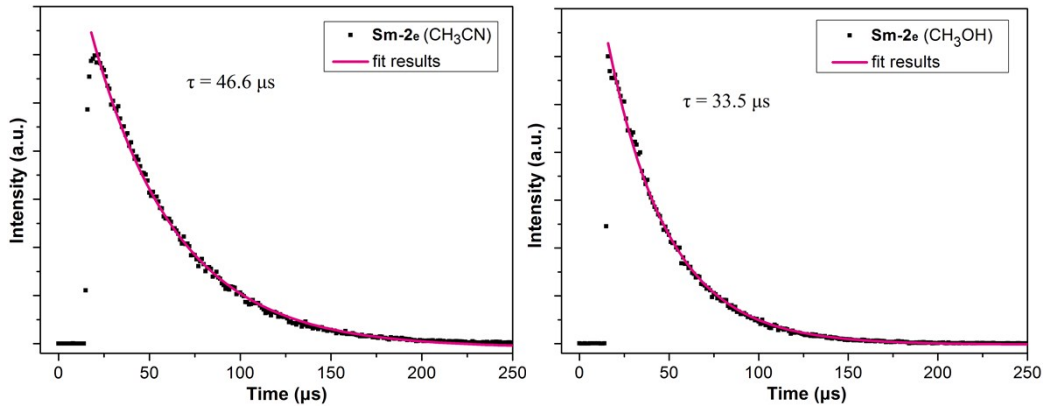
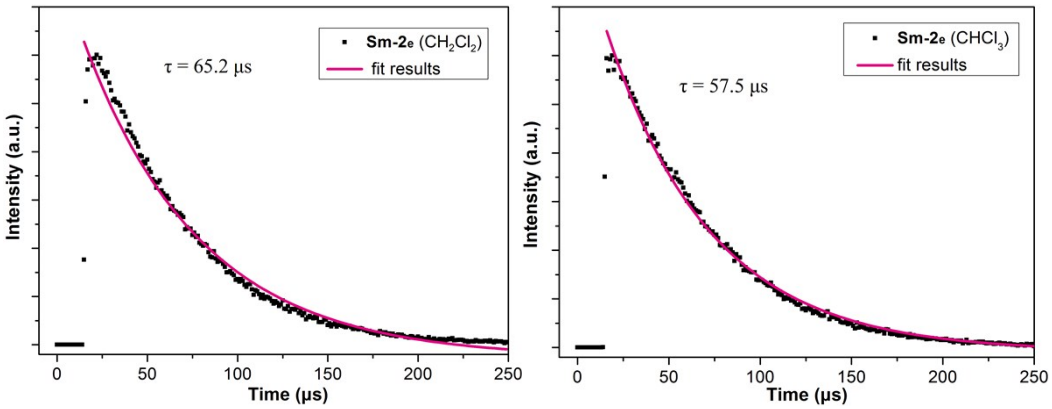


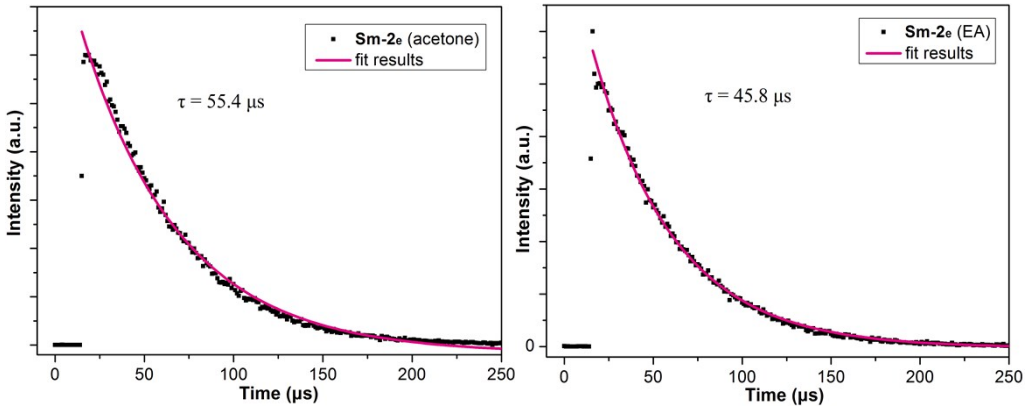
Fig. S4 The plot of (A_0-A) vs THF volume ratio in CH_3OH at 358nm for complex **Sm-2$_e$**.


Sm-2e (CH3CN)
fit results
τ = 46.6 μs
Intensity (a.u.)
Time (μs)
Sm-2e (CH3OH)
fit results
τ = 33.5 μs
Intensity (a.u.)
Time (μs)

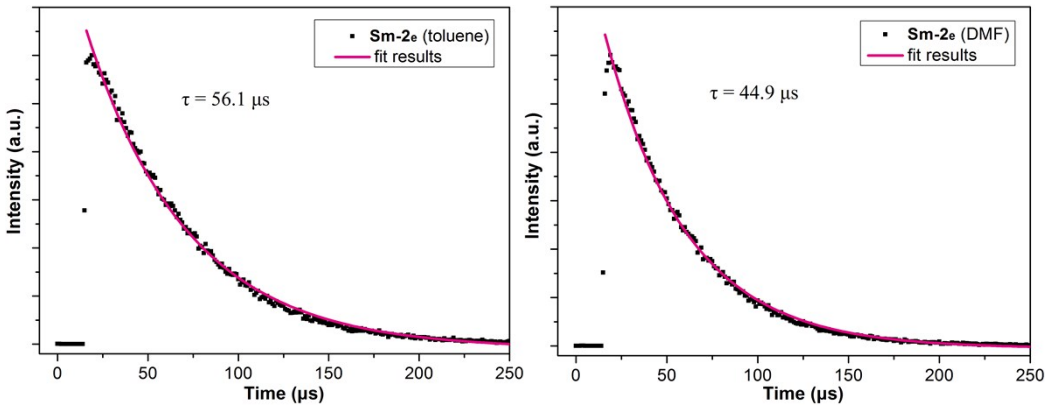
a b


Sm-2e (CH2Cl2)
fit results
τ = 65.2 μs
Intensity (a.u.)
Time (μs)
Sm-2e (CHCl3)
fit results
τ = 57.5 μs
Intensity (a.u.)
Time (μs)

c d


Sm-2e (acetone)
fit results
τ = 55.4 μs
Intensity (a.u.)
Time (μs)
Sm-2e (EA)
fit results
τ = 45.8 μs
Intensity (a.u.)
Time (μs)

e f


Sm-2e (toluene)
fit results
τ = 56.1 μs
Intensity (a.u.)
Time (μs)
Sm-2e (DMF)
fit results
τ = 44.9 μs
Intensity (a.u.)
Time (μs)

g h

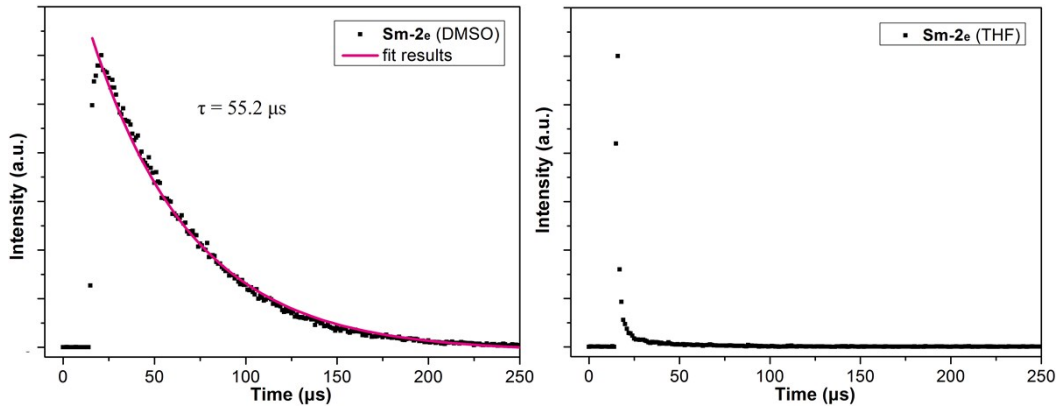


Fig. S5 Luminescence decay curves (λ_{em} = 643 nm) for macrocyclic Sm(III) complex **Sm-2$_e$** in different solvents (CH_3CN (**a**), CH_3OH (**b**), CH_2Cl_2 (**c**), $CHCl_3$ (d), acetone (**e**), EA (**f**), toluene (**g**), DMF (**h**), DMSO (**i**) and THF (**j**)) ([M] = 3 μM) at the room temperature.

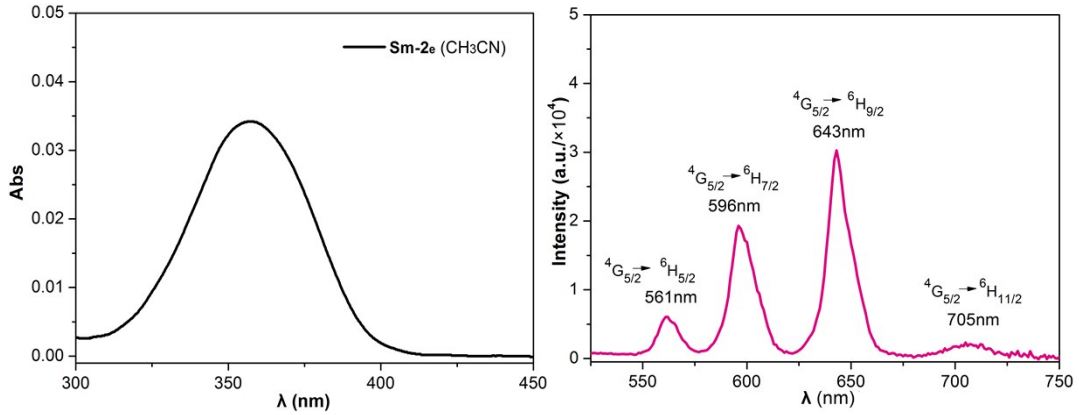


Fig. S6 UV-vis (left) and luminescence emission (right) spectra for macrocyclic Sm(III) complex **Sm-2$_e$** in CH_3CN ([M] = 3 μM) at the room temperature.

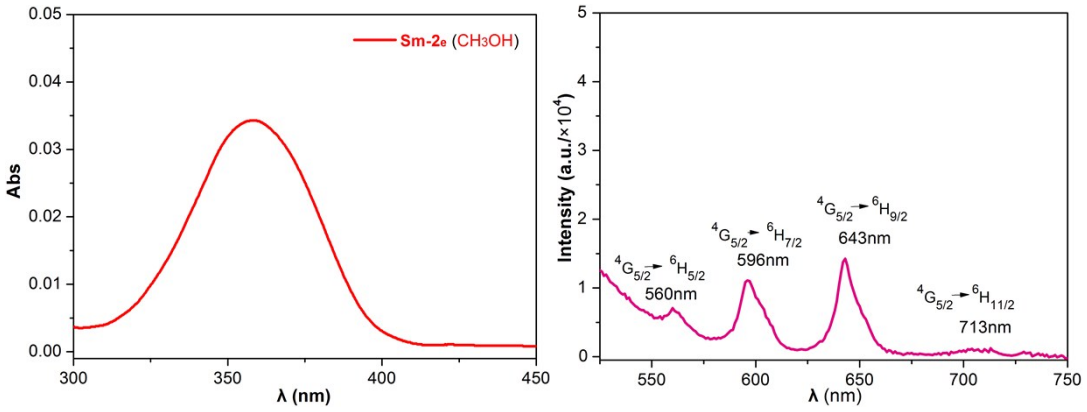


Fig. S7 UV-vis (left) and luminescence emission (right) spectra for macrocyclic Sm(III) complex **Sm-2$_e$** in CH_3OH ([M] = 3 μM) at the room temperature.

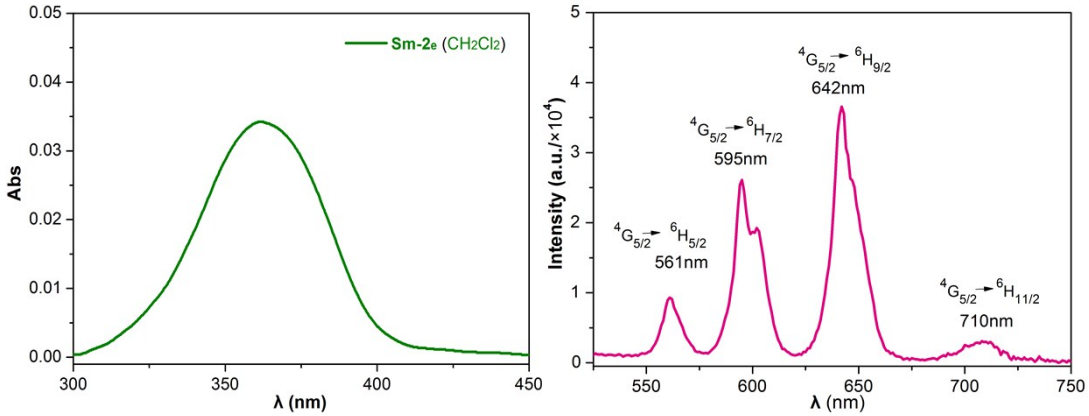


Fig. S8 UV-vis (left) and luminescence emission (right) spectra for macrocyclic Sm(III) complex **Sm-2$_e$** in CH_2Cl_2 ([M] = 3 μM) at the room temperature.

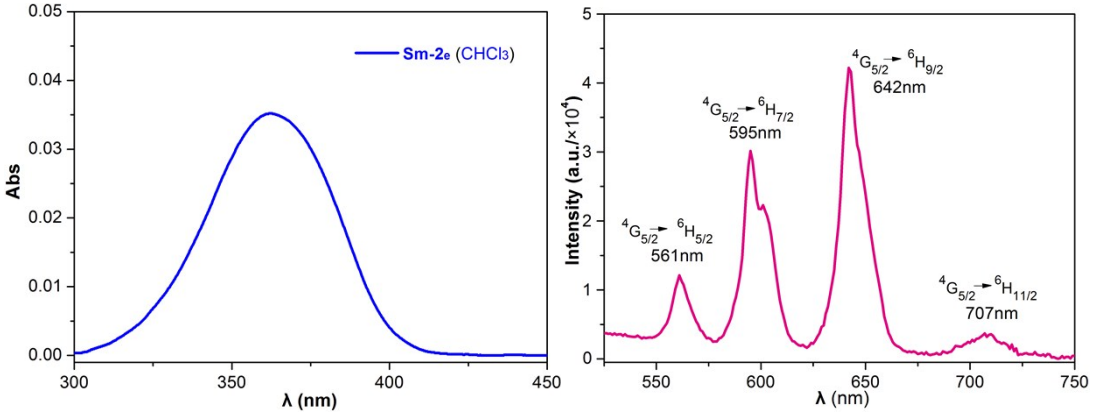


Fig. S9 UV-vis (left) and luminescence emission (right) spectra for macrocyclic Sm(III) complex **Sm-2$_e$** in $CHCl_3$ ([M] = 3 μM) at the room temperature.

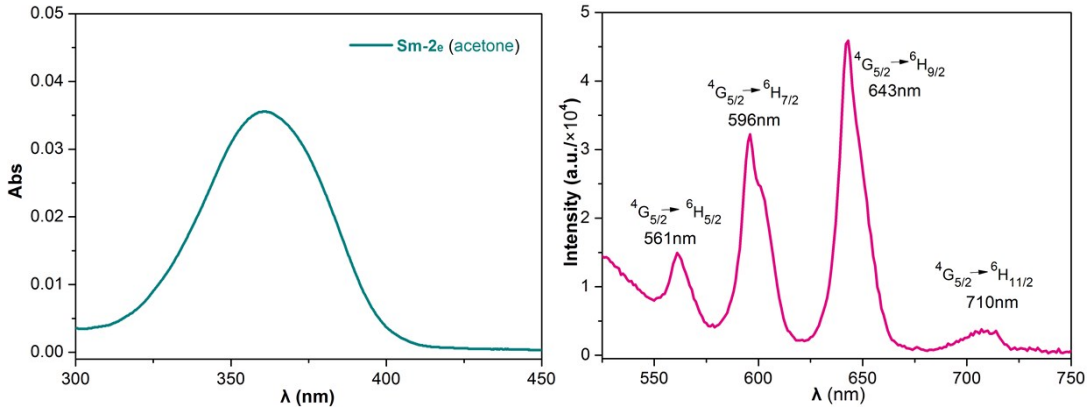


Fig. S10 UV-vis (left) and luminescence emission (right) spectra for macrocyclic Sm(III) complex **Sm-2$_e$** in acetone ([M] = 3 μM) at the room temperature.

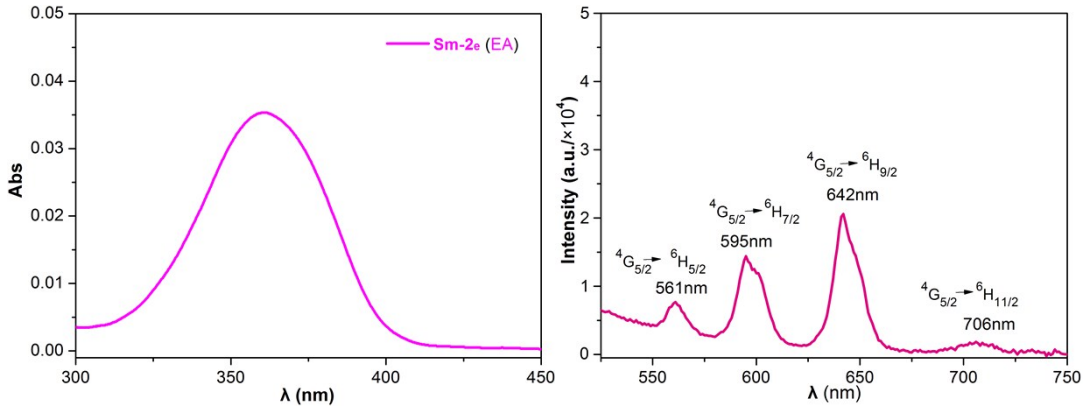


Fig. S11 UV-vis (left) and luminescence emission (right) spectra for macrocyclic Sm(III) complex **Sm-2$_e$** in EA ([M] = 3 μM) at the room temperature.

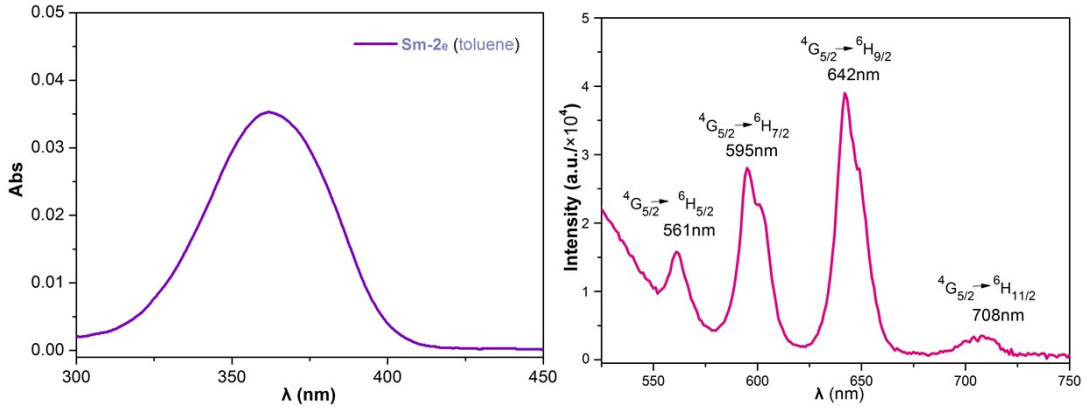


Fig. S12 UV-vis (left) and luminescence emission (right) spectra for macrocyclic Sm(III) complex **Sm-2$_e$** in toluene ([M] = 3 μM) at the room temperature.

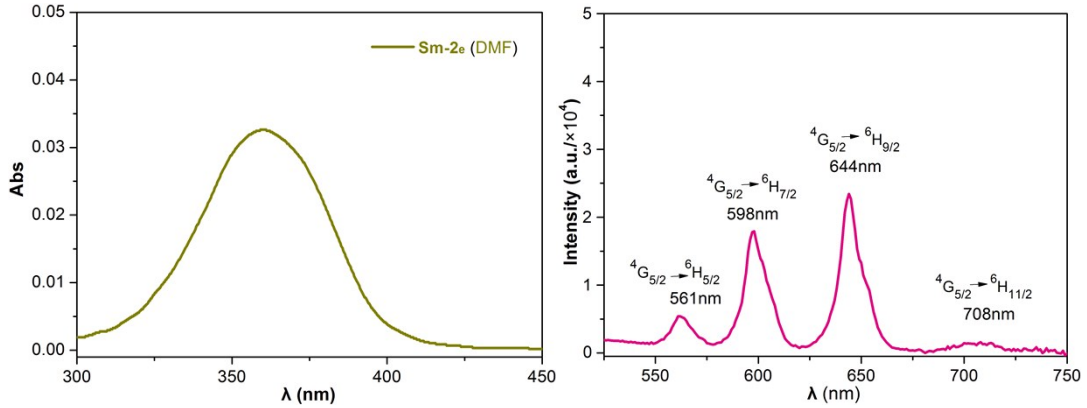


Fig. S13 UV-vis (left) and luminescence emission (right) spectra for macrocyclic Sm(III) complex **Sm-2$_e$** in DMF ([M] = 3 μM) at the room temperature.

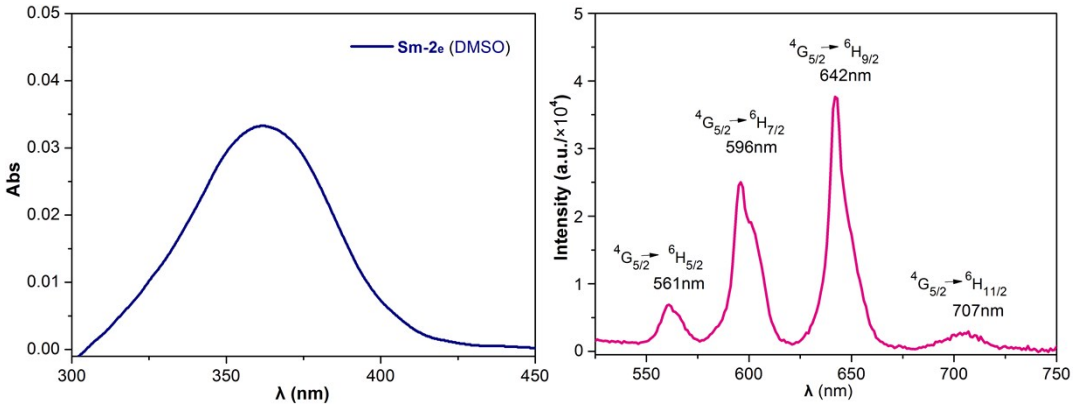


Fig. S14 UV-vis (left) and luminescence emission (right) spectra for macrocyclic Sm(III) complex **Sm-2$_e$** in DMSO ([M] = 3 μM) at the room temperature.

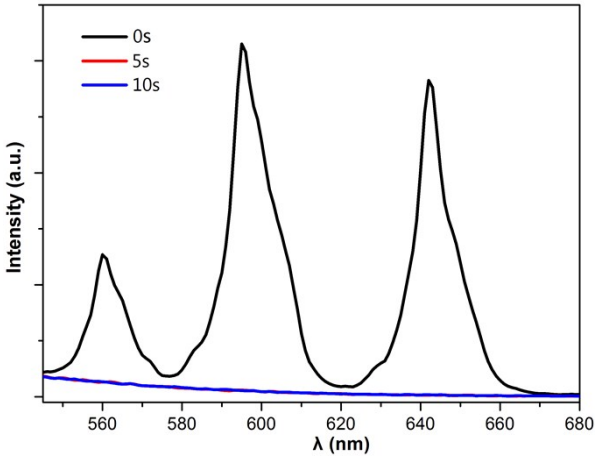


Fig. S15 The fluorescent emission spectra (λ_{ex}=358 nm) of probe **Sm-2$_e$** immersed in CH_3OH ([M] = 3 μM) with the THF content (volume ratio 25.6%) at two time intervals.

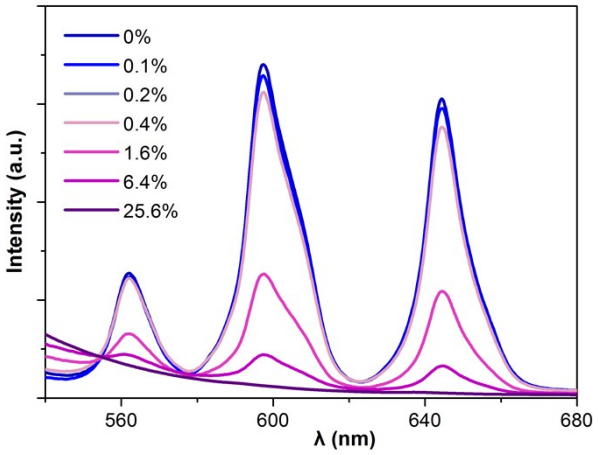


Fig. S16 The fluorescent spectra (λ_{ex}=358 nm) of probe **Sm-2$_e$** dispersed in mixed solvents ([M] = 3 μM) with increasing the volume ratio of THF at the room temperature.