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A Cu^{2+} ion-selective fluoroionophore with dual off/on switches

Takayo Moriuchi-Kawakami*, Youji Hisada, Yasuhiko Shibutani

Abstract

A new malonamide fluoroionophore possessing two pyrene moieties was synthesized. This bispyrene exhibited the fluorescence of the pyrene monomer (λ_{em} = 395 nm) and intramolecular excimer (λ_{em} = 467 nm) emissions. The designed derivative showed the excellent ion sensing ability to Cu^{2+}. The "on-off-off" and "off-on-off" fluorescence responses were demonstrated by the addition of the variable Cu^{2+} concentration. The utilization of the dual off/on responses could apply to the estimation of the rough Cu^{2+} concentration.

Findings

In recent years, researches on development of ion sensing with fluorescence emission have attracted considerable attention [1,2]. The rapid development of cation sensing is derived from the realization of the diverse roles played by cations in biological and chemical systems. For example, Cu^{2+} is a significant environmental pollutant and also an essential trace element in biological system [3]. Moreover, Cu^{2+} is a well-known paramagnetic ion with an unfilled *d* orbital and could strongly quench the fluorescence of the fluorophore near it via electron or energy transfer [4]. In most of the reported recognition of Cu^{2+}, the binding of Cu^{2+} causes quenching of the fluorescence emission [5-9]. Few reports are available for "off-on"-type fluorescent compounds that can selectively recognize Cu^{2+} [10-14]. However, the "off-on-off"-type sensing for Cu^{2+} has not been reported yet. The "off-on-off"-type sensing should be suitable for the simplified measurement, because the ion concentration could be roughly estimated.

Most of the fluoroionophore for cation recognition are composed of a cation recognition site with a fluorescent moiety [15]. Pyrene is one of the most useful fluorescent units due to their relatively efficient excimer formation and emission properties [16-21]. Fluorescent molecules with more than one pyrene moiety exhibit not only pyrene monomer emission but also intramolecular excimer emission because of strong π-π interaction between two pyrene moieties [22,23]. If both the emission signals are utilized for sensing, it would lead to the development of a novel sensing method. We herein report dual off/on fluorescence for Cu^{2+} ion sensing, in which both monomer and excimer emission signals of pyrene units change effectively and cooperatively. Therefore, the use of this dual off/on fluorescence responses could apply to estimate the rough Cu^{2+} concentration.

Bispyrene **1** was prepared by the synthetic routes depicted in Figure 1. Disubstituted malonic acid dichloride was synthesized by the reaction of corresponding disubstituted malonic acids with $(COCl)_2$ in benzene [24]. Subsequently, the reaction of disubstituted malonic acid dichlorides with 1-pyrenylmethylamine hydrochloride in benzene gave a desired bispyrene **1** in 2% isolated yield. Derivative **2** possessing only one pyrene moiety was also obtained with derivative **1**. Bispyrene **3** was prepared by similar method.

Derivatives **1** and **3** have two pyrene moieties as a fluorescent unit. As shown in Figure 2, bispyrenes **1** and **3** displayed both excimer (λ_{em} = 467 nm) and monomer (λ_{em} = 395 nm) emissions when excited at 344 nm in $CH_3CN/CHCl_3$ (9:1, v/v). The excimer emissions were dominant compared with the monomer emissions. Derivative **2** has only one pyrene moiety as a fluorescent unit. Monopyrene **2** exhibited only typical monomer (λ_{em} = 395 nm) emission by exciting at 344 nm in $CH_3CN/CHCl_3$ (9:1, v/v).

In ^1H NMR spectra, the amide NH resonances of bispyrenes **1** and **3** were detected in $CDCl_3$ at the lower field (δ 7.24 for **1** and δ 7.19 for **3**) than that of the monopyrene **2** possessing only one amide group (δ 5.53). Therefore, bispyrenes **1** and **3** seem to form

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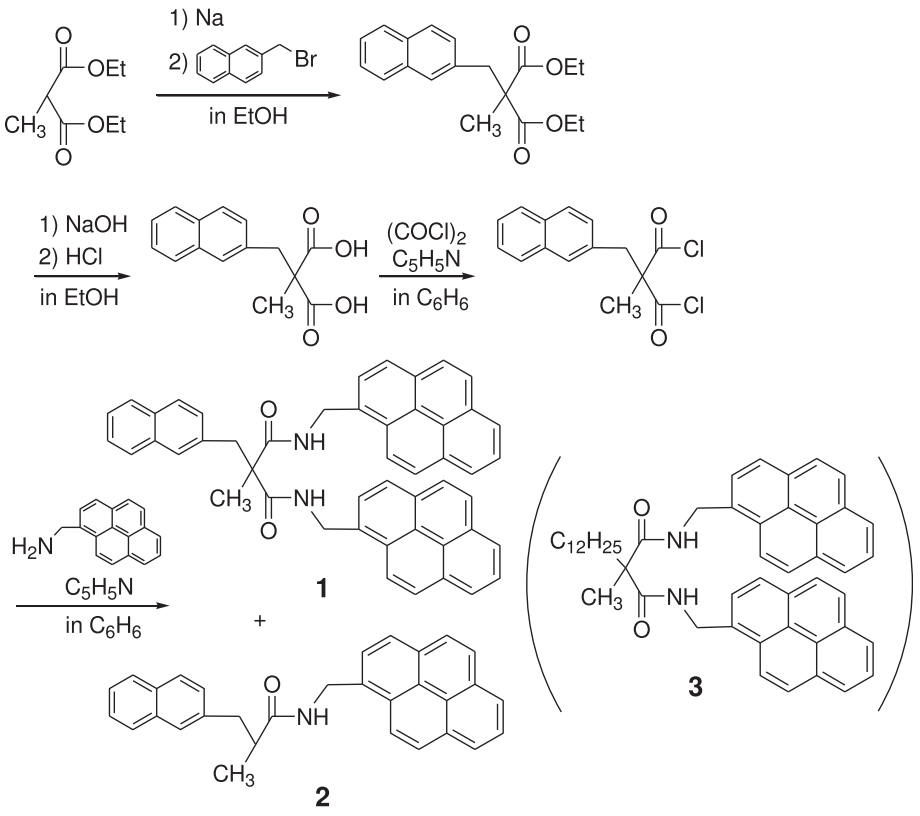

Figure 1 Syntheses of pyrene compounds.

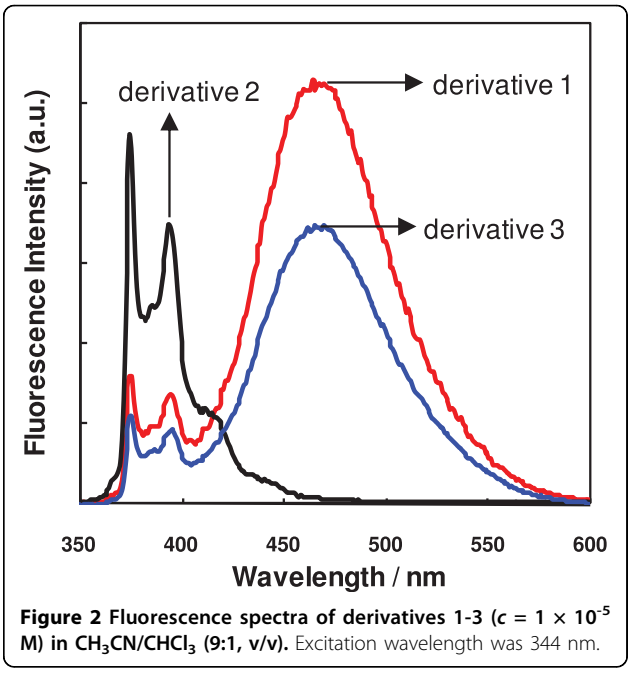

Figure 2 Fluorescence spectra of derivatives 1-3 (c = 1 × 10^{-5} M) in $CH_3CN/CHCl_3$ (9:1, v/v). Excitation wavelength was 344 nm.

intramolecular hydrogen bonds between both amide groups. The hydrogen bonds might structurally influence intramolecular π-π interaction of two pyrene moieties, which result in a relatively strong fluorescent in the excimer emission. Further, the excimer emission intensity of bispyrene **1** was reduces to about half by the addition of CH_3OH (CH_3CN:$CHCl_3$:CH_3OH = 99:10:1, v/v). ^1H NMR study in $CDCl_3$ demonstrated that the amide NH resonance of bispyrene **1** was slightly perturbed by the addition of 10 equiv and 100 equiv of CD_3OD (from δ 7.24 to δ 7.29 and 7.42). These results also support the formation of the intramolecular hydrogen bonds in bispyrene **1**.

To study cation recognition properties of new malonamide-substituted pyrene derivatives **1**-**3**, the fluorescence measurements were carried out. The fluorescence emissions for 1 × 10^{-5} M solution of **1**-**3** in CH_3CN/$CHCl_3$ (9:1, v/v) were measured in the presence of metal perchlorates by exciting them at 344 nm. The effect of K^+, Rb^+, Cs^+, Mg^{2+}, Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Ag^+ on the excimer and monomer

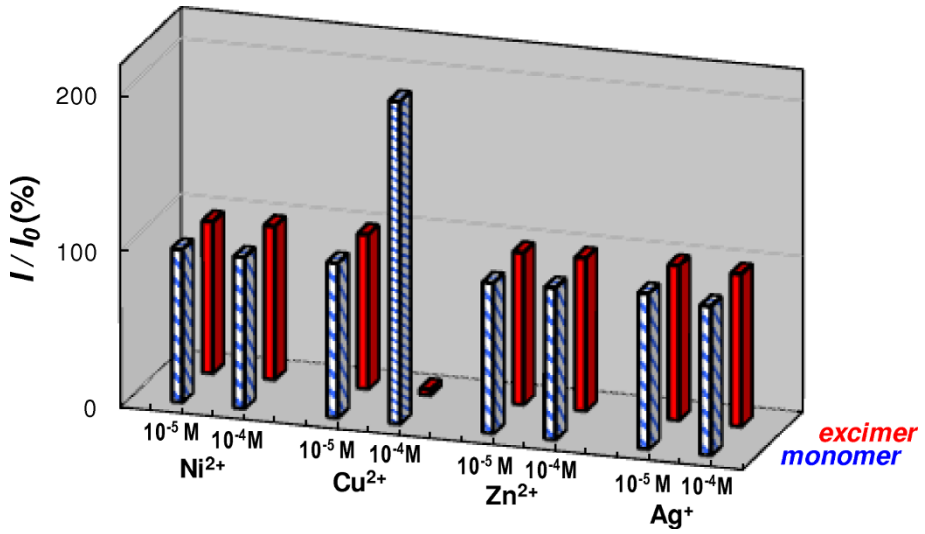

Figure 3 Intensity ratios of the excimer (λ_{em} = 467 nm) and monomer (λ_{em} = 395 nm) emissions (I) for 1 × 10^{-5} M of derivative 1 in the presence of 1 × 10^{-5} M and 1 × 10^{-4} M of metal ions to those emissions (I_0) without the addition of metal ions.

emission intensities of **1**-**3** was investigated. For derivative **1**, the effect of Li^+, Na^+, NH_4^+, Ca^{2+}, Fe^{2+}, Cd^{2+} and Pb^{2+} was also examined. The addition of 1 equiv (1 × 10^{-5} M) of Ni^{2+}, Cu^{2+}, Zn^{2+} and Ag^+ marginally affected the fluorescence emissions of **1**. Interestingly, the both monomer and excimer emission intensities of **1** were dramatically changed by the addition of 10 equiv (1 × 10^{-4} M) of Cu^{2+}. Figure 3 shows the intensity ratios (I/I_0) of the excimer and monomer emissions for 1 × 10^{-5} M solution of **1** in the presence of 1 × 10^{-5} and 1 × 10^{-4} M of Ni^{2+}, Cu^{2+}, Zn^{2+} and Ag^+ ions to the excimer and monomer emissions for 1 × 10^{-5} M solution of **1**. On the other hand, the addition of 1 equiv (1 × 10^{-5} M) of Cu^{2+} caused changes in the excimer and monomer emission intensities of bispyrene **3** significantly and selectively as illustrated in Figure 4. Bispyrenes **1** and **3** exhibited noteworthy responses to Cu^{2+} as compared to other metal ions examined. Unlike bispyrene compounds, monopyrene **2** showed nonselective response to most of metal perchlorates, increasing or decreasing the monomer emissions.

The fluorescence responses of derivatives **1**-**3** to Cu^{2+} were examined in detail. Figure 5 shows the fluorescence response of 1 × 10^{-5} M bispyrene **1** with the addition of Cu^{2+} in $CH_3CN/CHCl_3$ (9:1, v/v). The fluorescence spectra of **1** are characterized by the dual emission resulting from the excimer and the monomer. Until the addition of ca. 3 equiv (3 × 10^{-5} M) of Cu^{2+}, both fluorescence emissions of **1** were unaffected. However, by the addition of 10 equiv (1 × 10^{-4} M) of Cu^{2+}, the fluorescence intensity of the excimer emission decreased while the intensity of the monomer emission increased. Both fluorescence emissions of **1** were quenched by the further addition of

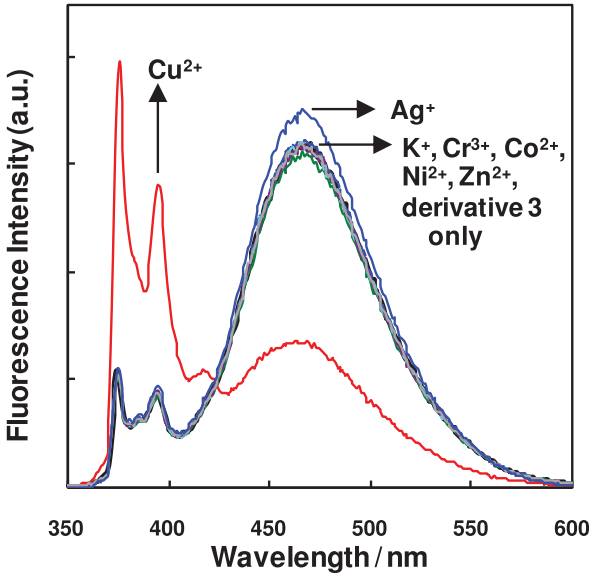

Figure 4 Fluorescence emission changes of derivative **3** (c = 1 × 10^{-5} M) upon addition of metal ions K^+, Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+ (1 equiv) in $CH_3CN/CHCl_3$ (9:1, v/v). Excitation wavelength was 344 nm.

Cu^{2+}. Thus, the addition of Cu^{2+} to **1** gave the "on-off-off" and "off-on-off" fluorescence responses to the excimer and monomer emissions, respectively. The discriminations between "on" and "off" states were determined from the abrupt change of fluorescence intensities in the excimer and monomer emissions, respectively. Bispyrene **1** exhibited two switching points that would be brought by the addition of ca. 3 and 10 equiv of Cu^{2+} respectively.

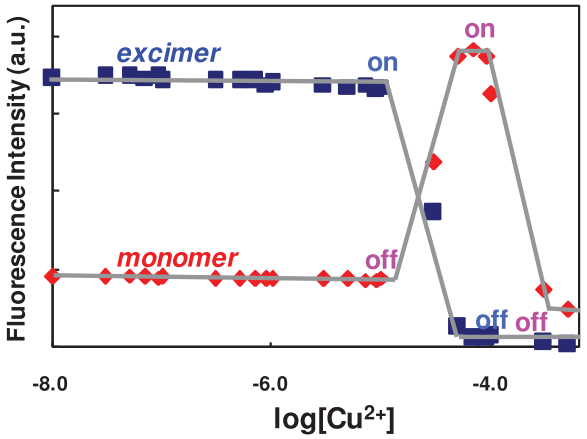

Figure 5 Fluorescence intensity changes during the titration of derivative 1 (c = 1 × 10^{-5} M) in $CH_3CN/CHCl_3$ (9:1, v/v) with Cu^{2+} (from 1 × 10^{-8} to 5 × 10^{-4} M). Excitation wavelength was 344 nm and emission was at 467 nm for excimer and 395 nm for monomer.

The fluorescence response of 1 × 10^{-6} M bispyrene **1** with the addition of Cu^{2+} provided the similar switching responses. Therefore, the utilization of both off/on fluorescence responses could apply to estimate the rough Cu^{2+} concentration. Figure 6 illustrates the switch function of bispyrene **1**. For example, the "on" signal of only the excimer emission displays the presence of ca. 1 equiv of Cu^{2+} and the "on" signal of only the monomer emission indicates the presence of ca. 10 equiv of Cu^{2+}. The "off" signals of both emissions mean the presence of ca. 100 equiv of Cu^{2+}. Bispyrene **3** also showed the similar sensing ability for Cu^{2+}. However, the off/on signals of **3** changed easily by a little change of the concentration of Cu^{2+}. Therefore, "on-off" responses of 1 × 10^{-5} M of **3** were observed under the presence of over 1 equiv (1 × 10^{-5} M) of Cu^{2+}.

On the other hand, 1 × 10^{-5} M of monopyrene **2** exhibited only inherent monomer emission. The fluorescence intensity of the monomer emission of **2** linearly decreased as the concentration of Cu^{2+} increased to ca. 1 × 10^{-4} M (10 equiv).

	Cu^{2+}		
	1 equiv	10 equiv	100 equiv
response 1 excimer	on	off	off
response 2 monomer	off	on	off

Figure 6 Switch function of derivative 1.

The "on-off-off" fluorescence response in the excimer emission and the "off-on-off" fluorescence response in the monomer emission of bispyrene **1** to Cu^{2+} could be interpreted as follows. The binding of Cu^{2+} to an amide moiety [25] is considered to cleave the intramolecular hydrogen bond resulting a conformational change to abolish intramolecular π-π interaction. Then the fluorescence intensity of the excimer emission decreases while the intensity of the inherent monomer emission increases. Upon the addition of excesses amount of Cu^{2+} (over 10 equiv), even the inherent monomer emission should be quenched due to paramagnetic property of Cu^{2+} [15] and the cation-π interations between pyrene moiety and Cu^{2+}. Kim et al. reported pyrene-armed calix[4]crown chemosensor for detection of Pb^{2+} and Cu^{2+} [25]. They illustrated that Cu^{2+} is coordinated with two facing amide nitrogen atoms and the two pyrenyl groups in the complex form a static excimer. From above results, the fluorescence mechanism of malonamide-substituted pyrene derivative **1** is thought to be different from their mechanism.

These malonamide-substituted bispyrenes **1**-**3** were found to exhibit the sensing ability to Cu^{2+} in the wide concentration range (from 1 × 10^{-5} M to 1 × 10^{-3} M for **1**, 1 × 10^{-4} M for **2** and **3**). These results are probably due to the weak binding ability to Cu^{2+}. In fact, binding constants of **1**-**3** for Cu^{2+} were determined as 1.28 × 10^{-1} (± 0.37) M^{-1} for **1**, 1.20 × 10^{-2} (± 0.41) M^{-1} for **2**, and 2.13 × 10^{-1} (± 0.56) M^{-1} for **3**, respectively, from the change in the UV absorption (λ = 342 nm for **1** and **3**, 311 nm for **2**) as a function of Cu^{2+} concentration (Based on the 1:1 binding stoichiometry, the binding constants (K_a) were calculated by means of the nonlinear least-squares method). Compared to derivative **1**, the strength of the binding of derivative **3** was a little strong relatively. It means that the off/on signals of **3** changed easily by a little change of the concentration of Cu^{2+}. Such difference between bispyrenes **1** and **3** might result from the steric hindrance of the sp^3 carbon of malonamides affecting the intramolecular hydrogen bonds between both amide groups.

New malonamide derivatives possessing two fluorescent pyrene moieties were synthesized. Bispyrenes **1** and **3** exhibited the fluorescence of pyrene monomer and intramolecular excimer emissions. Bispyrene **3** showed the excellent ion sensing ability to Cu^{2+}. Bispyrene **1** displays the Cu^{2+}-selective fluoroionophore with dual on/off switches by both monomer and excimer emissions. The information about the binding of bispyrene **1** to Cu^{2+} was provided from UV-Vis absorption spectra and it revealed that the strength of binding is extremely weak. Therefore, bispyrene **1** could show sensing ability to Cu^{2+} under the wide concentration range.

Experimental

2-Methyl-2-naphthalenylmethyl-malonyl dichloride for 1 and 2

Sodium metal (2.60 g) was added to dry ethyl alcohol (500 mL) at 0°C and stirred for 1.3 h until sodium metal dissolved completely to form sodium ethoxide. Methylmalonic acid diethyl ester (20.7 g) was added dropwise over period of 2 h. The reaction solution was stirred for 15 h. Then 2(-bromomethyl)naphthalene (25.0 g) was added and refluxed for 48 h. After concentration in vacuo for the removal of the solvent, the residue was added by water (70 mL). The solution was extracted with diethyl ether (80 × 3 mL) and the organic layer was washed with water (70 mL). The organic layer was dried over anhydrous magnesium sulfate, filtrated and evaporated under reduced pressure. The purification was performed by distillation under reduced pressure to give 2-methyl-2-naphthalenylmethyl-malonic acid diethyl ester. Yield: 22.1 g, 62%; pale yellow tough liquid; bp 155.0°C (0.3 mmHg). ^{1}H NMR (300 MHz NMR, $CDCl_3$): 1.26 (t, 6H, *J* = 7.2 Hz), 1.38 (s, 3H), 3.40 (s, 2H), 4.21 (q, 4H, *J* = 7.2 Hz), 7.23-7.90 (m, 7H). ^{13}C NMR (75 MHz NMR, $CDCl_3$): 14.0, 19.8, 41.2, 54.9, 61.3, 125.5, 125.9, 127.5, 127.5, 127.6, 128.3, 129.0, 132.4, 133.2, 133.8, 171.9. Sodium hydroxide (15.3 g) was added to dry ethyl alcohol (300 mL) at room temperature and stirred for 1 h until sodium hydroxide dissolved completely. The gained 2-methyl-2-naphthalenylmethyl-malonic acid diethyl ester (20.2 g) was added dropwise over period of 2 h. The reaction solution was refluxed for 23 h. After the filtration the pale yellow solid was obtained and washed with dry ethyl alcohol. After filtration, the precipitate was dried under reduced pressure. The obtained solid was dissolved in water (325 mL). Then the solution was became pH 1 by the addition of hydrochloric acid to form the precipitate. After filtration, the precipitate was dissolved in diethyl ether (100 mL) and the filtrate was washed with diethyl ether (100 × 2 mL). These diethyl ether solution was washed with water (100 × 2 mL). The organic layer was dried over anhydrous magnesium sulfate, filtrated and evaporated under reduced pressure. The gained solid was washed with ethyl acetate-hexane (1:20) to give 2-methyl-2-naphthalenylmethyl-malonic acid. Further purification was performed by recrystallization with acetone. Yield: 13.97 g, 84%; pale yellow crystal. ^{1}H NMR (300 MHz NMR, $(CD_3)_2CO$): 1.38 (s, 3H), 3.41 (s, 2H), 7.43-7.84 (m, 7H).^{13}C NMR (75 MHz NMR, $(CD_3)_2CO$): 20.4, 41.4, 74.2, 126.4, 126.5, 127.7, 127.7, 127.8, 128.5, 129.5, 130.6, 132.8, 133.2, 171.0. 2-Methyl-2-naphthalenylmethyl-malonic acid (6.03 g) and dry pyridine (3.2 mL) were added in dry benzene (90 mL) and stirred for 2 h at room temperature. In a dark room, oxalyl chloride (9.0 mL) was added dropwise and stirred for 22 h. Then the reaction solution was refluxed for 20 h outside a dark room. After concentration in vacuo for the removal of the solvent, the residue was distilled under reduced pressure to give 2-methyl-2-naphthalenylmethyl-malonyl dichloride. Yield: 3.45 g, 50%; pale yellow crystal; bp 114.0°C (0.1 mmHg). IR (KBr): 1788, 943 cm^{-1}.

N, N'-bis(1-pyrenylmethyl)-2-methyl-2-naphthalenylmethyl-malonamide 1

1-Pyrenylmethylamine hydrochloride (5.68 g) was dissolved in dry benzene (150 mL). Dry pyridine (5.2 mL) was added to the solution and stirred for 1 h. In a dark room, the dry benzene solution (35 mL) of 2-methyl-2-naphthalenylmethyl-malonyl dichloride (3.19 g) was added dropwise to the solution and stirred for 93 h at room temperature. The reaction solution evaporated under reduced pressure. 0.5 M hydrochloric acid aqueous solution (130 mL) was added to the residue. The solution was extracted with chloroform (150 × 2 mL) and washed with water (50 × 2 mL). The organic layer was dried over anhydrous magnesium sulfate, filtrated and evaporated under reduced pressure. The purification was performed by liquid chromatography (CHEMCOSORB 5-ODS-H) with methanol-chloroform (14:3). Yield: 0.14 g, 2%; pale yellow solid; mp 184.8-185.5°C. ^{1}H NMR (300 MHz NMR, $CDCl_3$): 1.39 (s, 3H), 3.42 (s, 2H), 5.05 (dd, 2H, *J* = 5.40 and 14.6 Hz), 5.14 (dd, 2H, *J* = 5.40 and 14.7 Hz), 7.18-7.24 (m, 1H), 7.24 (br, 2H), 7.32-7.40 (m, 1H), 7.40-7.47 (m, 1H), 7.52-7.62 (m, 3H), 7.68-7.74 (m, 1H), 7.74-7.82 (m, 4H), 7.94-8.02 (m, 8H), 8.03-8.09 (m, 4H), 8.16-8.21 (m, 2H). ^{13}C NMR (75 MHz NMR, $CDCl_3$):18.7, 42.4, 45.5, 54.7, 122.4, 124.4, 124.6, 124.7, 124.9, 125.3, 125.3, 125.7, 126.0, 1267.0, 127.3, 127.5, 127.7, 128.1, 128.3, 128.4, 128.8, 128.8, 128.9, 130.4, 130.6, 131.1, 131.2, 131.3, 132.4, 133.3, 133.8, 172.4. HRMS: m/z calcd for C49H36N2O2 684.2777, found (FAB+) 684.2779, (EI+) 684.2784.

N-(1-pyrenylmethyl)-2-naphthalenylmethyl-propionamide 2

N-(1-pyrenylmethyl)-2-naphthalenylmethyl-propionamide was obtained by liquid chromatography with earlier retention time than derivative **1**. Pale yellow solid; mp 95.6-96.5°C. ^{1}H NMR (300 MHz NMR, $CDCl_3$): 1.27 (d, 3H, *J* = 6.9 Hz), 2.53 (m, 1H), 2.86 (dd, 1H, *J* = 5.7 and 13.5 Hz), 3.15 (dd, 1H, *J* = 9.0 and 13.3 Hz), 4.94 (dd, 1H, *J* = 4.8 and 14.4 Hz), 4.94 (dd, 1H, *J* = 5.40 and 14.4 Hz), 5.53 (s, 1H), 7.36-7.81 (m, 7H), 7.90-8.14 (m, 9H). ^{13}C NMR (75 MHz NMR, $CDCl_3$): 18.1, 40.8, 41.9, 44.0, 122.5, 124.5, 124.8, 125.2, 125.3, 125.3, 125.9, 127.0, 127.3, 127.3, 127.4, 127.6, 127.6, 128.0, 128.0,

128.1, 128.8, 130.6, 130.7, 131.0, 131.1, 131.2, 132.2, 133.5, 137.3, 175.0. HRMS(EI+): m/z calcd for C31H25NO 427.1936, found 427.1944.

2-Dodecyl-2-methyl-malonyl dichloride for 3

2-Dodecyl-2-methyl-malonic acid diethyl ester was gained by the reaction between methyl-malonic acid diethyl ester (40.0 g) and lauryl chloride (51.1 g). Yield: 58.7 g, 75%; clear liquid; bp 140.0°C (0.4 mmHg). ^{1}H NMR (300 MHz NMR, $CDCl_3$): 0.88 (t, 3H, J = 7.2 Hz), 1.16-1.35 (m, 23H), 1.39 (s, 3H), 1.80-1.90 (m, 2H), 4.17 (q, 4H, J = 7.2 Hz).^{13}C NMR (75 MHz NMR, $CDCl_3$): 13.9, 13.9, 19.6, 22.5, 24.1, 29.2, 29.4, 29.5, 29.5, 29.5, 29.7, 31.8, 35.4, 53.5, 60.8, 172.3. 2-Dodecyl-2-methyl-malonic acid was obtained from 2-dodecyl-2-methyl-malonic acid diethyl ester (16.7 g). Yield: 11.8 g, 85%; white crystal. ^{1}H NMR (300 MHz NMR, $(CD_3)_2CO$): 0.88 (t, 3H, J = 5.1 Hz), 1.25-1.39 (m, 20H), 1.39 (s, 3H), 1.82-2.00 (m, 2H), 10.96 (br).^{13}C NMR (75 MHz NMR, $(CD_3)_2CO$): 12.1, 18.1, 21.0, 22.8, 27.7, 27.8, 27.8, 28.0, 28.0, 28.0, 28.4, 30.3, 34.1, 51.4, 171.7. 2-Dodecyl-2-methyl-malonyl dichloride was synthesized by the reaction between 2-dodecyl-2-methyl-malonic acid (2.12 g) and oxalyl chloride (5 mL). Yield: 0.98 g, 41%; pale yellow liquid; bp 90.2°C (0.2 mmHg).^{1}H NMR (300 MHz NMR, $CDCl_3$): 0.88 (t, 3H, J = 7.2 Hz), 1.19-1.42 (m, 20H), 1.64 (s, 3H), 2.02-2.13 (m, 2H).^{13}C NMR (75 MHz NMR, $CDCl_3$): 14.1, 20.2, 22.7, 23.8, 29.1, 29.4, 29.4, 29.6, 29.6, 29.6, 31.9, 35.8, 73.1, 171.3. IR (neat): 1790 cm^{-1}.

N, N'-bis(1-pyrenylmethyl)-2-dodecyl-2-methyl-malonamide 3

N, *N*'-bis(1-pyrenylmethyl)-2-dodecyl-2-methyl-malonamide was gained by the reaction between 2-dodecyl-2-methyl-malonyl dichloride (0.94 g) and 1-pyrenylmethylamine hydrochloride (0.76 g). The purification was performed by liquid chromatography (CHEMCOSORB 5-ODS-H) with methanol-chloroform (17:7). Yield: 0.04 g, 2%; white solid; mp 147.8-148.3°C. ^{1}H NMR (300 MHz NMR, $CDCl_3$): 0.89 (t, 3H, J = 6.9 Hz), 1.03-1.39 (m, 20H), 1.40 (s, 3H), 5.07 (d, 2H, J = 5.4 Hz), 5.08 (d, 2H, J = 5.4 Hz), 7.19 (t, 2H, J = 5.4 Hz), 7.83-7.88 (m, 2H), 7.94-7.98 (m, 10H), 7.98-8.20 (m, 6H).^{13}C NMR (75 MHz NMR, $CDCl_3$):14.1, 14.3, 19.2, 19.3, 22.7, 24.9, 26.8, 29.4, 29.4, 29.5, 29.6, 29.6, 29.6, 29.7, 29.8, 31.9, 33.2, 39.6, 40.0, 42.2, 43.3, 53.5, 122.7, 123.3, 124.7, 124.8, 125.0, 125.0, 125.1, 125.3, 125.4, 125.6, 126.1, 126.4, 127.0, 127.4, 127.5, 128.2, 128.4, 128.9, 129.3, 130.7, 130.9, 131.0, 131.2, 131.3, 131.4, 172.9, 254.3. HRMS(EI+): m/z calcd for C50H52N2O2 712.4029, found 712.4036.

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Authors' contributions

TM conceived of the study, designed the fluoroionophores, participated in its syntheses and performed the analysis. YH performed the syntheses and the analysis. YS participated in its design and analysis.

Competing interests

The authors declare that they have no competing interests.

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