Electronic Supplementary Material (ESI) for ChemComm.

Fluorescent Monitoring on the Reaction Kinetics of Nonfluorescent Molecules Enabled by a Fluorescent Receptor

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Table of Contents

1. Experimental Section

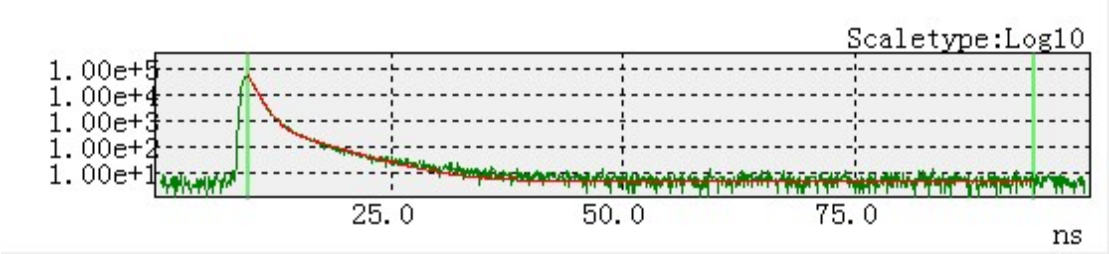
1.1 General Method. Reagents and solvents are commercially available and used without further purification. ^{1}H NMR spectra were recorded on a Bruker Avance-400 NMR spectrometer. All chemical shifts are reported in ppm with sodium methanesulfonate as the internal standard. Fluorescence spectra were recorded on a Shimadzu RF-5301pc spectrometer. The determination methods of binding constants using fluorescence titrations and ^{1}H NMR titrations were reported earlier.[1] The synthesis of molecular tubes **1** has been reported.[2]

1.2 Monitoring the Hydrolysis Kinetics of Esters. For fluorescence monitoring, **1** (5.0 μM) was dissovled in the buffer solution (pH= 11.9, confirmed by pH meter) which was prepared from Na_2HPO_4 (25 mM) and NaOH (27 mM). This solution (2.0 ml) was placed in a cuvette at 25 ^{o}C. 330 nm was selected as excitation wavelength, and the emission intensity at 403 nm was monitored. Ester was added to this solution containing **1**, and fluorescence intensity at 403 nm was monitored to follow the hydrolysis kinetics of ester.

1 H. Yao, H. Ke, X. Zhang, S.-J. Pan, M.-S. Li, L.-P. Yang, G. Schreckenbach and W. Jiang, *J. Am. Chem. Soc.*, 2018, **140**, 13466.

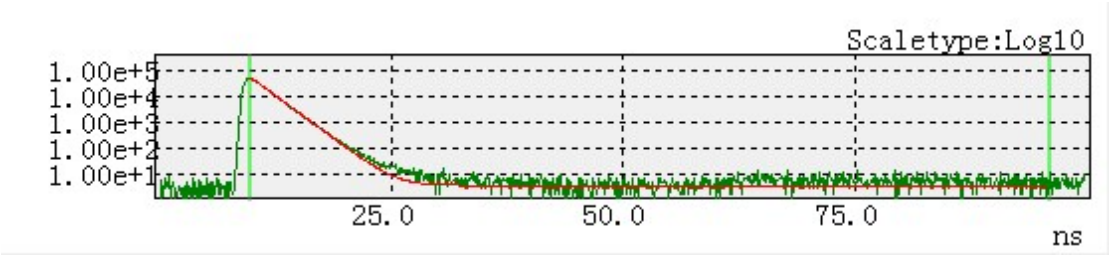
2 G.-B. Huang, S.-H. Wang, H. Ke, L.-P. Yang and W. Jiang, *J. Am. Chem. Soc.*, 2016, **138**, 14550.

2. Fluorescence Quantum Yield and Lifetime



excitation wavelength (nm)	fluorescence quantum yield (%)
330	1.7
340	1.8
350	1.8
360	1.9
370	1.8

Fig. S1 Curve fit of the fluorescence lifetime of **1** (20 μM) in water. excitation wavelength= 340 nm, emission wavelength= 403 nm, and the fluorescence quantum yield of different excitation wavelength of **1**.



excitation wavelength (nm)	fluorescence quantum yield (%)
330	5.4
340	5.2
350	5.4
360	5.5
370	5.2

Fig. S2 Curve fit of the fluorescence lifetime of **1** (20 μM) in the presence of ethyl acetate (8 mM). excitation wavelength= 340 nm, emission wavelength= 403 nm. The fluorescence quantum yields of the host-guest complex at different excitation wavelengths were listed in the Table.

3. Binding Constants of 1 to Esters

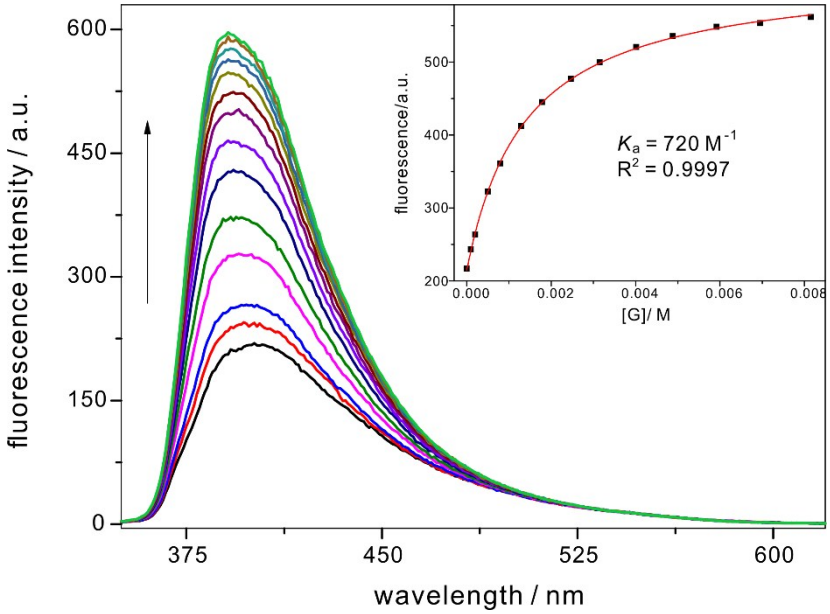


Fig. S3 Fluorescence spectra of **1** (5.0 μM) when titrated with methyl acetate in deionized H_2O at 25 °C. Inset: curve fit of the titration data according to a 1:1 binding stoichiometry.

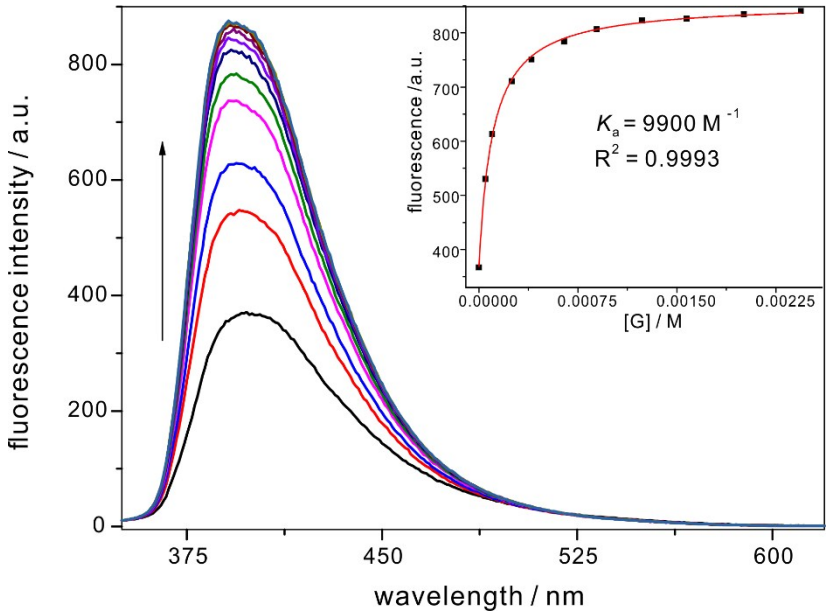


Fig. S4 Fluorescence spectra of **1** (5.0 μM) when titrated with propyl acetate in deionized H_2O at 25 °C. Inset: curve fit of the titration data according to a 1:1 binding stoichiometry.

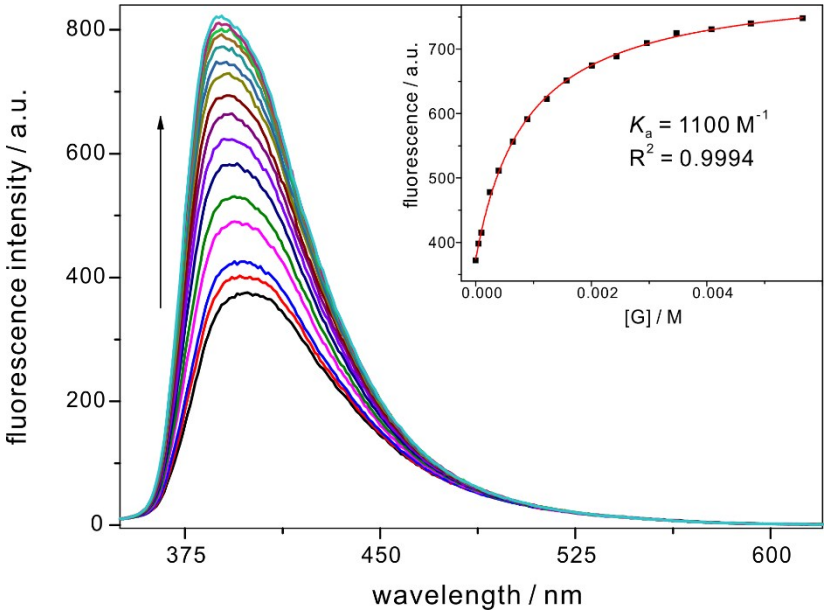


Fig. S5 Fluorescence spectra of **1** (5.0 μM) when titrated with isopropyl acetate in deionized H_2O at 25 °C. Inset: curve fit of the titration data according to a 1:1 binding stoichiometry.

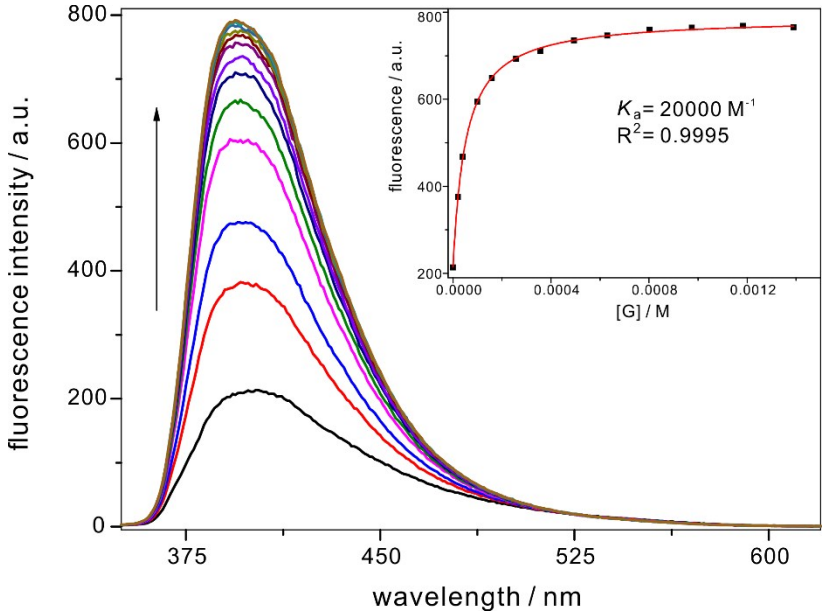


Fig. S6 Fluorescence spectra of **1** (5.0 μM) when titrated with butyl acetate in deionized H_2O at 25 °C. Inset: curve fit of the titration data according to a 1:1 binding stoichiometry.

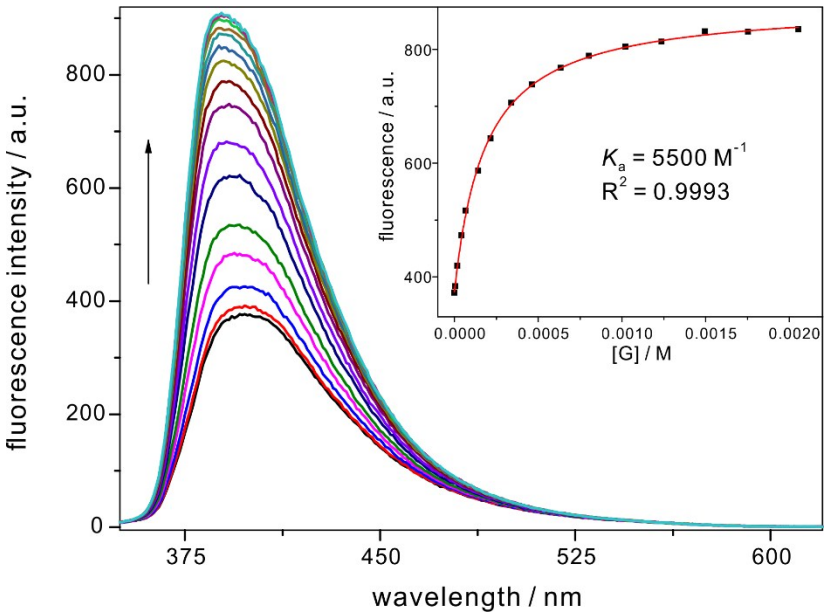


Fig. S7 Fluorescence spectra of **1** (5.0 μM) when titrated with isobutyl acetate in deionized H_2O at 25 °C. Inset: curve fit of the titration data according to a 1:1 binding stoichiometry.

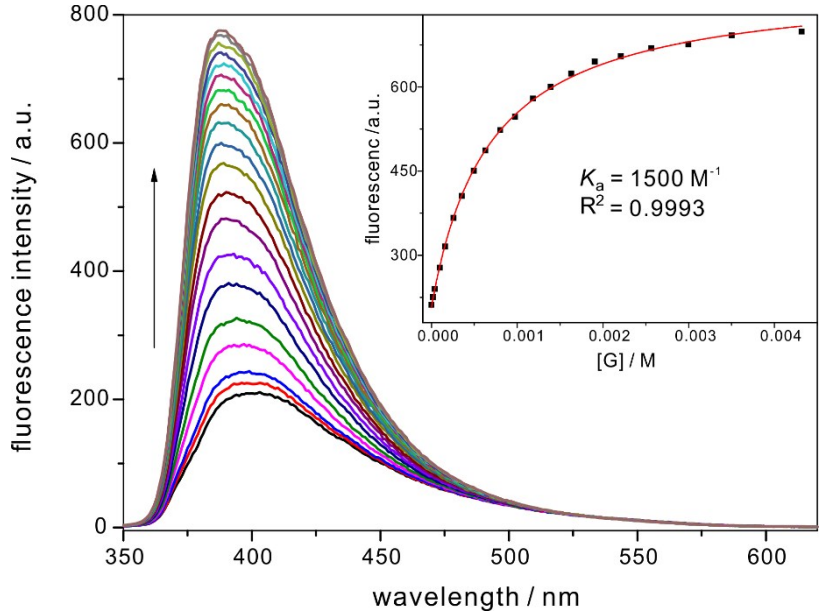


Fig. S8 Fluorescence spectra of **1** (5.0 μM) when titrated with sec-butyl acetate in deionized H_2O at 25 °C. Inset: curve fit of the titration data according to a 1:1 binding stoichiometry.

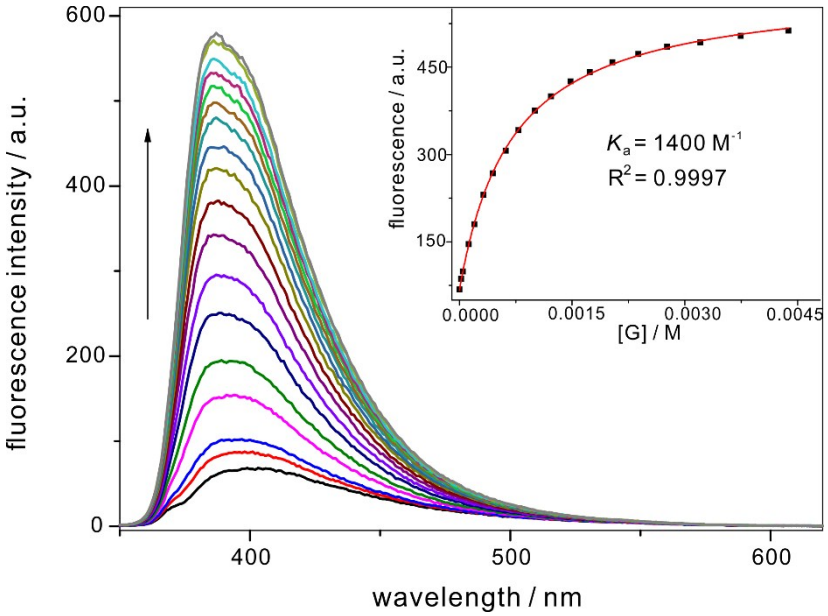


Fig. S9 Fluorescence spectra of **1** (5.0 μM) when titrated with tert-butyl acetate in deionized H_2O at 25 °C. Inset: curve fit of the titration data according to a 1:1 binding stoichiometry.

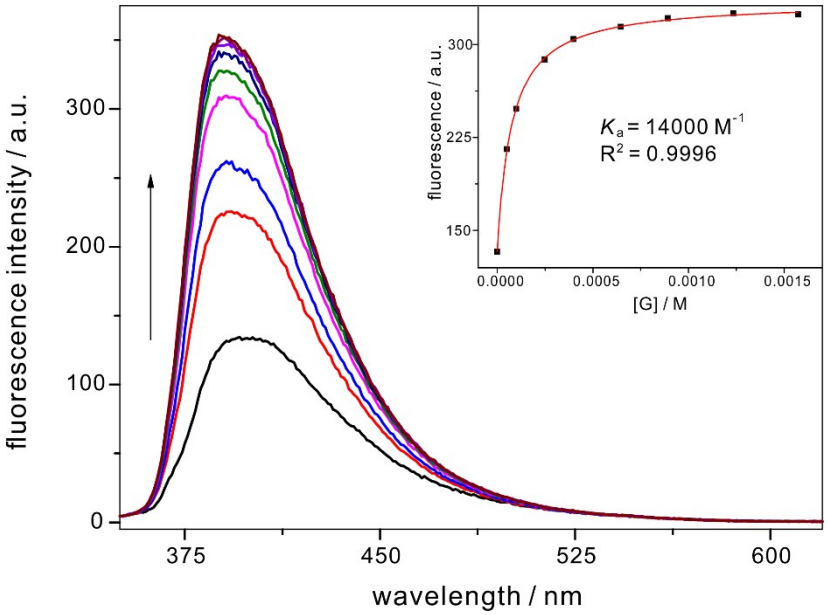


Fig. S10 Fluorescence spectra of **1** (5.0 μM) when titrated with ethyl propionate in deionized H_2O at 25 °C. Inset: curve fit of the titration data according to a 1:1 binding stoichiometry.

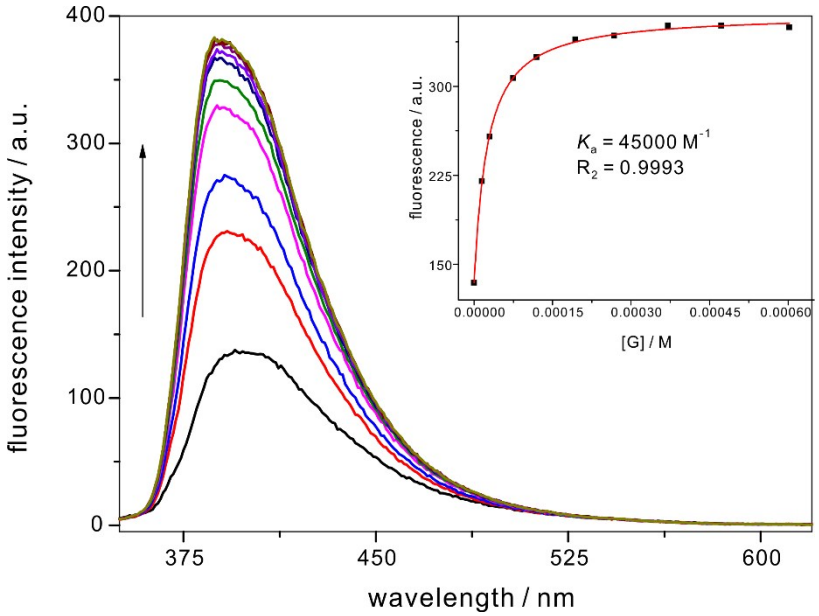


Fig. S11 Fluorescence spectra of **1** (5.0 μM) when titrated with ethyl butyrate in deionized H_2O at 25 °C. Inset: curve fit of the titration data according to a 1:1 binding stoichiometry.

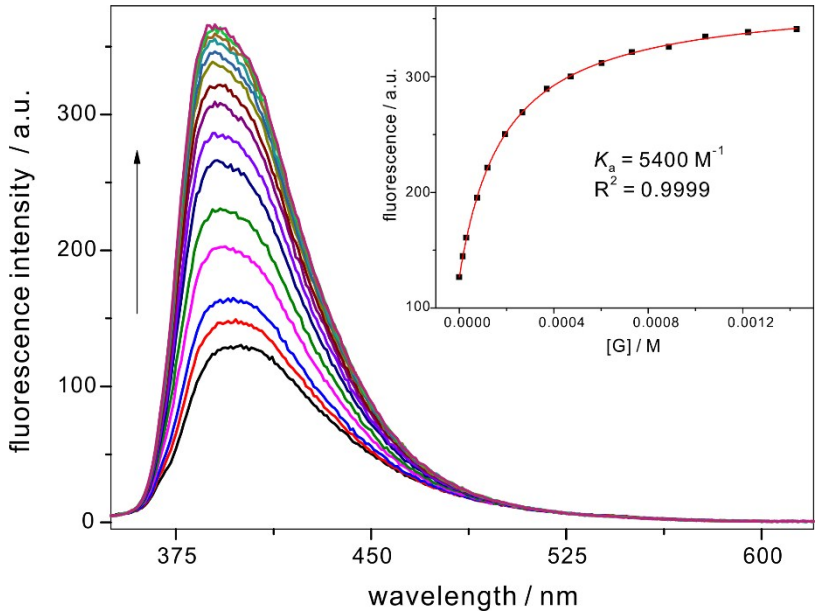


Fig. S12 Fluorescence spectra of **1** (5.0 μM) when titrated with ethyl isobutyrate in deionized H_2O at 25 °C. Inset: curve fit of the titration data according to a 1:1 binding stoichiometry.

4. Binding Constants of 1 to Alcohols

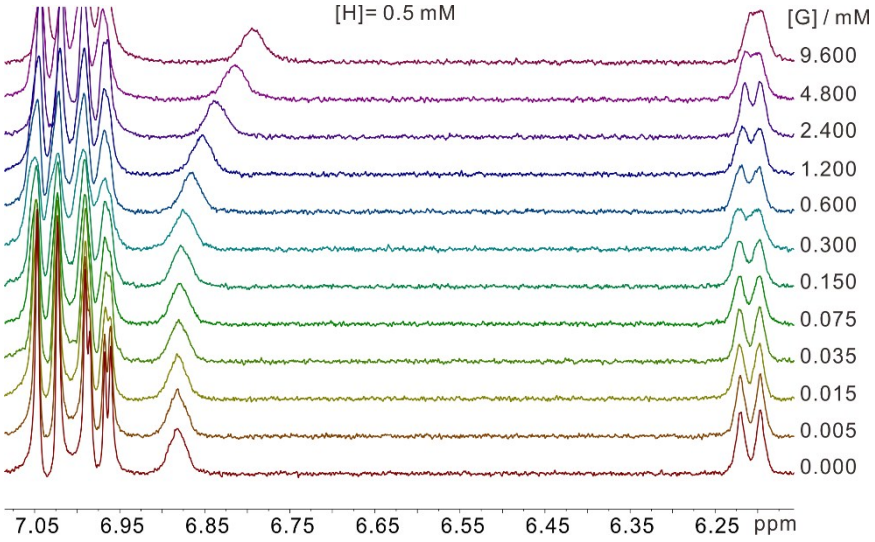


Fig. S13 Partial ^{1}H NMR spectra (400 MHz, H_2O: D_2O = 9: 1, 25 °C) of **1** (0.5 mM) when titrated by propyl alcohol (0~9.6 mM).

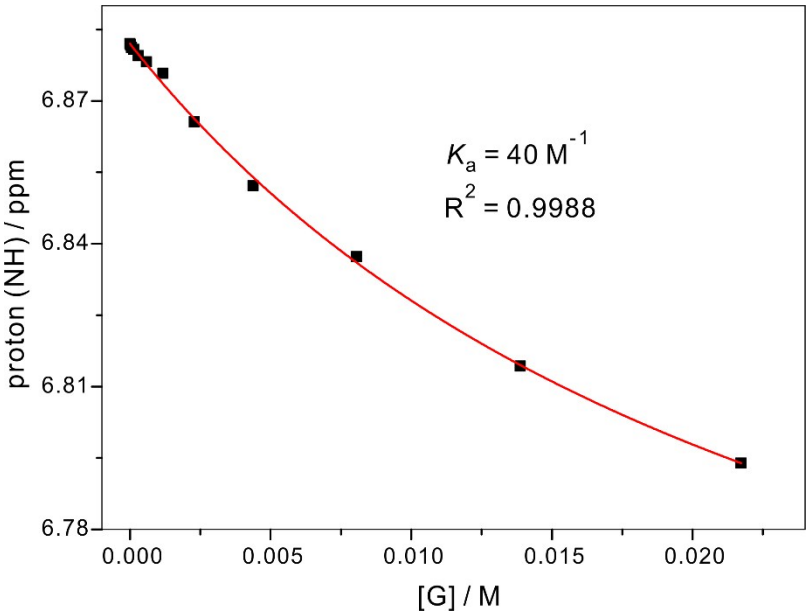


Fig. S14 Nonlinear fitting of the NMR titration curve of **1** by propyl alcohol. The chemical shift of amide NH protons on **1** is monitored.

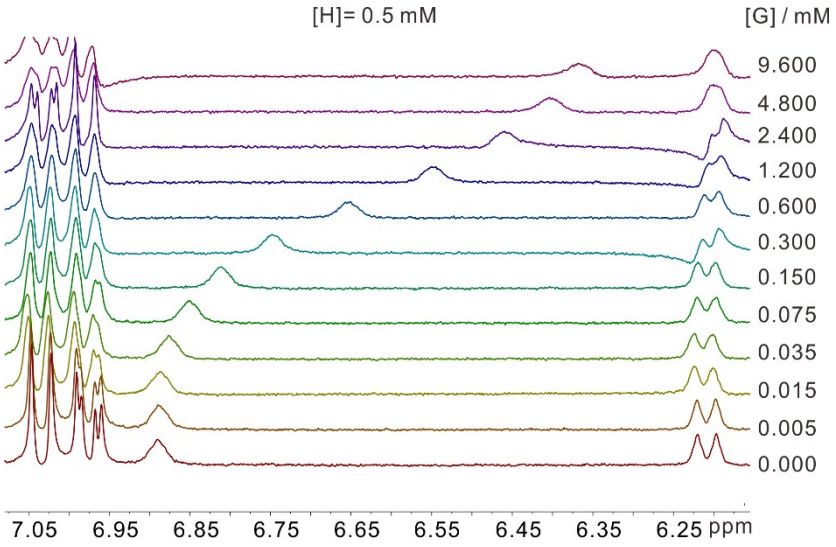


Fig. S15 Partial ^{1}H NMR spectra (400 MHz, H_2O: D_2O = 9: 1, 25 °C) of **1** (0.5 mM) titrated by butyl alcohol (0~9.6 mM).

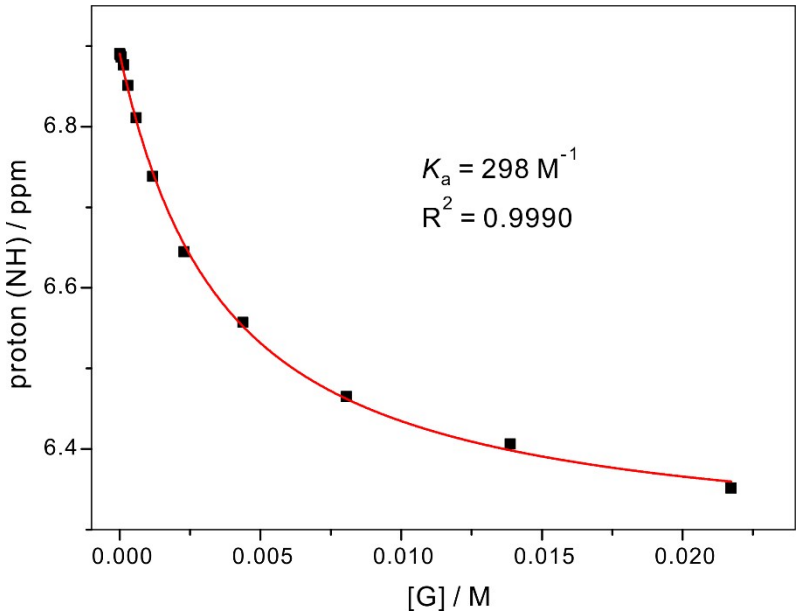


Fig. S16 Nonlinear fitting of the NMR titration curve of **1** by butyl alcohol. The chemical shift of amide NH protons on **1** is monitored.

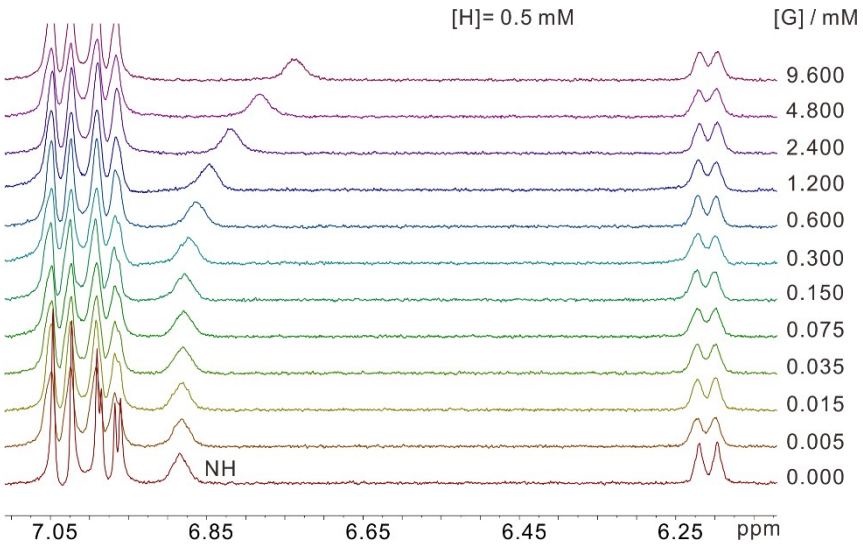


Fig. S17 Partial ^{1}H NMR spectra (400 MHz, H_2O: D_2O = 9: 1, 25 °C) of **1** (0.5 mM) titrated by isobutyl alcohol (0~9.6 mM).

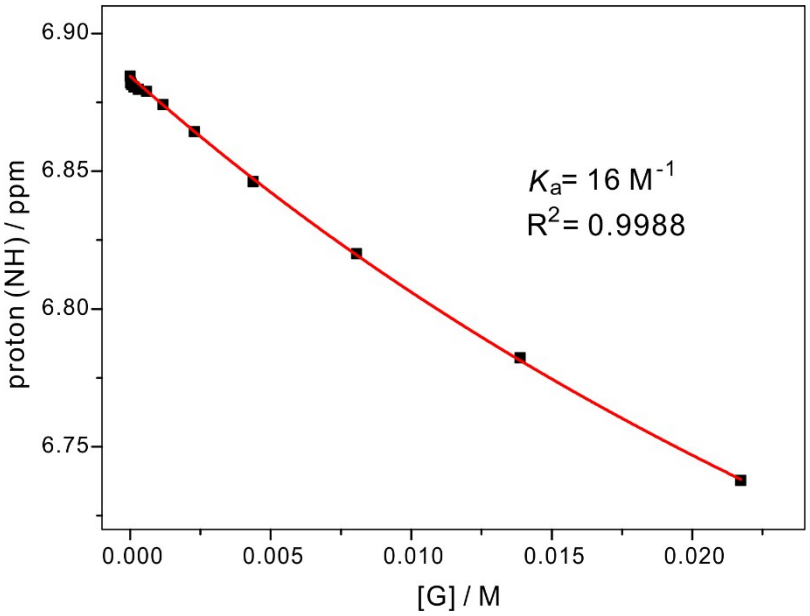


Fig. S18 Nonlinear fitting of the NMR titration curve of **1** by isobutyl alcohol. The chemical shift of amide NH protons on **1** is monitored.

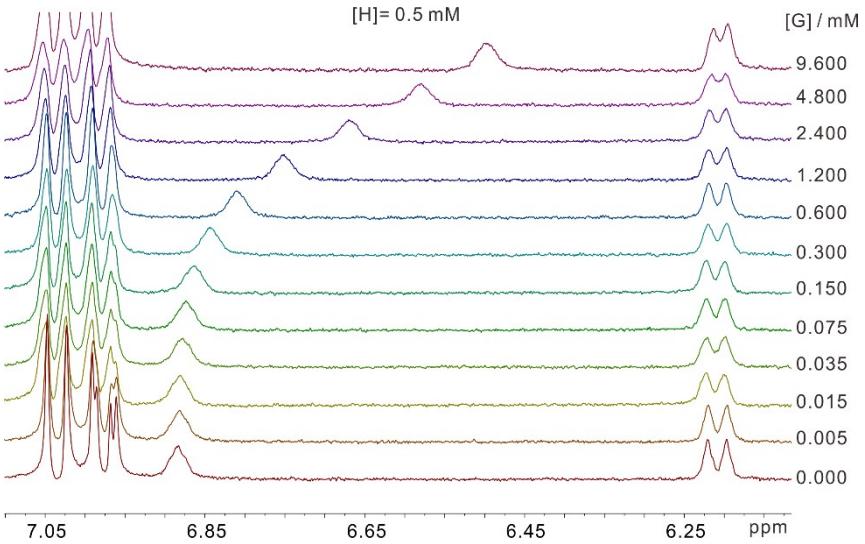


Fig. S19 Partial ^{1}H NMR spectra (400 MHz, H_2O: D_2O = 9: 1, 25 °C) of **1** (0.5 mM) titrated by sec-butyl alcohol (0~9.6 mM).

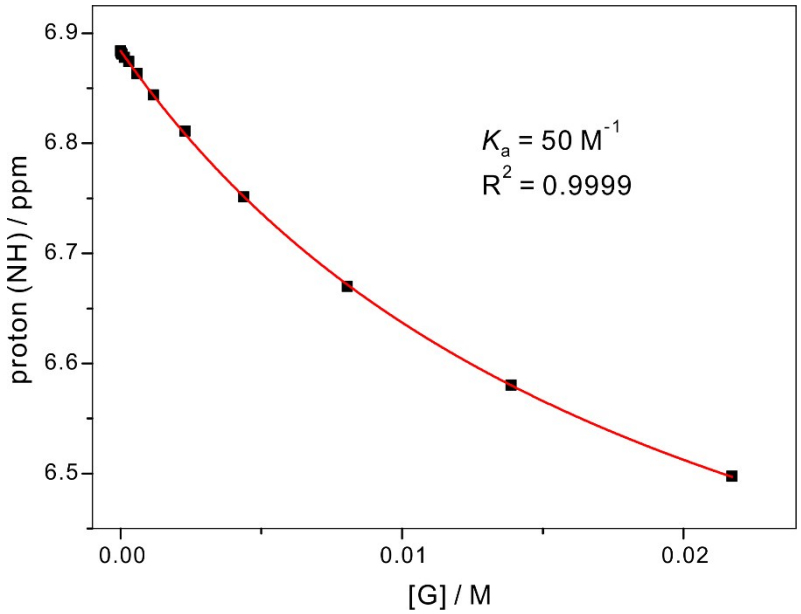


Fig. S20 Nonlinear fitting of the NMR titration curve of **1** by sec-butyl alcohol. The chemical shift of amide NH protons on **1** is monitored.

5. Monitoring the Hydrolysis Kinetics of Esters

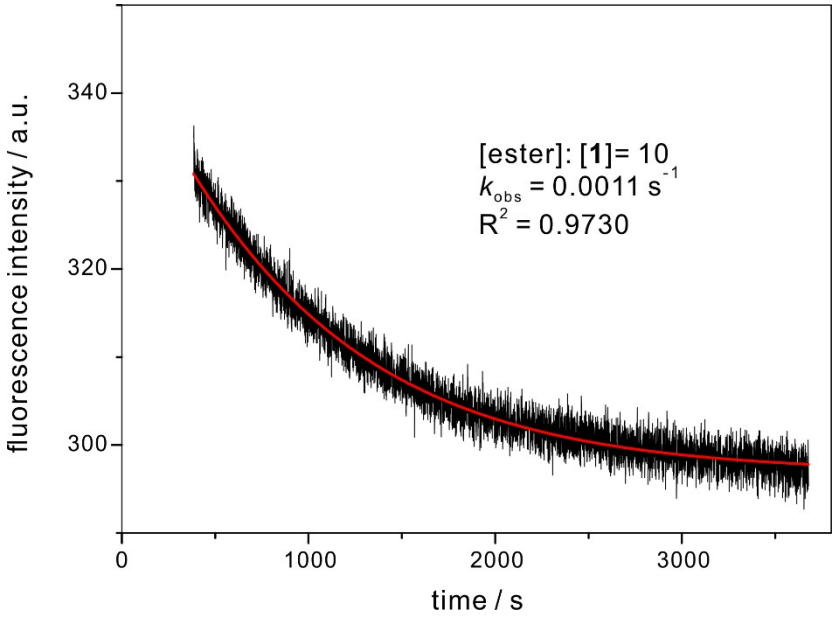


Fig. S21 Curve fitting of the hydrolytic data of ethyl acetate ([G]: [H] = 10: 1).

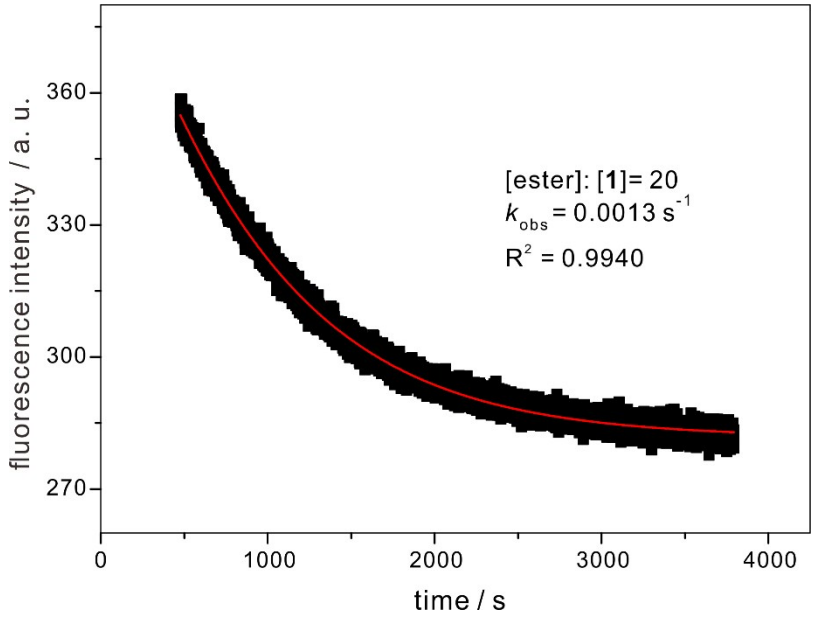


Fig. S22 Curve fitting of the hydrolytic data of ethyl acetate ([G]: [H] = 20: 1).

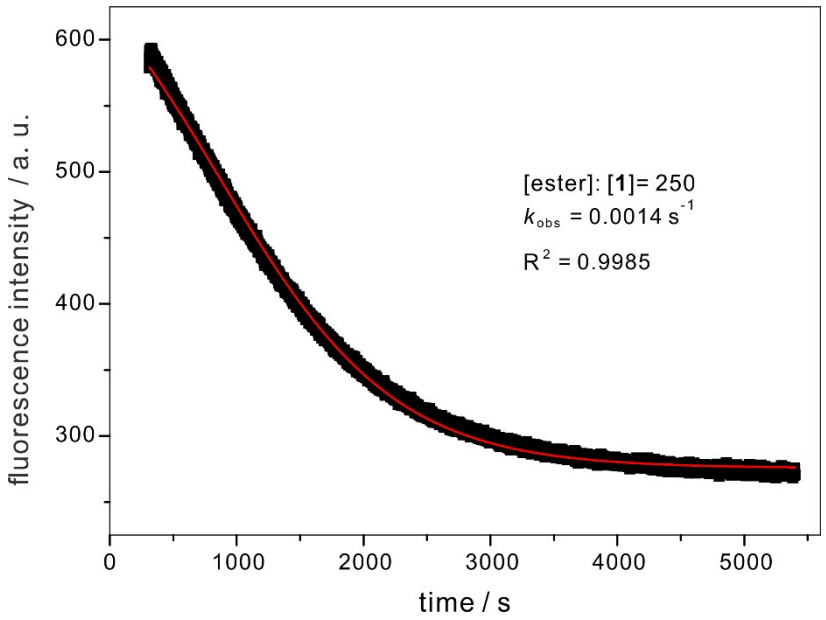


Fig. S23 Curve fitting of the hydrolytic data of ethyl acetate ([G]: [H] = 250: 1).

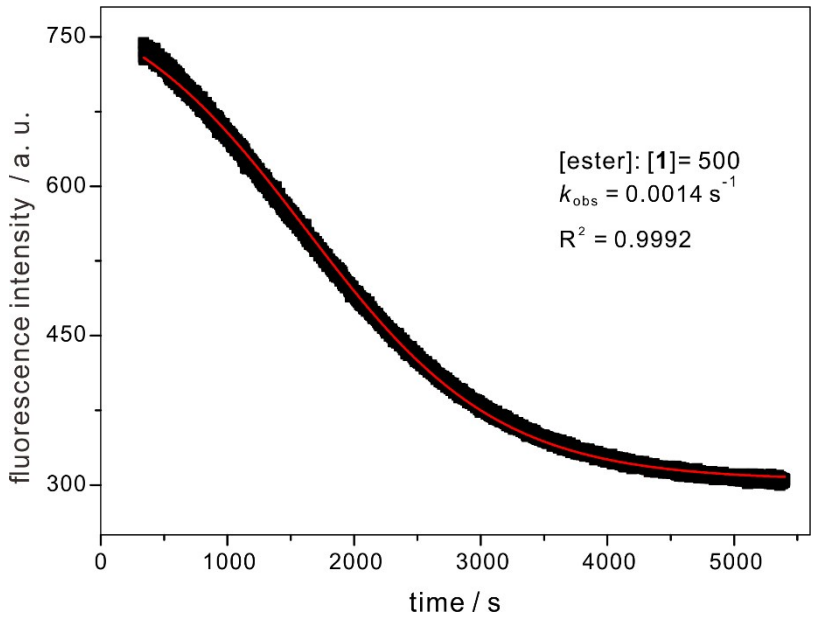


Fig. S24 Curve fitting of the hydrolytic data of ethyl acetate ([G]: [H] = 500: 1).

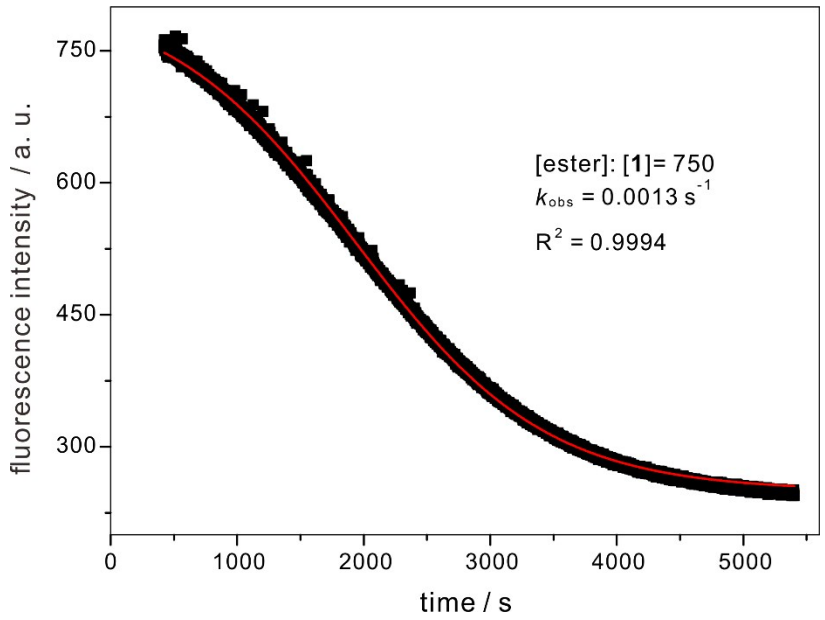


Fig. S25 Curve fitting of the hydrolytic data of ethyl acetate ([G]: [H] = 750: 1).

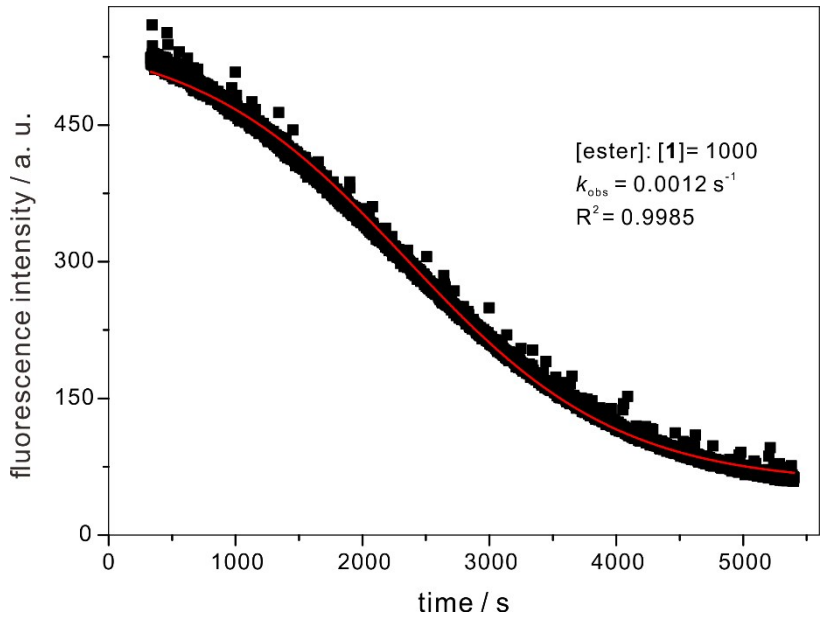


Fig. S26 Curve fitting of the hydrolytic data of ethyl acetate ([G] : [H] = 1000 : 1).

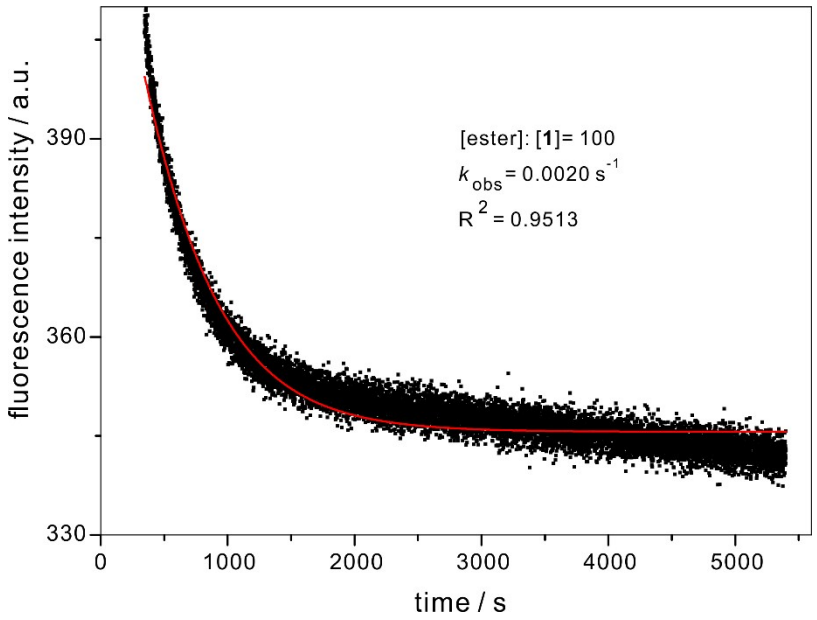


Fig. S27 Curve fitting of the hydrolytic data of methyl acetate ([G]: [H] = 100: 1).

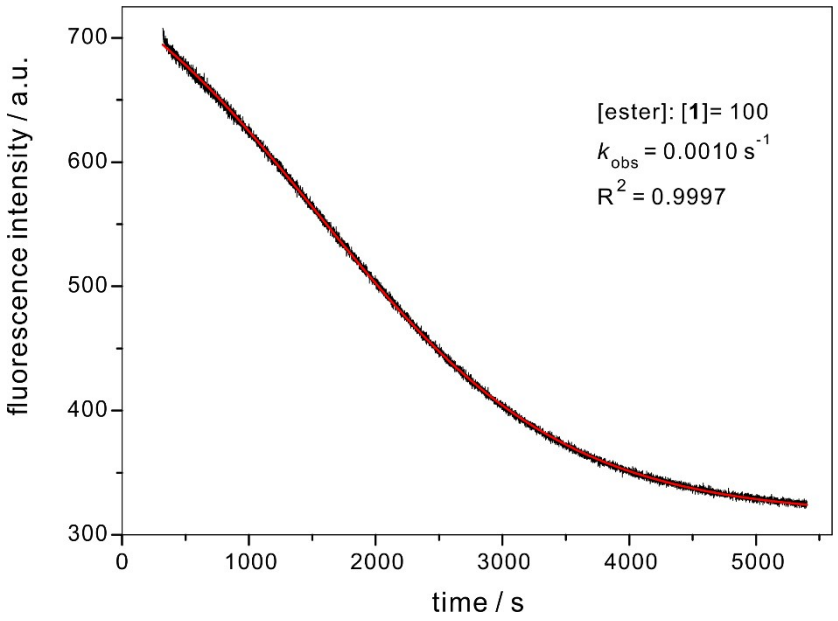


Fig. S28 Curve fitting of the hydrolytic data of propyl acetate ([G]: [H] = 100: 1).

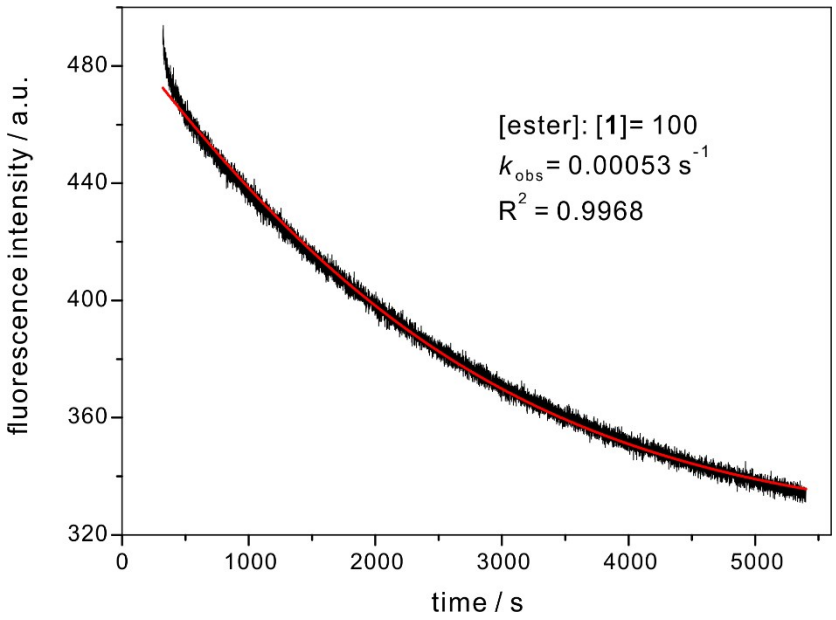


Fig. S29 Curve fitting of the hydrolytic data of isopropyl acetate ([G]: [H] = 100: 1).

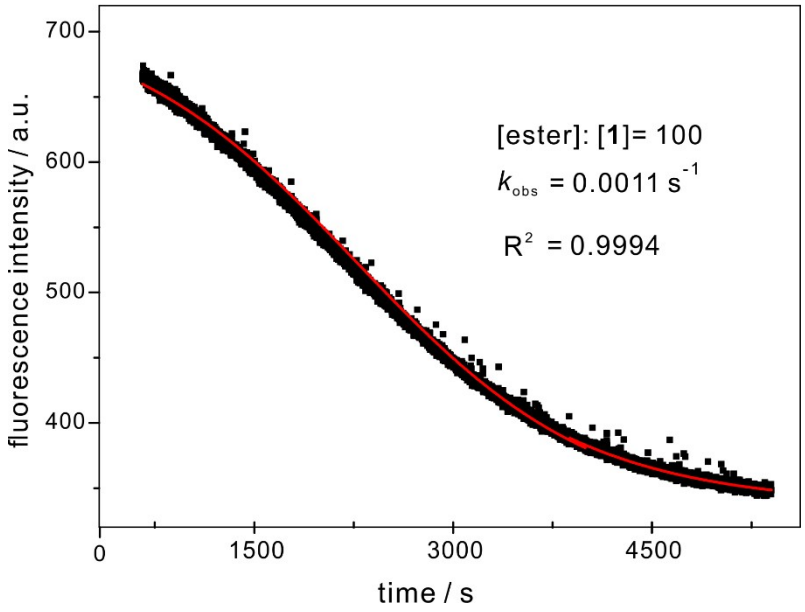


Fig. S30 Curve fitting of the hydrolytic data of butyl acetate ([G]: [H] = 100: 1).

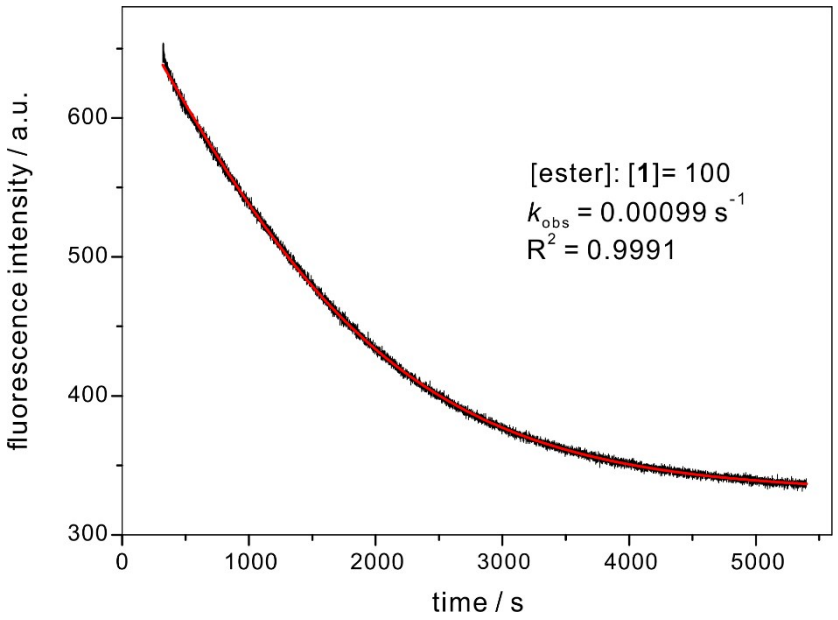


Fig. S31 Curve fitting of the hydrolytic data of isobutyl acetate ([G]: [H] = 100: 1).

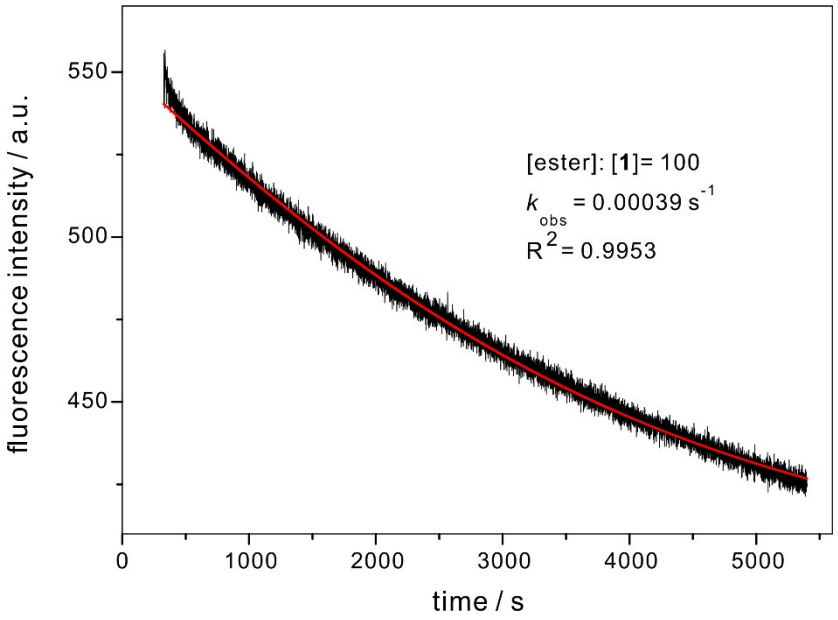


Fig. S32 Curve fitting of the hydrolytic data of sec-butyl acetate ([G]: [H] = 100: 1).

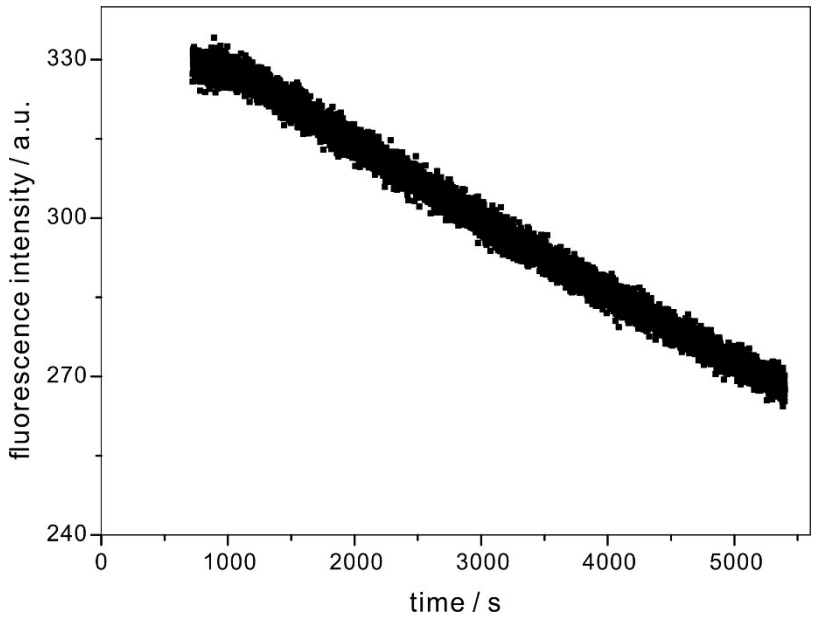


Fig. S33 Fluorescence change during the hydrolysis of *tert*-butyl acetate ([G]: [H] = 100: 1). The hydrolysis is too slow to allow the determination of the apparent rate constant.

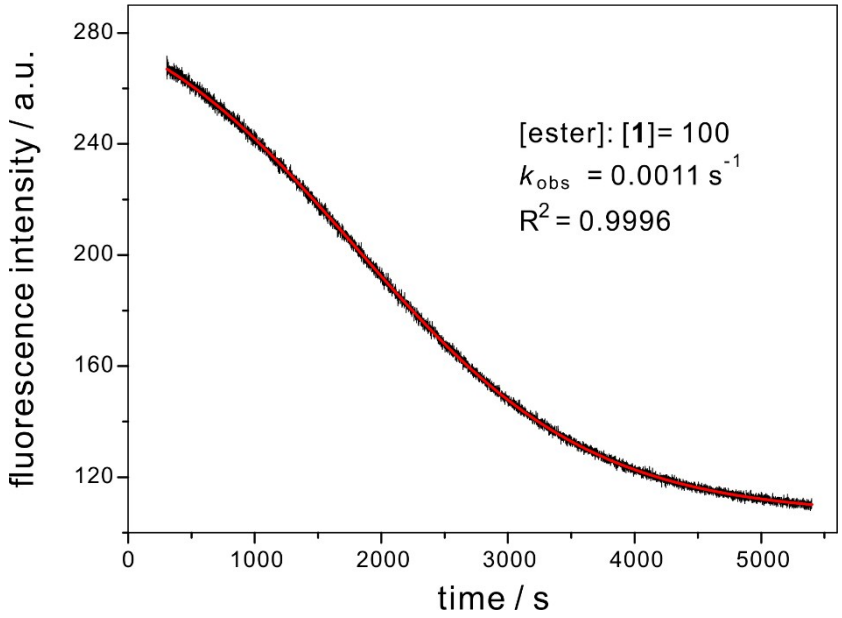


Fig. S34 Curve fitting of the hydrolytic data of ethyl propionate ([G]: [H] = 100: 1).

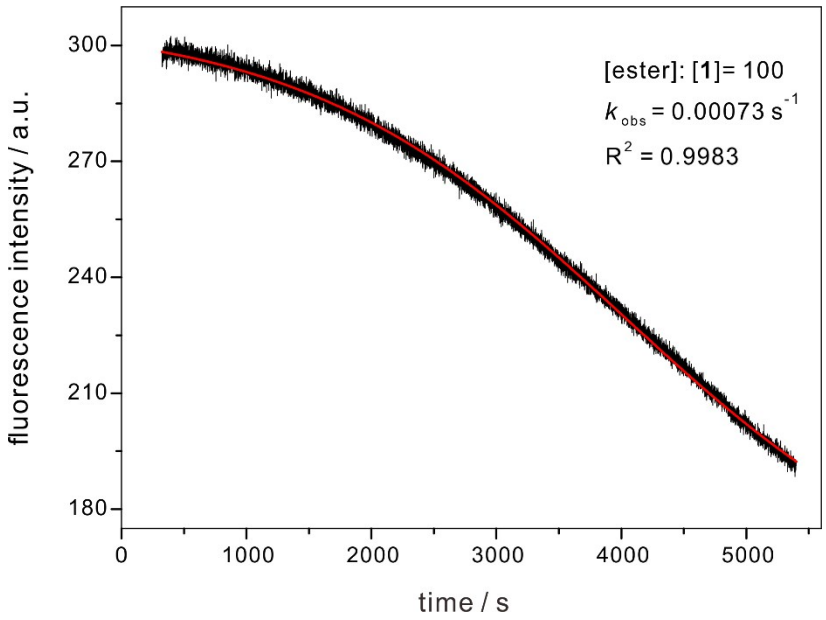


Fig. S35 Curve fitting of the hydrolytic data of ethyl butyrate ([G]: [H] = 100: 1).

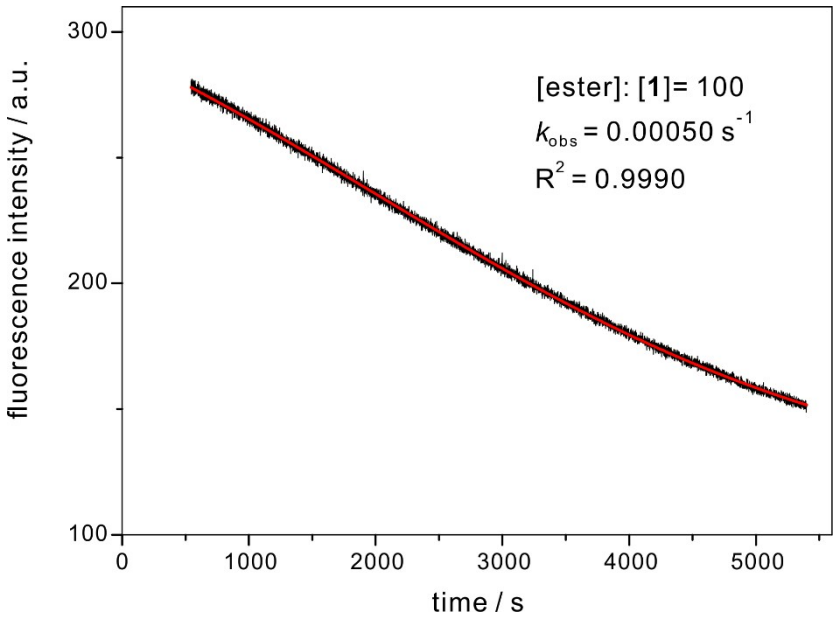
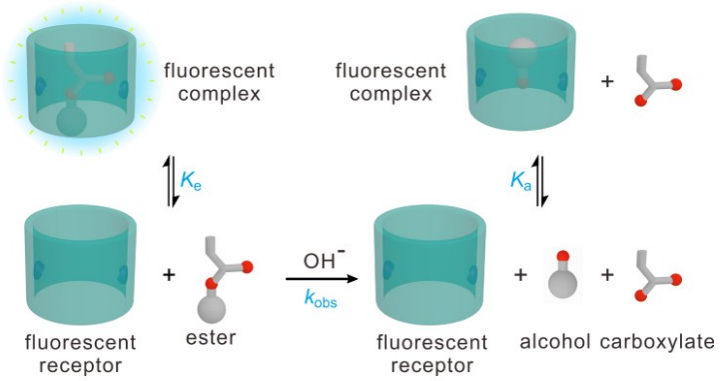


Fig. S36 Curve fitting of the hydrolytic data of ethyl isobutyrate ([G]: [H] = 100: 1).

6. Derivation of Equations on the Hydrolysis Kinetics

The experimentally derived data for the hydrolysis of esters in the presence of molecular tube **1** was fitted to the kinetic scheme defined by (7). In this scheme, K_e and K_a corresponds to the binding constant of the molecular tube **1** (flurescent receptor) to the ester (substrate) and alcohol (product), repectively. Due to there is no obviuos binding behaviour bwteewn molecular tube and all the carboxylates, this binding is ignored. k_{obs} is the apparent rate constant of ester hydrolysis reaction (pseudo first-order reaction) under the experimental conditions.



H + Ester $\overset{K_e}{\rightleftharpoons}$ H·Ester (eq.1)

H + Alcohol $\overset{K_a}{\rightleftharpoons}$ H·Alcohol (eq.2)

Ester $\xrightarrow{k_{obs}}$ Acid + Alcohol (eq.3)

According to eq.1, eq.2 and eq.3, the following equations could be obtained:

$$\frac{[H{\cdot}ester]}{[H] \times [ester]} = K_e \quad (1)$$

$$\frac{[H{\cdot}alcohol]}{[H] \times [alcohol]} = K_a \quad (2)$$

$$[ester] = [ester]_0 \times e^{-k_{obs} \times t} \quad (3)$$

$$[alcohol] = [ester]_0 \times (1 - e^{-k_{obs} \times t}) \quad (4)$$

$$[H]_0 = [H] + [H{\cdot}ester] + [H{\cdot}alcohol] \quad (5)$$

The observed fluorescence intensity F_t consisted of free molecular tube **H**, host-guest complex **H • ester** and **H • alcohol** at different time in the system follows (5) since it obeys similar Lambert-Beer law:

$$F_t = F_H + F_{H{\cdot}ester} + F_{H{\cdot}alcohol} = [H] \times F_H^{\theta} + [H{\cdot}ester] \times F_{H{\cdot}ester}^{\theta} + [H{\cdot}alcohol$$

(6)

The final equation $F_t = f(t, [H]_0, [ester]_0, K_e, K_a, k_{obs})$ is obtained from (1) to (6):

$$F_t = \frac{[H]_0(F_H^{\theta} + K_e[ester]_0 e^{-k_{obs}t} F_{H{\cdot}ester}^{\theta} + K_a[ester]_0\left(1 - e^{-k_{obs}t}\right)F_{H{\cdot}alcohol}^{\theta})}{1 + K_e[ester]_0 e^{-k_{obs}t} + K_a[ester]_0(1 - e^{-k_{obs}t})}$$

(7)

F_t : observed fluorescence intensity at different time,

$[H]_0$, $[ester]_0$: the initial concentration of molecular tube and ester,

F_H^{θ}, $F_{H{\cdot}ester}^{\theta}$ and $F_{H{\cdot}alcohol}^{\theta}$: fluorescence intensity of molecular tube **H**, complex **H** • ester and **H** • alcohol per mole,

K_e , K_a : the binding constants of macrocyle tube **H** to the esterand alcohol, repectively.

k_{obs} : the apparent rate constant of ester hydrolysis reaction (pseudo first-order reaction) under the chosen experimental conditions.