Supplementary Information

"Turn-on" fluorescent sensor array for basic amino acids in water

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General

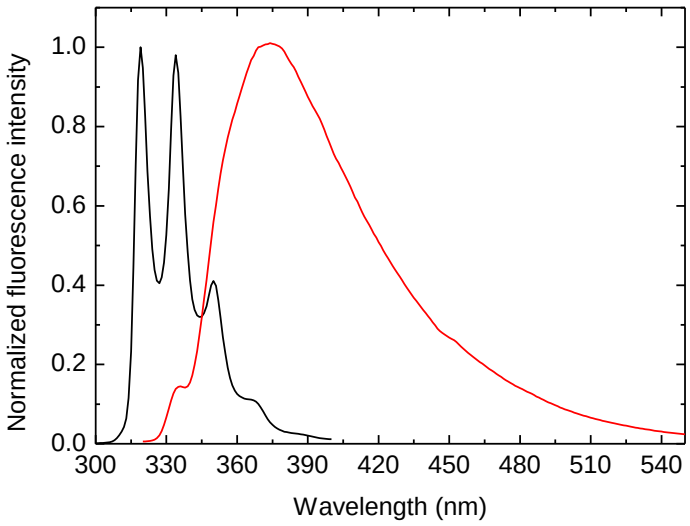
Starting materials were purchased from commercial suppliers and used without further purification. Compounds **1** and **2** were prepared according to the literature procedures.[1,2] Mass spectrometry was performed using Shimadzu LCMS-8030 liquid chromatograph mass spectrometer (ESI).

Fluorescence measurements were performed on a single photon counting spectrofluorimeter from Edinburgh Analytical Instruments (FL/FS 920). Diluted solutions used for all photophysical experiments were prepared using nanopure water in quartz cuvettes. Solutions of **1** were excited at 266 nm or 280 nm. Solutions of **2** were excited at 301 nm. Fluorescence emission spectra were recorded between 300 nm and 400 nm for **1**, between 320 nm and 550 nm for **2**, respectively. The slits of both excitation and emission monochrometers were set to 2.2 nm for **1**, 2.5 nm for **2**, respectively. The emission was scanned in 1 nm steps with a dwell time of 0.20 sec under ambient room conditions. Guest titrations were performed in water in the presence or the absence of Eu^{3+} ion (0.3 mM). Titration isotherms were constructed from changes in the fluorescence maximum at 319 nm for **1**, 369 nm for **2**, respectively. Data analysis was performed according to previously published methods.[3]

The array experiments were performed in 1536-well plates using a Beckman BioRAPTR microfluidic robotic dispenser. The fluids (water, probe, Eu^{3+} ion and analyte solutions) were contact-free dispensed at 200 nL/s as follows. Each experiment was performed in 24 repetitions. Each well received 1 μL of water at pH 3, 5, and 7 followed by 1 μL of **1** or **2** (12 μM), and 1 μL of Eu^{3+} ion solution (0, 0.1, 0.3, and 1 mM), after which the mixture was equilibrated for 2 min to establish a probe-metal ion

complex. Subsequently, 1 μL of analyte solutions ([lisinopril], [histidine], [ornithine], [histidinol], [arginine], [lysine], [histamine] = 50 μM, [putrescine], [agmatine], [cadaverine] = 12 μM) were added. For control experiments, 1 μL of water was added instead of analyte solution. After the analyte was dispensed, the plate was centrifuged (2 min, 3000 rpm, 21 °C) and immediately measured by a BMG PheraStar microplate reader using 280 nm excitation, 320 nm emission for **1** and 300 nm excitation, 370 nm emission for **2**. The resulting emission data were subjected to the Student's t-test to exclude 4 outlier data-points (of 24 repetitions). The coefficient of variability among the data within the class of 20 repetitions was lower than 5%. Thus obtained data were then analyzed using LDA or HCA without any further pretreatment.

Fluorescence property



Property of **1**

φ = 42.3%; τ = 45.18 ns.

Property of **2**

φ = 22.5%; τ = 6.55 ns.

Fig. S1. Fluorescence spectra of **1** (black line) and **2** (red line) in water. λ_{ex} = 266 nm for **1**, λ_{ex} = 301 nm for **2**. Fluorescence quantum yields were determined by using tryptophan in water as a standard.

Examples of fluorescence titrations

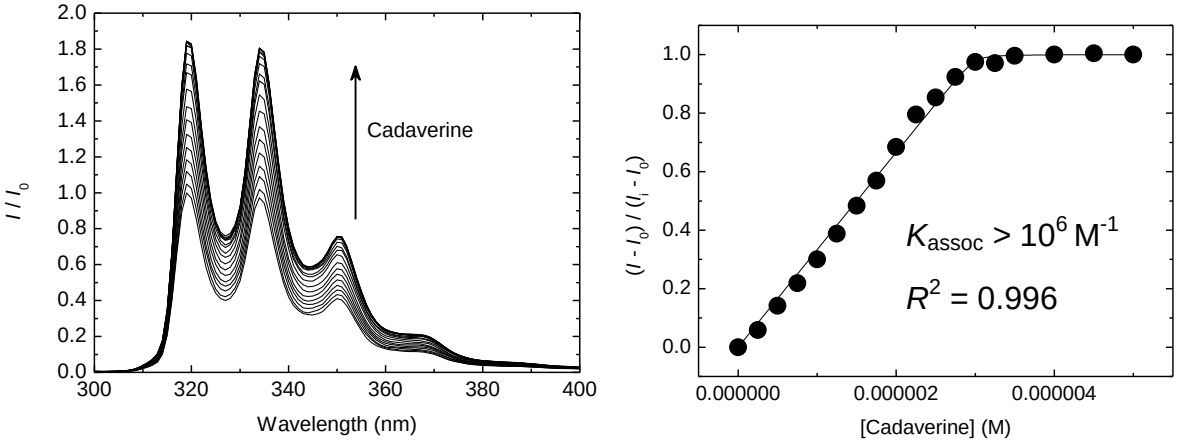


Fig. S2. Fluorescence spectra of **1** (3 μM) upon addition of incremental amounts of cadaverine in water with $Eu(NO_3)_3$ (300 μM) at pH 7. λ_{ex} = 266 nm. [Cadaverine] = 0 ─ 5 μM.

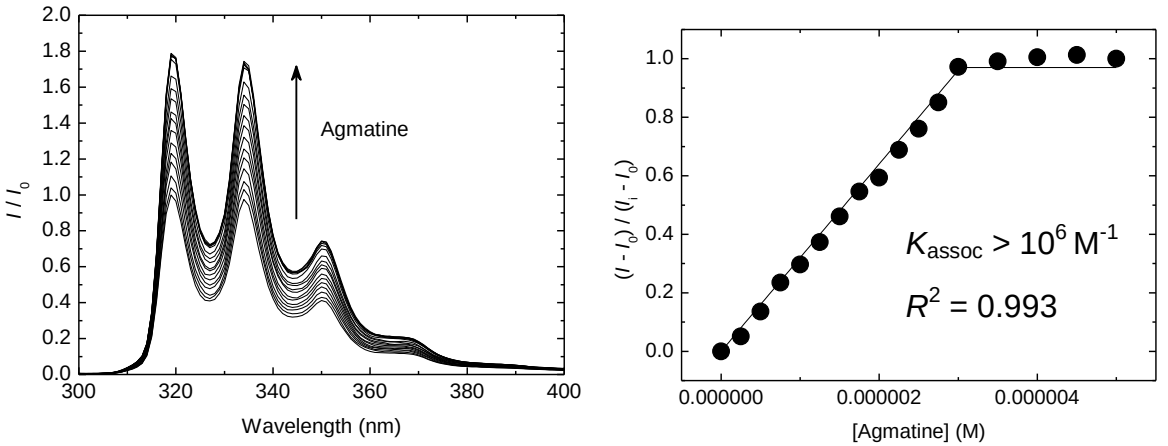


Fig. S3. Fluorescence spectra of **1** (3 μM) upon addition of incremental amounts of agmatine in water with $Eu(NO_3)_3$ (300 μM) at pH 7. λ_{ex} = 266 nm. [Agmatine] = 0 ─ 5 μM.

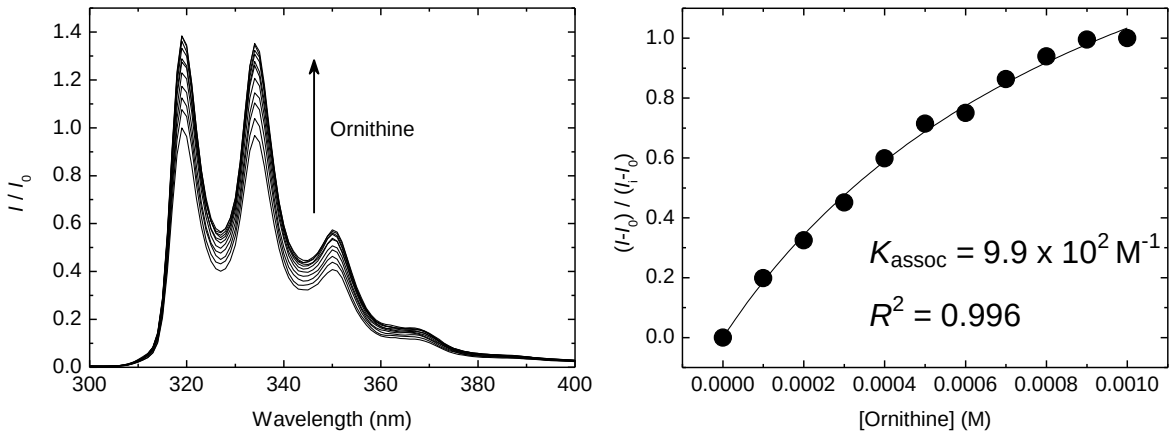


Fig. S4. Fluorescence spectra of **2** (3 μM) upon addition of incremental amounts of ornithine in water with $Eu(NO_3)_3$ (300 μM) at pH 7. λ_{ex} = 266 nm. [Ornithine] = 0 ─ 1 mM.

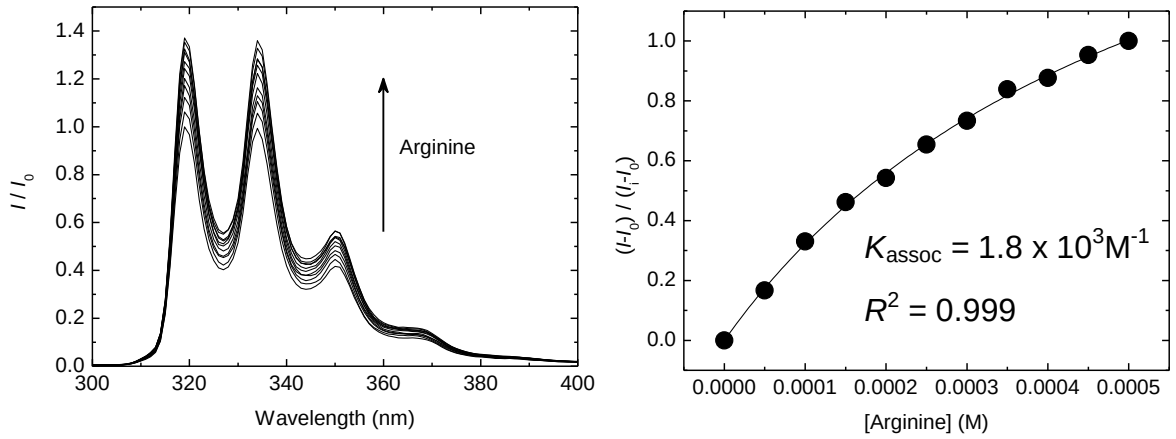


Fig. S5. Fluorescence spectra of **1** (3 μM) upon addition of incremental amounts of arginine in water with $Eu(NO_3)_3$ (300 μM) at pH 7. λ_{ex} = 266 nm. [Arginine] = 0 ─ 500 μM.

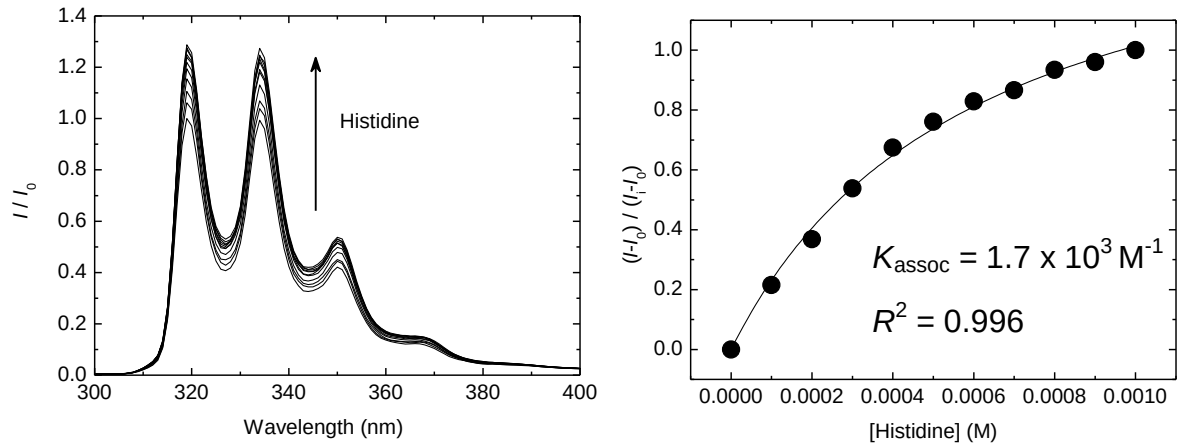


Fig. S6. Fluorescence spectra of **1** (3 μM) upon addition of incremental amounts of histidine in water with $Eu(NO_3)_3$ (300 μM) at pH 7. λ_{ex} = 266 nm. [Histidine] = 0 ─ 1 mM.

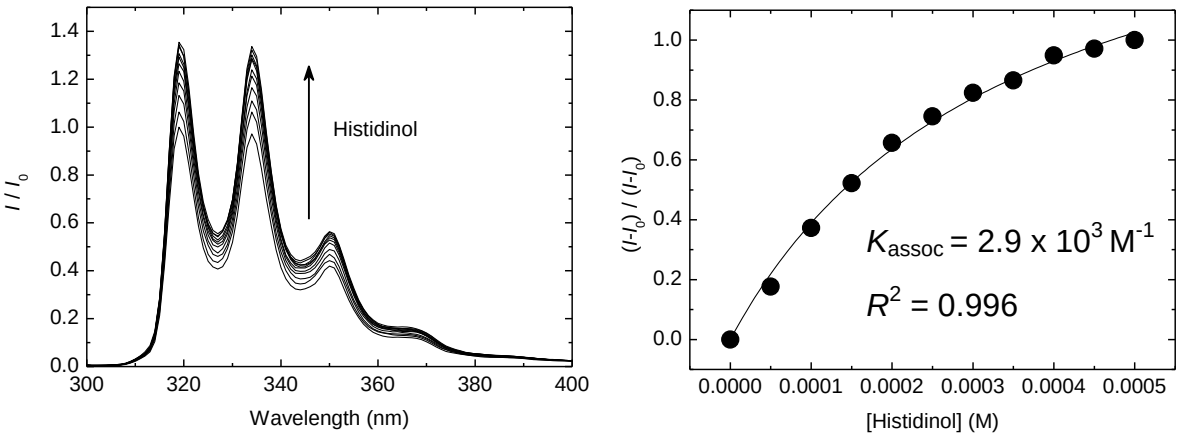


Fig. S7. Fluorescence spectra of **1** (3 μM) upon addition of incremental amounts of histidinol in water with $Eu(NO_3)_3$ (300 μM) at pH 7. λ_{ex} = 266 nm. [Histidinol] = 0 ─ 500 μM.

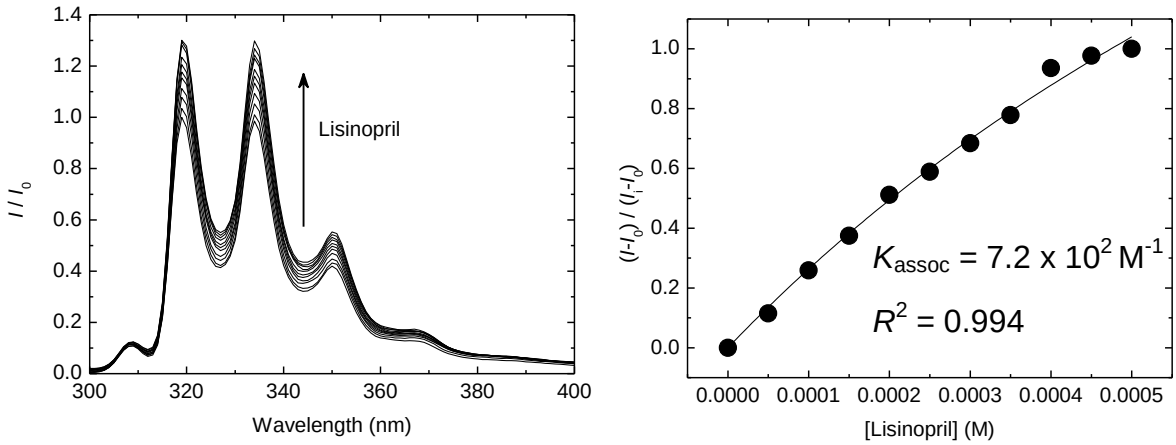


Fig. S8. Fluorescence spectra of **1** (3 μM) upon addition of incremental amounts of lisinopril in water with $Eu(NO_3)_3$ (300 μM) at pH 3. λ_{ex} = 280 nm. [Lisinopril] = 0 ─ 500 μM.

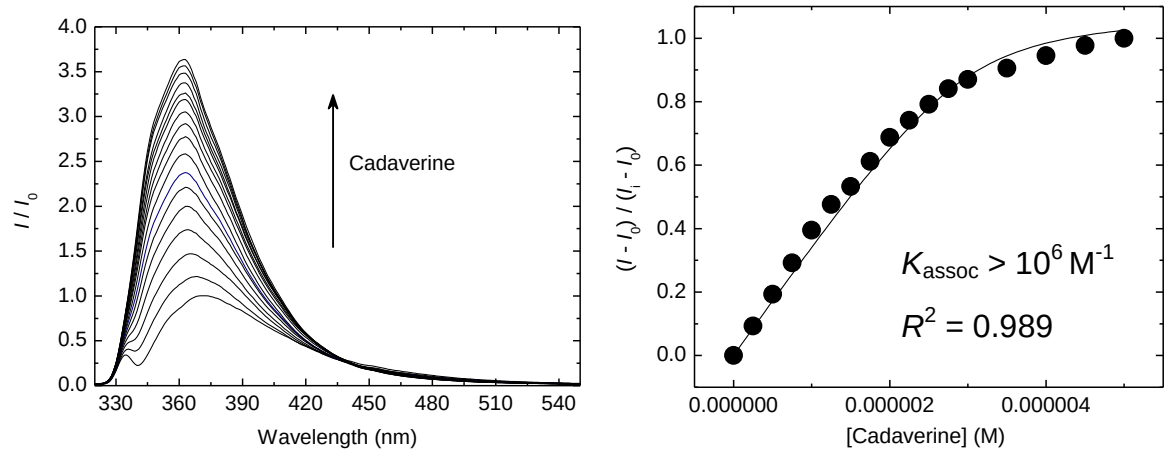


Fig. S9. Fluorescence spectra of **2** (3 μM) upon addition of incremental amounts of cadaverine in water with $Eu(NO_3)_3$ (300 μM) at pH 7. λ_{ex} = 301 nm. [Cadaverine] = 0 ─ 5 μM.

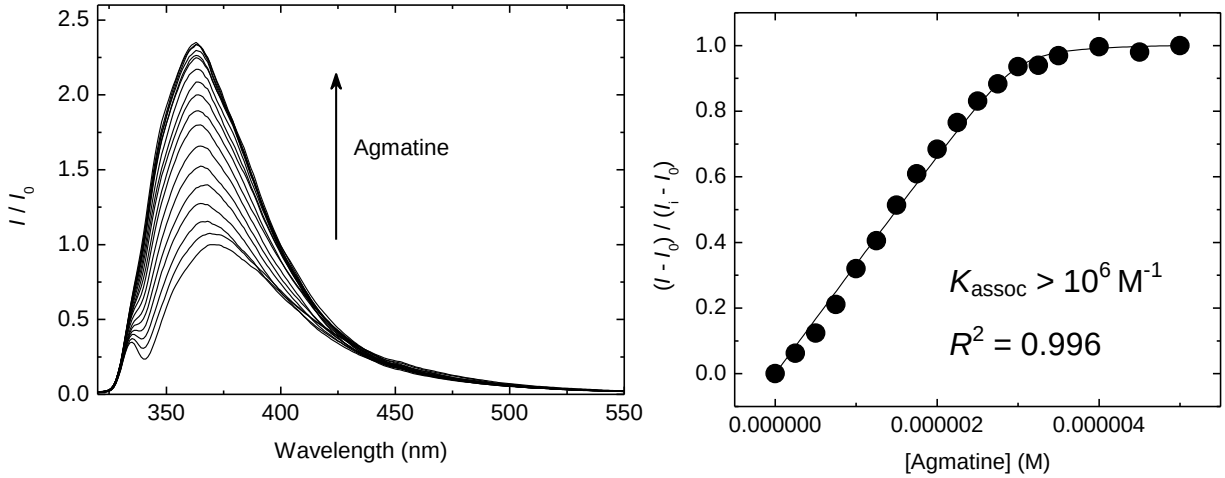


Fig. S10. Fluorescence spectra of **2** (3 μM) upon the addition of incremental amounts of agmatine in water with $Eu(NO_3)_3$ (300 μM) at pH 7. λ_{ex} = 301 nm. [Agmatine] = 0 ─ 5 μM.

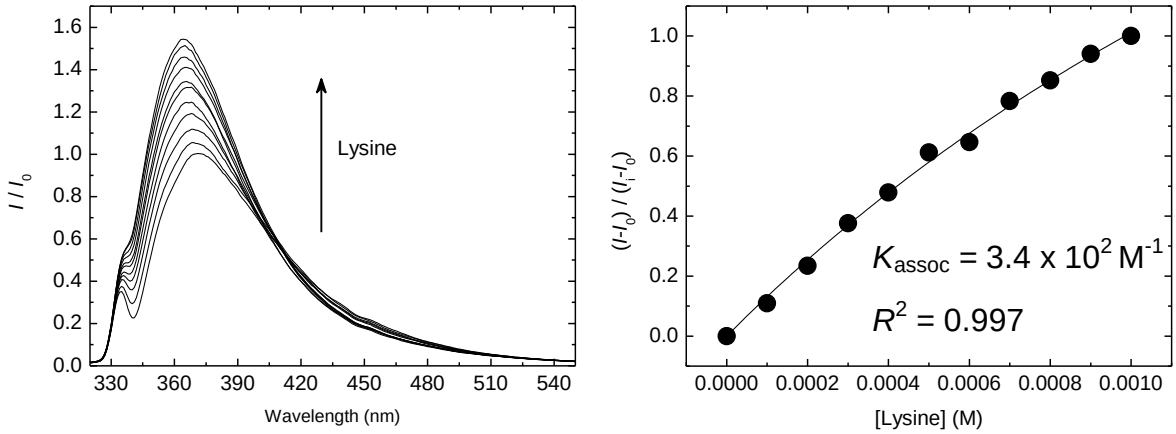


Fig. S11. Fluorescence spectra of **2** (3 μM) upon addition of incremental amounts of lysine in water with $Eu(NO_3)_3$ (300 μM) at pH 7. λ_{ex} = 301 nm. [Lysine] = 0 ─ 1 mM.

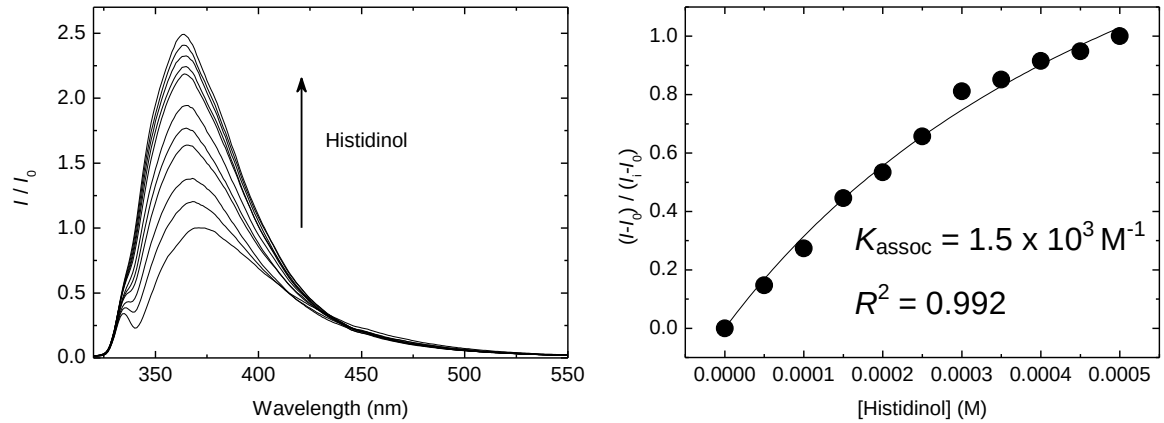


Fig. S12. Fluorescence spectra of **2** (3 μM) upon addition of incremental amounts of histidinol in water with $Eu(NO_3)_3$ (300 μM) at pH 7. λ_{ex} = 301 nm. [Histidinol] = 0 ─ 500 μM.

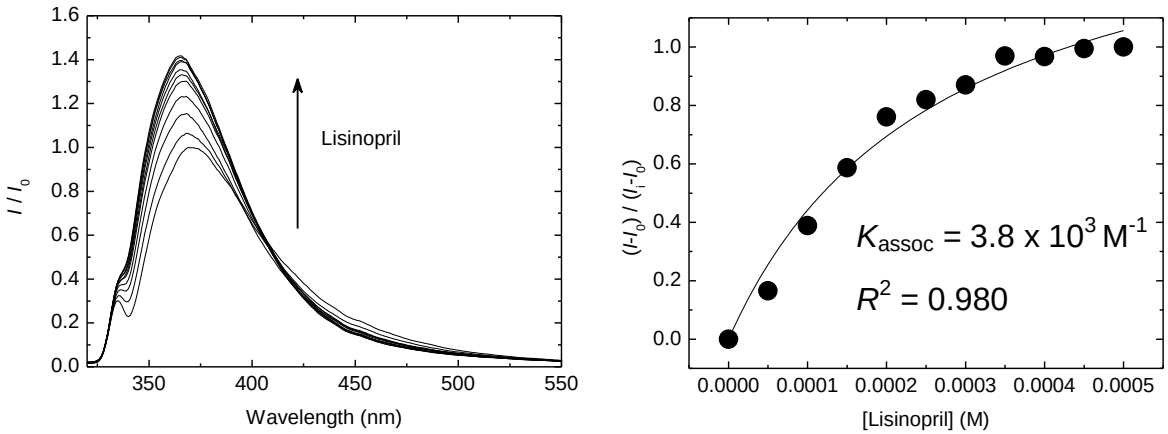


Fig. S13. Fluorescence spectra of **2** (3 μM) upon addition of incremental amounts of lisinopril in water with $Eu(NO_3)_3$ at pH 3. λ_{ex} = 301 nm. [Lisinopril] = 0 ─ 500 μM.

Qualitative analysis

Table 1. The Jackknifed classification matrix.

Jackknifed Classification Matrix

	A1 Putrescine	A10 Lisinopril	A2 Agmatine	A3 Cadaverine	A4 Lysine	A5 Arginine	A6 Histidinol	A7 L-Ornitine
A1 Putrescine	20	0	0	0	0	0	0	0
A10 Lisinopril	0	20	0	0	0	0	0	0
A2 Agmatine	0	0	20	0	0	0	0	0
A3 Cadaverine	0	0	0	20	0	0	0	0
A4 Lysine	0	0	0	0	20	0	0	0
A5 Arginine	0	0	0	0	0	20	0	0
A6 Histidinol	0	0	0	0	0	0	20	0
A7 Ornitine	0	0	0	0	0	0	0	20
A8 Histidine	0	0	0	0	0	0	0	0
A9 Histamine	0	0	0	0	0	0	0	0
Ctrl	0	0	0	0	0	0	0	0
Total	20	20	20	20	20	20	20	20

Jackknifed Classification Matrix (contd...)

	A8 Histidine	A9 Histamine	Ctrl	%correct
A1 Putrescine	0	0	0	100
A10 Lisinopril	0	0	0	100
A2 Agmatine	0	0	0	100
A3 Cadaverine	0	0	0	100
A4 Lysine	0	0	0	100
A5 Arginine	0	0	0	100
A6 Histidinol	0	0	0	100
A7 Ornitine	0	0	0	100
A8 Histidine	20	0	0	100
A9 Histamine	0	20	0	100
Ctrl	0	0	20	100
Total	20	20	20	100

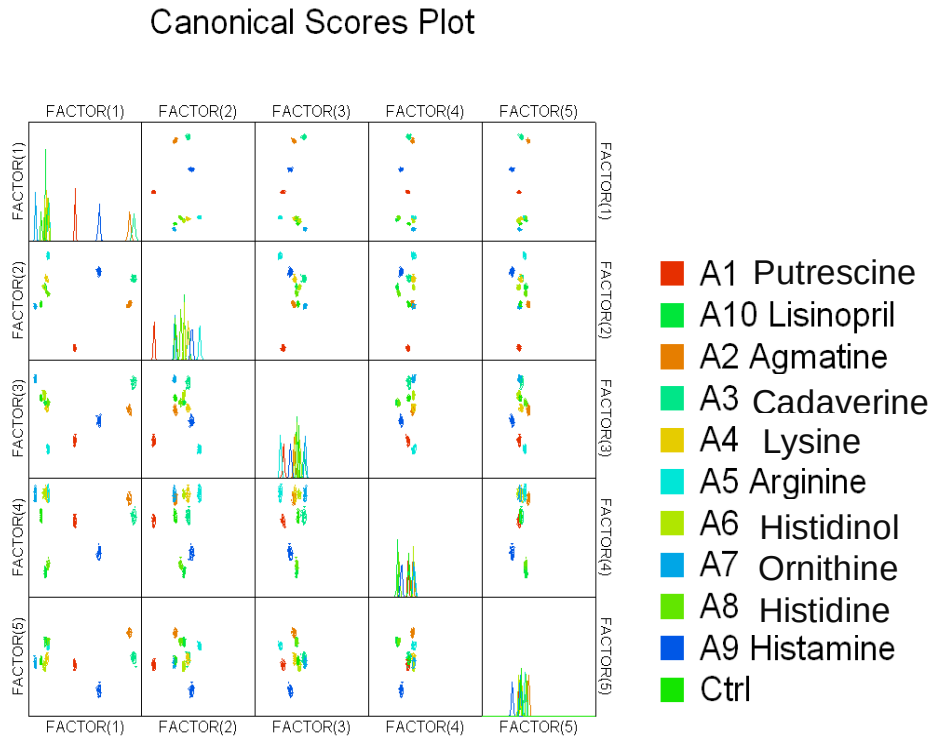


Fig. S14. The canonical scores plot.

References

1. D. Lucas, T. Minami, G. Iannuzzi, L. Cao, J. B. Wittenberg, P. Anzenbacher Jr., L. Isaacs, *J. Am. Chem. Soc.*, 2011, **133**, 17966.

2. T. Minami, N. A. Esipenko, B. Zhang, M. E. Kozelkova, L. Isaacs, R. Nishiyabu, Y. Kubo, P. Anzenbacher Jr., *J. Am. Chem. Soc.*, 2012, **134**, 20021.

3. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy 3rd Ed.*, Springer, New York, 2006.