Electronic Supplementary Information

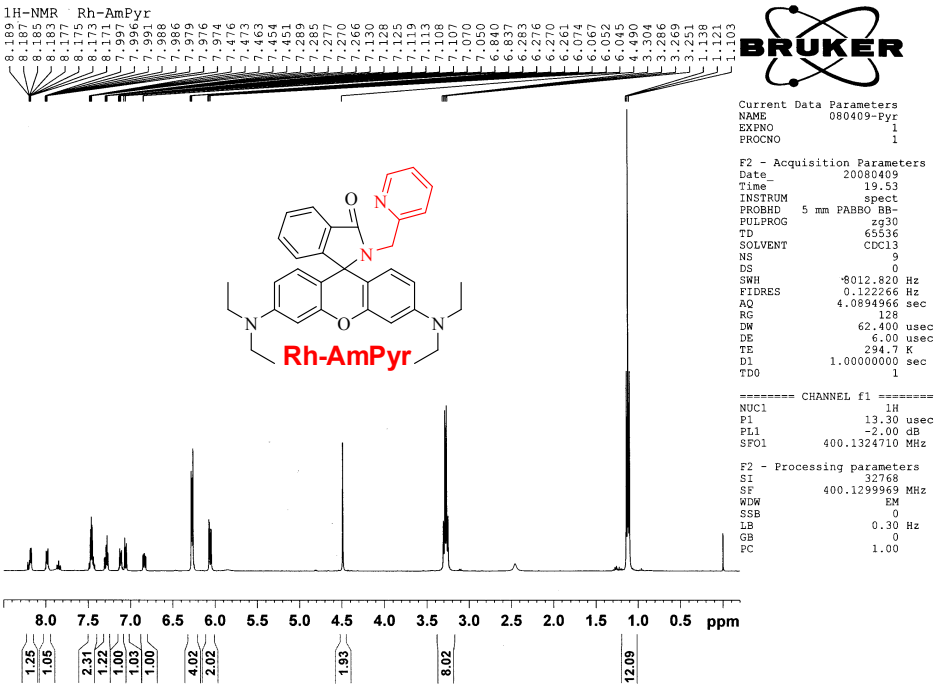
Rhodamine-based Fluorescent off/on Sensor for Fe^{3+} in Aqueous Solution and in Living Cells: 8-Aminoquinoline receptor and 2:1 binding

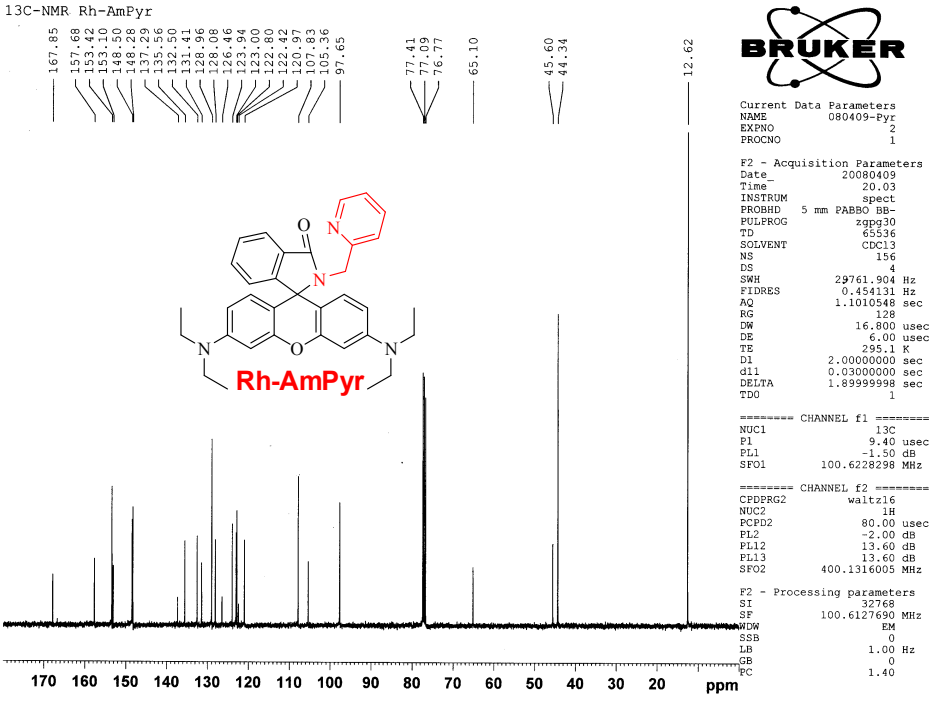
Junhai Huang[a,b], Yufang Xu[a], Xuhong Qian[a*]

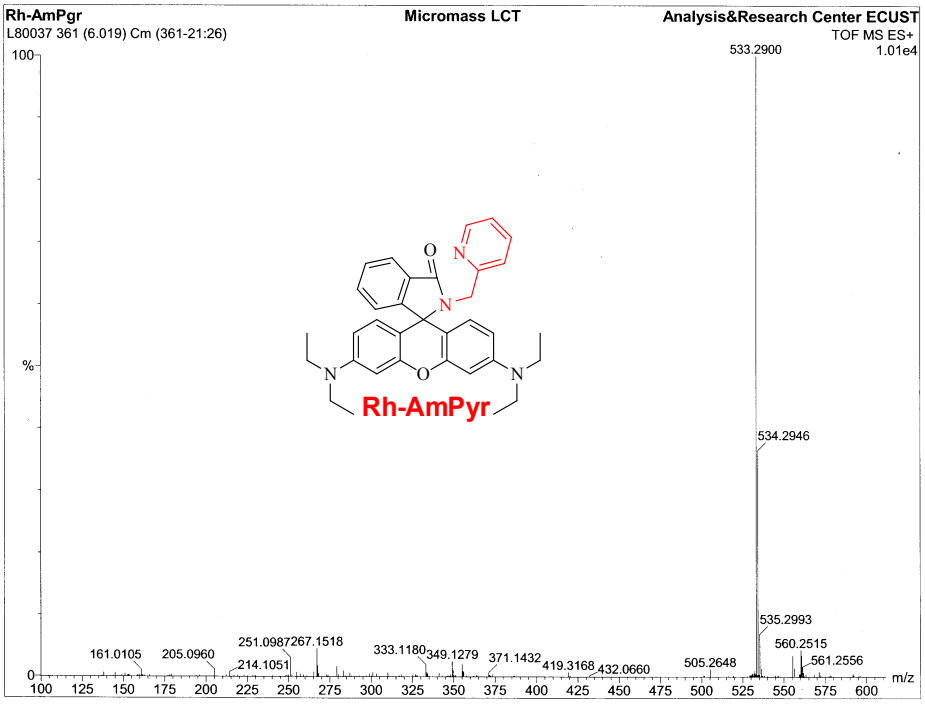
a State Key Laboratory of Bioreactor Engineering and Shanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology, Shanghai 200237, China; Email: xhqian@ecust.edu.cn; Fax: +86 21 6425 2603; Tel: +86 21 6425 3589;

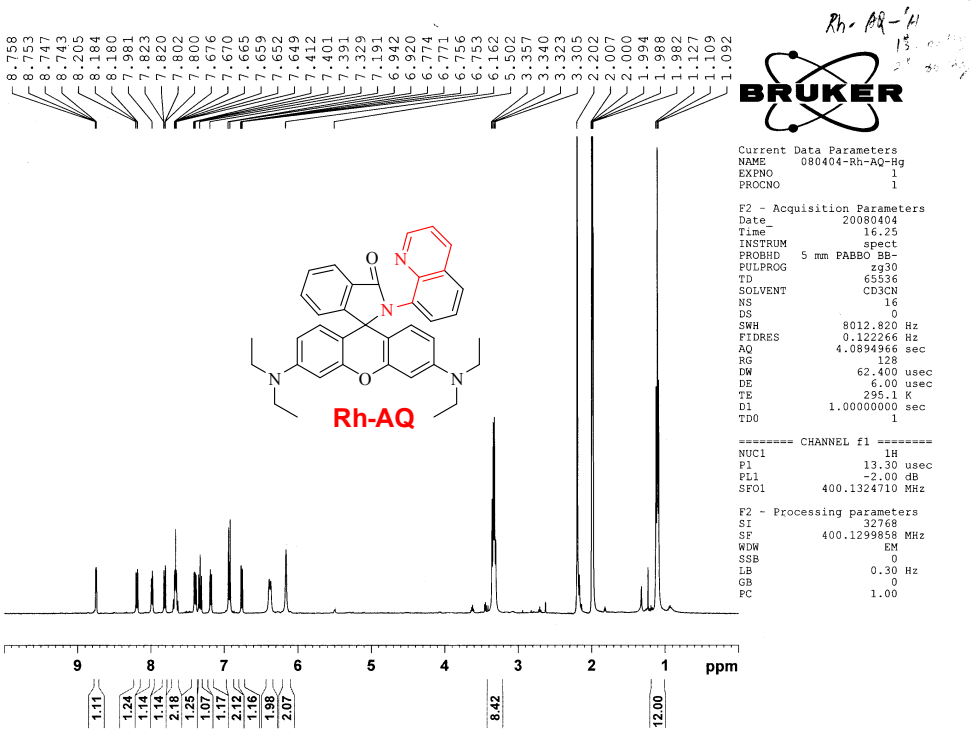
b Zhangjiang R&D center, Shanghai Institute of Pharmaceutical Industry, Shanghai, 200040

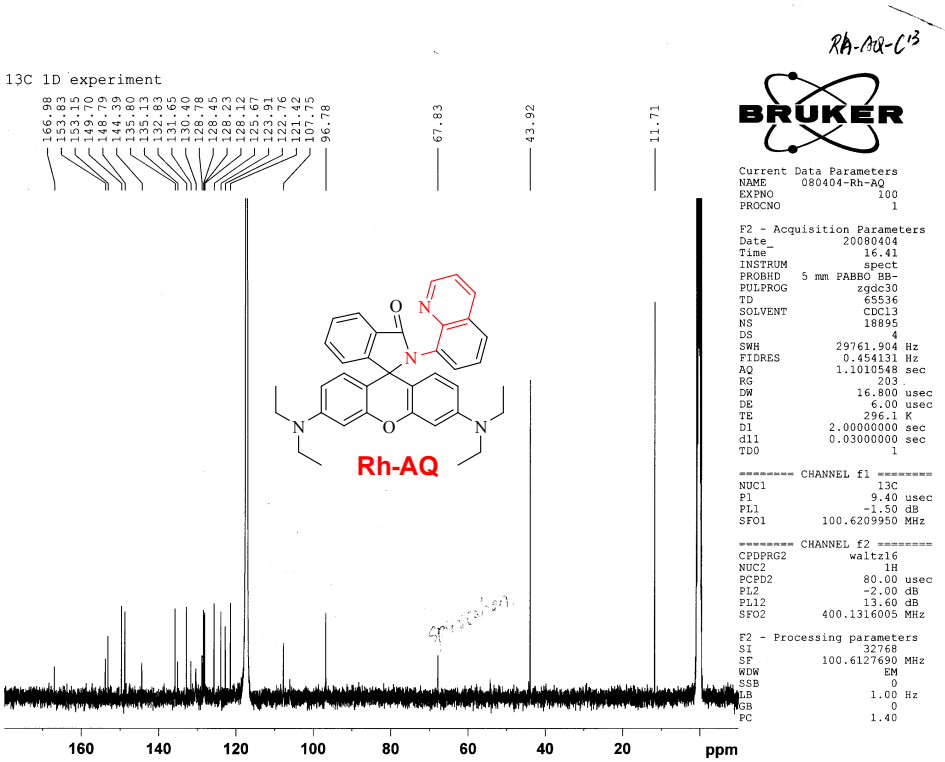
S1. Syntheses and characterization

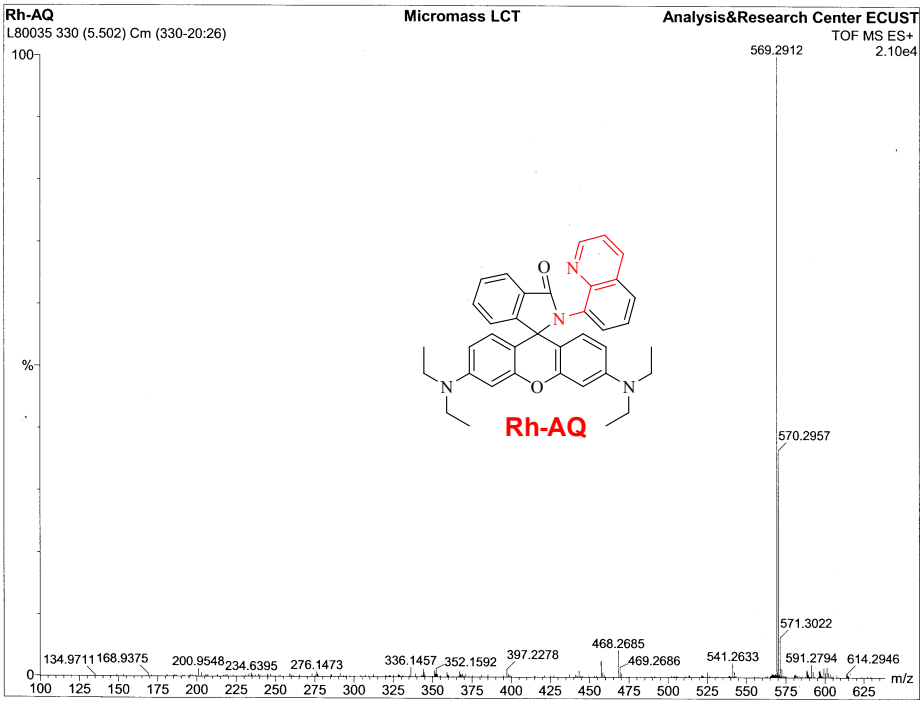


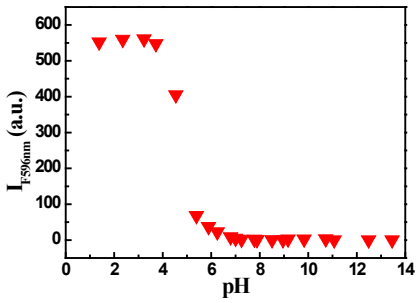



Rh-AmPgr
Micromass LCT
Analysis&Research Center ECUST
L80037 361 (6.019) Cm (361-21:26)
TOF MS ES+
1.01e4
533.2900
534.2946
535.2993
560.2515
561.2556
505.2648
161.0105
205.0960
214.1051
251.0987
267.1518
333.1180
349.1279
371.1432
419.3168
432.0660
%
m/z
Rh-AmPyr

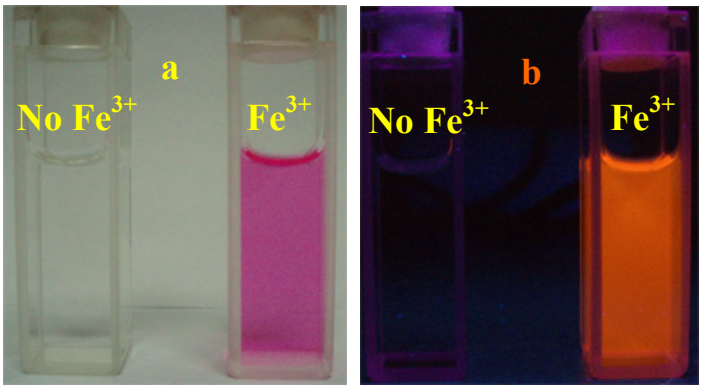

Rh-AQ-1H
BRUKER
Rh-AQ
Current Data Parameters
NAME 080404-Rh-AQ-Hg
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080404
Time 16.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 128
DW 62.400 usec
DE 6.00 usec
TE 295.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1299858 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm
1.11
1.24
1.14
1.14
2.18
1.25
1.07
1.17
2.12
1.16
1.98
2.07
8.42
12.00


RA-AQ-C13
13C 1D experiment
166.98
153.83
153.15
149.70
148.79
144.39
135.80
135.13
132.83
131.65
130.40
128.78
128.45
128.23
128.12
125.67
123.91
122.76
121.42
107.75
96.78
67.83
43.92
11.71
Rh-AQ
BRUKER
Current Data Parameters
NAME 080404-Rh-AQ
EXPNO 100
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080404
Time 16.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 18895
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 203
DW 16.800 usec
DE 6.00 usec
TE 296.1 K
D1 2.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.40 usec
PL1 -1.50 dB
SFO1 100.6209950 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 13.60 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160
140
120
100
80
60
40
20
ppm

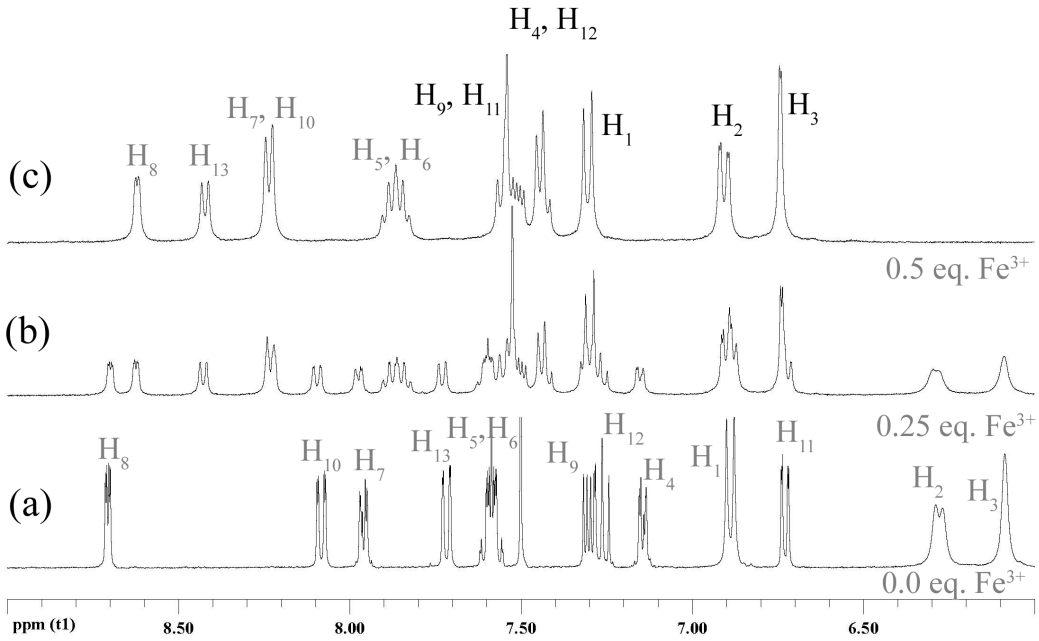

Rh-AQ
L80035 330 (5.502) Cm (330-20:26)
Micromass LCT
Analysis&Research Center ECUST
TOF MS ES+
2.10e4
100
%
0
Rh-AQ
569.2912
570.2957
571.3022
134.9711
168.9375
200.9548
234.6395
276.1473
336.1457
352.1592
397.2278
468.2685
469.2686
541.2633
591.2794
614.2946
100
125
150
175
200
225
250
275
300
325
350
375
400
425
450
475
500
525
550
575
600
625
m/z



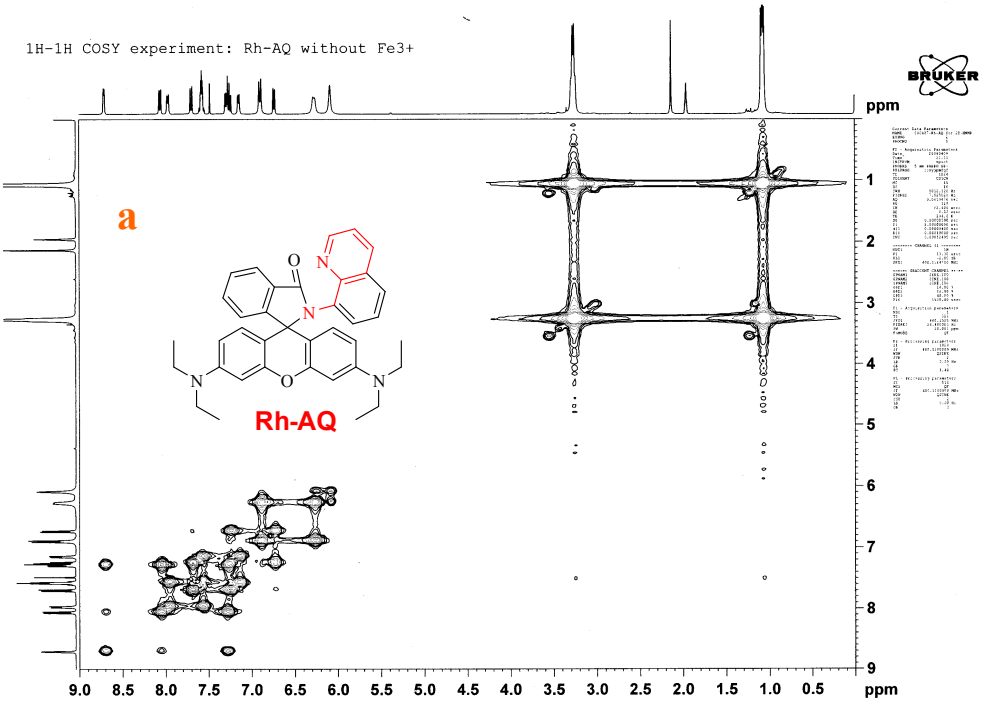
S2 pH-titration curves of Rh-AQ in CH_3CN/H_2O solution (v/v, 5/5). pK_a value inferred for the curve was 4.7.

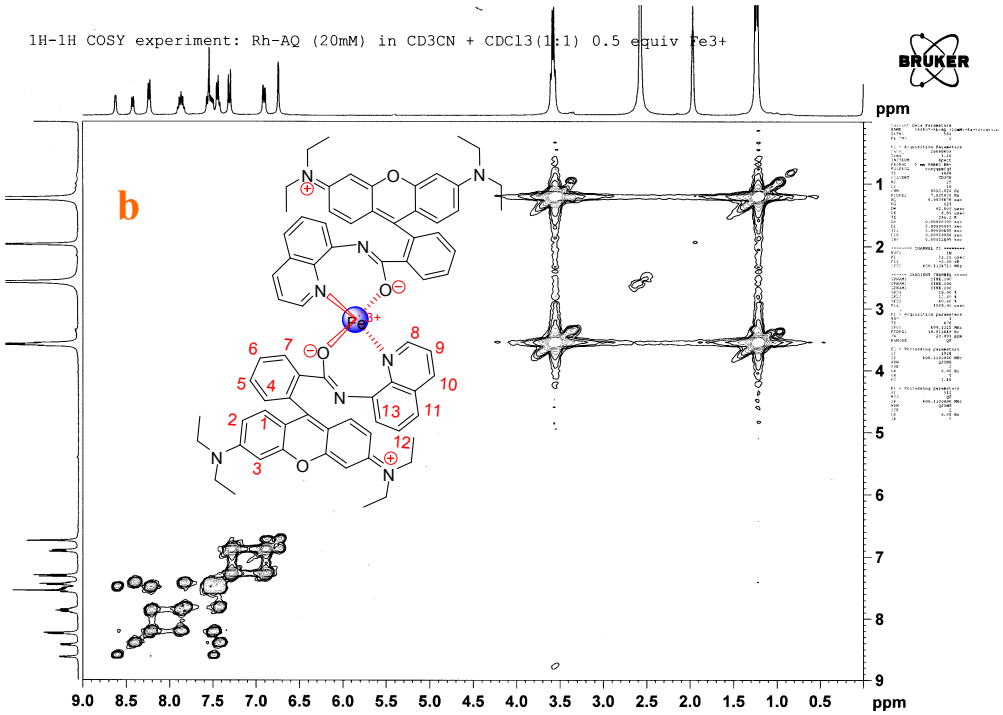


S3 Change in color (a) and fluorescence (b).

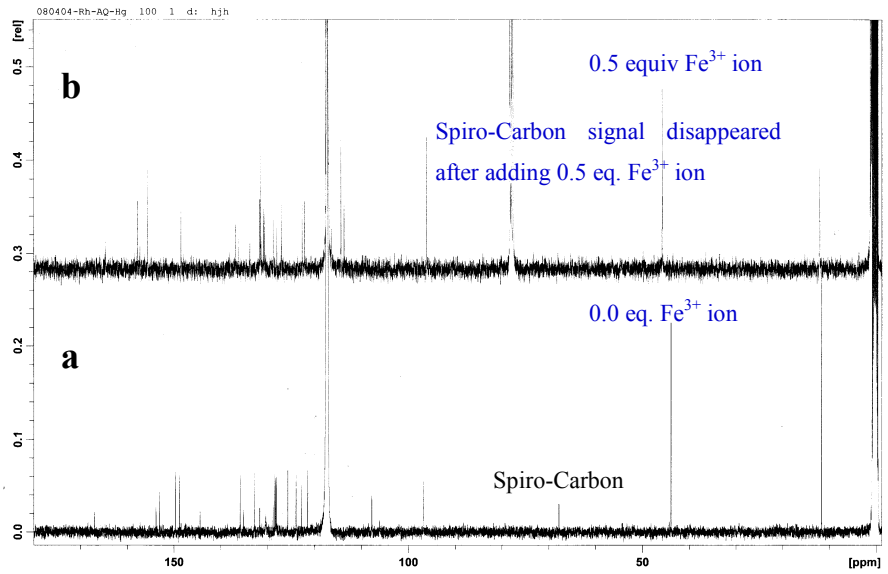


S4 Evolution of the ^{1}H-NMR spectrum of Rh-AQ (20 mM) in CD_3CN and $CDCl_3$ (1:1) upon addition of increasing amounts of Fe^{3+}: a) 0.0 eq.; b) 0.25 eq.; c) 0.5 eq..

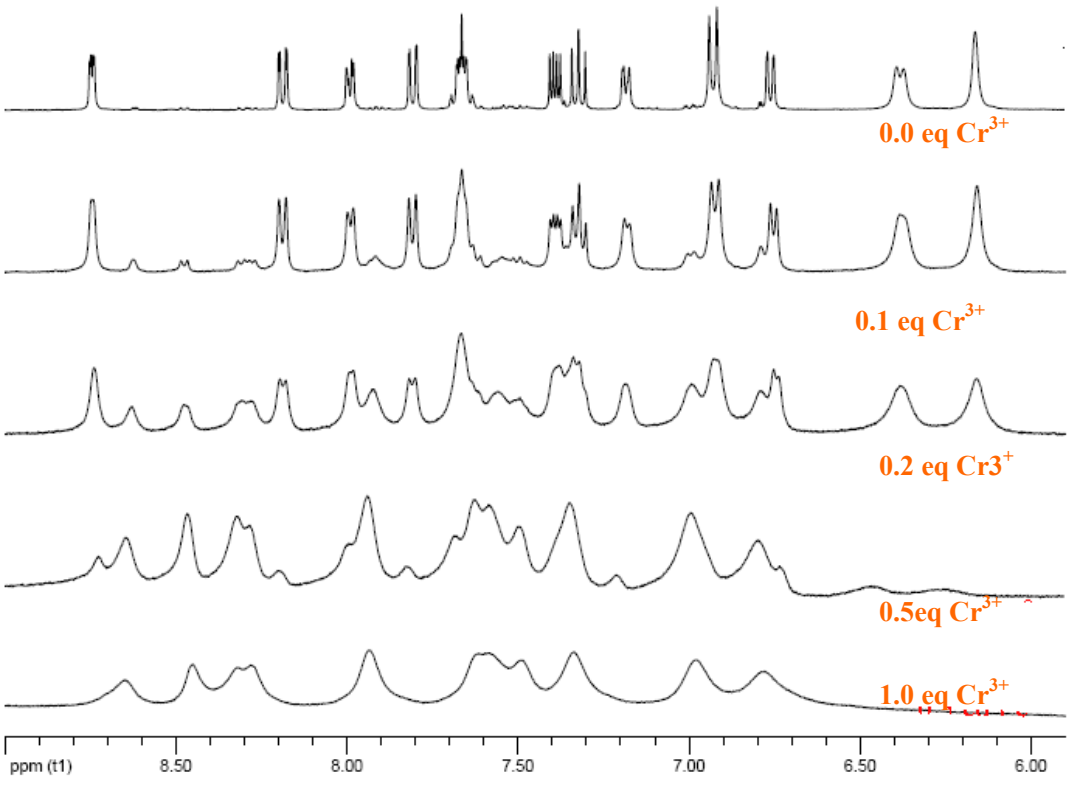




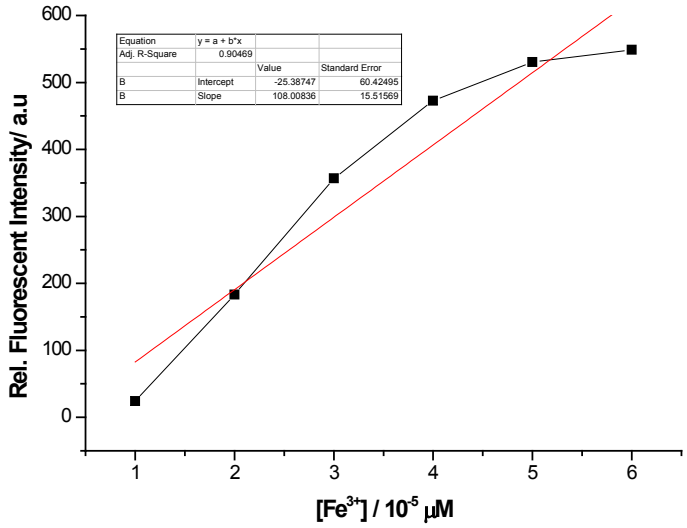
S5: ^{1}H-^{1}H COSY NMR of Rh-AQ in CD_3CN and $CDCl_3$ (1:1) in the absence (a) or (b) presence of 0.5 eq. Fe^{3+} ion.



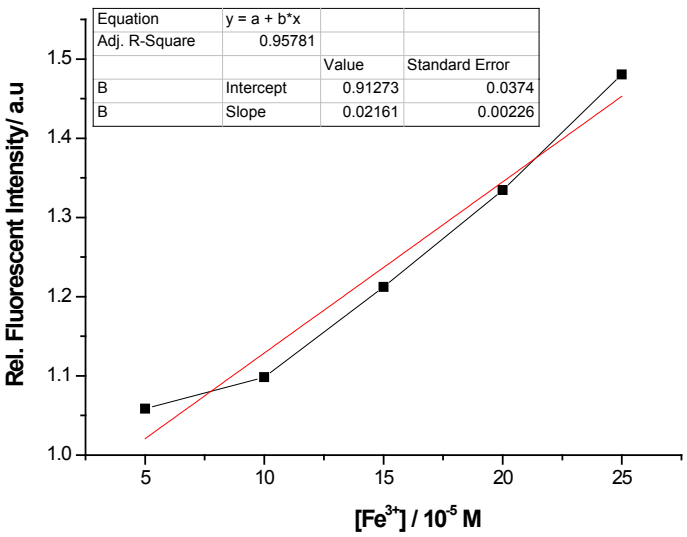
S6 ^{13}C-NMR of Rh-AQ in CD_3CN and $CDCl_3$ (1:1) in the absence (a) or (b) presence of 0.5 eq. Fe^{3+} ion.



S7 Evolution of the ^{1}H-NMR spectrum of Rh-AQ (20 mM) in $CDCl_3/CD_3CN$ (1:1) upon addition of increasing amounts of Cr^{3+}: 0.0 eq.; 0.1 eq.; 0.2 eq., 0.5 eq., 1.0 eq..



S8: The linear relationship was observed between I_{590} and [Fe^{3+}] in the range of 10-60 µM. The relationship between emission at 590 nm and Fe^{3+} concentration was: y =-25.387+ 108.008*x, where y was the fluorescence intensity under the emission at 590 nm and x was the concentration of Fe^{3+}. The linear range of the method was found to be at least 10~60 µM Fe^{3+} with a correlation coefficient of R^2 = 0.905. The detection limit, based on the definition by IUPAC (CDL=3 Sbm^{-1}) was found to be 3.2×10^{-7} M which is lower enough than TLV (10 ppb). The relative standard deviation (R.S.D.) for three repeated measurements of 1.8×10^{-6} M Fe^{3+} was 3.3%. (Ref. H.M.N.H. Irving, H. Freiser, T.S. West, IUPAC Compendium of Analytical Nomenclature, Definitive Rules Pergamon Press, Oxford (1981)



S9: The linear range of the method was found to be at least 5–25 * 10^{-5} M [Fe^{3+}] with a correlation coefficient of R^2= 0.9578. The detection limit, based on the definition by IUPAC (CDL = 3 Sb

m−1) was found to be 3.5×10^{-6} M. The relative standard deviation (R.S.D.) for three repeated measurements of 5.2×10^{-5} M [Fe^{3+}] was 3.6%. (Ref. H.M.N.H. Irving, H. Freiser, T.S. West, IUPAC Compendium of Analytical Nomenclature, Definitive Rules Pergamon Press, Oxford (1981)