Photophysical study of a polyoxo ethylene linked naphthalene-based fluorescent chemosensor for Mg^{2+} and Ca^{2+} detection

Xiaoyan Xiang , Dan Wang， Yali Guo, Weisheng Liu , Wenwu Qin[1]

[Revised- Mar 27, 2013]

Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province and State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China.

[1] To whom correspondence should be addressed. E-mail for W. Qin: qinww@lzu.edu.cn, Tel.: +86 -931-8912582; Fax: +86-931-8912582

Table S1. Global analyst results of N-Acetyl-1-aminonaphthalene (10 μM) in alcoholic solvents.

solvent	monitored wavelength/ nm	τ_1/ns	τ_2/ns	α_1 (%)	α_2 (%)
ethanol	407	5.87±0.001	1.48±0.006	77%	23%
	430			71%	29%
	460			64%	36%
1-pentanol	407	8.60±0.001	1.75±0.010	86%	14%
	430			79%	21%
	460			70%	30%
1-pentanol(high concentration)*	407	8.45±0.001	1.62±0.009	85%	15%
	430			81%	19%
	460			68%	32%

* The concentration of N-Acetyl-1-aminonaphthalene is 40 μM.

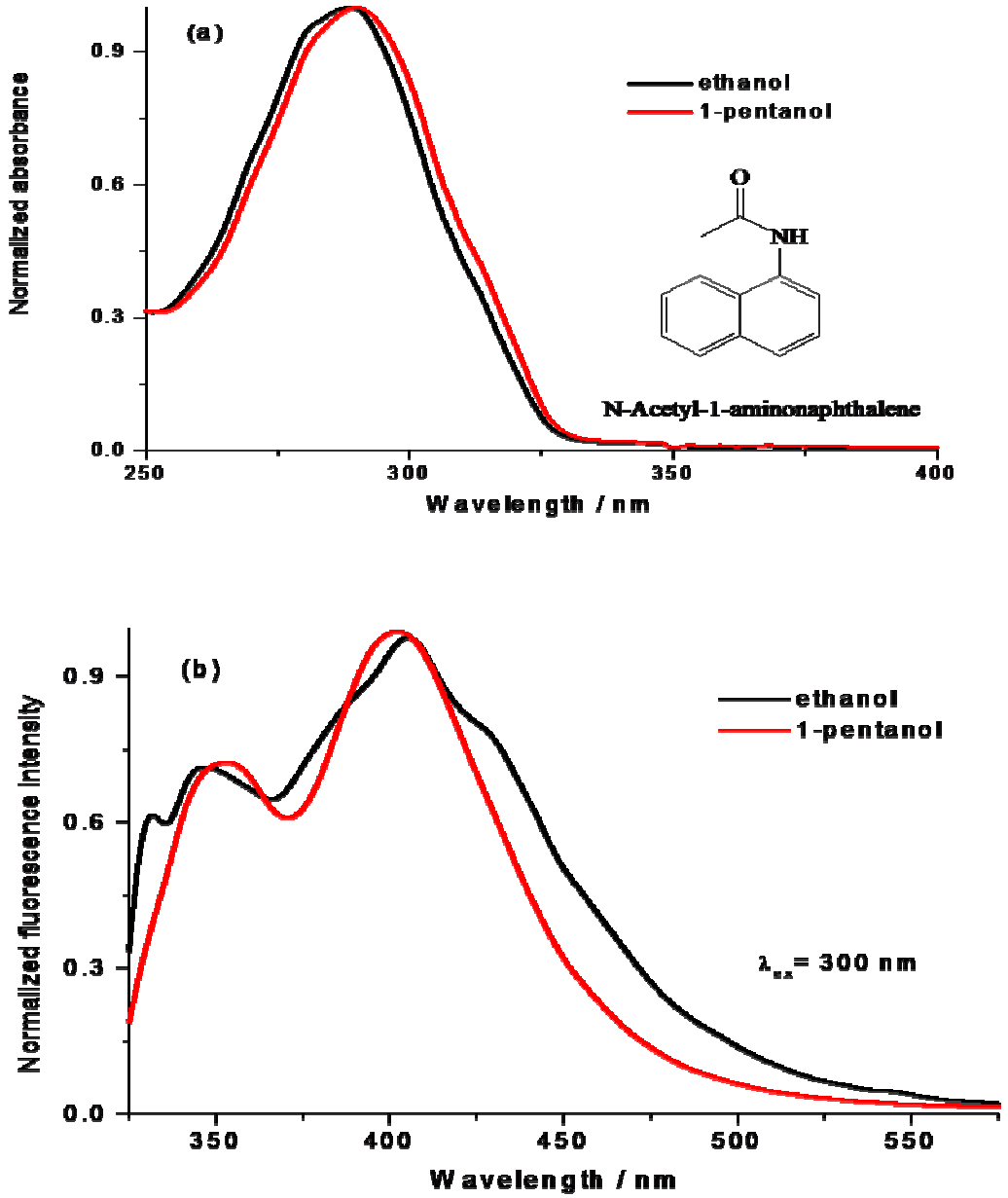
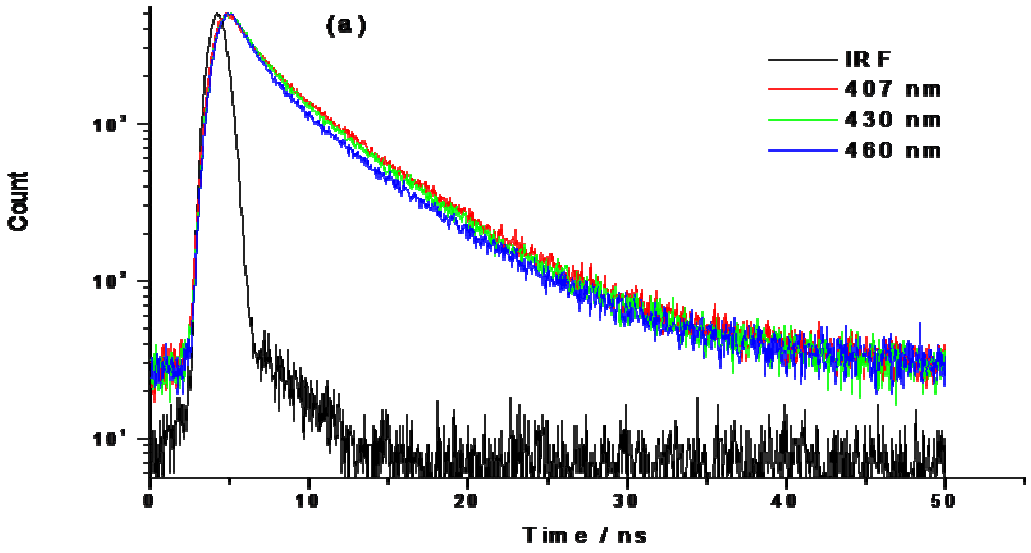
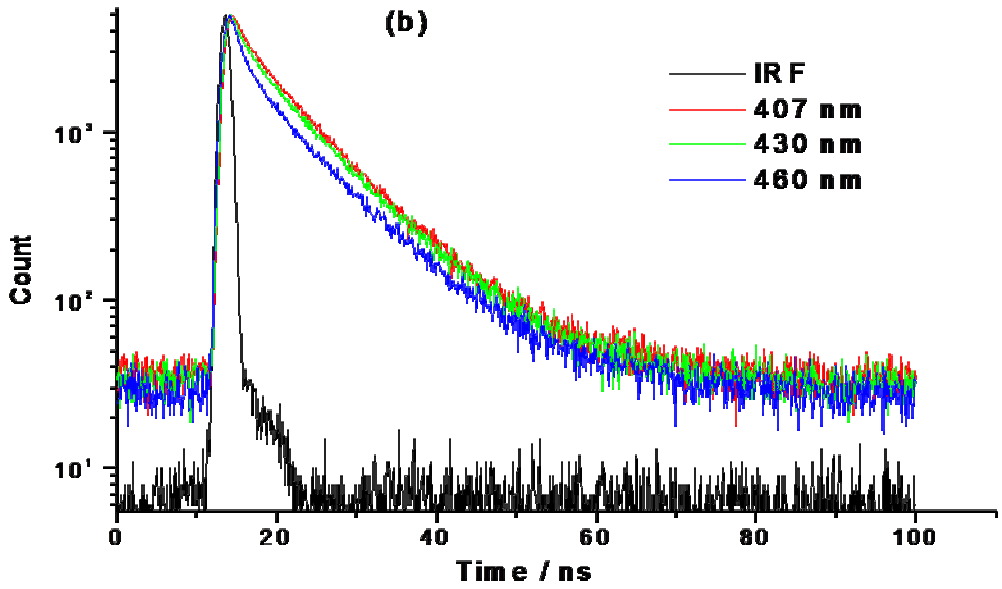


Figure S1. (a) Normalized absorption spectra of N-Acetyl-1-aminonaphthalene in two solvents. (b) Corresponding normalized fluorescence emission spectra (**λ_{ex}** = 300 nm).





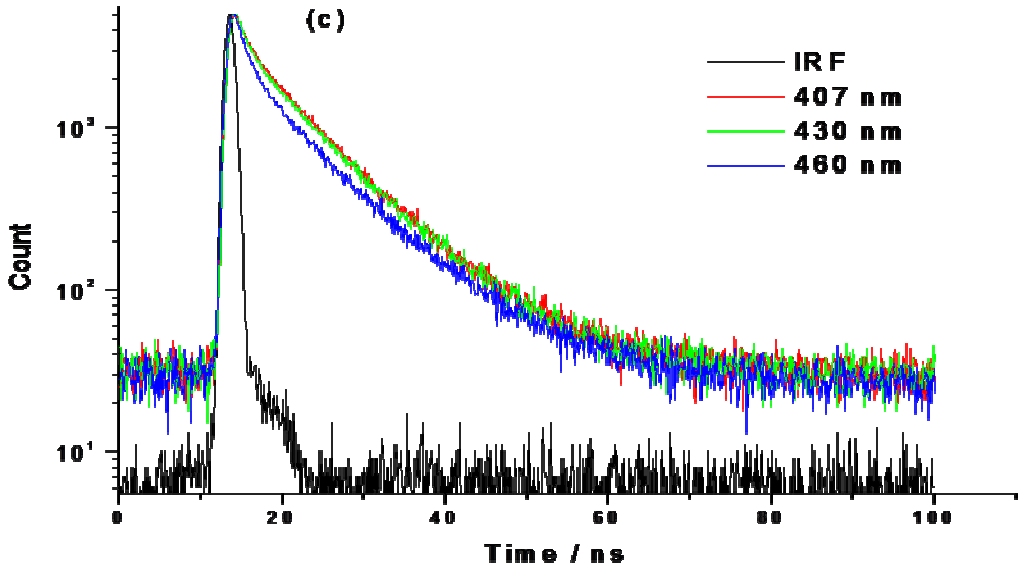
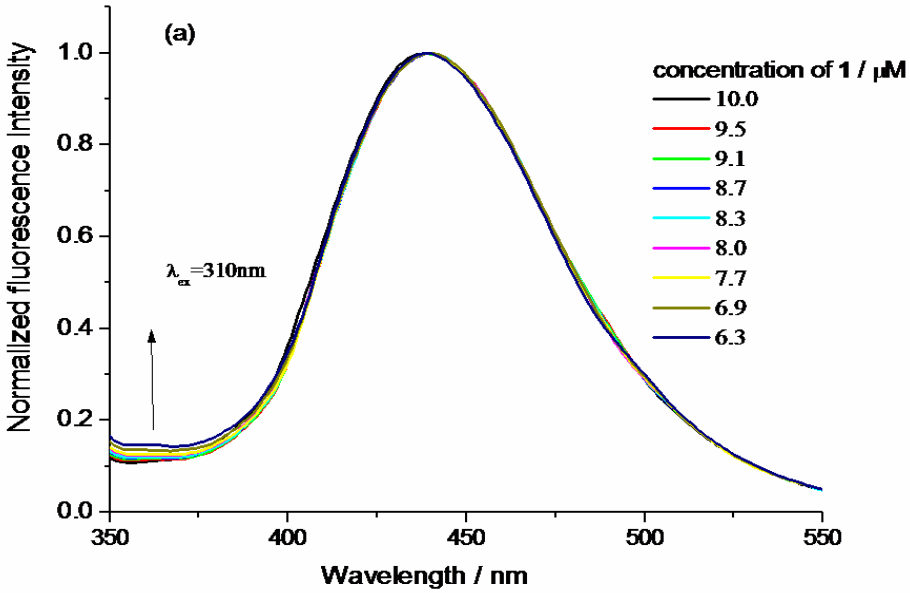
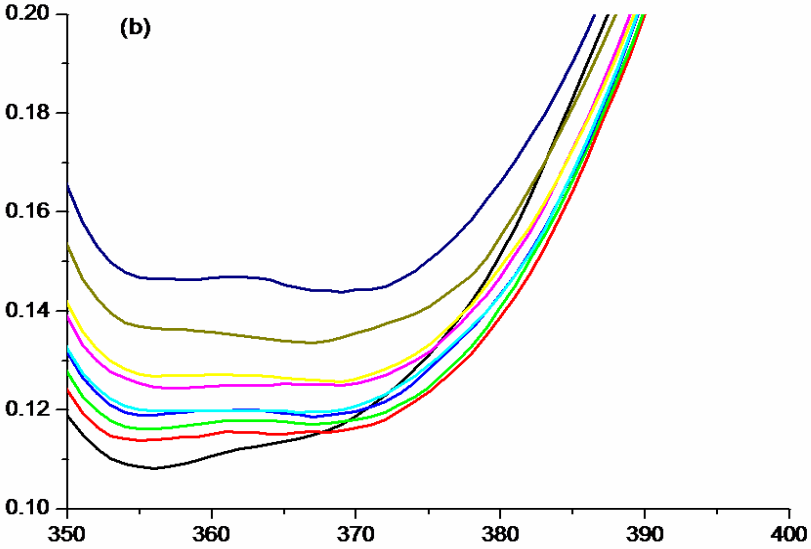


Figure S2. The decay curves of N-Acetyl-1-aminonaphthalene (10 μM) collected at different wavelengths in (a) 1- Ethanol (in 50 ns time windows), (b) 1-Pentanol (in 100 ns time windows) and (c) 1-Pentanol (The concentration of N-Acetyl-1-aminonaphthalene is 40 μM, in 100 ns time windows).





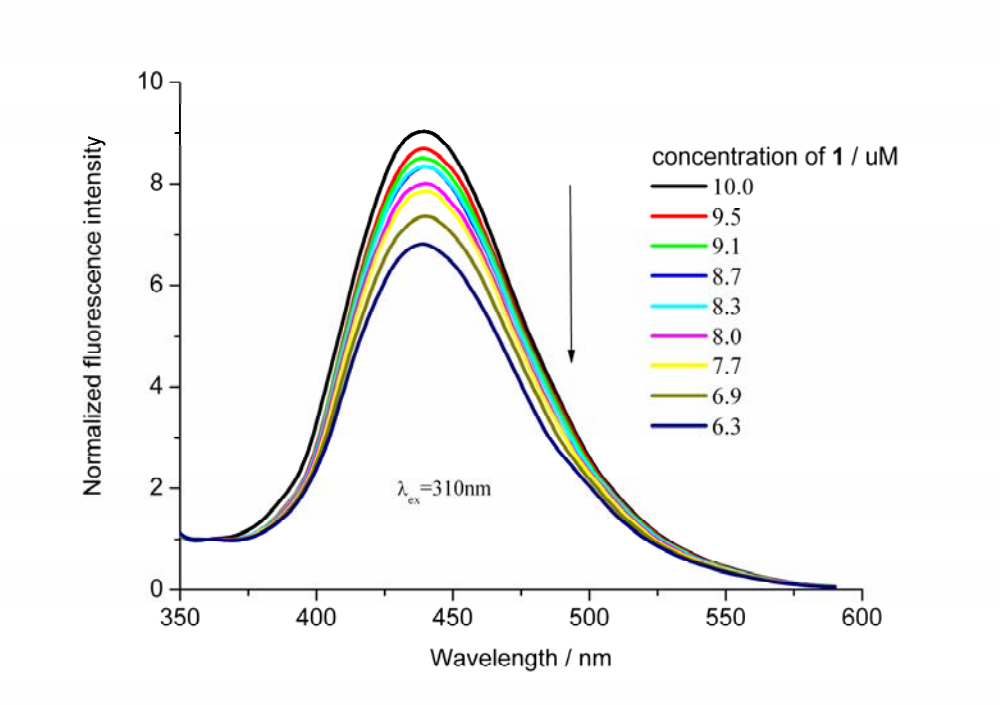


Figure S3. (a) Normalized (440nm) emission spectra of **1** (λ_{ex}= 310 nm) in ethanol at different concentrations. (b) Enlargement part of the blue side (350-400 nm) of the fluorescence emission spectra. (c) Normalized (360nm) emission spectra of **1** (λ_{ex}= 310 nm) in ethanol at different concentrations.

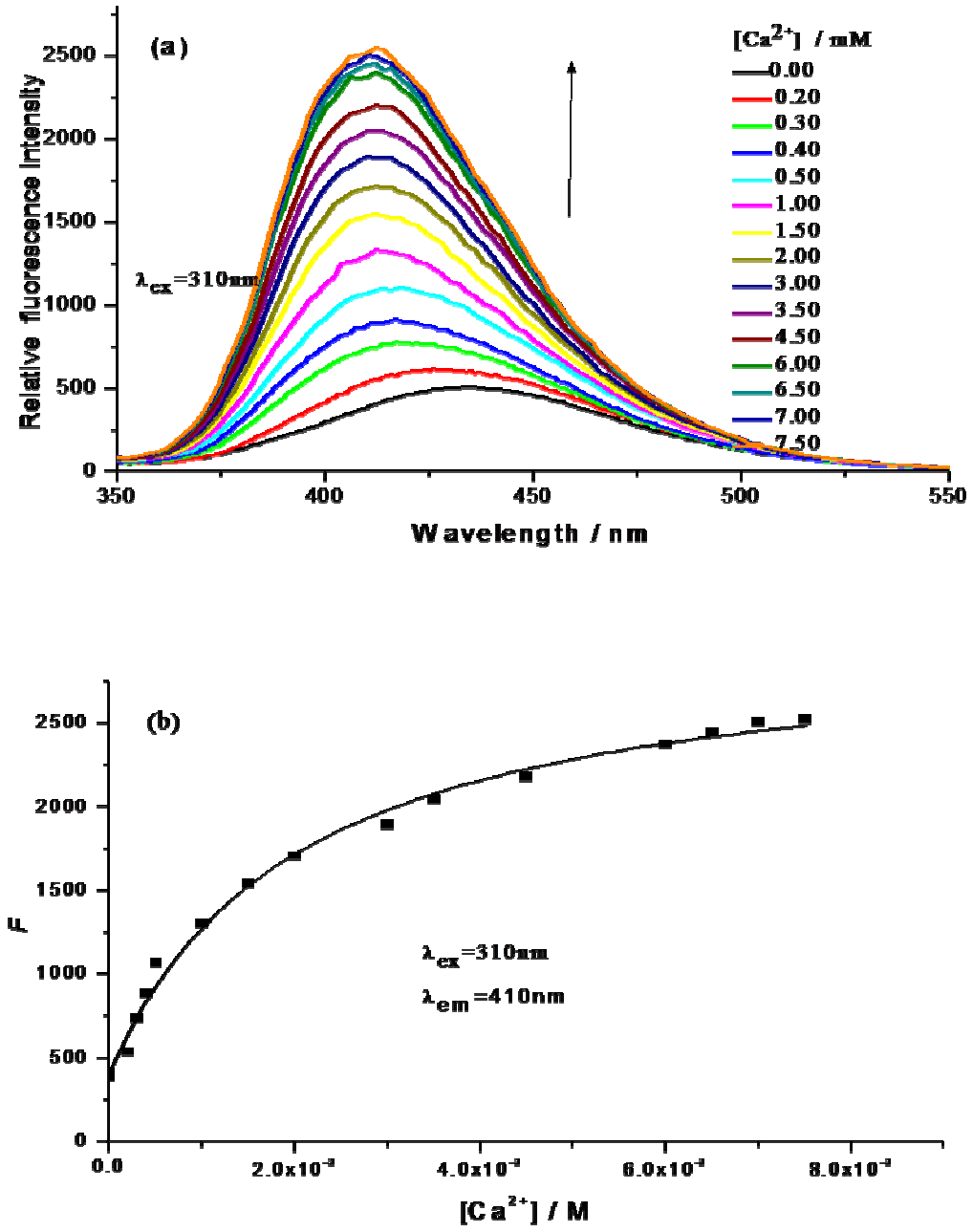


Figure S4. (a) Fluorescence emission (λ_{ex} = 310 nm) spectra of **1** (10 μM) in EtOH as a probe of [Ca^{2+}]. (b) Best fit of eq **1** with n = 1 to the *direct* emission fluorescence titration data of **1** obtained from the spectra of fig S4a (λ_{ex} = 310 nm, λ_{em} = 410 nm).

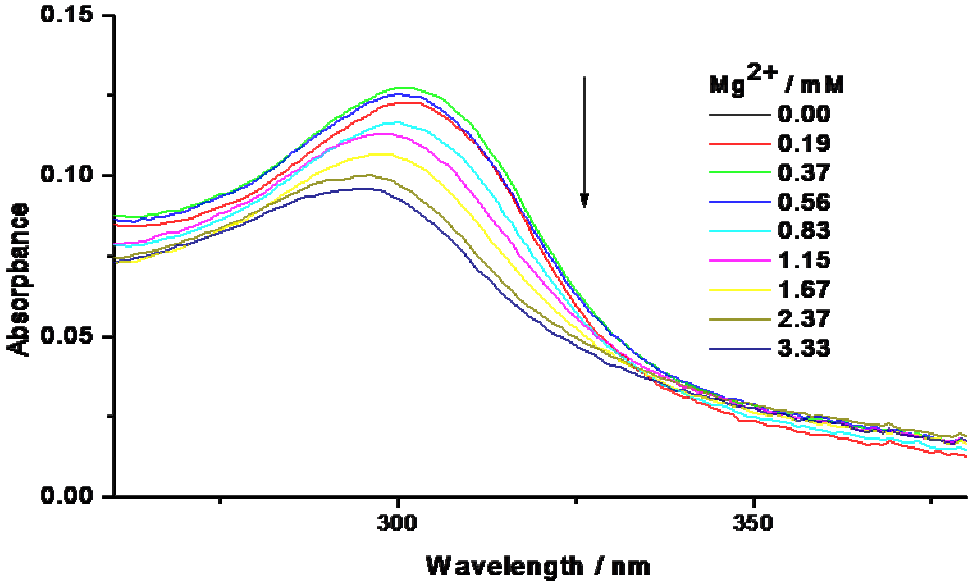
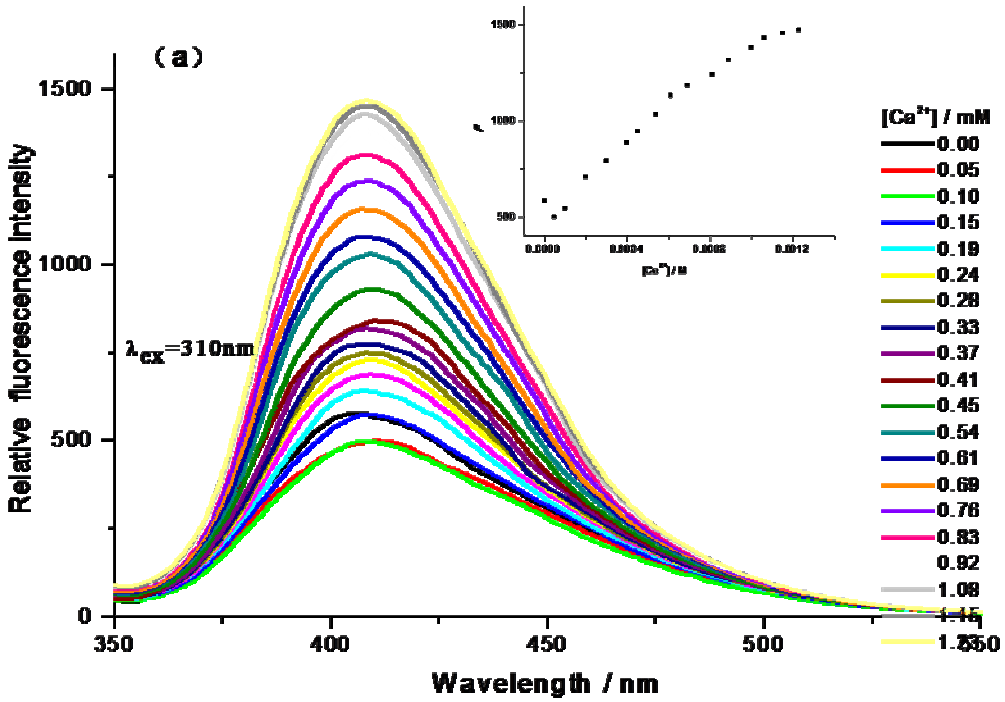


Figure S5. Absorption spectra of **1** (10 μM) in EtOH/H_2O (9/1 V/V) as a function of [Mg^{2+}].



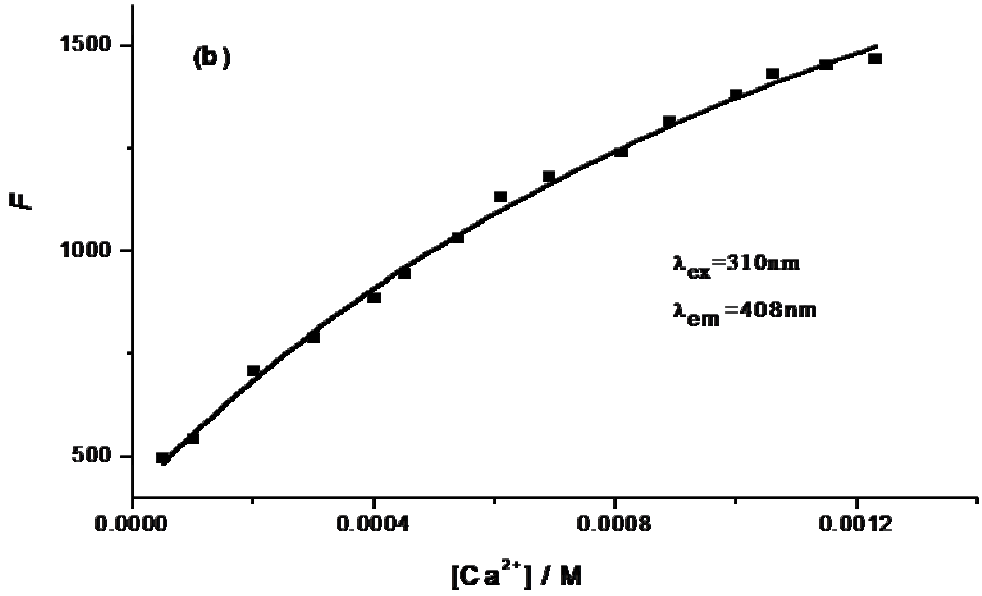


Figure S6. (a) Fluorescence emission (λ_{ex} = 310 nm) spectra of **1** (10 μM) in EtOH/H_2O (9/1 V/V) as a probe of [Ca^{2+}]. (b) Best fit of eq 1with n = 1 to the direct emission fluorescence titration data of **1** obtained from the spectra of 5a(from 0.05 mM to 1.23 mM) (λ_{ex}= 310 nm, λ_{em}= 408 nm).

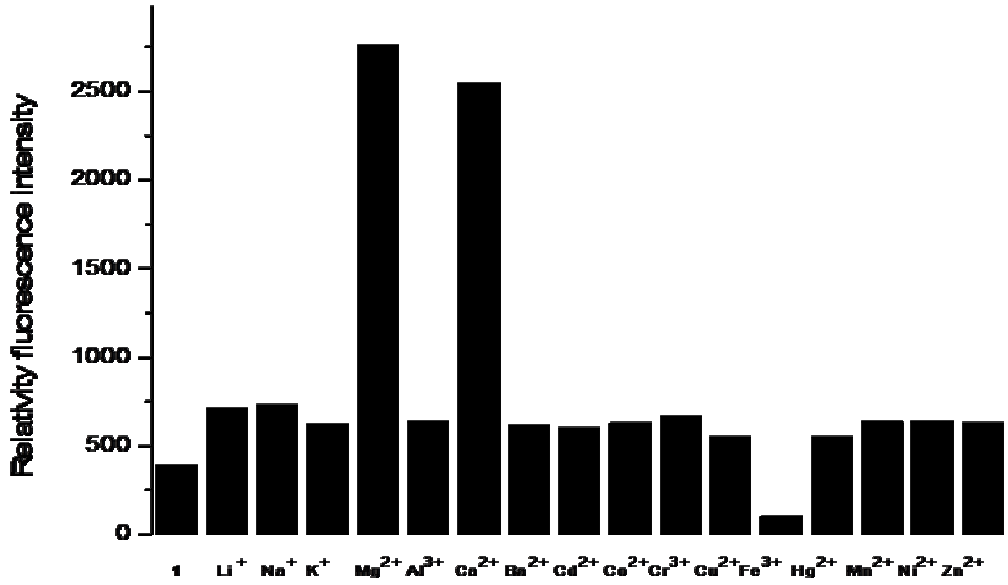


Figure S7. Bars represent the final fluorescence intensity response the addition of 2 mM various cations to the solution of **1** (10 μM) in the EtOH/H_2O (9/1 V/V) solution.

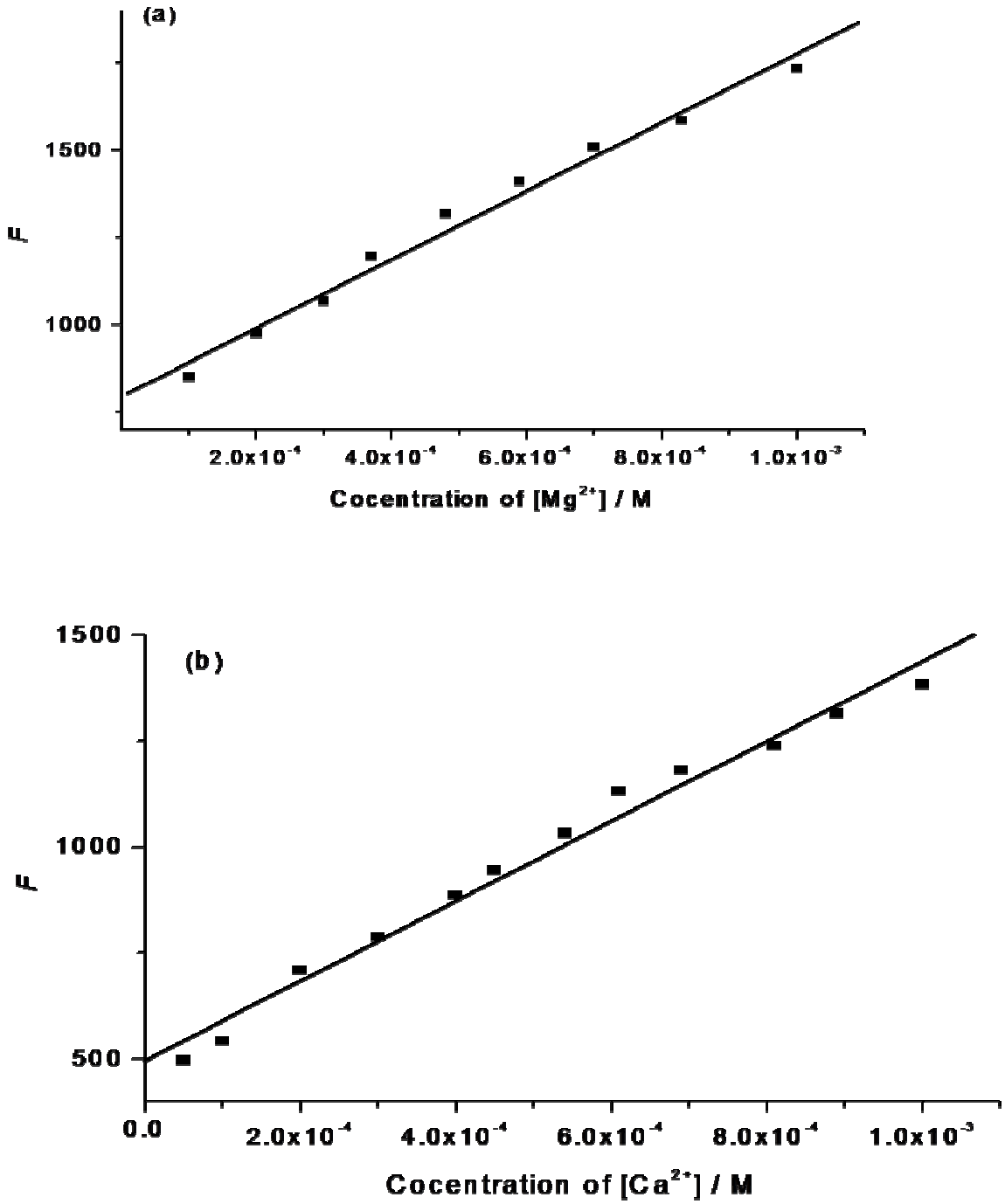


Figure S8. The linear relationship between fluorescence intensity at 407 nm and (a) concentration of Mg^{2+} within the range 0.1–1.0 mM, (b) concentration of Ca^{2+} within the range 0.05–1.08 mM in EtOH/H_2O (9/1 V/V).(data obtained from part of the spectra of Fig 6b and Fig S6b)

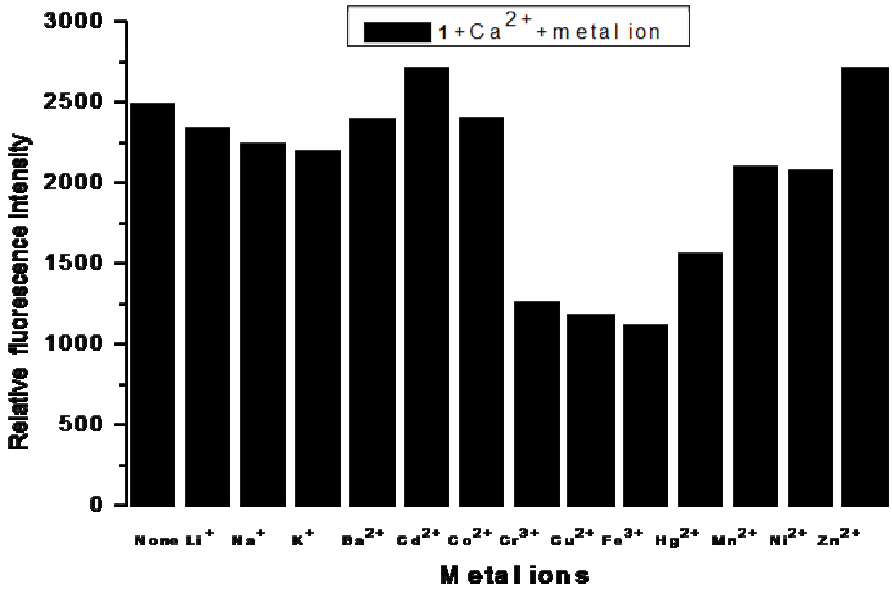
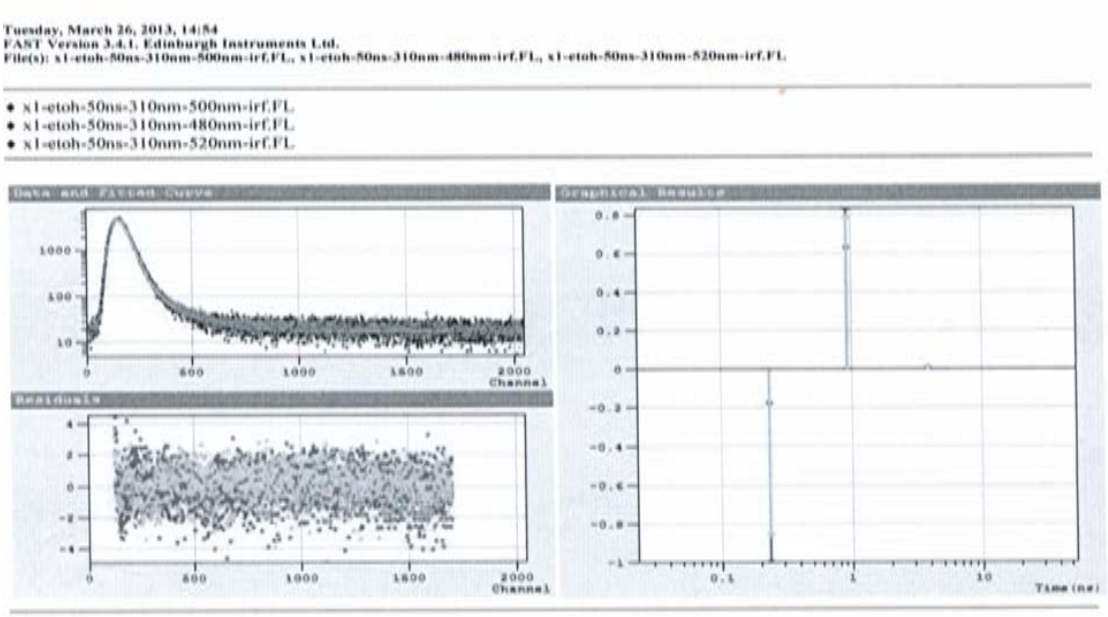


Figure S9. Selectivity of **1** (10 μM) for Ca^{2+} (1.2 mM) over other cations. The bars indicate the fluorescence change that occurs immediately following the addition of interfering ions (10 equiv of the Ca^{2+} ions) to the EtOH/H_2O (9/1 V/V) solution. The emission wavelength is 407 nm.



File: x1-etoh-50ns-310nm-500nm-irf.FL

❖ **Global Analysis (Reconvolution)**

Fitting range : [120; 1700] channels
Global χ^2 : 1.198
χ^2 : 1.169

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	-0.0727	0.0024	22.44	-23.14	0.226 linked	0.2225
2	0.0606	0.0009	73.85	1.7619	0.891 linked	0.0069
3	0.0007	4.4e-5	3.7114	0.2518	3.737 linked	0.0064

Shift : -0.2888 ns (± 0 ns)
Decay Background : 15.67 (± 0)
IRF Background : 18.30

File: x1-etoh-50ns-310nm-480nm-irf.FL

❖ **Global Analysis (Reconvolution)**

Fitting range : [120; 1700] channels
Global χ^2 : 1.198
χ^2 : 1.343

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	-0.0130	0.0010	6.2830	-7.1540	0.226 linked	0.2384
2	0.0459	0.0005	87.88	2.0087	0.891 linked	0.0074
3	0.0007	4.7e-5	5.8342	0.4455	3.737 linked	0.0069

Shift : -0.0363 ns (± 0 ns)
Decay Background : 19.69 (± 0)
IRF Background : 18.30

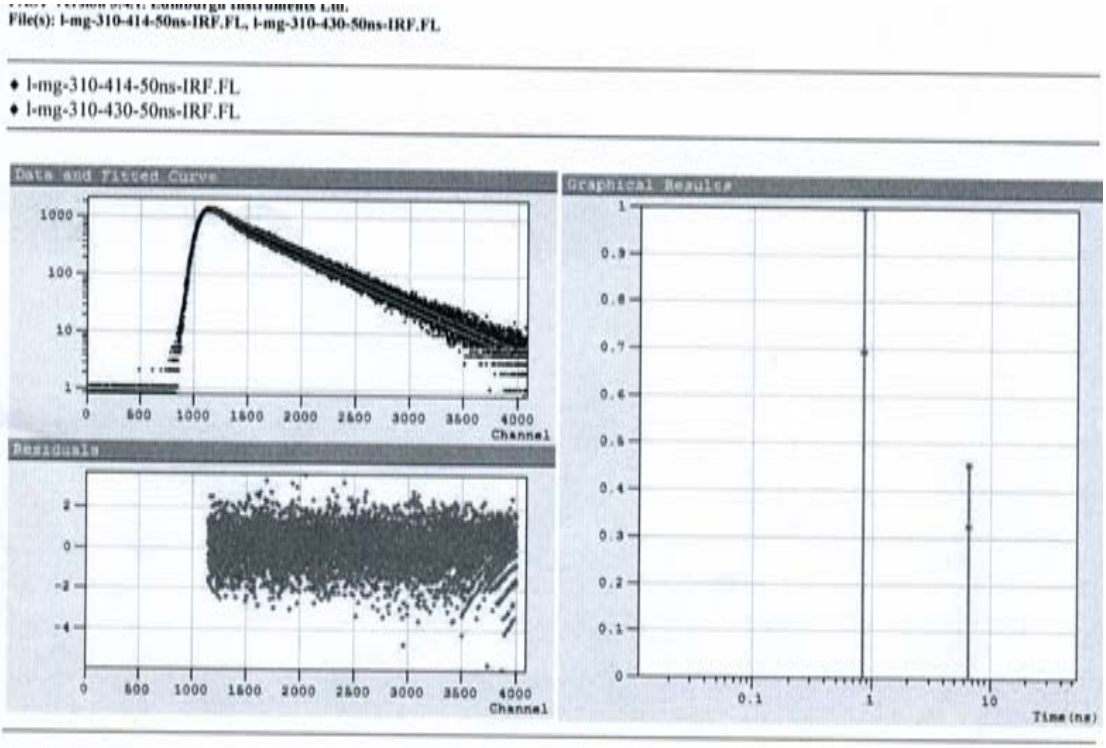
❖ **Global Analysis (Reconvolution)**

Fitting range : [120; 1700] channels
Global χ^2 : 1.198
χ^2 : 1.083

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	-0.0626	0.0019	20.73	-19.81	0.226 linked	0.2142
2	0.0574	0.0008	75.00	1.6178	0.891 linked	0.0067
3	0.0008	4.5e-5	4.2690	0.2622	3.737 linked	0.0062

Shift : -0.2620 ns (± 0 ns)
Decay Background : 17.67 (± 0)
IRF Background : 18.30

Figure S10. The global fitting results of **1** (10 μM) collected at 480 nm, 500 nm and 520 nm.



File: l-mg-310-414-50ns-IRF.FL

❖ **Global Analysis (Reconvolution)**

Fitting range : [1141; 4000] channels
Global χ^2 : 1.058
χ^2 : 1.029

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.0078	0.0002	16.60	0.8889	0.813 linked	0.0239
2	0.0051	1.8e-5	83.40	0.2932	6.244 linked	0.0003

Shift : -0.0244 ns (± 0 ns)
Decay : 0.5467 (± 0)
Background
IRF Background : 0

File: l-mg-310-430-50ns-IRF.FL

❖ **Global Analysis (Reconvolution)**

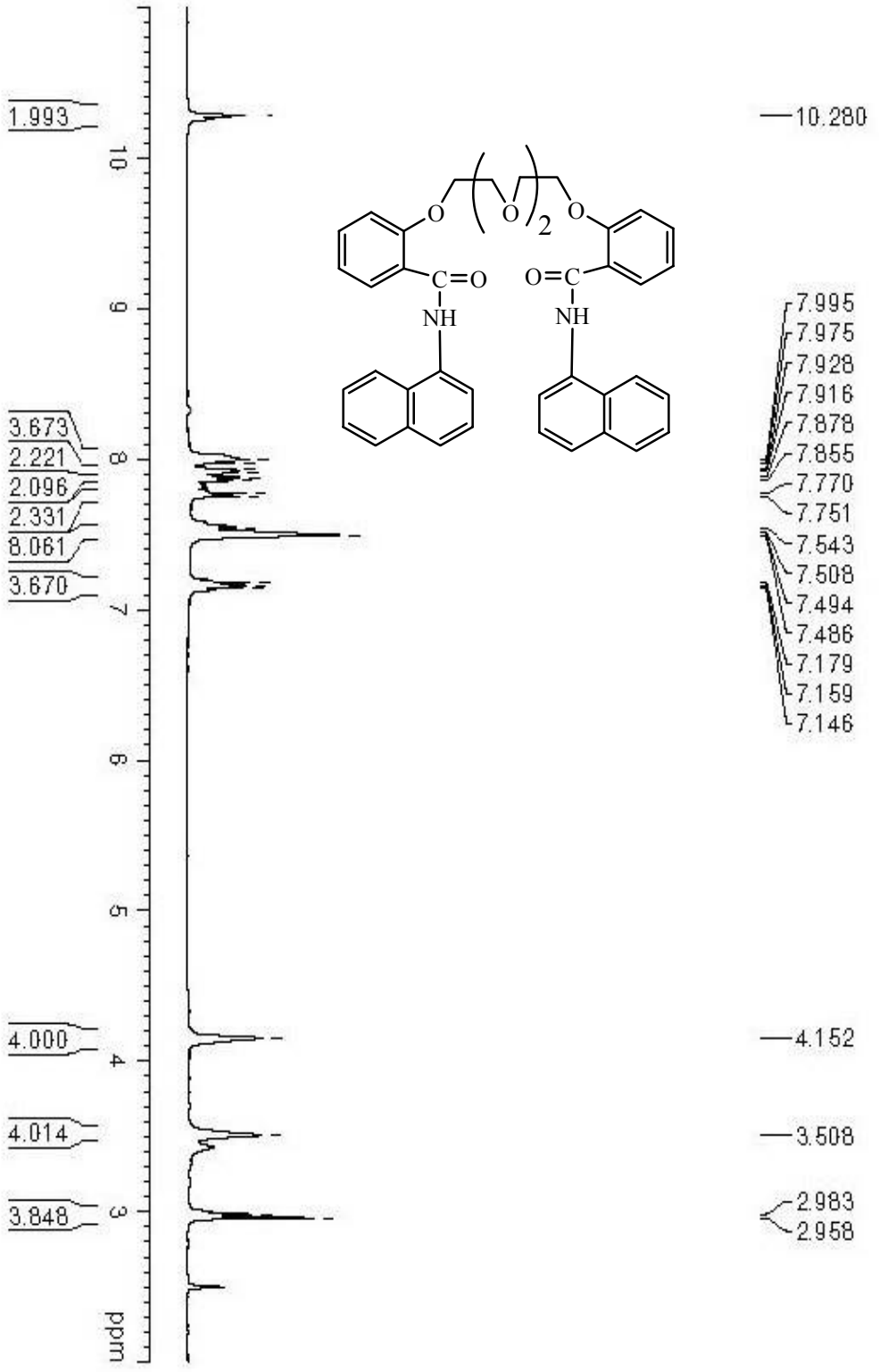
Fitting range : [1141; 4000] channels
Global χ^2 : 1.058
χ^2 : 1.087

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.0113	0.0003	28.78	1.5902	0.813 linked	0.0245
2	0.0036	1.5e-5	71.22	0.3051	6.244 linked	0.0003

Shift : 0.1464 ns (± 0 ns)
Decay : 0.6447 (± 0)
Background
IRF Background : 0

Figure S11.The global fitting results of **1** (10 μM) in addition of Mg^{2+} (6.0 mM)in ethanol as a function of λ_{em}.

^{1}H NMR (DMSO, 400 MHz) spectrum of 1



^{13}C NMR (DMSO, 400 MHz) spectrum of 1

MS Spectrum of 1(1+ H^+) (calcd. For $C_{40}H_{36}N_2O_6$:640.3)