Supporting Information

A colorimetric and ratiometric fluorescent sensor for sequentially detecting Cu^{2+} and arginine based on coumarin-rhodamine B derivative and its application for bioimaging

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Contents

Fig. S6. Spectroscopic changes of **1**-Cu^{2+} induced by the addition of various amino acids (50.0 eq.) in CH_3CN-H_2O (9/1, v/v) solutions. (A) Absorption spectral changes. (B) Fluorescence emission intensity changes. (C) The color image set upon the addition of various amino acids. (D) The fluorescence image set upon the addition of various amino acids. λ_{ex} = 350 nm.

Fig. S7. Competition experiments of **1**-Cu^{2+} in the presence of different amino acids (50 eq., black bar) and subsequent addition of Arg (30 eq., red bar) in CH_3CN-H_2O (9/1, v/v). (A) Absorption changes (B) Fluorescence intensity ratio changes (I_{615}/I_{490}), λ_{ex} = 350 nm, slit: 5 nm/5 nm.

Fig. S8. Nonlinear curve fitting of the absorbance titration data from 0 to 200 μM for **1**-Cu^{2+} complex towards different concentrations of Arg at 564 nm in CH_3CN–H_2O (9/1, v/v) solutions at room temperature. R^2 = 0.99714.

Fig. S9. Limit of detection (LOD) of the **1**-Cu^{2+} complex towards Arg by UV-vis method.

Fig. S10. Fluorescent intensities ratio (I_{615}/I_{490}) change of **1**-Cu^{2+} solution towards different concentrations of Arg (0-200 μM). R^2 = 0.97889.

Fig. S11. Limit of detection (LOD) of the **1**-Cu^{2+} complex towards Arg by fluorescence method.

Fig. S12. Normalized spectral overlap of fluorescence spectrum of coumarin (blue) and absorption spectrum of rhodamine B (pink) in CH_3CN-H_2O (9/1, v/v) solution.

Fig. S13. ^1H NMR spectrum of **1** in CD_2Cl_2.

Fig. S14. ^{13}C NMR spectrum of **1** in CD_2Cl_2.

Fig. S15. The ESI-MS spectrum of **1**.

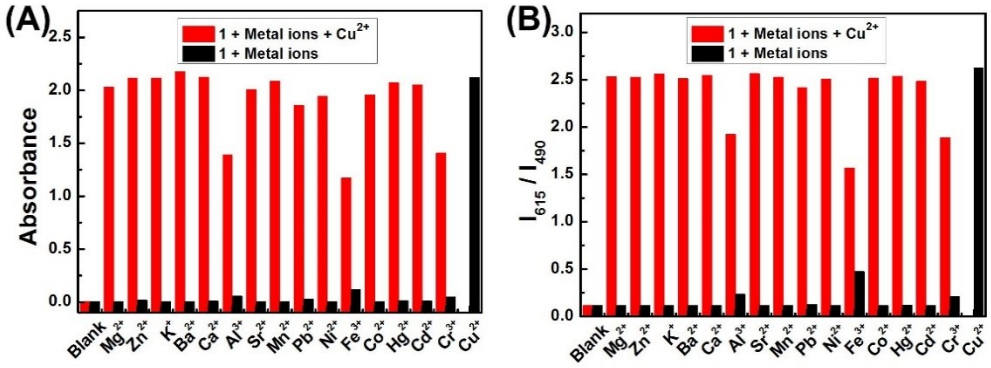
(A)
Absorbance
1 + Metal ions + Cu2+
1 + Metal ions
Blank
Mg2+
Zn2+
K+
Ba2+
Ca2+
Al3+
Sr2+
Mn2+
Pb2+
Ni2+
Fe3+
Co2+
Hg2+
Cd2+
Cr3+
Cu2+
(B)
I615 / I490
1 + Metal ions + Cu2+
1 + Metal ions

Fig. S1.

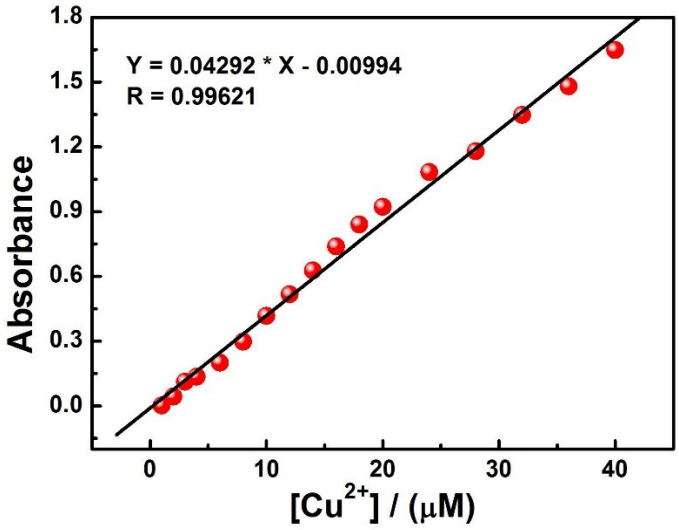
Y = 0.04292 * X - 0.00994
R = 0.99621
Absorbance
[Cu2+] / (μM)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
10
20
30
40

Fig. S2.

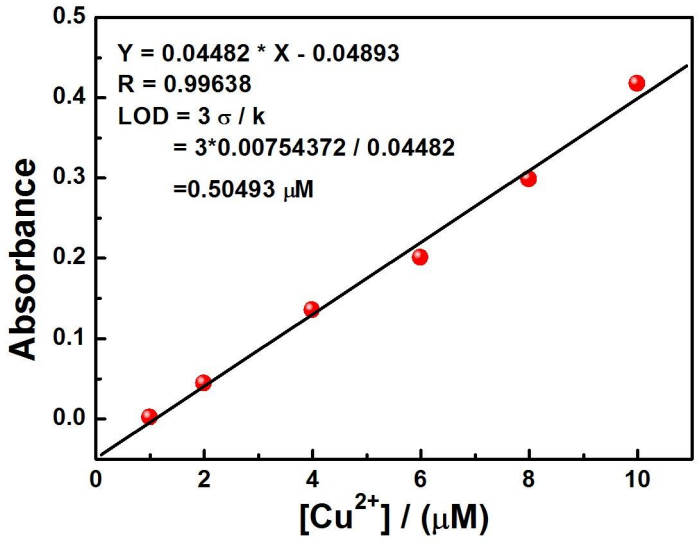
Y = 0.04482 * X - 0.04893
R = 0.99638
LOD = 3 σ / k
= 3*0.00754372 / 0.04482
=0.50493 μM
Absorbance
0.0
0.1
0.2
0.3
0.4
0.5
0
2
4
6
8
10
[Cu2+] / (μM)

Fig. S3.

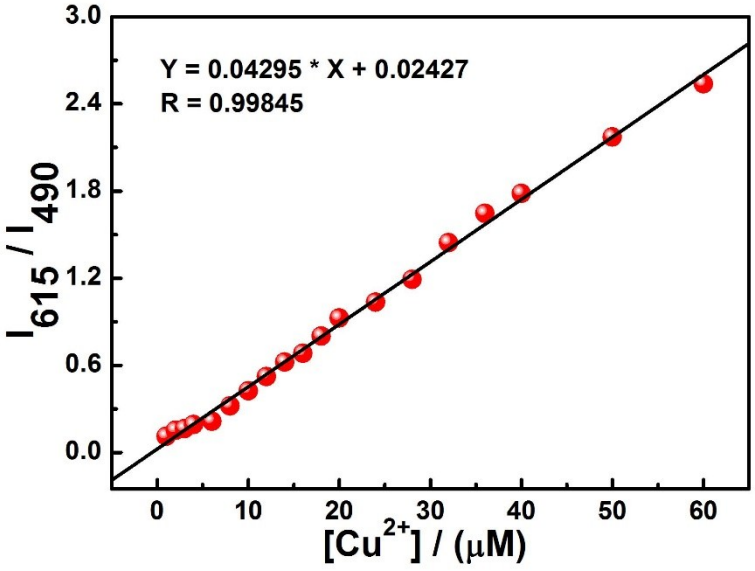
Y = 0.04295 * X + 0.02427
R = 0.99845
I_{615} / I_{490}
$[Cu^{2+}]$ / (μM)
3.0
2.4
1.8
1.2
0.6
0.0
0
10
20
30
40
50
60

Fig. S4.

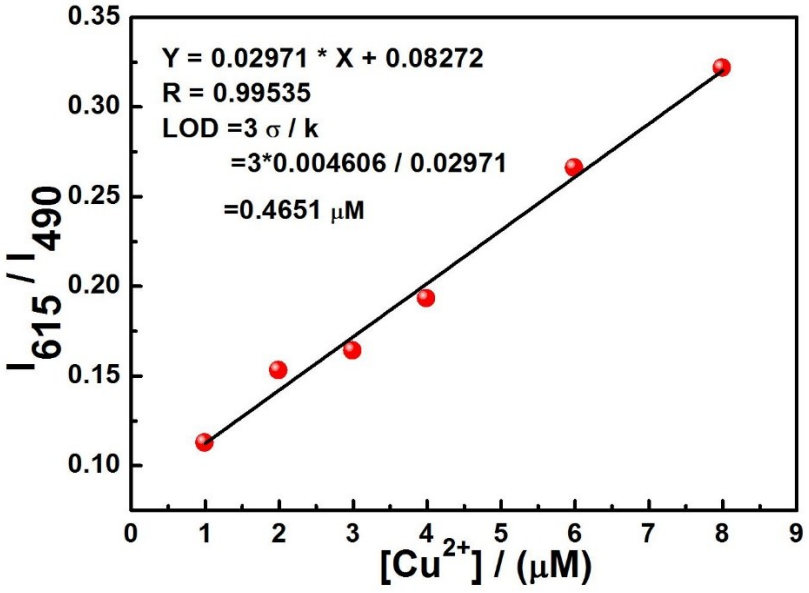
Y = 0.02971 * X + 0.08272
R = 0.99535
LOD =3 σ / k
=3*0.004606 / 0.02971
=0.4651 μM
I615 / I490
[Cu2+] / (μM)
0.35
0.30
0.25
0.20
0.15
0.10
0
1
2
3
4
5
6
7
8
9

Fig. S5.

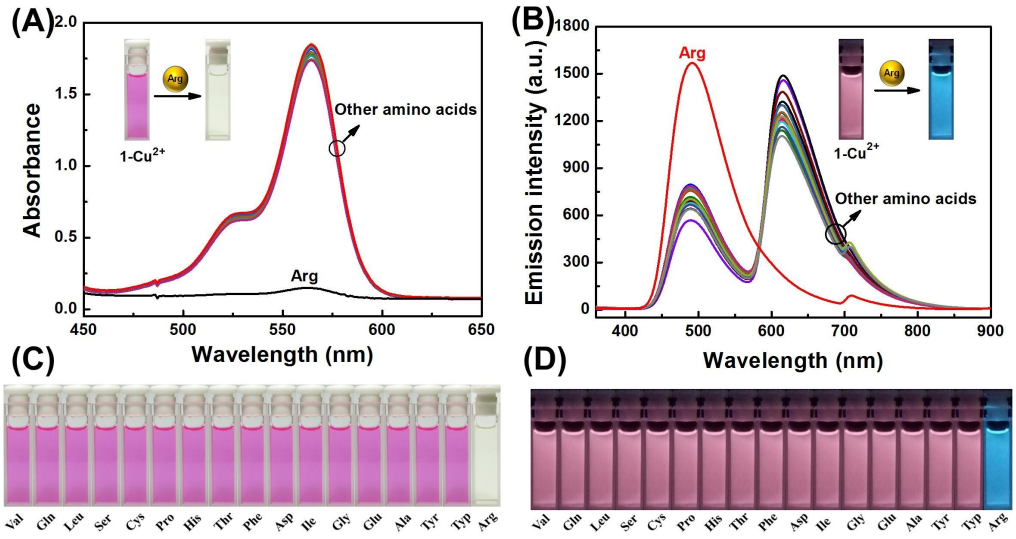
(A)
Absorbance
Wavelength (nm)
Other amino acids
Arg
1-Cu2+
(B)
Emission intensity (a.u.)
Wavelength (nm)
Arg
Other amino acids
1-Cu2+
(C)
(D)
Val Gln Leu Ser Cys Pro His Thr Phe Asp Ile Gly Glu Ala Tyr Typ Arg

Fig. S6.

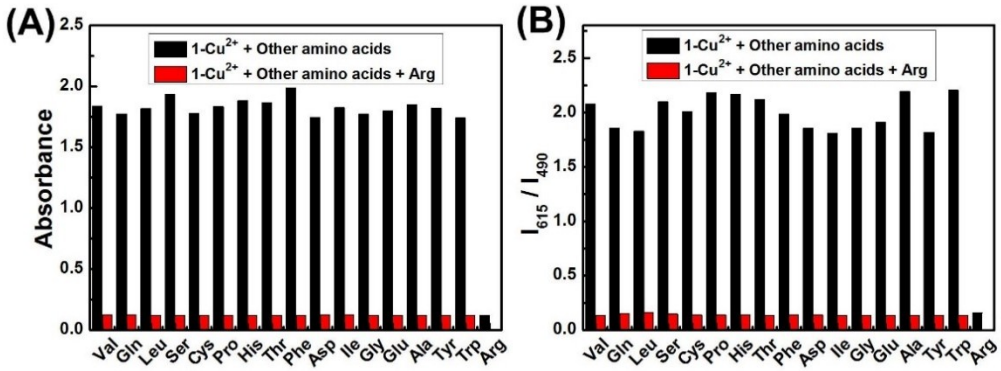
(A)
Absorbance
1-Cu2+ + Other amino acids
1-Cu2+ + Other amino acids + Arg
0.0
0.5
1.0
1.5
2.0
2.5
Val Gln Leu Ser Cys Pro His Thr Phe Asp Ile Gly Glu Ala Tyr Trp Arg
(B)
I615 / I490
1-Cu2+ + Other amino acids
1-Cu2+ + Other amino acids + Arg
0.0
0.5
1.0
1.5
2.0
2.5
Val Gln Leu Ser Cys Pro His Thr Phe Asp Ile Gly Glu Ala Tyr Trp Arg

Fig. S7.

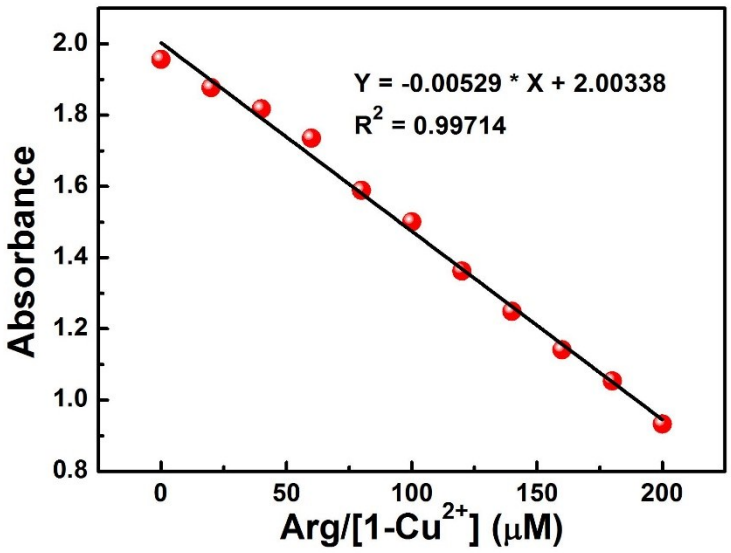
Y = -0.00529 * X + 2.00338
R2 = 0.99714
Absorbance
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0
50
100
150
200
Arg/[1-Cu2+] (μM)

Fig. S8.

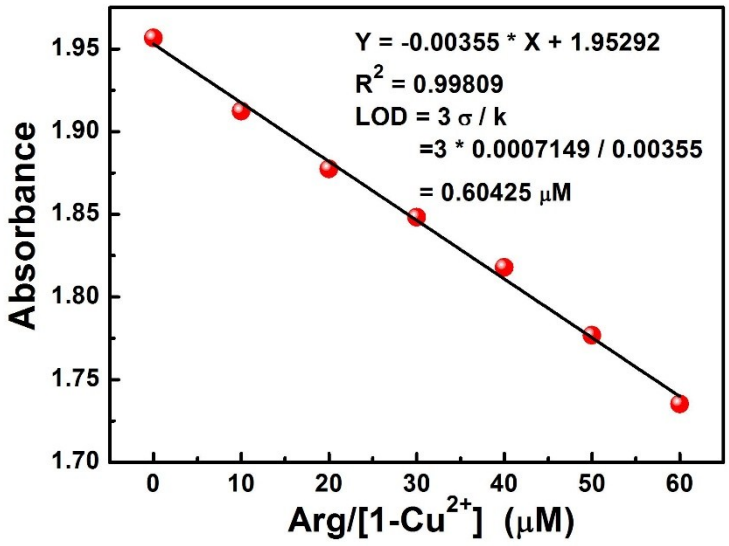
Y = -0.00355 * X + 1.95292
R2 = 0.99809
LOD = 3 σ / k
=3 * 0.0007149 / 0.00355
= 0.60425 μM
Absorbance
1.95
1.90
1.85
1.80
1.75
1.70
0
10
20
30
40
50
60
Arg/[1-Cu2+] (μM)

Fig. S9.

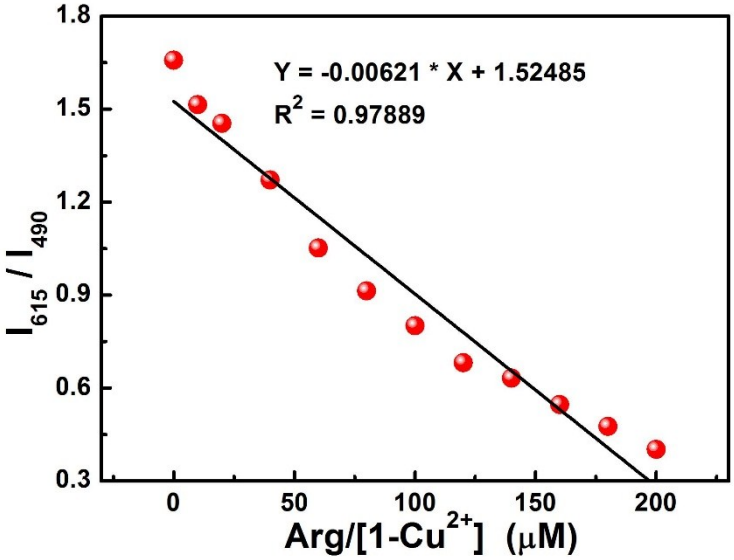
Y = -0.00621 * X + 1.52485
R2 = 0.97889
I615 / I490
Arg/[1-Cu2+] (μM)
1.8
1.5
1.2
0.9
0.6
0.3
0
50
100
150
200

Fig. S10.

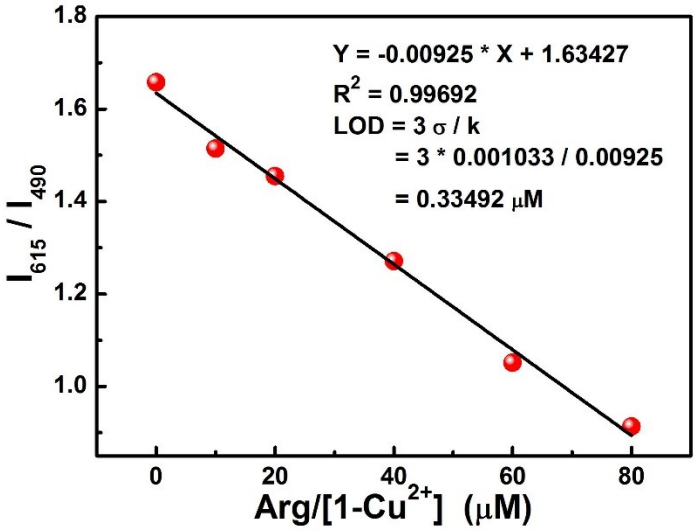
Y = -0.00925 * X + 1.63427
R2 = 0.99692
LOD = 3 σ / k
= 3 * 0.001033 / 0.00925
= 0.33492 μM
I615 / I490
Arg/[1-Cu2+] (μM)
1.8
1.6
1.4
1.2
1.0
0
20
40
60
80

Fig. S11.

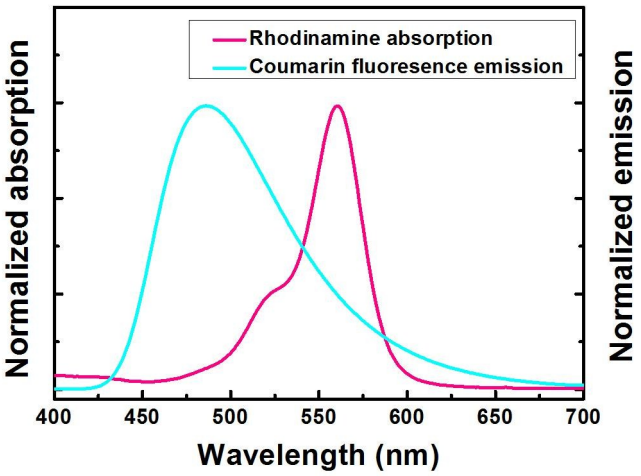
Rhodinamine absorption
Coumarin fluoresence emission
Normalized absorption
Normalized emission
400
450
500
550
600
650
700
Wavelength (nm)

Fig. S12.

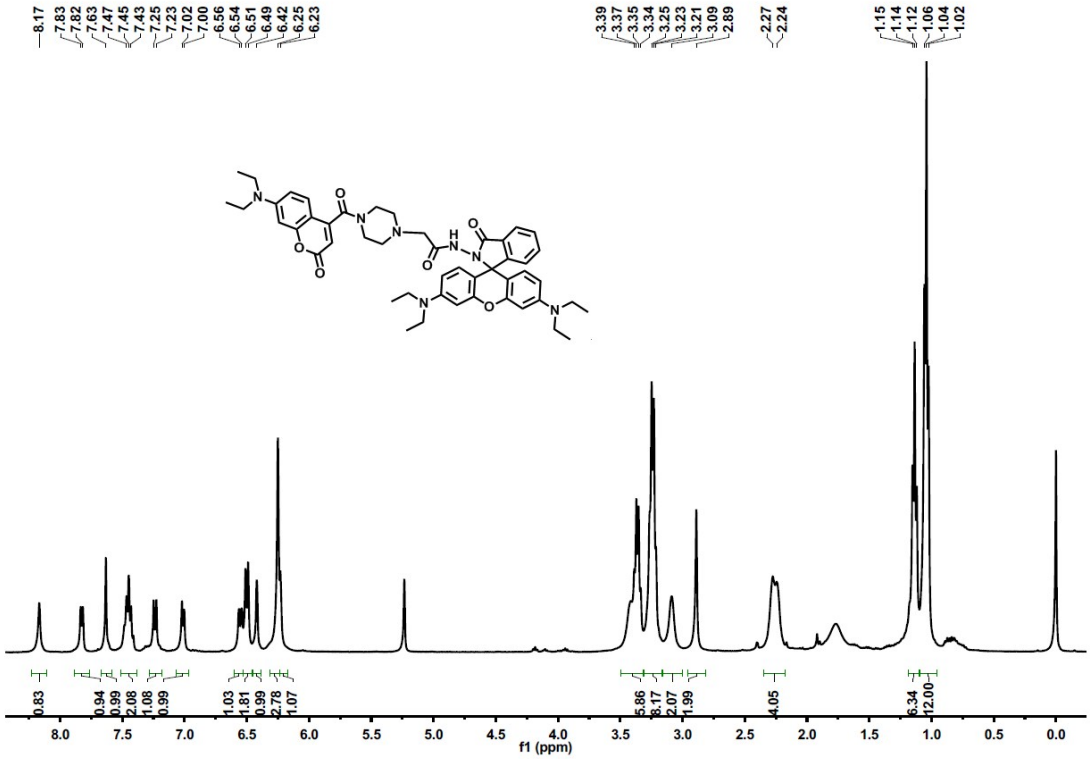
8.17
7.83
7.82
7.63
7.47
7.45
7.43
7.25
7.23
7.02
7.00
6.56
6.54
6.51
6.49
6.42
6.25
6.23
3.39
3.37
3.35
3.34
3.25
3.23
3.21
3.09
2.89
2.27
2.24
1.15
1.14
1.12
1.06
1.04
1.02
0.83
0.94
0.99
2.08
1.08
0.99
1.03
1.81
0.99
2.78
1.07
5.86
6.17
2.07
1.99
4.05
6.34
12.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Fig. S13.

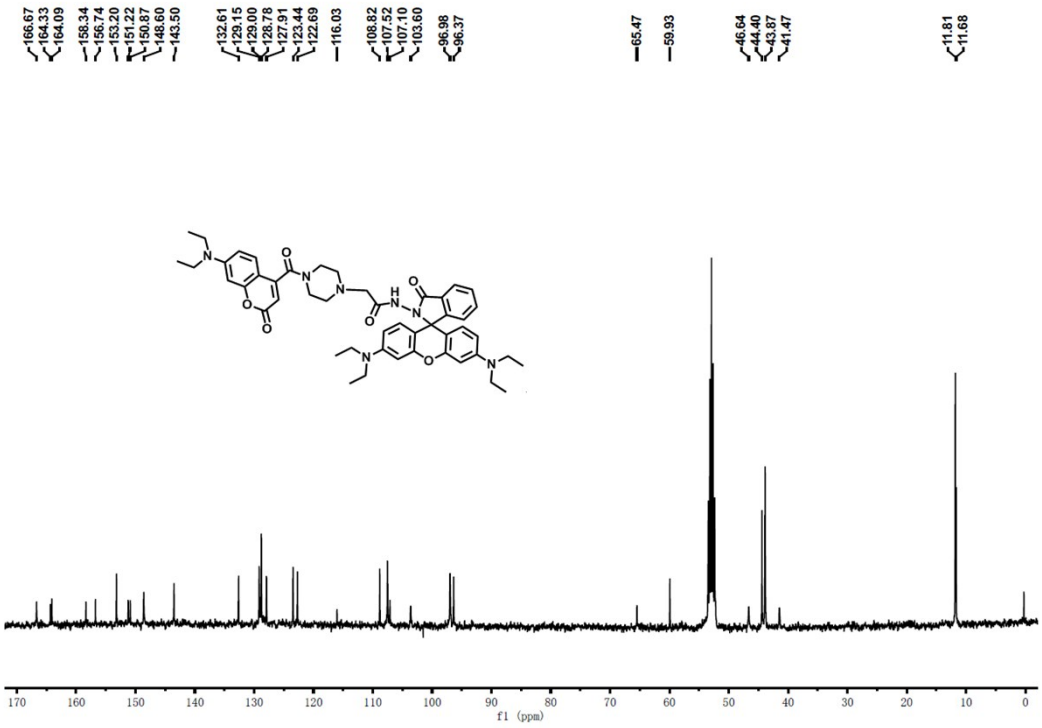
166.67
164.33
164.09
158.34
156.74
153.20
151.22
150.87
148.60
143.50
132.61
129.15
129.00
128.78
127.91
123.44
122.69
116.03
108.82
107.52
107.10
103.60
96.98
96.37
65.47
59.93
46.64
44.40
43.87
41.47
11.81
11.68
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Fig. S14.

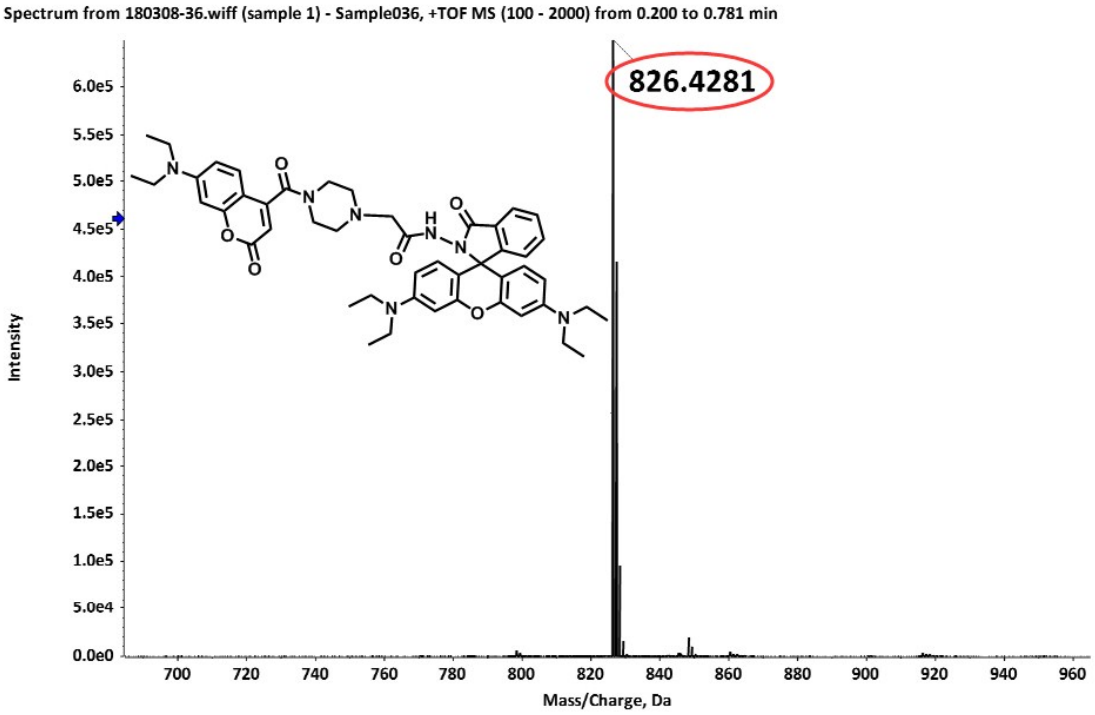
Spectrum from 180308-36.wiff (sample 1) - Sample036, +TOF MS (100 - 2000) from 0.200 to 0.781 min
826.4281
Intensity
6.0e5
5.5e5
5.0e5
4.5e5
4.0e5
3.5e5
3.0e5
2.5e5
2.0e5
1.5e5
1.0e5
5.0e4
0.0e0
700
720
740
760
780
800
820
840
860
880
900
920
940
960
Mass/Charge, Da

Fig. S15.