Supplementary Material (ESI) for Organic & Biomolecular Chemistry

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A Red-shift Colorimetric and Fluorescent Sensor for Cu^{2+} in Aqueous Solution: Unsymmetrical 4,5-Diaminonaphalimide with N-H Deprotonaton Induced by Metal Ion

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S1. Reagents and general methods

1.1 Reagents

All the reagents and solvents were commercial available and used without purification. ^{1}H-NMR spectra were collected in CDCl3 at 25 °C on a Bruker AV-400 spectrometer. Electrospray ionization (ESI) spectroscopy was performed in Mass Instrumentation Facility of Analysis&Research Center of ECUST.

UV-vis spectra were obtained using a Varian Cary 100 spectrophotometer (1 cm quartz cell) at room temperature; Fluorescence spectra were obtained using a Varian Cary Eclipse fluorescent spectrophotometer (1 cm quartz cell) at room temperature; Melting points were determined by using an Büchi Melting point B-540 apparatus (uncorrected when using); pH was measured with a Sartorius pH-Meter PB-20.

The metal salts employed are $LiClO_4$, $NaClO_4$, $KClO_4$, $Mg(ClO_4)_2$, $Cd(ClO_4)_2{\cdot}6H_2O$, $Hg(ClO_4)_2{\cdot}3H_2O$, $Mg(ClO_4)_2$, $Cr(ClO_4)_3{\cdot}6H_2O$, $FeCl_3$, $FeSO_4{\cdot}7H_2O$, $Zn(ClO_4)_2{\cdot}6H2O$, $AgClO_4{\cdot}H_2O$, $Co(ClO_4)_2{\cdot}6H_2O$, $Mn(ClO_4)_2{\cdot}6H_2O$, $Cu(ClO4)_2{\cdot}6H_2O$, $Ni(ClO_4)_2{\cdot}6H_2O$, and $Pb(ClO_4)_2{\cdot}3H_2O$, respectively.

Metal ions and sensors were dissolved in water or ethanol to obtain 1 mM stock solutions.

1.2 Association Constants and Curve fitting

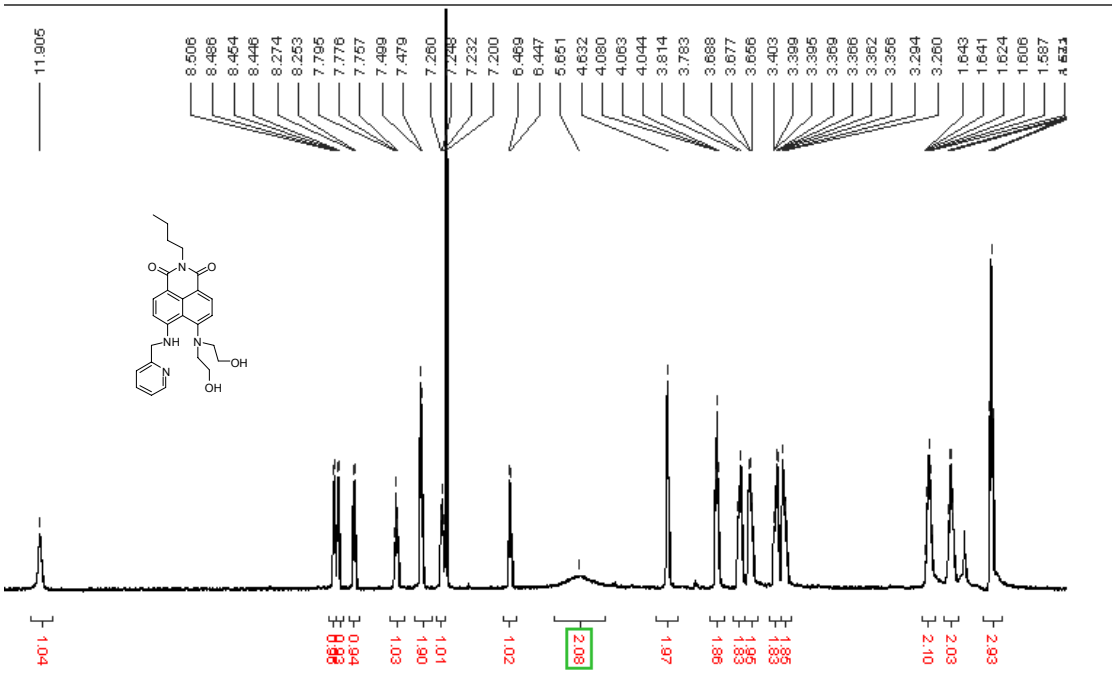
The following equation was used for the nonlinear least squares analysis to determine the binding constant (Ka):

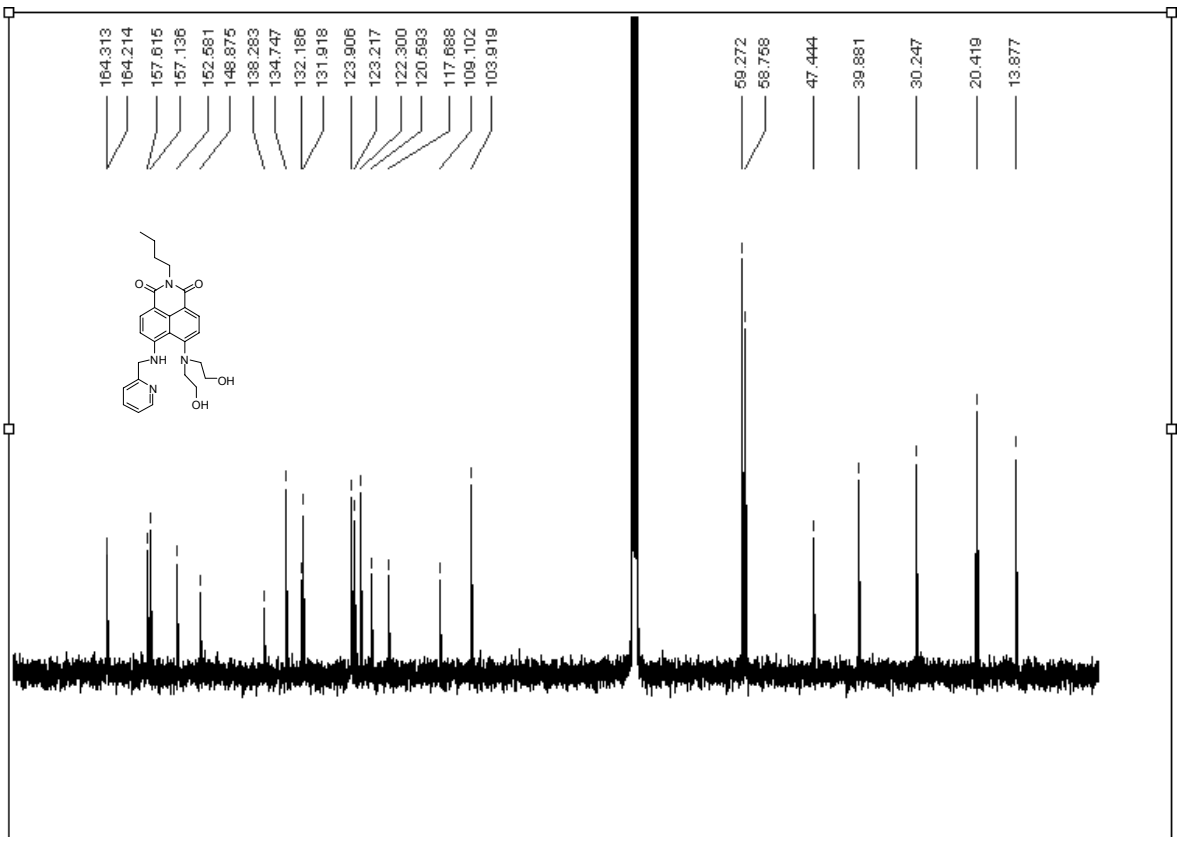
$$Y = Y_0 + \frac{Y_{\lim} - Y_0}{2}\left\{1 + \frac{c_M}{c_L} + \frac{1}{K_s c_L} - \left[\left(1 + \frac{c_M}{c_L} + \frac{1}{K_s c_L}\right)^2 - 4\frac{c_M}{c_L}\right]^{1/2}\right\}$$

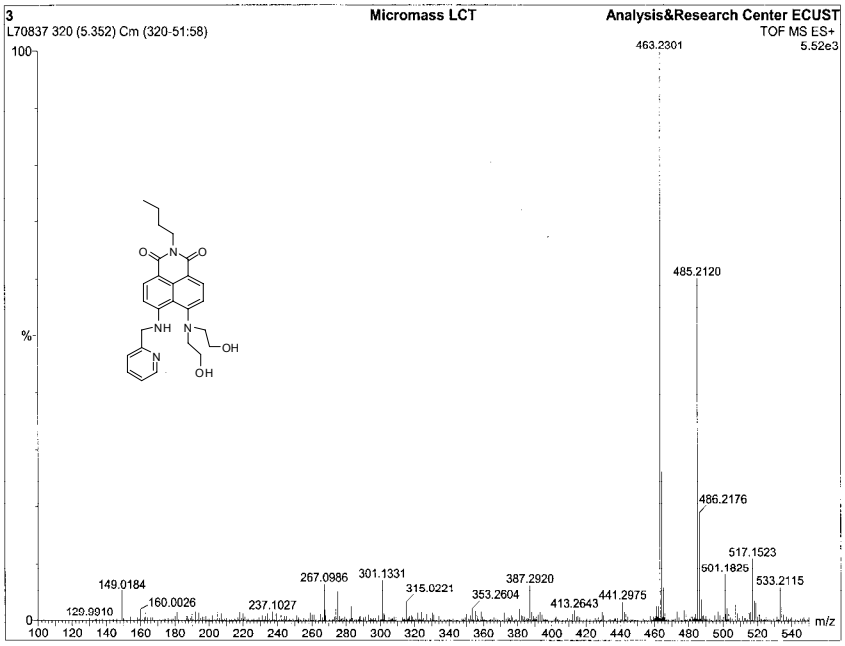
Here, Y was the recorded fluorescent intensity, Y_0 was the start value without the addition of Cu^{2+} ion, Y_{lim} was the limiting value (left as a floating parameter), C_M was the Cu^{2+} concentration, and C_L was the sensor concentration. (B. Valeur, *Moleucular Fluorescence: Principle and Applications*, Wiley-VCH, Germany, 2002)

S2 Spectra (^{1}HNMR, ^{13}CNMR, HRMS) of H1

6-(bis(2-hydroxyethyl)amino)-2-butyl-7-(pyridin-2-ylmethylamino)-1H-benzo[de]isoquinoline-1,3(2H)-dione






3
Micromass LCT
Analysis&Research Center ECUST
L70837 320 (5.352) Cm (320-51:58)
TOF MS ES+
5.52e3
100
%
0
463.2301
485.2120
486.2176
517.1523
501.1825
533.2115
149.0184
160.0026
129.9910
237.1027
267.0986
301.1331
315.0221
353.2604
387.2920
413.2643
441.2975
m/z
100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540

S3. The ESI(+)-Ms of H1 and Cu^{2+} (equimolar H1/Cu2+, 2 μM/2 μM) in water/ethanol (9/1) solution.

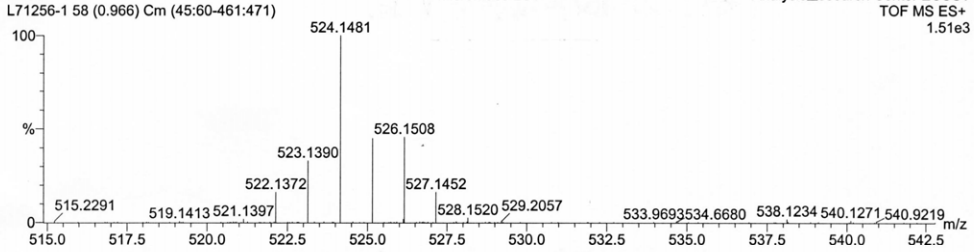
Elemental Composition Report Page 1

Multiple Mass Analysis: 6 mass(es) processed
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
40 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)

H1Cu
L71256-1 58 (0.966) Cm (45:60-461:471)

Micromass LCT
AnalysisResearch Center ECUST
TOF MS ES+
1.51e3



Minimum:	10.00				-1.5		
Maximum:	100.00		5.0	5.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
522.1372	16.17	---					
523.1390	33.06	---					
524.1481	100.00	524.1485	-0.4	-0.7	14.5	n/a	12C26 1H29 14N4 16O4 63Cu
525.1519	44.93	525.1518	0.1	0.1	14.5	n/a	12C25 13C 1H29 14N4 16O4 63Cu
526.1508	*45.54*	*526.1467*	*4.1*	*7.8*	*14.5*	*n/a*	*12C26 1H29 14N4 16O4 65Cu*
527.1452	16.17	527.1500	-4.8	-9.2	14.5	n/a	12C25 13C 1H29 14N4 16O4 65Cu

S4. Influence of pH on the absorption spectra of H1/Cu^{2+} adduct

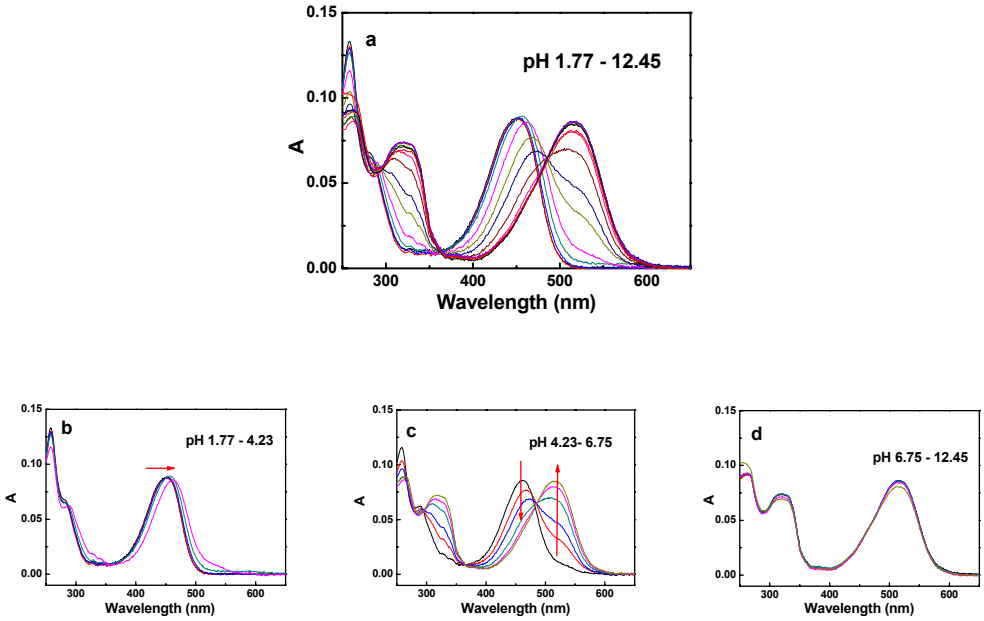


Fig. S4. (a). Influence of pH on the absorption spectra of **H1**/Cu^{2+} adduct (5 μM **H1** and 5 μM Cu^{2+}) in ethanol-water solutions (1/9, v/v). (b) Influence of pH from 1.77 to 4.23. (c) Influence of pH from 4.23 to 6.75. d) Influence of pH from 6.75 to 12.45.

S5. Influence of pH on the fluorescent spectra of H1/Cu^{2+} adduct

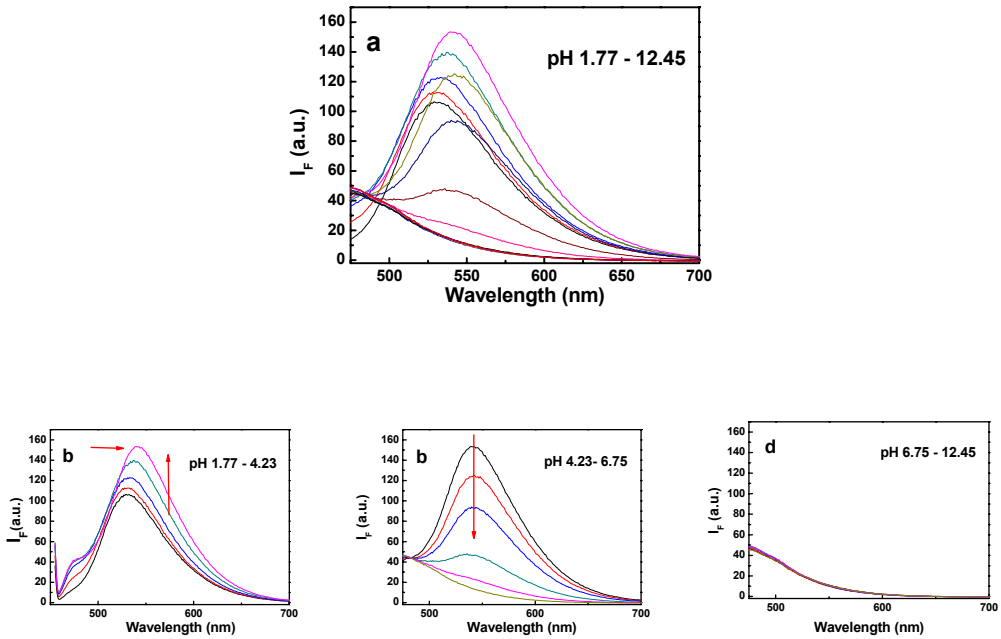


Fig. S5. (a) Influence of pH on fluorescent spectra of **H1**/Cu^{2+} adducts (5 μM **H1** and 5 μM Cu^{2+}) in ethanol-water solutions (1/9, v/v). (b) Influence of pH from 1.77 to 4.23. (c) Influence of pH from 4.23 to 6.75. (d) Influence of pH from 6.75 to 12.45.

S6. Cu^{2+}-titration at pH 11.59 in aqueous ethanol (ethanol/water = 1/9) solution

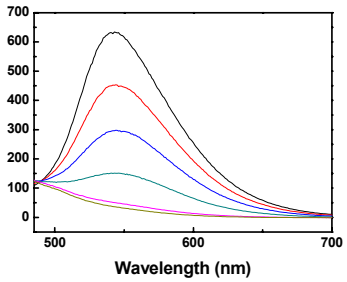


Fig. S6. Cu^{2+} ion titration-induced the fluorescent spectra changes of sensor **H1** (10 μM) at **pH11.59** in aqueous ethanol (ethanol/water = 1/9) solution (Cu^{2+} amount was 0.25 , 0.5, 0.75, 1.0 equiv respectively).