Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

A Highly Selective and instantaneous responsive Schiff Base Fluorescent Sensor for the "Turn-off" Detection of Iron(III), Iron(II), Copper(II) Ions

Xiaoyu Zhu,[a] Yuai Duan,[a] Po Li,[a] Haiming Fan,[b*] Tianyu Han[a*] and Xiaonan Huang[a*]

a. Department of Chemistry, Capital Normal University, 105 West 3rd Ring North Rd, Beijing 100048, PR China

b. Shandong Provincial Key Laboratory of Oilfield Chemistry, School of Petroleum Engineering, China University of Petroleum (East China), Qingdao 266580, Shandong Province, P. R. China

E-mail: huangxn@cnu.edu.cn (X.N. Huang); Haimingfan@126.com

Indexes

Fig. S1

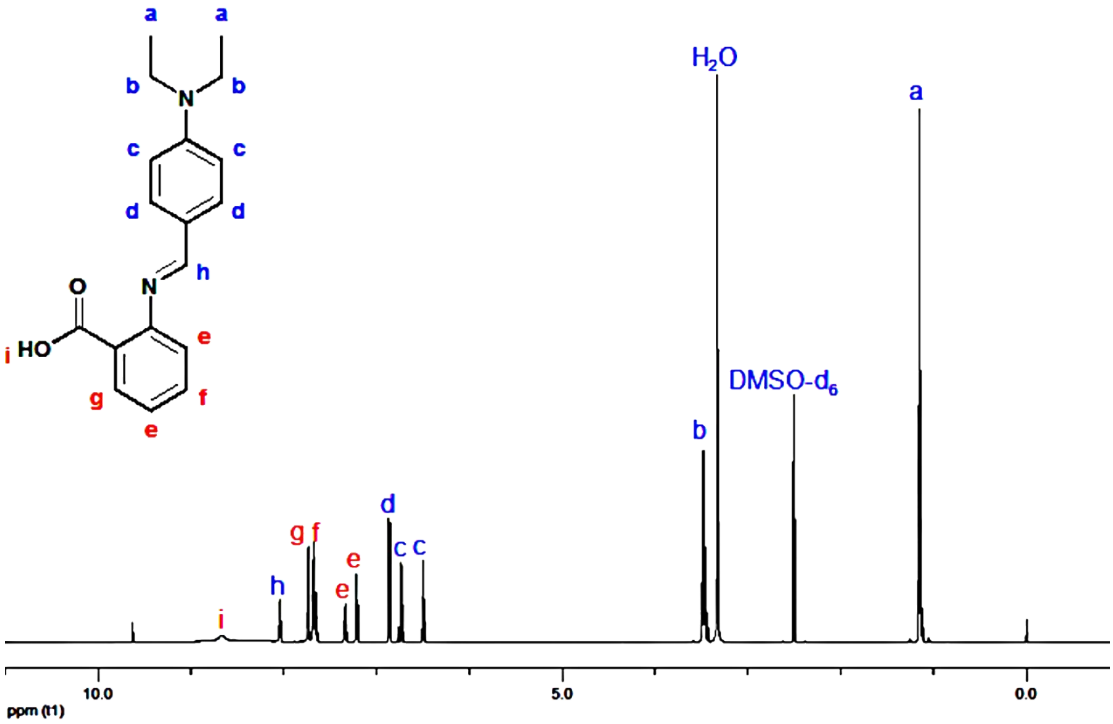

a
a
b
b
N
c
c
d
d
h
N
O
i HO
e
g
f
e
H2O
a
DMSO-d6
b
d
g f
e
c c
h
e
i
10.0
5.0
0.0
ppm (t1)

Fig. S2

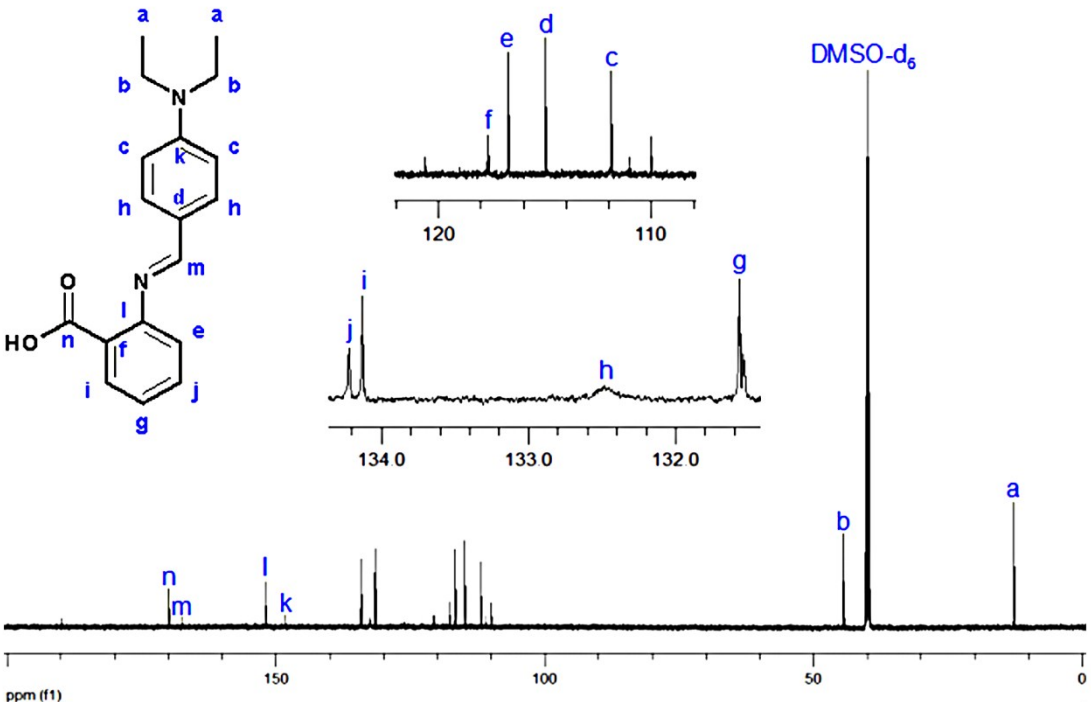
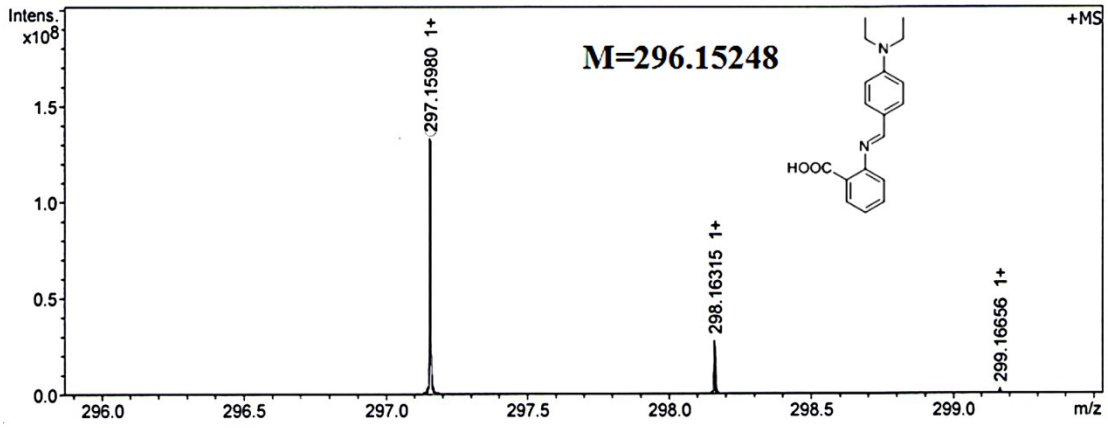

a
a
b
b
N
c
c
k
h
d
h
m
N
O
l
HO
n
f
e
i
j
g
e
d
f
c
120
110
g
i
j
h
134.0
133.0
132.0
DMSO-d6
a
b
n
m
l
k
150
100
50
0
ppm (f1)

Fig. S3

Acquisition Parameter

Polarity	Positive	Calibration Date	Wed Nov 15 08:44:13 2017
Broadband Low Mass	57.7 m/z		
Broadband High Mass	800.0 m/z	Acquired Scans	6



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
297.159797	1	C18H21N2O2	100.00	297.159754	0.1	-0.3	4.3	9.5	even	ok

Fig. S4

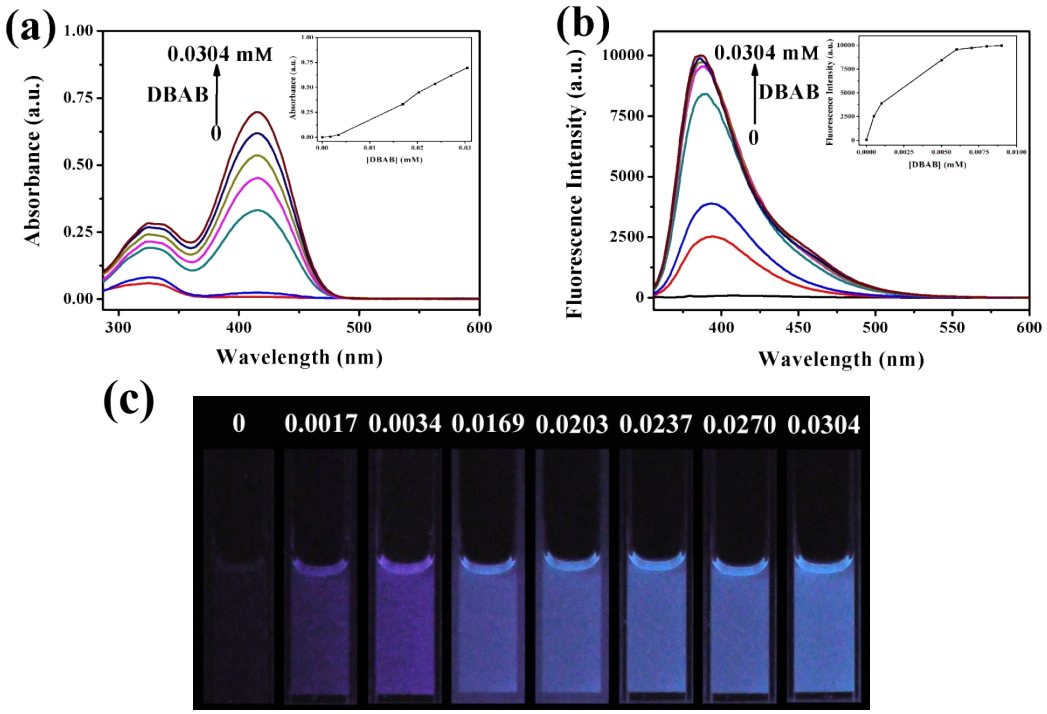
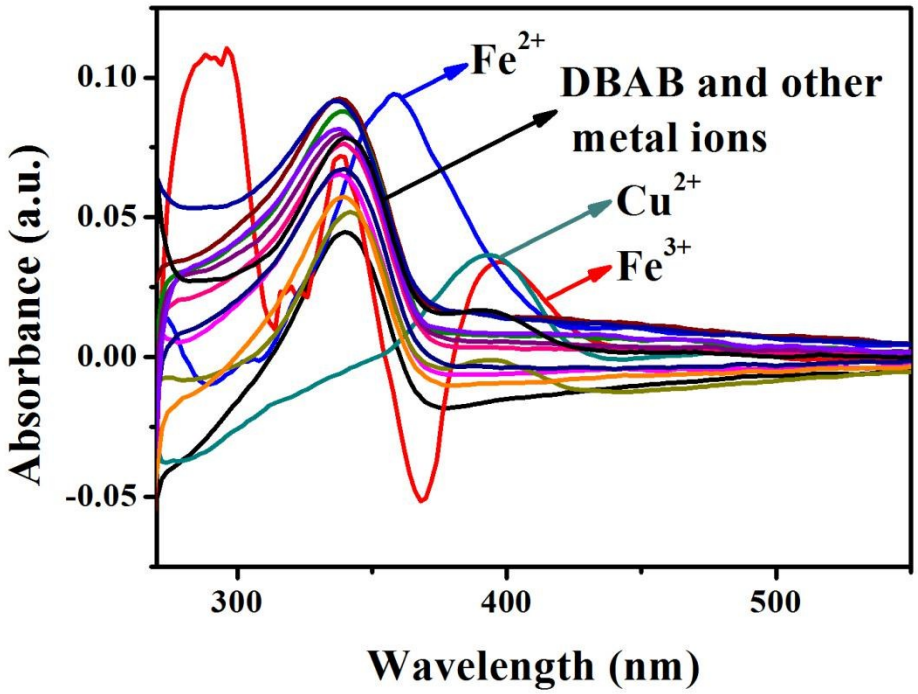

(a)
Absorbance (a.u.)
Wavelength (nm)
0.0304 mM
DBAB
0
[DBAB] (mM)
(b)
Fluorescence Intensity (a.u.)
Wavelength (nm)
0.0304 mM
DBAB
0
[DBAB] (mM)
(c)
0
0.0017
0.0034
0.0169
0.0203
0.0237
0.0270
0.0304

Fig. S5


Fe2+
DBAB and other metal ions
Cu2+
Fe3+
0.10
0.05
0.00
-0.05
Absorbance (a.u.)
300
400
500
Wavelength (nm)

The limit of detection and association constant

The limit of detection (LOD) was calculated based on the fluorescence titration according to the following equation (Eq. S1) [1-3], where Sb_1 is the standard deviation of the blank solution and S is the slope of the calibration curve. To determine Sb_1, the emission intensity of DBAB in DMF solution without any metal ions was measured 10 times, respectively.

$$LOD = 3 \times Sb_1 / S \quad \text{(Eq. S1)}$$

The association constant (Ka) of DBAB-metal ion was obtained from nonlinear curve fitting of the fluorescence titration data according to Benesi-Hildebrand equation (Eq. S2) [4-6], where F_0, F, and F_{min} are the fluorescence intensity of DBAB in the absence of metal ions, at a certain concentration of metal ions, and the minimum fluorescence intensity of [QLBM-Fe^{3+}/Fe^{2+}/Cu^{2+}] in the linear range, [M] is the metal ion concentration, n is the binding stoichiometry.

$$\log[\frac{F_{\max} - F}{F - F_0}] = n \log[M] + \log K_a \quad \text{(Eq. S2)}$$

References

[1] T. Mistri, M. Dolai, D. Chakraborty, A.R. Khuda-Bukhsh, K.K. Das, M. Ali, A highly selective and sensitive in vivo fluorosensor for zinc(II) without cytotoxicity, Org. Biomol. Chem. 10 (2012) 2380-2384.

[2] J.L. Zhang, Y.M. Zhou, W.P. Hu, L. Zhang, Q. Huang, T.S. Ma, Highly selective fluorescence enhancement chemosensor for Hg2+ based on rhodamine and its application in living cells and aqueous media, Sens. Actuators B 183 (2013) 290-296.

[3] A. Barba-Bon, A.M. Costero, S. Gil, M. Parra, J. Soto, R. Martinez-Manez, et al., A new selective fluorogenic probe for trivalent cations, Chem. Commun. 48 (2012) 3000-3002.

[4] A.K. Mandal, M. Suresh, P. Das, E. Suresh, M. Baidya, S.K. Ghosh, et al., Recognition of Hg2+ Ion through Restricted Imine Isomerization: Crystallographic Evidence and Imaging in Live Cells, Org. Lett. 14(2012) 2980-2983.

[5] A.F. Liu, L. Yang, Z.Y. Zhang, Z.L. Zhang, D.M. Xu, A novel rhodamine-based colorimetric and fluorescent sensor for the dual-channel detection of Cu2+ and Fe3+ in aqueous solutions, Dyes Pigments 99 (2013) 472-479.

[6] H.A. Benesi, J.H. Hildebrand, A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons, J. Am. Chem. Soc. 71 (1949) 2703-2707.