Supporting information for

# An "off-on" fluorescent naphthalimide-based sensor for anions: application for visual $\mathrm{F}^{-}$and $\mathrm{AcO}^{-}$discrimination in a self-assembly gel <br> Xuelei Pang, Junqi Ge, Xudong Yu*, Yajuan Li, Fengjuan Shen, Yanqiu Wang, Jujie Ren 

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Scheme S1 the synthesis procedure of Y1
Synthesis of N -haxanioc acid-4-Br-1, 8- naphthalic anhydride (1)
A mixture of aminocaproic acid ( $1 \mathrm{mmol}, 131 \mathrm{mg}$ ), and sodium hydroxide $(40 \mathrm{mg}, 1 \mathrm{mmol})$ was stirred at $40^{\circ} \mathrm{C}$ for 20 minutes, then 4-Br-1,8-naphthalic anhydride ( $277 \mathrm{mg}, 1 \mathrm{mmol}$ ) was added, and refluxed for 24 hours under nitrogen atmosphere. The reaction mixture was concentrated in vacuo, the residue was neutralized by dilute hydrochloric acid, the filtrate was purified by column chromatography $\left(\mathrm{SiO}_{2}: \mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{CH}_{3} \mathrm{OH}=20: 1\right)$ to yield 1 as a white solid $(179 \mathrm{mg}, 46 \%)$.

Mp: 166-168 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{HNMR}\left(400 \mathrm{M}, \mathrm{CDCl}_{3}, \delta\right): 1.45-1.52\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 1.69-1.80\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right)$, 2.36-2.40 (t, 2H, J=7.6 Hz, CH2 ), 4.16-4.19 (t, 2H, J=7.6 Hz, CH2 ), 7.83-7.87 (t, 2H, J=7.2 Hz, ArH), 8.03-8.05(d, 1H, J=8 Hz, ArH), 8.40-8.42 (d, 1H, J=8 Hz, ArH), 8.56-8.58 (d, 1H, J=7.2 Hz), 8.64-8.67 (d, 1H, J=7.2 Hz, ArH). ${ }^{13} \mathrm{CNMR}\left(125 \mathrm{M}, \mathrm{CDCl}_{3}, \delta\right): 24.68,26.51,27.60,33.96,122.11$, $122.89,128.39,129.01,129.48,129.97,131.19,131.61,131.83,132.81$. HRMS for calc. for. $\left(\mathrm{C}_{18} \mathrm{H}_{16} \mathrm{BrNO}_{4}+\mathrm{H}\right)^{+}: 390.0296,392.0276$; Found: 390.0328, 392.0310.

## Synthesis of N-ethyl amine-3- $\beta$-cholest-5-en-3-yl-ester-N-Lysine acid ethyl ester (2)

The synthesis of $\mathbf{2}$ was according to the literature 29.

Synthesis of 4-Br-1, 8-naphthalic anhydride-N-haxanioc acid imide-N-ethyl amine-3- $\beta$ -cholest-5-en-3-yl-ester-N-Lysine acid ethyl ester (3)

Compound 1 ( $1 \mathrm{mmol}, 389 \mathrm{mg}$ ) and $2(1 \mathrm{mmol}, 472 \mathrm{mg})$, Dcc ( $102.6 \mathrm{mg}, 3$ equiv) and HOBt (150 mg ) were stirred in dry $\mathrm{CHCl}_{3}$ for 24 h . The reaction mixture was concentrated and purified by chromatography $\left(\mathrm{SiO}_{2}, \mathrm{CHCl}_{3} / \mathrm{CH}_{3} \mathrm{OH}=80: 1\right)$ to give $\mathbf{3}$ as a white solid ( 422 mg , yield: $50 \%$ ). Mp : $199-201^{\circ} \mathrm{C} .{ }^{1} \mathrm{HNMR}\left(500 \mathrm{M}, \mathrm{CDCl}_{3}, \delta\right): 0.66\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 0.87\left(\mathrm{~d}, 3 \mathrm{H}, \mathrm{J}=2 \mathrm{~Hz}, \mathrm{CH}_{3}\right), 0.88(\mathrm{~d}, 3 \mathrm{H}$, $\left.\mathrm{J}=2 \mathrm{~Hz}, \mathrm{CH}_{3}\right), 0.91-0.93\left(\mathrm{~d}, 2 \mathrm{H}, \mathrm{J}=6.5 \mathrm{~Hz}, \mathrm{CH}_{2}\right), 0.98-2.35(\mathrm{~m}, 41 \mathrm{H}$, Cholesterol), 3.32-3.39(m, 4H, $\mathrm{CH}_{2}$ ), 4.16-4.19 (t, 2H, J=7.5Hz, $\mathrm{CH}_{2}$ ), 5.15-5.35 ( $\mathrm{s}, 1 \mathrm{H}$, cholesterol), 7.85-7.88 (t, $1 \mathrm{H}, \mathrm{J}=8.5 \mathrm{~Hz}$, ArH), 8.05-8.07 (d, 1H, J=8 Hz, ArH), 8.42-8.44 (d, 1H, J=8Hz, ArH), 8.58-8.60 (d, 1H, J=8.5Hz), 8.67-8.68 (d, 1H, J=7.5Hz, ArH). ${ }^{13} \mathrm{CNMR}\left(125 \mathrm{M}, \mathrm{CDCl}_{3}, \delta\right): 10.82,17.70,18.28,19.98,21.55$, $21.81,22.83,23.24,24.14,25.52,26.51,27.00,27.13,30.82,34.77,35.17,35.37,35.49,35.92$, $37.53,38.50,38.70,39.34,41.26,48.96,55.12,73.61,121.18,121.48,122.05,127.07,129.29$, 129.61, $130.10,131.01,132.28,138.71,150.62,162.59,172.67$. HRMS for calc. for. $\left(\mathrm{C}_{48} \mathrm{H}_{66} \mathrm{BrN}_{3} \mathrm{O}_{5}+\mathrm{Na}\right)^{+}: 866.4084,868.4063$; Found: 866.4085, 868.4073.

Synthesis of 4-diamine-1, 8-naphthalic anhydride-N-haxanioc acid imide-N-ethyl amine-3- $\beta$ -cholest-5-en-3-yl-ester-N-Lysine acid ethyl ester (Y1)

The compound 3 ( $1 \mathrm{mmol}, 843 \mathrm{mg}$ ), and hydrazine hydrate ( 8 mL ) were refluxed in ethanol for 3 days, the reaction mixture was then concentrated and purified by chromatography $\left(\mathrm{SiO}_{2}, \mathrm{CHCl}_{3} /\right.$ $\mathrm{CH}_{3} \mathrm{OH}=10: 1$ ) to give Y1 as a yellow solid (mg, yield: $30 \%$ ). Mp: $186-189{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{HNMR}(500 \mathrm{M}$, $\left.\mathrm{CDCl}_{3}, \delta\right): 0.60(\mathrm{~s}, 3 \mathrm{H}), 0.83-1.59(\mathrm{~m}, 39 \mathrm{H}$, Cholesterol), 1.76-1.92(m, 5 H$), 2.03-2.06(\mathrm{t}, 2 \mathrm{H}$, $\mathrm{J}=6 \mathrm{~Hz}), 2.15-2.28(\mathrm{~m}, 2 \mathrm{H}), 2.99-3.01(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}=6 \mathrm{~Hz}), 3.04-3.06(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}=5.5 \mathrm{~Hz}), 3.31(\mathrm{~s}, 1 \mathrm{H}), 3.96-$ $3.99(\mathrm{~T}, 2 \mathrm{H}, \mathrm{J}=8 \mathrm{~Hz}), 4.29(\mathrm{~m}, 1 \mathrm{H}), 4.63(\mathrm{~s}, 1 \mathrm{H}), 5.28(\mathrm{~s}, 1 \mathrm{H}), 6.97-6.99(\mathrm{t}, 1 \mathrm{H}, \mathrm{J}=5.0 \mathrm{~Hz}), 7.22-7.24$ $(\mathrm{d}, 1 \mathrm{H}, \mathrm{J}=8.5 \mathrm{~Hz}), 7.60-7.63(\mathrm{t}, 1 \mathrm{H}, \mathrm{J}=8 \mathrm{~Hz}), 7.75-7.77(\mathrm{~d}, 1 \mathrm{H}, \mathrm{J}=5.5 \mathrm{~Hz}), 8.26-8.28(\mathrm{~d}, 1 \mathrm{H}, \mathrm{J}=8.5 \mathrm{~Hz})$, 8.39-8.41 (d, 1H, J=7.5Hz),8.59-8.61 (d, 1H, J=8.5Hz), $9.10(\mathrm{~s}, 1 \mathrm{H})$.

Table S1. The gelation properties of $\mathbf{Y} 1(20 \mathrm{mg} / \mathrm{mL})$ in different organic solvents

| Solvent | H-C | Sonication |
| :---: | :---: | :---: |
| dichloromethane | P | P |
| trichloromethane | P | P |
| acetone | P | P |
| methanol | P | P |
| tetrahydrofuran | S | S |
| ethanol | P | G |
| ethyl acetate | P | TG |
| benzene | G | P |
| cyclohexane | P | P |
| isopropanol | S | G |
| acetonitril | P | P |
| n-propanol | S | G |
| toluene | P | PG |
| dioxane | S | TG |
| n-butyl alcohol | S | G |
| dimethylfomamide | S | S |

H-C: heating-cooling process; G: gel; P: precipitate; S: solution; PG: partial gel.


Fig. S1 (a) Bar charts of the absorbance at 347 nm of $\mathbf{Y} 1$ in benzene solution, (b) bar charts of luminescent intensities at 409 nm of $\mathbf{Y} 1$ in benzene solutions $(20 \mathrm{mg} / \mathrm{mL})$ upon the addition of different anions ( 50 equiv.).


Fig. S2 (a) Luminescent intensities of $\mathbf{Y} 1$ in benzene solutions $\left(1.0 \times 10^{-4} \mathrm{M}\right)$ upon the addition of all anions ( 50 equiv.), (b) Luminescent intensities of $\mathbf{Y} 1$ in benzene solutions ( $1.0 \times 10^{-4} \mathrm{M}$ ) after the addition of all anions ( 50 equiv.), except $\mathrm{F}^{-}$, change over time. The inset shows the corresponding luminescence under UV-light irradiation at 365 nm .


Figure S3 Reciprocal of fluorescent intensity of $\mathbf{Y} 1\left(1.0 \times 10^{-4} \mathrm{M}\right)$ at 409 nm with addition of $\mathrm{F}^{-}$.


Figure S4 Reciprocal of fluorescent intensity of Y1 $\left(1.0 \times 10^{-4} \mathrm{M}\right)$ at 409 nm with addition of $\mathrm{OAc}^{-}$.


Fig. S5 The visual sensing process of organogel toward $\mathrm{F}^{-}$.


Fig. S6 The visual sensing process of organogel toward $\mathrm{OAc}^{-}$recognition.

