Electronic Supplementary Material (ESI) for RSC Advances

Electronic Supporting Information (ESI):

Multifunctional BODIPY derivatives to image cancer cells and sense copper(II) ions in living cells.

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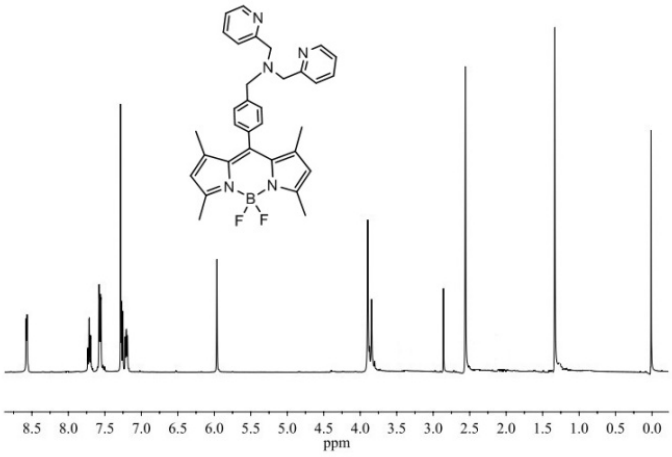

Fig. S1(a) ^{1}HNMR spectrum of 8-[di(2-picolyl)amine-4-benzyl]-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (**L1**) in chloroform ($CDCl_3$).

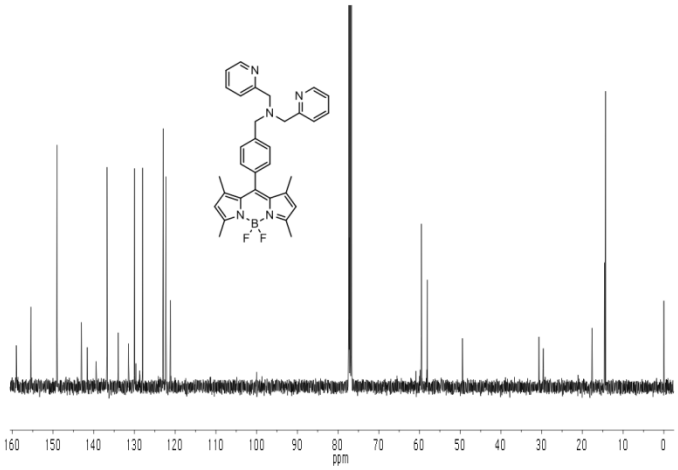

Fig. S1(b) ^{13}CNMR spectrum of 8-[di(2-picolyl)amine-4-benzyl]-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (**L1**) in chloroform ($CDCl_3$).

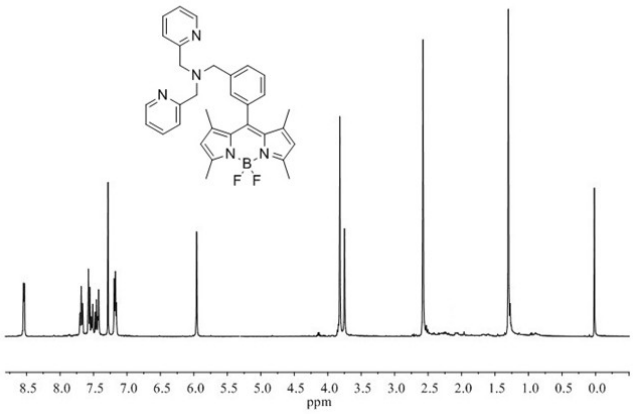

Fig.S2(a) ^{1}HNMR spectrum of 8-[di(2-picolyl)amine-3-benzyl]-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (**L2**) in chloroform ($CDCl_3$).

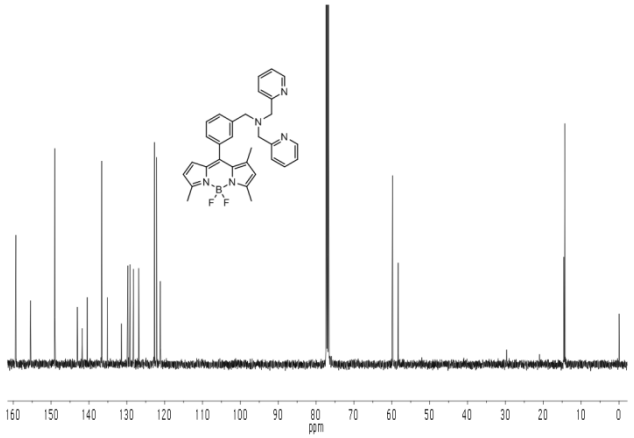

Fig.S2(b) ^{13}CNMR spectrum of 8-[di(2-picolyl)amine-3-benzyl]-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (**L2**) in chloroform ($CDCl_3$).

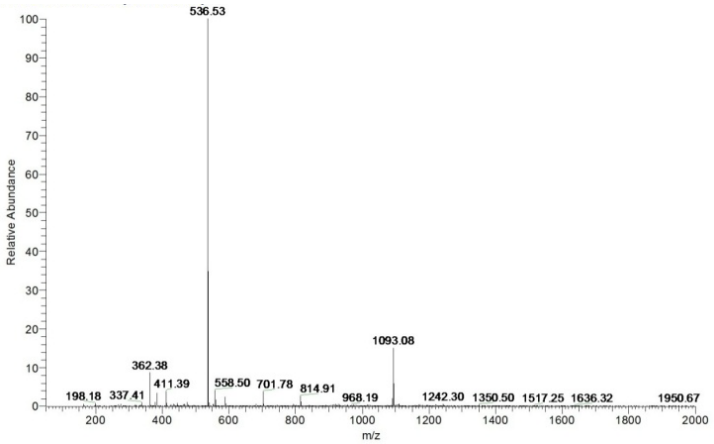

Fig. S3(a) ESI-MS spectrum of [**L1**+H^+], m/z=536.53.

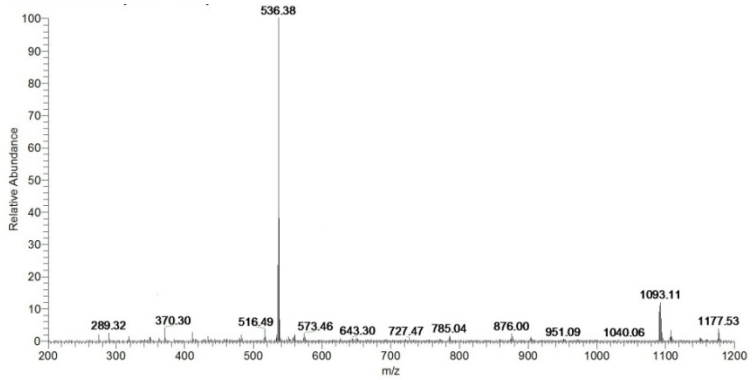

Fig. S3 (b) ESI-MS spectrum of [**L2**+H^+], m/z=536.38.

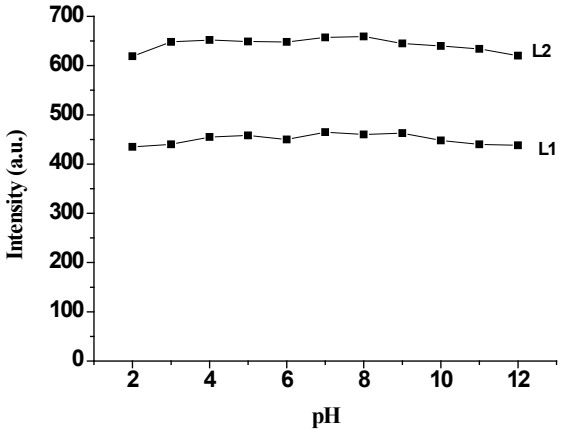

Fig. S4 Fluorescence intensities at 510 nm of **L1** and **L2** at various pH values. Tris-DMSO (pH 7.4, 9:1, v/v). λ_{ex}=460 nm. Slit width was 5 nm. All measurements were taken at 25 °C.

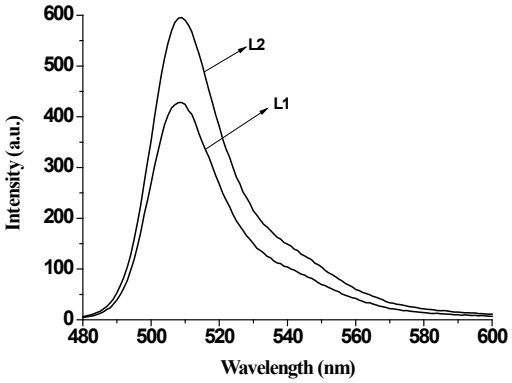

Fig. S5 Fluorescence spectra of probe **L1, L2** (2 μM) measured in Tris-DMSO (9:1, v/v) solution, λ_{ex}=460 nm. Measurements were taken at 25°C, Slit width was 5 nm.

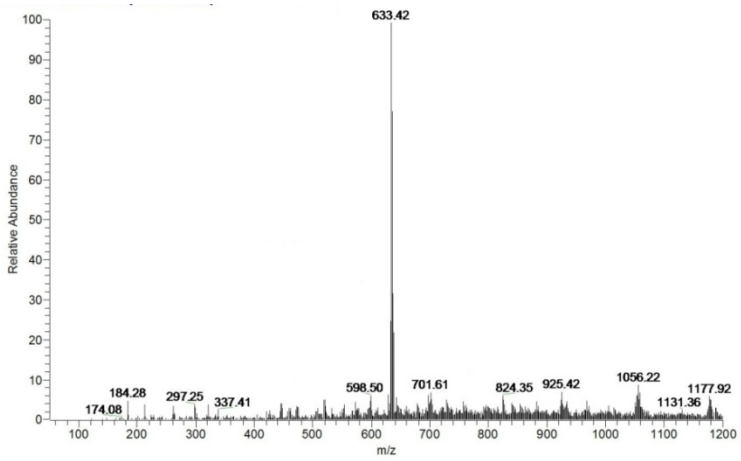

Fig. S6(a) ESI-MS spectrum of [**L1**+Cu^{2+}+Cl^{-}], m/z=633.42.

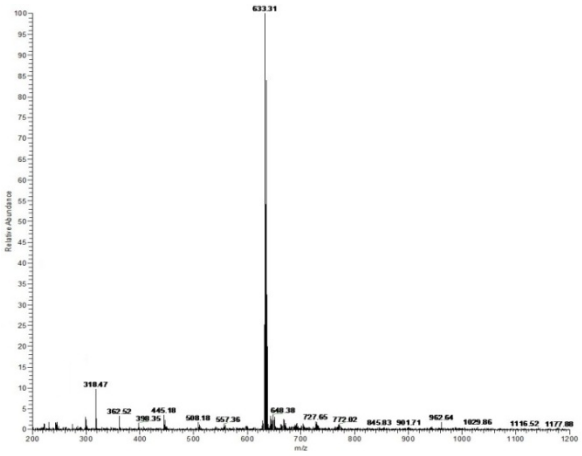

Fig. S6(b) ESI-MS spectrum of [**L2**+Cu^{2+}+Cl^{-}], m/z=633.31.

Determination of quantum yields [1]

Quantum yields were determined at 25°C, Fluorescein (Φ= 0.90) in 0.1 M NaOH was used as a standard. The absorption of standard was adjusted to the same value (abs < 0.1, 491nm) as that of probe L. Excitation was chosen at 460 nm; the emission spectra were corrected and integrated from 480 to 600 nm. The quantum yields were calculated with the following equation:

$$U_{sample} = U_{standard} \times \int_{emission\ sample} / \int_{emission\ standard}$$

Association constant[2]

The association constant was calculated from the emission intensity-titration curves according to the equation:

$$I_F^0/(I_F - I_F^0)=(1/f)[(1/K_S[M])+1]$$

Where I_F^0 is the emission intensity of probe L1 and L2 at 510 nm, I_F is the emission intensity of probe L at 510 nm upon the addition of different amount of Cu^{2+}, f is the fraction of the initial fluorescence which is accessible to the sensor, [M] is the concentration of Cu^{2+}. The association constant values K_S is given by the ratio intercept/slope.

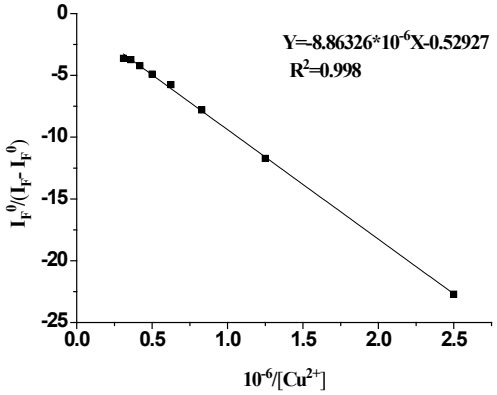

Fig. S7 Fitting of Fluorescence titration curve of **L1** in Tris-DMSO (9:1, v/v). The association constant is $Ks=5.97\times10^4\ M^{-1}$.

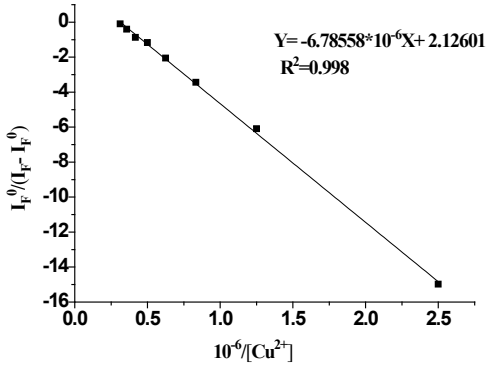

Fig. S8 Fitting of Fluorescence titration curve of **L2** in Tris-DMSO (9:1, v/v). The association constant is $Ks=3.13\times10^5\ M^{-1}$.

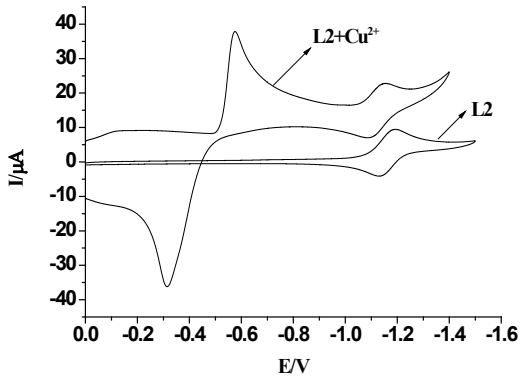

Fig.S9 Cyclic voltammogram of complex [**L2+Cu^{2+}**] in MeCN + 0.1 M Bu_4NClO_4 . Scan rate: 100 mV S^{-1}.

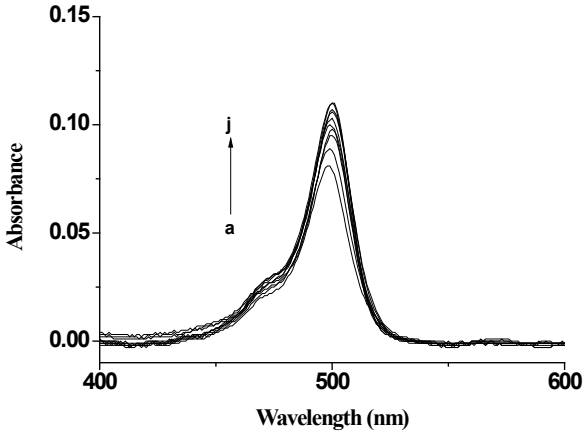

Fig. S10 UV-vis absorption spectra of probe **L2** (2 μM) in Tris-DMSO (9:1, v/v) solution with titration of Cu^{2+} (a-j: 0, 0.4 , 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 4.0 μM). All measurements were taken at 25°C, The data were recorded 1 min after Cu^{2+} was added.

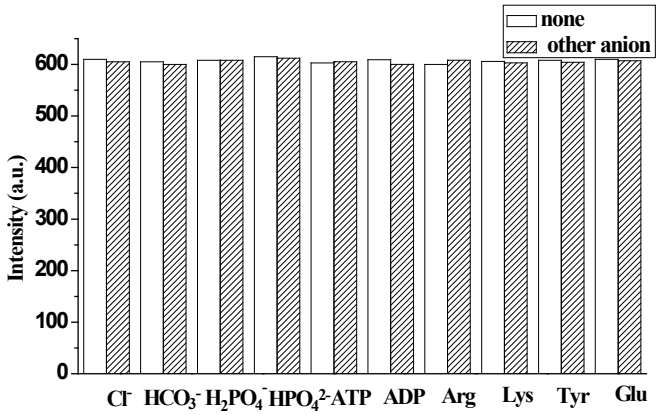

Fig. S11 Fluorescence of the chemosensor **L2** (2 μM) in the presence of important anions and molecules (2 μM) within cancer cells. Measured in Tris-DMSO (9:1, v/v) solution at 25°C, λ_{ex}=460 nm, Slit width was 5 nm.

Notes and references

1. J. N. Demas and G. A. Crosby, J. Phys. Chem., 1971, **75**, 991-1024.

2. F.-P. Hou, J. Cheng, P.-X. Xi, F.-J. Chen, L. Huang, G.-Q. Xie, Y.-J. Shi, Dalton Trans., 2012, **41**, 5799 -5804.