Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Borondipyrromethene-derived Cu^{2+} sensing chemodosimeter for fast and selective detection

Chunchang Zhao, Peng Feng, Jian Cao, Xuzhe Wang, Yang Yang, Yulin Zhang, Jinxing Zhang, Yanfen Zhang*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, P. R. China; Tel: +86-21-64252388; E-mail: zhaocchang@ecust.edu.cn

General Methods

All chemical reagents and solvents for synthesis were purchased from commercial suppliers and were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer with chemical shifts reported in ppm at room temperature. Mass spectra were measured on a HP 1100 LC-MS spectrometer.

UV-vis absorption spectra were recorded on a Varian Cary 100 spectrophotometer. Fluorescence spectra were measured with a Varian Cary Eclipse Fluorescence spectrophotometer. Spectral-grade solvents were used for measurements of UV-vis absorption and fluorescence.

Fluorometric measurements. A stock solution of probe (5×10^{-3} M) was prepared in DMSO. The test solutions of probe (5μM) in H_2O/DMSO buffer solution (0.05 M Tris-HCl, 50% DMSO, pH = 7.5) were prepared by placing 3 μL of the stock solution, 3 mL H_2O/DMSO buffer solution into a quartz cell.

Preparation of Cells. HEK293A cells were cultured in Dulbecco's modified Eagle's medium (DMEM) (GIBCO), supplemented with 10% fetal bovine serum (HyClone), at 37 °C in a 5/95 CO_2/air incubator.

For fluorescence imaging, cells were passed on a 24-well plate (3×10^4 cells per well) and incubated for 24 h. Copper uptake experiments were performed in the same medium for 30 min at 37°C. Then cells were washed with PBS buffer, incubated with 5 μM **BODIPY-EP** in culture medium containing 10% DMSO for 30 min at 37 °C, washed with PBS, and mounted on the microscope stage. The cell images were collected with a fluorescence microscope (OLYMPUS) with a 530-550 nm filter.

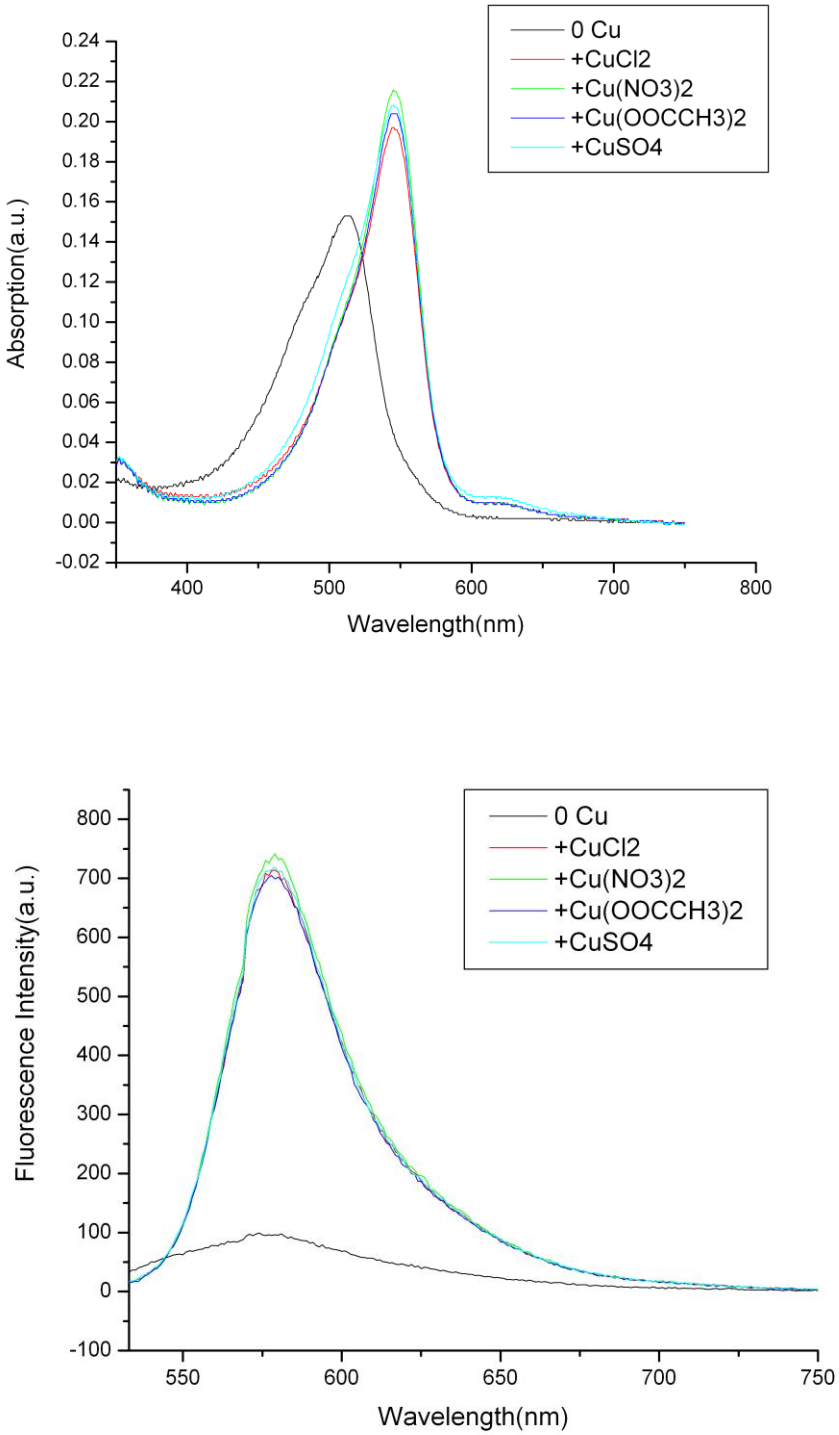


Figure S1. Spectra of **BODIPY-EP** (5×10^{-6} M) in the presence 6equiv of Cu^{2+} with different counter anions in H_2O/DMSO buffer solution (0.05 M Tris-HCl, 50% DMSO, pH = 7.5). (up) Absorption spectra. (bottom) Fluorescence titration spectra (λ_{ex} = 523 nm).

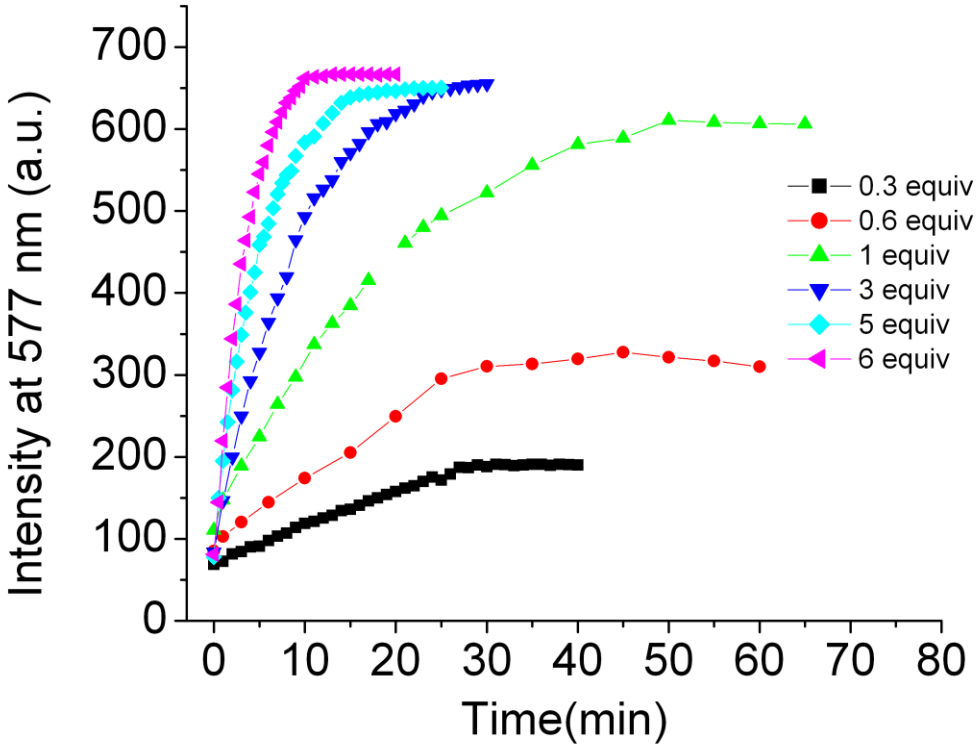


Figure S2. Kinetics of fluorescence enhancement profile of **BODIPY-EP** (5 μM) at 577 nm in the presence of various concentrations of Cu^{2+}. The experiment was carried out in H_2O/DMSO buffer solution (0.05 M Tris-HCl, 50% DMSO, pH = 7.5) at room temperature. λ_{ex} = 523 nm. The observed rate constant is calculated to be: $K_{0.3equiv}$ = 0.071, $K_{0.6equiv}$ = 0.068, K_{1equiv} = 0.06, K_{3equiv} = 0.138, K_{5equiv} = 0.206, K_{6equiv} = 0.372.

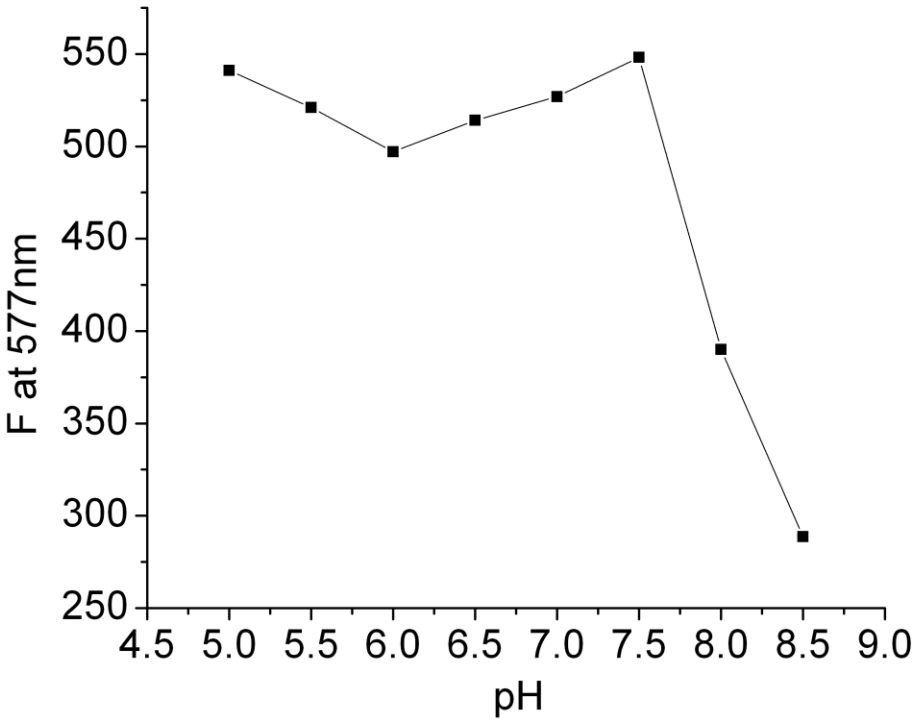
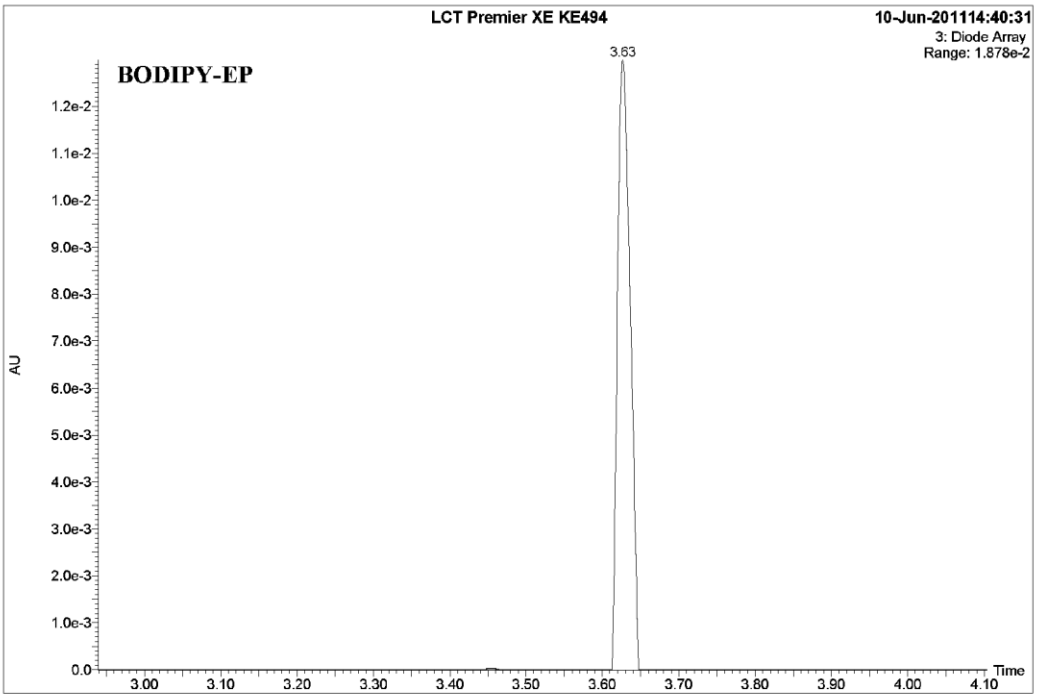


Figure S3. Fluorescence change of **BODIPY-EP** (5 μM) in intensity at 577 nm as function of pH. The experiment was carried out in H_2O/DMSO buffer solution (50% DMSO). λ_{ex} = 523 nm.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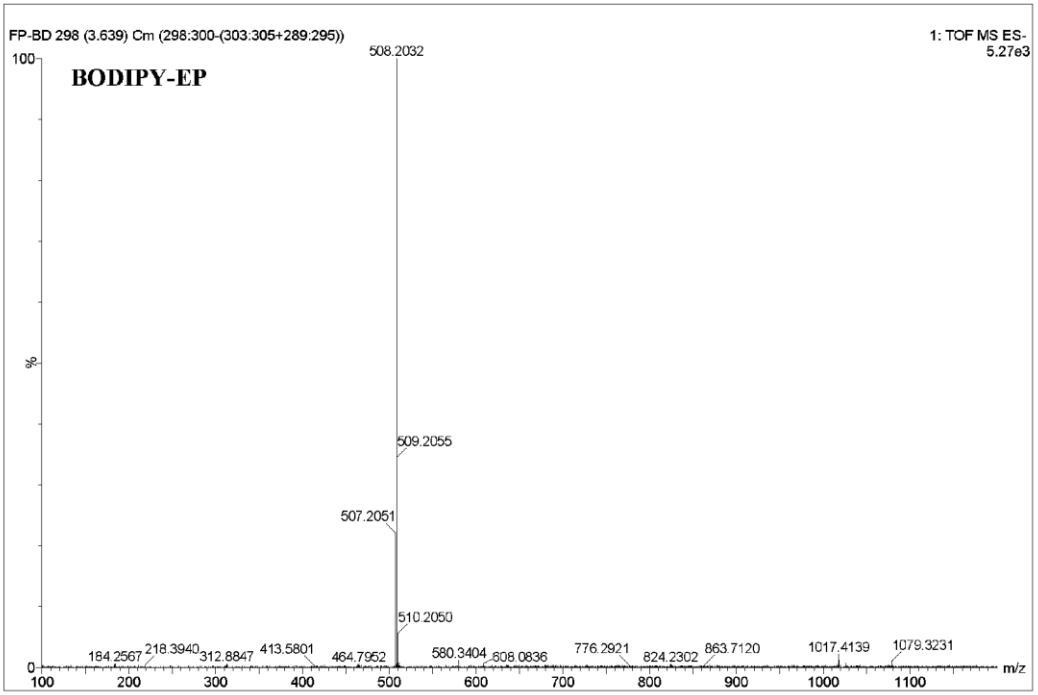
10-Jun-201114:40:31
3: Diode Array
Range: 1.878e-2
BODIPY-EP
3.63
AU
Time


FP-BD 298 (3.639) Cm (298:300-(303:305+289:295))
1: TOF MS ES-
5.27e3
BODIPY-EP
508.2032
509.2055
507.2051
510.2050
%
m/z

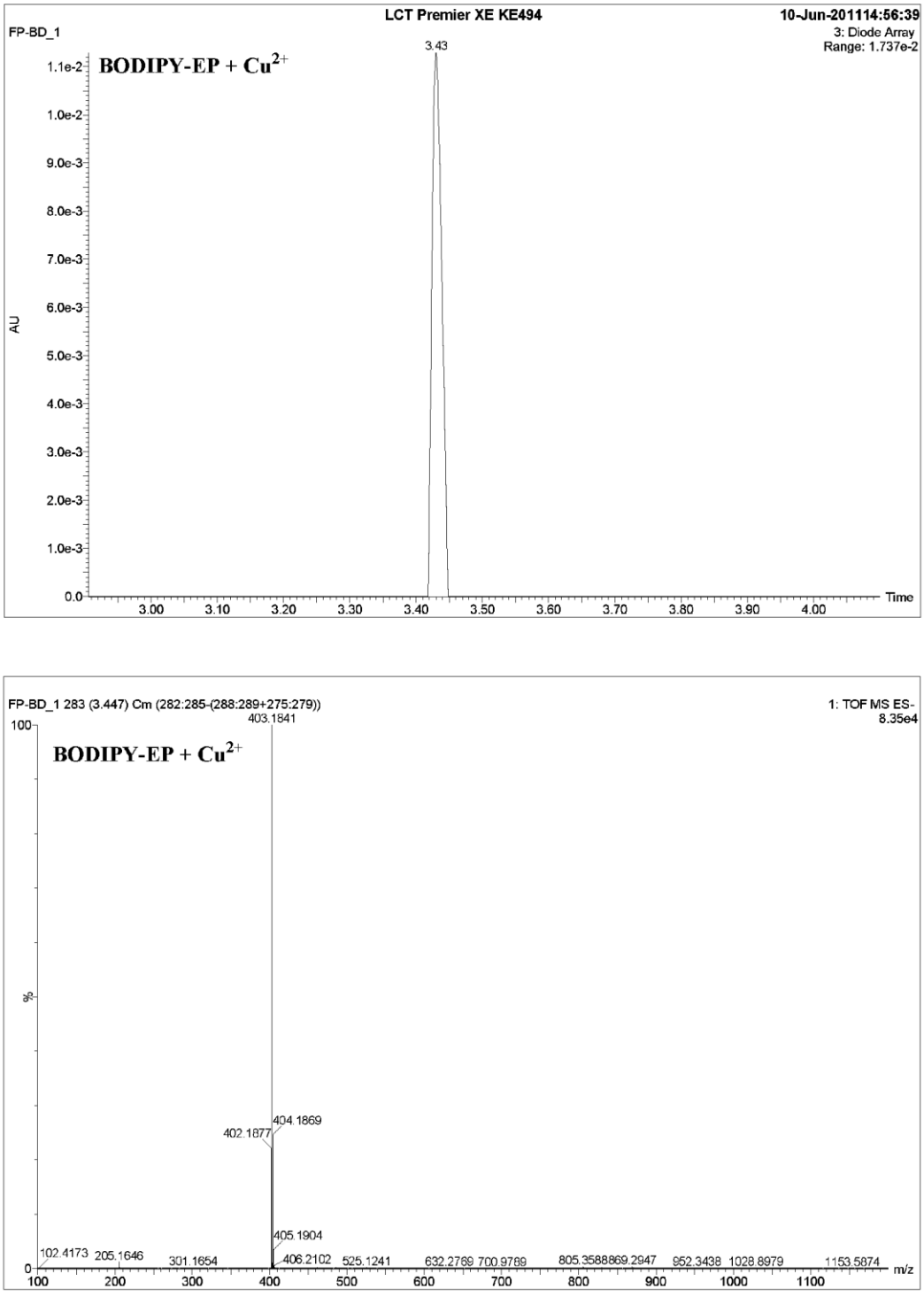


Figure S4. UPLC-Mass spectra of **BODIPY-EP** and **BODIPY-EPY** + $CuCl_2$.

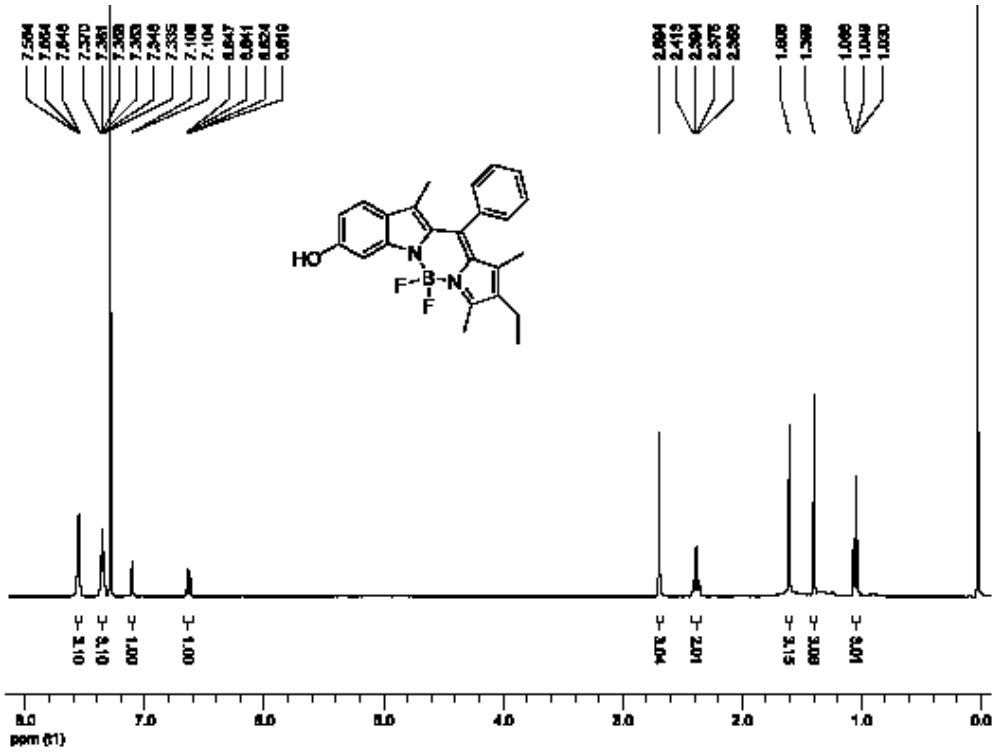


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **BODIPY-OH** from the reaction of **BODIPY-EP** with Cu^{2+} in H_2O/DMSO buffer solution.

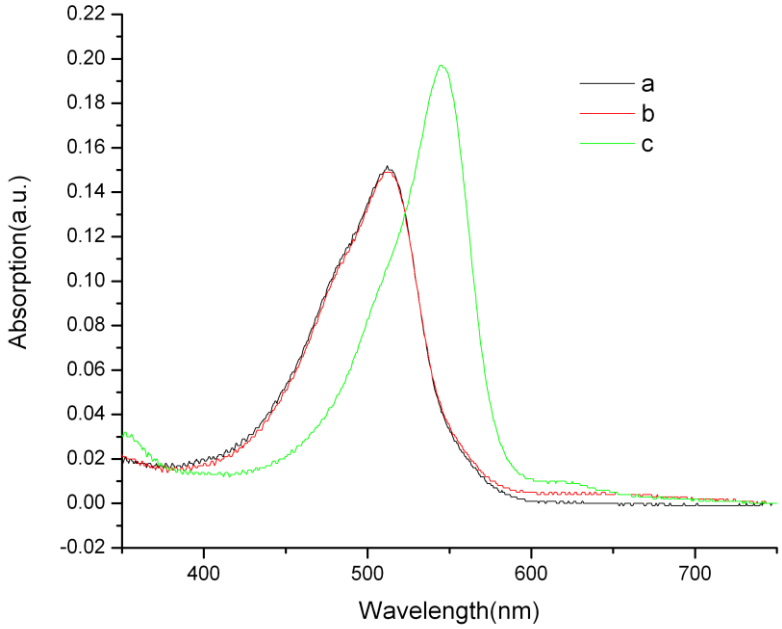


Figure S6. Absorption spectra of **BODIPY-EP** (5×10^{-6} M) in the absence and presence of 2-pyridinecarboxylic acid (PCA, 1000 equiv) upon addition of 6 equiv of Cu^{2+} in H_2O/DMSO buffer solution (0.05 M Tris-HCl, 50% DMSO, pH = 7.5). (a) **BODIPY-EP** only. (b) **BODIPY-EP** + PCA + Cu^{2+}. (c) **BODIPY-EP** + Cu^{2+}.

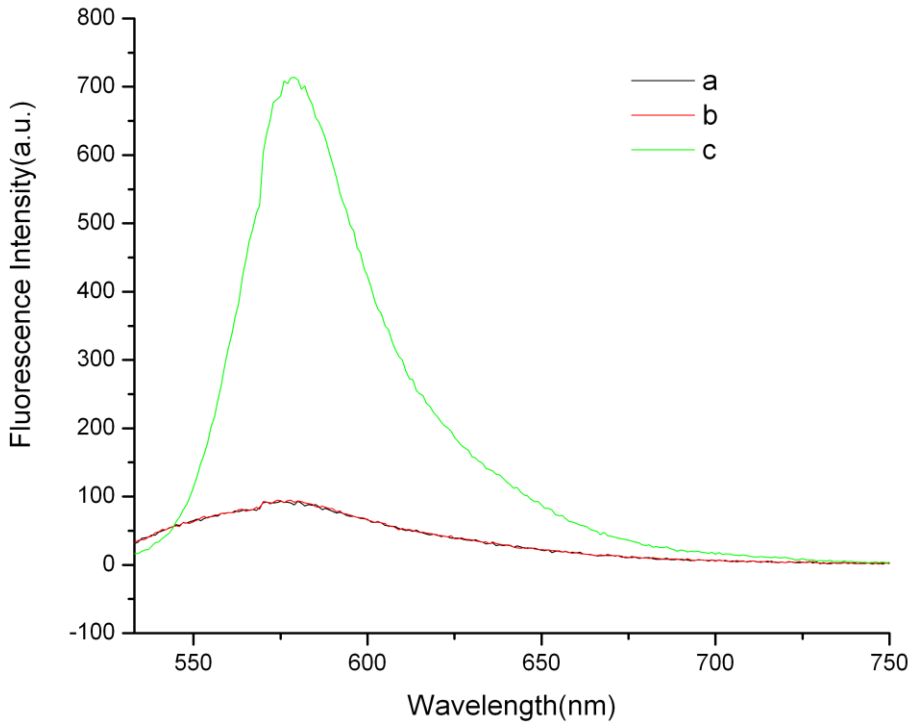


Figure S7. Fluorescnce spectra of **BODIPY-EP** (5×10^{-6} M) in the absence and presence of 2-pyridinecarboxylic acid (PCA, 1000 equiv) upon addition of 6equiv of Cu^{2+} in H_2O/DMSO buffer solution (0.05 M Tris-HCl, 50% DMSO, pH = 7.5). (a) **BODIPY-EP** only. (b) **BODIPY-EP** + PCA + Cu^{2+}. (c) **BODIPY-EP** + Cu^{2+}.

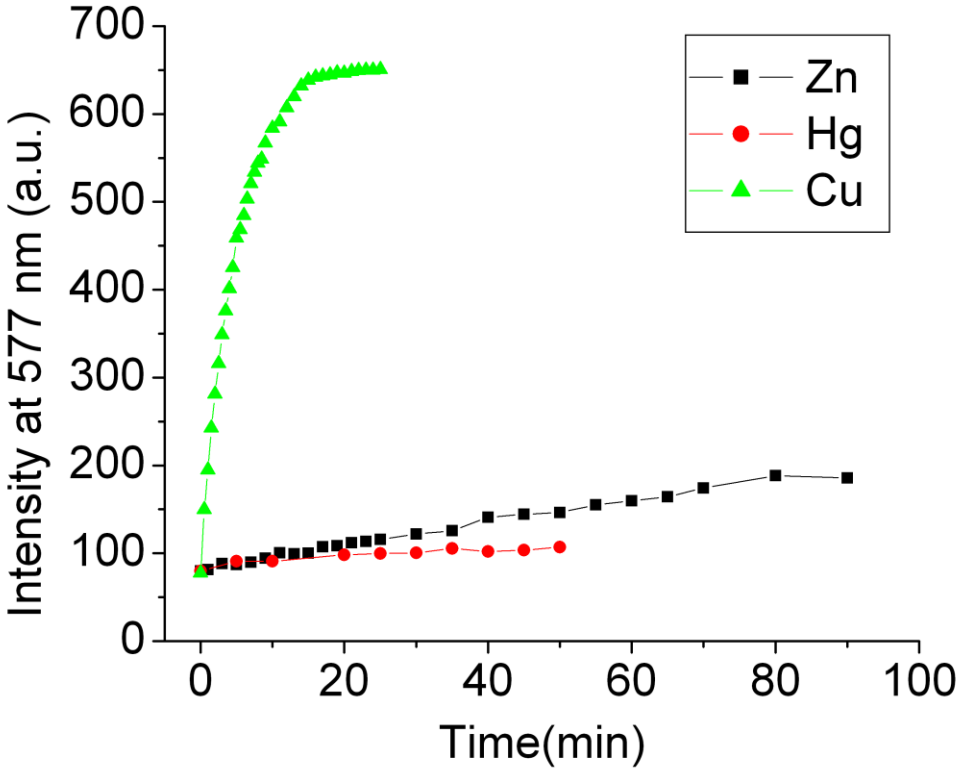


Figure S8. Kinetics of fluorescence enhancement profile of **BODIPY-EP** (5 μM) at 577 nm in the presence 6 equiv of Zn^{2+}, Hg^{2+}, Cu^{2+}. The experiment was carried out in H_2O/DMSO buffer solution (0.05 M Tris-HCl, 50% DMSO, pH = 7.5) at room temperature. λ_{ex} = 523 nm.

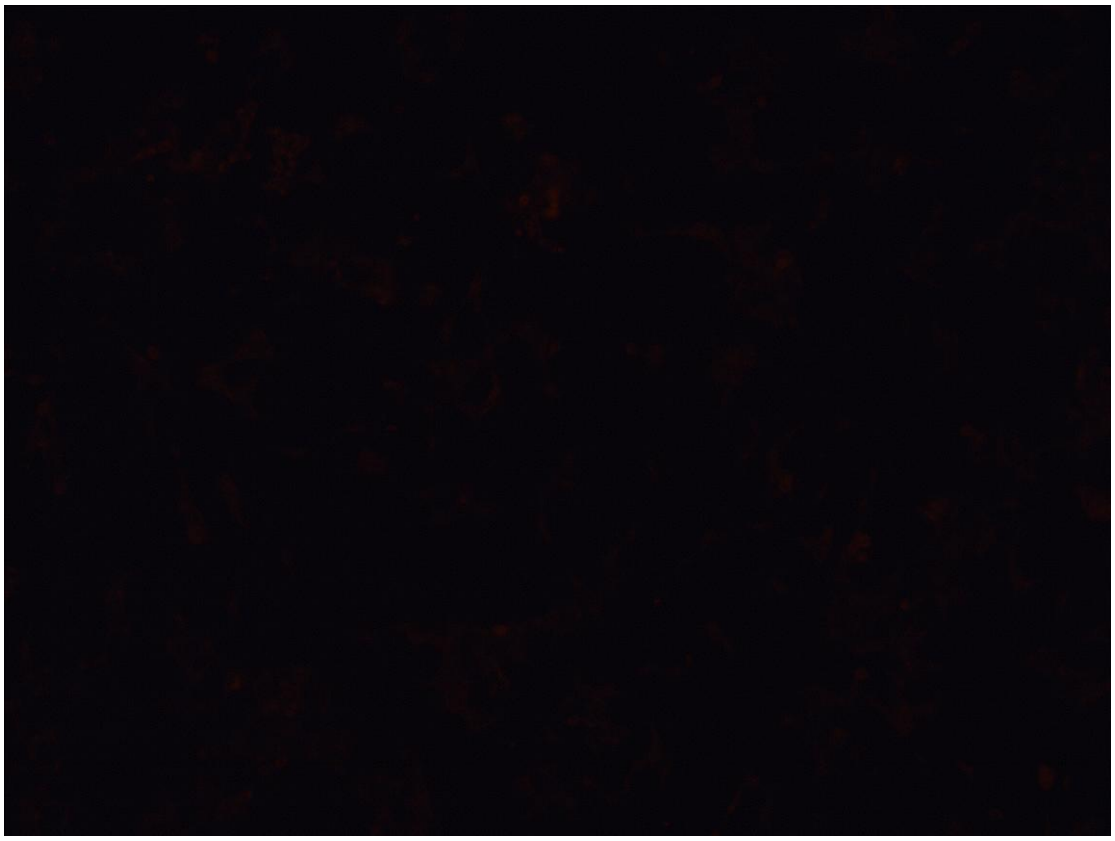


Figure S9. Fluorescence image of HEK293A cells incubated with 10 μM **BODIPY-EP** for 120 min.

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0.5ml/min 514 nm CH3cn

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Sample Name     : 0106                          Location : Vial 1
Acq. Operator   : ml
Acq. Instrument : Instrument 1
Method          : C:\HPCHEM\1\METHODS\JPW.M
Last changed    : 2012-1-7 17:29:37     by ml
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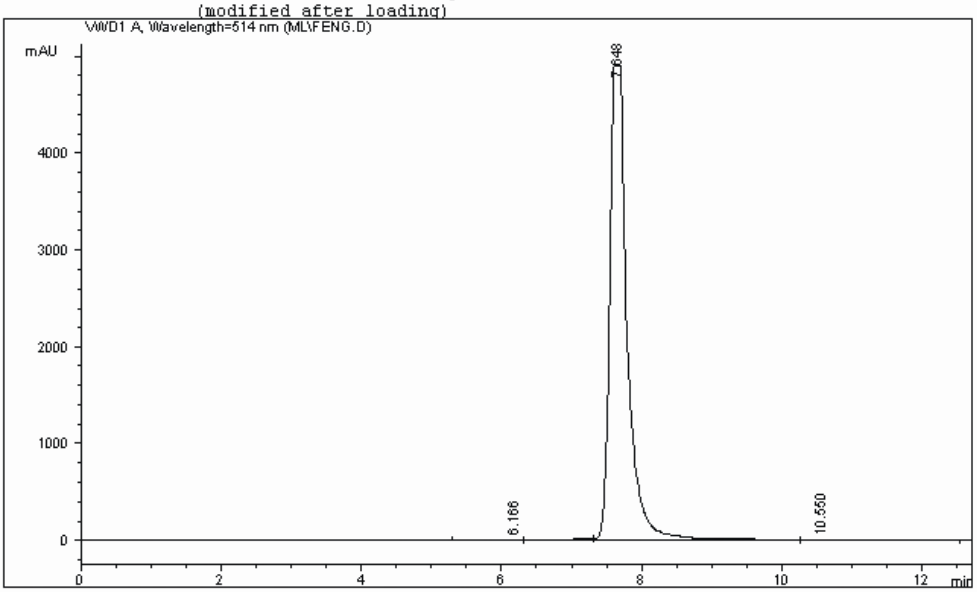


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==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      2.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=514 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.166 BV    0.3802  104.87571    3.49971   0.1207
   2   7.648 VB    0.2333 8.62643e4  4893.51172  99.2674
   3  10.550 BV    1.0141  531.73151    6.45074   0.6119

Totals :                  8.69009e4  4903.46217

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
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Instrument 1 2012-1-7 18:17:41 下午 ml Page 1 of 1

Figure S10. HPLC analysis of **BODIPY-EP**.