

Supporting information

A Schiff base sensor for relay monitoring In^{3+} and Fe^{3+} through an “off-on-off” fluorescence signals

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Experimental section

Materials

All metal salts such as MgCl_2 , CaCl_2 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 3\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, AgCl , $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, InCl_3 , $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, KCl , ZnCl_2 , HgCl_2 , LiCl and $\text{Ga}(\text{NO}_3)_3$ were analytical grade and used without further purification.

All other organic reagents were purchased and used as received.

Instruments

UV-vis spectra were recorded through a Shimadzu 3100 spectrometer.

Fluorescence measurements were carried out using an Edinburgh

Instruments Ltd-FLS920 fluorescence spectrophotometer Fluorescence measurements were performed when excitation at 410 nm. The slits of excitation and emission were 10 nm and 20 nm, respectively. ¹H NMR spectra were executed with a Bruker AV III 400 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal standard. ¹³C NMR spectral data were obtained using a Bruker AV III 100 MHz NMR spectrometer with tetramethylsilane (TMS) as the internal standard and DMSO as the solvent. Infrared spectral data were obtained using a Bruker Vertex 70 FT-IR spectrometer and samples as KBr pellets.

Sample preparation

All tests involved in this work were carried out with distilled water at room temperature (25 °C). In the experiments of titration with various metal ions, the sensor was dissolved in Tris DMF – H₂O (9 : 1, v/v) buffer solution to afford the test solution (1 × 10⁻⁵ M). Stock solutions (1 × 10⁻⁵ M) of KCl, AlCl₃, MgCl₂, CaCl₂, LiCl, FeCl₂, HgCl₂, NiCl₂, CuCl₂, ZnCl₂, AgCl, MnCl₂, FeCl₃, CoCl₂, CrCl₃, CdCl₂, InCl₃, Ga(NO₃)₃ were prepared at a concentration of 0.03 M with distilled water.

Calculation of quantum yield

The quantum yield of **LB2**, [**LB2**+In³⁺] and [**LB2**+Fe³⁺] were determined according to the following equation:

$$\phi_u = \phi_s \frac{F_u A_s n_u^2}{F_s A_u n_s^2}$$

where ϕ is quantum yield; F is integrated area under the corrected emission

spectra; A is the absorbance at the excitation wavelength; n is the refractive index of the solution; the subscripts u and s refer to the unknown and the standard, fluorescence respectively. Rhodamine B in ethanol solution was used as the standard, which has a quantum yield of 0.97.⁵⁹

Theoretical calculation

Density functional theory (DFT) structural optimizations were performed on the Gaussian 09 program. In all conditions, the structures were optimized via the B3LYP functional and the mixed basis sets 6-31G(d) and LANL2DZ. Each structure was subsequently subjected to TD-DFT calculation using the B3LYP functional soon afterwards. The absence of imaginary frequencies for all the optimized structures were confirmed through executing the frequency calculations. The molecular orbitals were visualized and plotted with the GaussView 09 program.⁶⁰

Synthesis of **LB2**

Compound **methyl 4,5-dihydronaphtho[1,2-*b*]thiophene-2-carboxylate(1)** and **4,5-dihydronaphtho[1,2-*b*]thiophene-2-carbohydrazide(2)** was synthesized according to the previous work.⁶¹⁻⁶²

Synthesize of *N'*-(3-ethoxy-2-hydroxybenzylidene)-4,5-dihydronaphtho[1,2-*b*]thiophene-2-carbohydrazide (LB2)

Compound **2** (25 mg, 0.1 mmol) and 3-ethoxy-2-hydroxybenzaldehyde (20 mg, 0.12 mmol) was mixed in ethanol (2 ml). The mixture was then stirred at room temperature overnight. The precipitate was filtered and washed

with ethanol to afford the target product (white solid). Yield: 25 mg, 64.9%.
ESI-MS: $m/z = 393.1388$ $[M + H]^+$. FTIR (KBr, cm^{-1}): 3128(N-H),
1400(C=N). ^1H NMR (400 MHz, DMSO) δ 11.93 (d, $J = 142.8$ Hz, 0H),
9.93 (d, $J = 655.0$ Hz, 0H), 8.57 (d, $J = 51.2$ Hz, 0H), 7.87 (d, $J = 40.6$ Hz,
1H), 7.47 (d, $J = 5.9$ Hz, 1H), 7.30 (dd, $J = 13.8, 6.3$ Hz, 1H), 7.17 (d, $J =$
7.3 Hz, 0H), 7.03 (d, $J = 7.8$ Hz, 0H), 6.86 (d, $J = 7.6$ Hz, 1H), 4.08 (d, $J =$
6.6 Hz, 1H), 2.95 (d, $J = 6.8$ Hz, 1H), 2.85 (t, $J = 7.3$ Hz, 2H), 1.37 (t, $J =$
6.7 Hz, 1H).

Sample Name	200710-LB-2	Position	P1-C6	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
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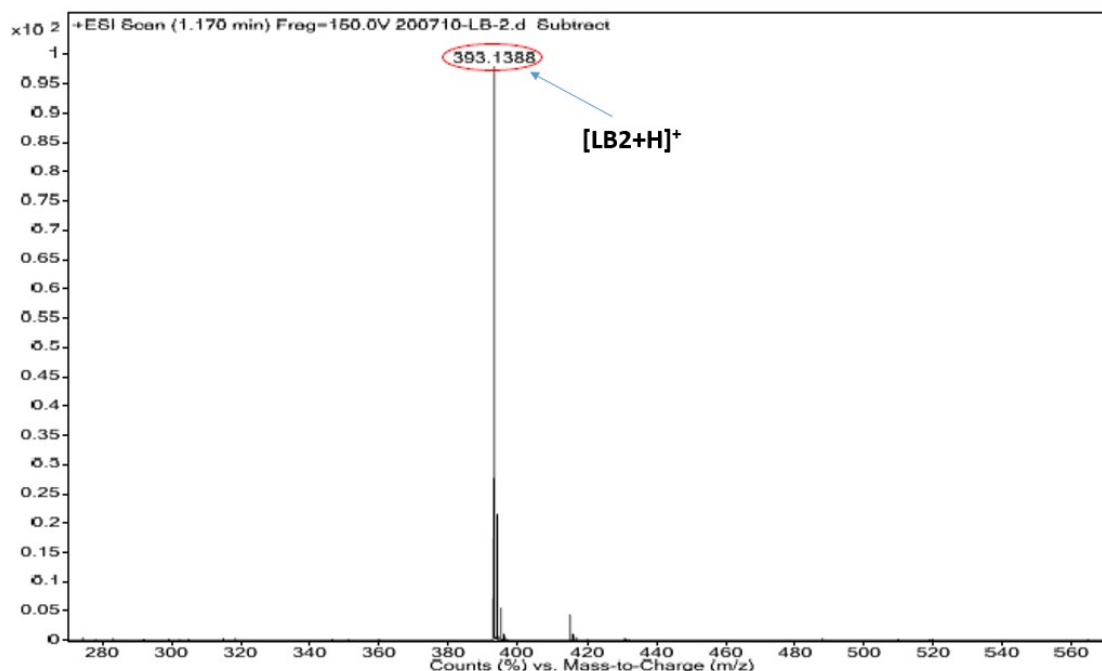


Fig.S1 ESI mass spectrum of probe **LB2**.

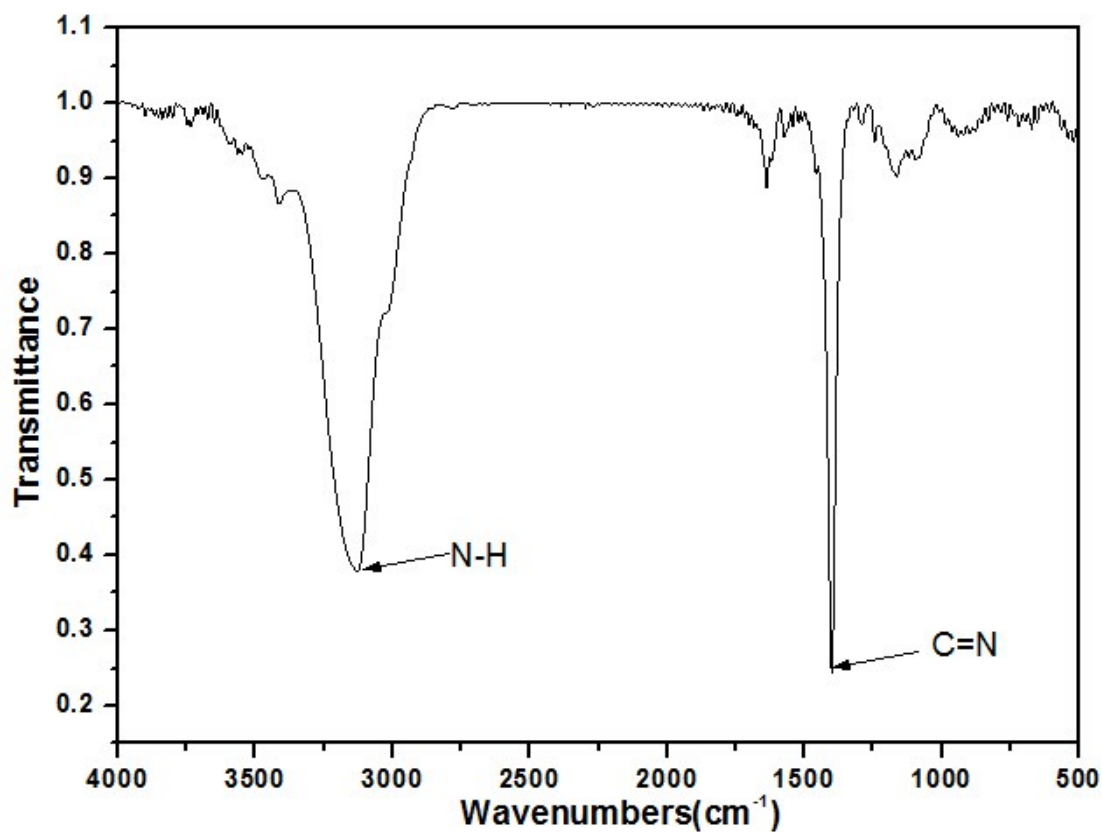


Fig.S2 The FTIR spectra of **LB2**

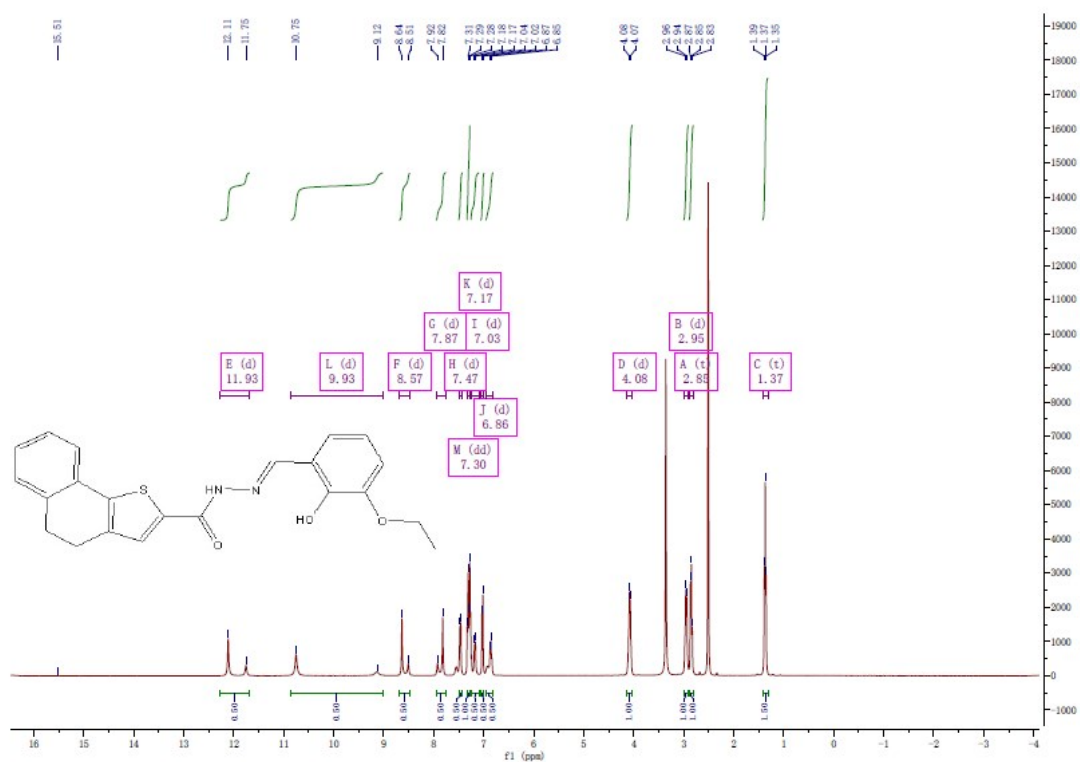


Fig.S3 ¹H NMR spectrum of compound **LB2**.

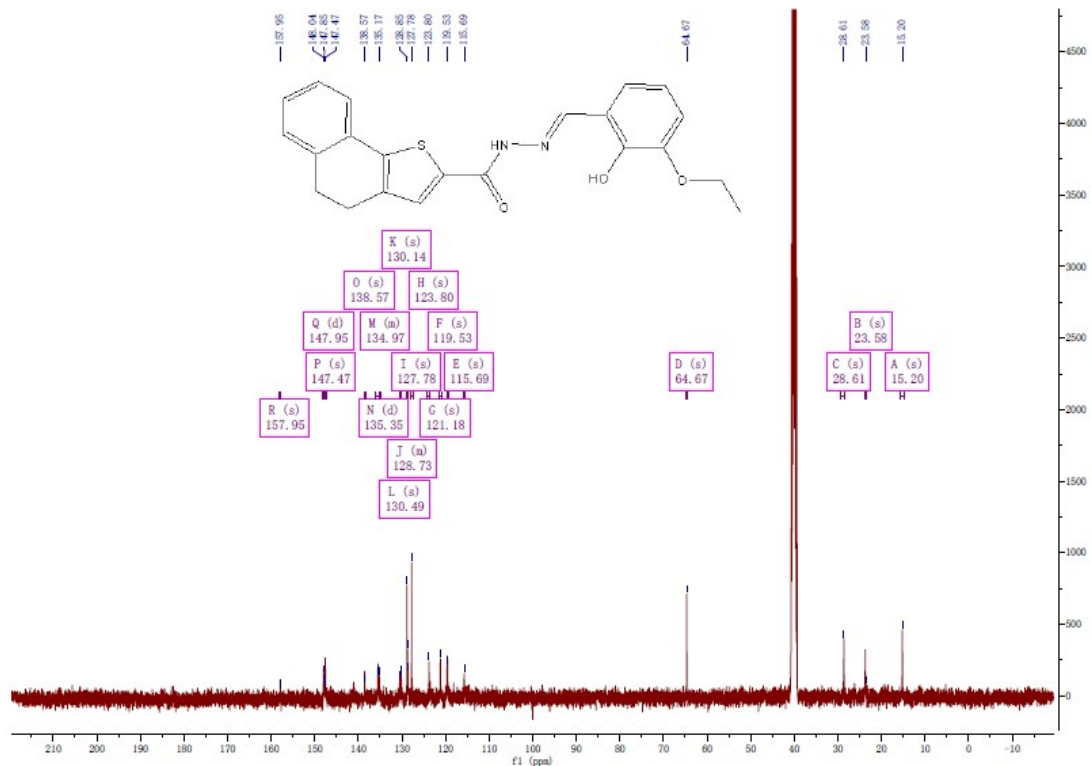


Fig.S4 ^{13}C NMR spectrum of compound **LB2**.

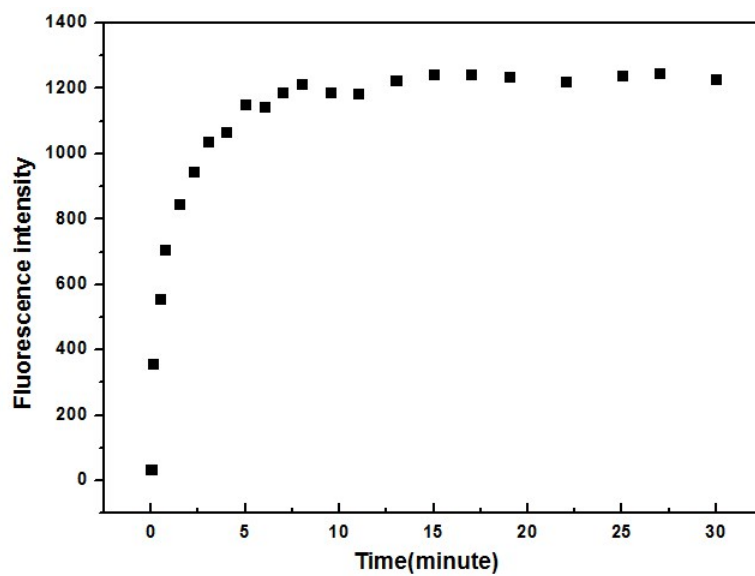


Fig.S5 Time dependent fluorescence response of **LB2** ($30\ \mu\text{M}$) at $\lambda=516\text{nm}$ in the presence of In^{3+} (3 eq.) in $\text{DMF-H}_2\text{O}$ (9:1, v:v) 10 mM of Tris buffer solution at pH 7.4. $\lambda_{\text{ex}} = 410\ \text{nm}$

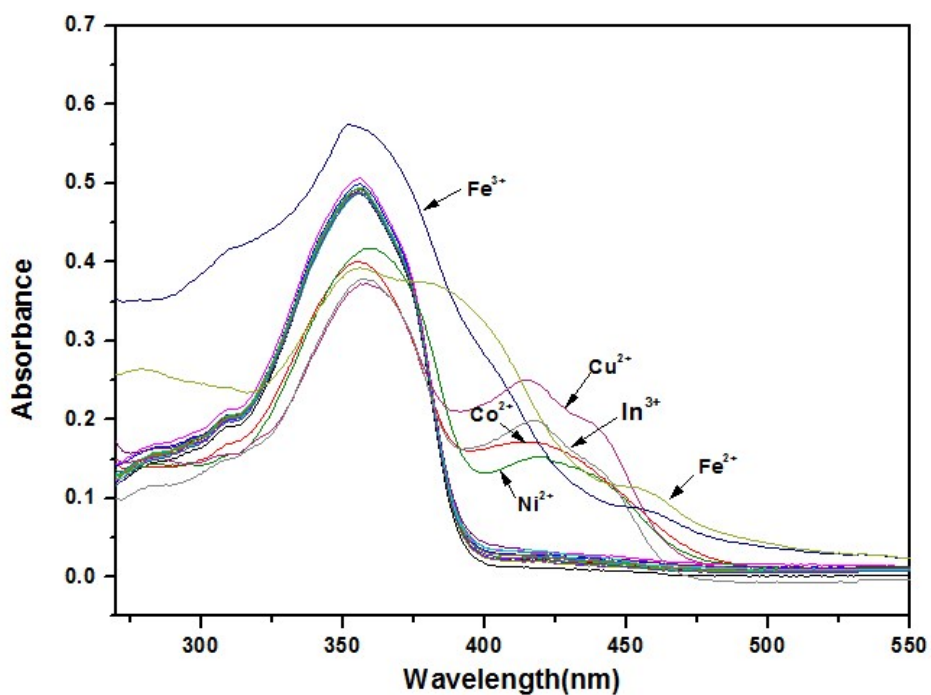


Fig.S6 Changes in absorption spectroscopy of **LB2** (30 μM) with different ions (30 μM) in DMF- H_2O (9:1, v:v) 10 mM of Tris buffer solution at pH 7.4.

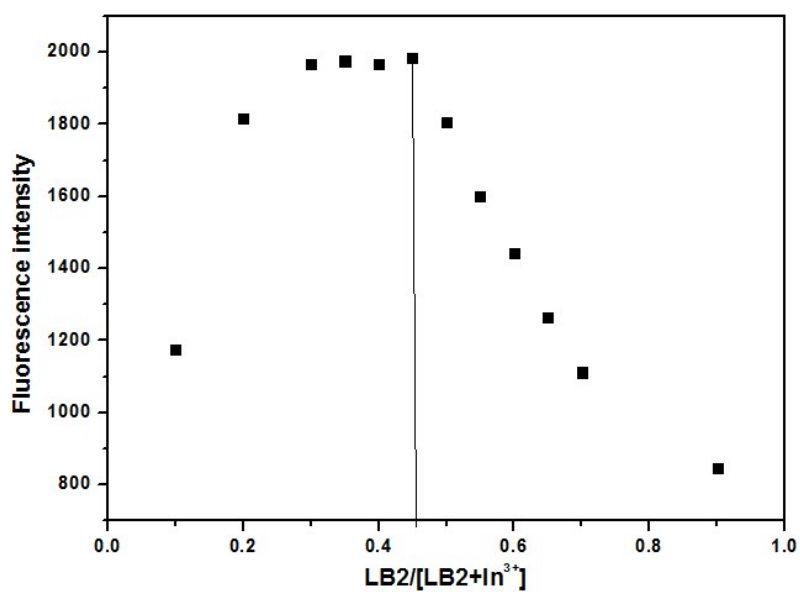


Fig.S7 Job's plot of the **LB2** in DMF- H_2O (9 : 1, Tris 0.01 M, pH=7.4) at 25 $^{\circ}\text{C}$. The total concentration of **LB2** and In^{3+} was 0.05 mM. Excitation is at 410 nm, and emission is monitored at 516 nm.

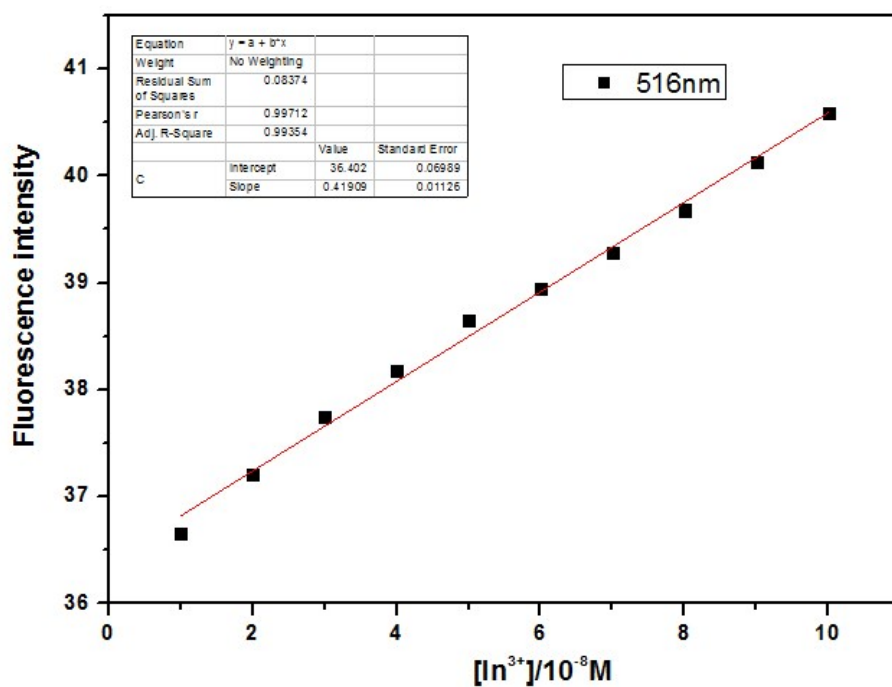


Fig.S8 Fluorescence intensity of **LB2** at 516 nm with the addition of In^{3+} (0 - 1 equiv.) in DMF- H_2O (9 : 1, Tris 0.01 M, pH =7.4).

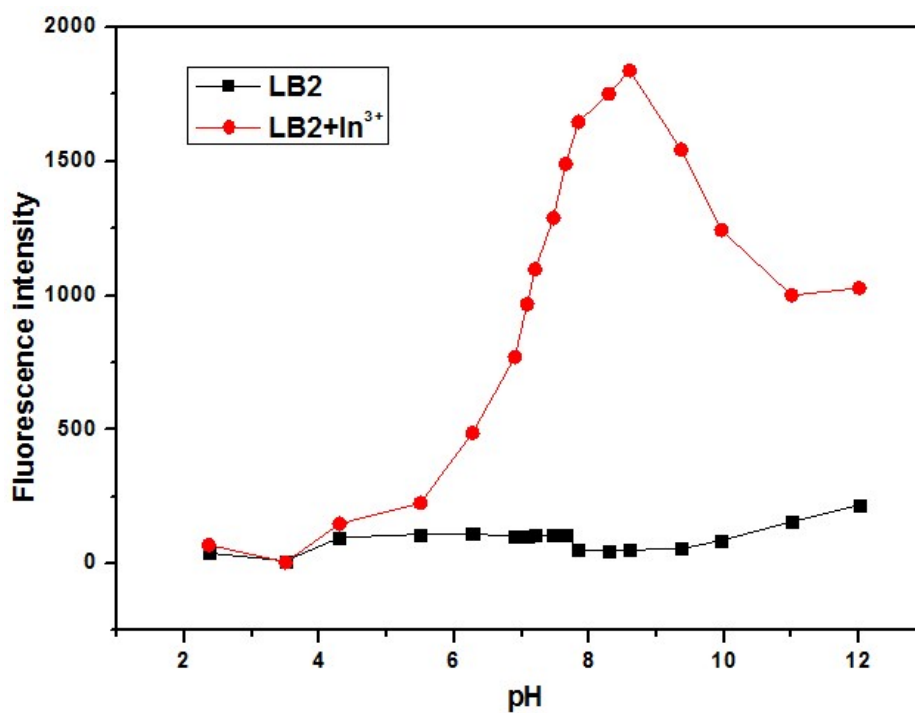


Fig.S9 Fluorescence intensity of **LB2** and **LB2** in the presence of In^{3+} at various pH values in DMF- H_2O (9 : 1, v/v) 10 mM of Tris buffer solution.

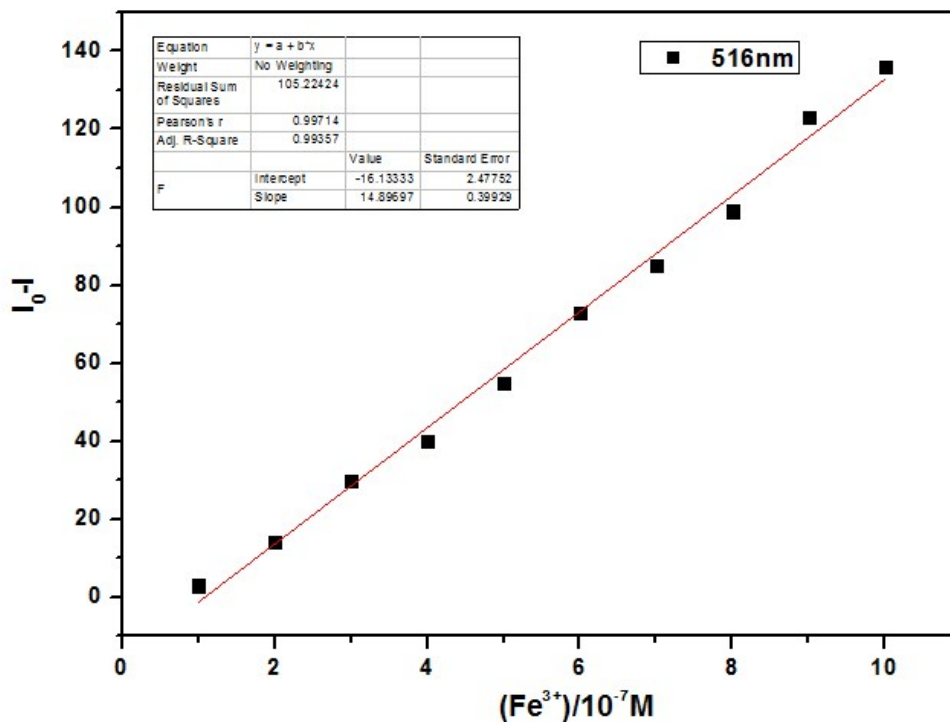


Fig.S10 Fluorescence intensity of [LB2+In³⁺] at 516 nm with the addition of Fe³⁺ (0 - 1 equiv.) in DMF-H₂O (9 : 1, Tris 0.01 M, pH =7.4).

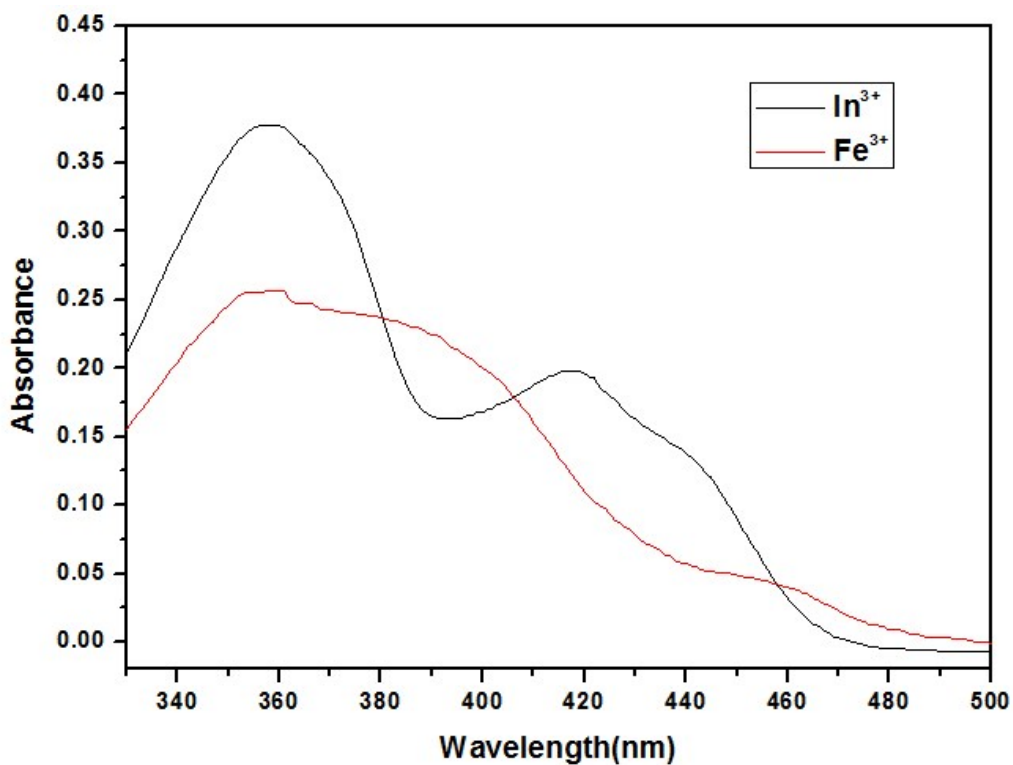


Fig.S11 Absorption spectra of [LB2+In³⁺] and [LB2+Fe³⁺] in DMF-H₂O buffer solution (v/v = 9:1, Tris = 10 mM, pH = 7.4).

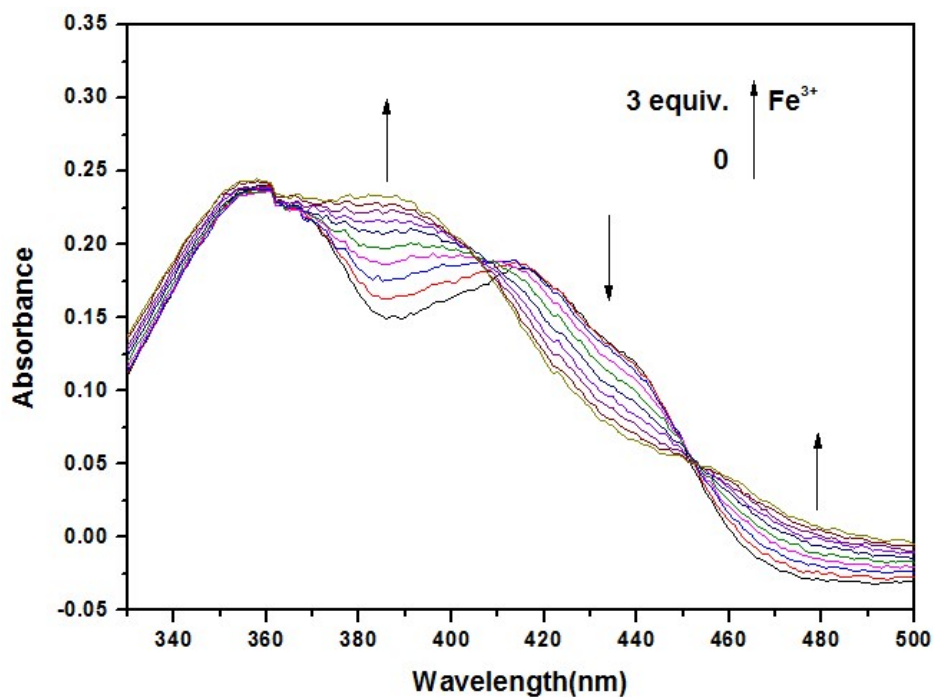


Fig.S12 Changes in absorption spectroscopy of [LB2+In³⁺] (30 μM) with incremental addition of In³⁺ (0–30 μM) in DMF–H₂O (9 : 1, v/v) 10 mM of Tris buffer solution at pH 7.4.

Sample Name	200710-LB-6	Position	P1-B6	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	200710-LB-6.d	ACQ Method	0103.m	Comment		Acquired Time	7/10/2020 12:06:46 PM

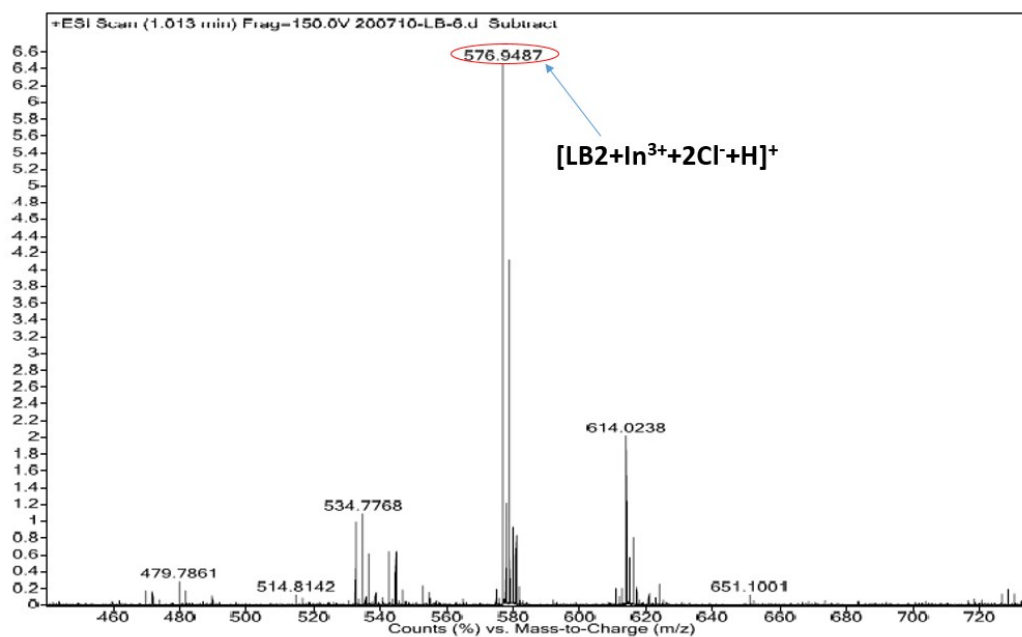


Fig.S13 ESI mass spectrum of complex [LB2+In³⁺].

Sample Name	200710-LB-7	Position	P1-05	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	200710-LB-7.d	ACQ Method	0103.m	Comment		Acquired Time	7/10/2020 11:47:42 AM

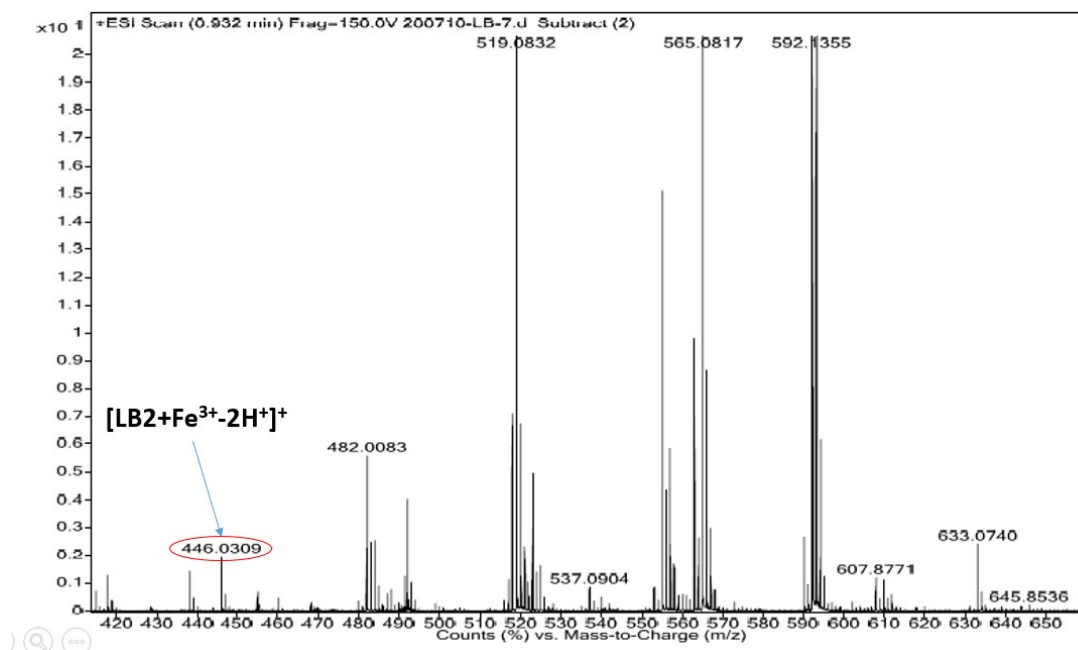


Fig.S14 ESI mass spectrum of complex $[\text{LB2}+\text{Fe}^{3+}]$.

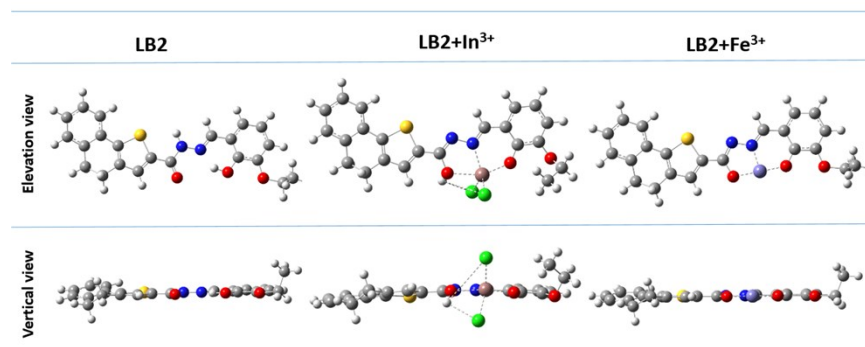


Fig.S15 The optimized geometry of LB2 , $[\text{LB2}+\text{In}^{3+}]$ and $[\text{LB2}+\text{Fe}^{3+}]$ at the B3LYP level of theory, where light-gray, red, blue, white, purple-gray, grayish-blue and green spheres denote C, O, N, H, In, Fe and Cl atoms, respectively.

Table S1 Determination of the In^{3+} concentration in tap water samples

sample	In^{3+} added (mol L ⁻¹)	In^{3+} recovered (mol L ⁻¹)	Recovery (%)	RSD (%)
1	3×10^{-5}	3.2×10^{-5}	107.6	0.61
2	4×10^{-5}	4.2×10^{-5}	106.5	0.86
3	5×10^{-5}	5.3×10^{-5}	105.4	0.97

Table S2 Determination of the Fe^{3+} concentration in tap water samples

sample	Fe^{3+} added (mol L ⁻¹)	Fe^{3+} recovered (mol L ⁻¹)	Recovery (%)	RSD (%)
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1	1×10^{-5}	1.1×10^{-5}	113.1	2.08
2	2×10^{-5}	2.2×10^{-5}	110.2	2.43
3	4×10^{-5}	3.8×10^{-5}	95.3	2.29

Table S3 Determination of the In³⁺ concentration in drink water samples

sample	In ³⁺ added (mol L ⁻¹)	In ³⁺ recovered (mol L ⁻¹)	Recovery (%)	RSD (%)
1	2×10^{-5}	1.9×10^{-5}	96.8	1.34
2	3×10^{-5}	3.1×10^{-5}	104.5	0.63
3	5×10^{-5}	5.2×10^{-5}	104.7	1.52

Table S4 Determination of the Fe³⁺ concentration in drink water samples

sample	Fe ³⁺ added (mol L ⁻¹)	Fe ³⁺ recovered (mol L ⁻¹)	Recovery (%)	RSD (%)
1	1×10^{-5}	1.0×10^{-5}	109.3	1.38
2	2×10^{-5}	2.2×10^{-5}	111.8	1.69
3	3×10^{-5}	2.8×10^{-5}	94.6	1.21

Table S5 Comparison of type of indium sensors and their detection limits

Solvent system	Detection limit	Response	Reference
DMF	5.3×10^{-7} M	-	2
CH ₃ CN	6.4×10^{-8} M	-	13
Ethanol	6.1×10^{-7} M	turn-on	19
Methanol	2×10^{-6} M	turn-on	28
DMF/H ₂ O(v/v,9:1)	8.05×10^{-9} M	off-on	this work

Table S6 Comparison of type of ferric ion sensors and their detection limits

Solvent system	Detection limit	Response	Reference
DMF	4.4×10^{-7} M	-	2
DMSO/H ₂ O(v/v,9:1)	6.7×10^{-8} M	off-on	30
Pure aqueous	2.49×10^{-7} M	on-off	33
THF/H ₂ O(40:60)	2.95×10^{-6} M	turn-on	34
DMF/H ₂ O(v/v,9:1)	2.59×10^{-8} M	on-off	this work