Electronic Supplementary Material (ESI) for RSC Advances.
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Supporting Information

Experiment

1. The synthesis of sensor Fluorescein-Ad moiety

1.1 The synthesis of S1 and S2

According to the literature [8], fluorescein (6 g, 18.1 mmol), 24 mL hydrazine hydrate (hydrazine content >80 mass %), 50ml MeOH were dropwised. The cude product was purified by recrystallization from MeCN to give 4.7g as an off-white solid (83%).

Adamantanecarboxylic-acid(3.44g,19.1mmol),DMAP(0.192g,1.7mmol),EDCI(3.15g,17.1mmol),and 2,4-2 hydroxyl benzaldehyde (1.89g,13,7mmol) were dissolved into 50ml DMF.The residue was purified by flash chromatography with CH_2Cl_2/ PE(10:1) as the eluent to afford S2 (3.14g, yield: 75%) off-white solid.

1.2 The synthesis of S3

S1 (1.048g,3,03mmol)and S2 (0.925g,3.08mmol) were dissolved in 100ml dry ethanol, and the reaction mixture was stirred under reflux and N_2.Removing the solvent, the residue was purified by flash chromatography with CH_2Cl_2/MeOH,50:1 as the eluent to obtain light pink solid (1.14g,yield 60%).

^{1}H NMR (400 MHz, DMSO) δ 10.55 (s, 1H), 9.94 (s, 2H), 9.08 (s, 1H), 7.91 (s, 1H), 7.62 (s, 2H), 7.36 (s, 1H), 7.12 (s, 1H), 6.93 – 6.25 (m, 8H), 1.86 (dd, *J* = 84.6, 23.0 Hz, 15H).

^{13}C NMR (101 MHz, DMSO) δ 178.54 – 177.80 (m), 174.84 (s), 163.51 (s), 158.35 (d, *J* = 72.3 Hz), 157.98 – 157.25 (m), 153.25 (s), 152.10 (s), 150.57 (s), 148.87 (s), 134.23 – 133.81 (m), 129.28 (d,

J = 20.3 Hz), 128.58 (s), 128.02 (s), 123.51 (d, *J* = 55.2 Hz), 116.93 (s), 112.88 (d, *J* = 70.0 Hz), 112.31 – 111.32 (m), 109.51 (d, *J* = 18.9 Hz), 102.55 (s), 65.15 (s), 54.91 (s), 40.41 (s), 38.49 (s), 38.09 (s), 35.91 (d, *J* = 24.7 Hz), 27.31 (d, *J* = 16.7 Hz).

ESI-MS (m/z): [M+H] + calcd for C38H32N2O7, 629; found, 628.

2. Preparation of Fe_3O_4@SiO_2-β-CD.

2.1 preparation of magnetic microspheres

According to the literature [4], 1.35g $FeCl_3 \cdot 6H_2O$ (5 mmol) was dissolved in 40mL glycol adding 3.6g NaAc and stirring for 30min.Then the mixture was put into high pressure reactor with 200℃ for 12h.Cooling to indoor temperature ,the product was washed by alcohol for 6 times, then vacuum drying at 60℃ for 6h.

2.2 Preparation of magnetic sillica microspheres

0.5g above-mentioned magnetic microspheres, 2ml TEOS was mixed uniformly, dropwising 20ml H_2O and emulsifying 1h with ultrasonic compulsively. After that, 6ml ammonia (25%) and 25ml ethanol were dropwised stirring for 4h at room temperature with ultrasonic. The product was obtained by centrifugation, washed with alcohol, then separated magnetically

2. 3 Preparation of β-CD-SiO_2@Fe_3O_4

2.5gβ-CD was dissolved in 50ml DMF, then added 0.5g NaH stirring at room temperature. After 15min ,the mixture was filtered to get colatuie in which we added 4ml GTMS(KH560) at 90℃ under the protection of nitrogen. After 5h, 50ml DMF, 1g magnetic sillica microspheres and 1.5ml ammonia (25%) was added one by one stirring for 12h fiercely. The product was separated by magnet and washed with ethanol and water, then vacuum desiccated at 60℃for 24 h.

Scheme S1. The synthesis of sensor Fluorescein-Ad moiety S3

Scheme S2. The preparation of Fe_3O_4@SiO_2-β-CD

Fig.S1. The SEM and TEM images (a, b) of FFIC MNPs

Fig.S2a. The magnetic hysteresis loops of Fe_3O_4 (black line), FFIC MNPs (red line)

Fig.S3a. 1H NMR spectrum of organic molecule fluorophore moiety in DMSO-d6

Fig.S3b. 1C NMR spectrum of organic molecule fluorophore moiety in DMSO-d6

Fig.S4. X-ray powder diffraction pattern analysis

Fig.S5. Photograph of FFIC MNPs in the presence of various metal ions (5.0×10^{-4} M except Zn^{2+} that is 1.0×10^{-5} M) in CH_3CN-H_2O (1:4, v/v, pH=7.10)

Fig.S6. The different pH, 0.1g/L FFIC MNPs, 2.5×10^{-6}mol/L Zn^{2+}, excitation was at 390 nm, emission was monitored at 485 nm. Slit 2.50×5.00mm

Fig.S7. From left to right was FFIC MNPs (CH_3CN–H_2O, 1: 4, and v/v, buffered at pH=7.1 with Tris-HCl) with no Zn^{2+},0.25μmol/L,2.5μmol/L,25μmol/L.

Fig.S8. The different volume proportion of CH_3CN and water, 0.1g/L FFIC MNPs, 5×10^{-6}mol/L Zn^{2+} in 4ml, excitation was at 390 nm, emission was monitored at 485 nm. Slit 2.50×5.00mm

Fig.S9. S3 and Zn^{2+} in CH_3CN-H_2O (1/4, v/v), conditions:[**S3** + Zn^{2+}] = 2.5×10^{-5} mol/L， excitation was at 390 nm, emission was monitored at 485nm.

Fig.S10. Time course of fluorescence intensity of FFIC MNPs (0.1 g/L), the concentration of Zn^{2+} 2.5×10^{-7} (CH^3CN–H^2O, 1:4, v/v) buffered at pH=7.1 with tris-HCl(0.1M), excitation was at 390 nm, emission was monitored at 485nm)

Fig.S11. The equilibrium adsorption amounts

Fig.S12. The Langmuir curve

Fig.S1

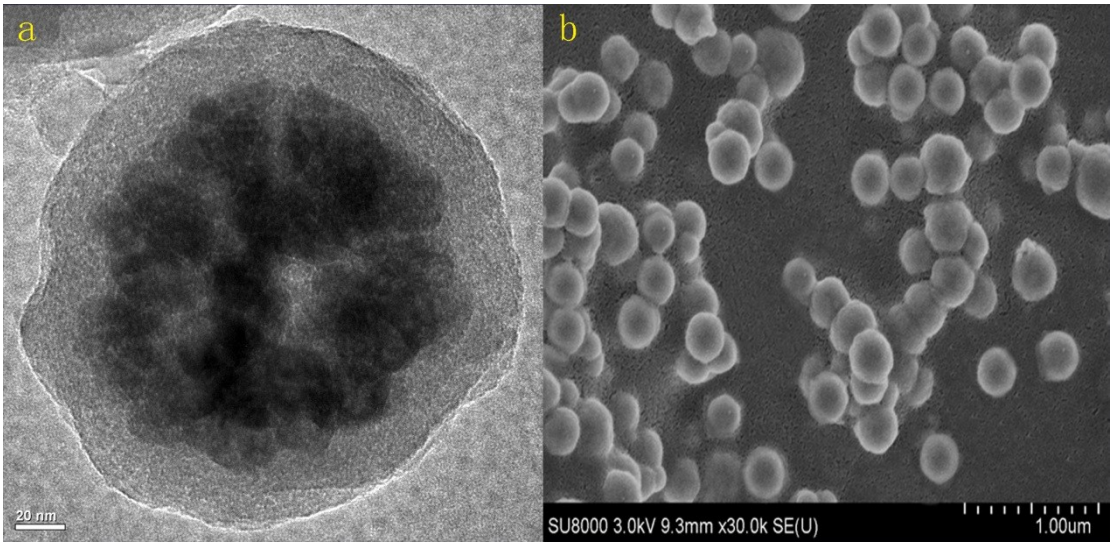

Fig.S2a

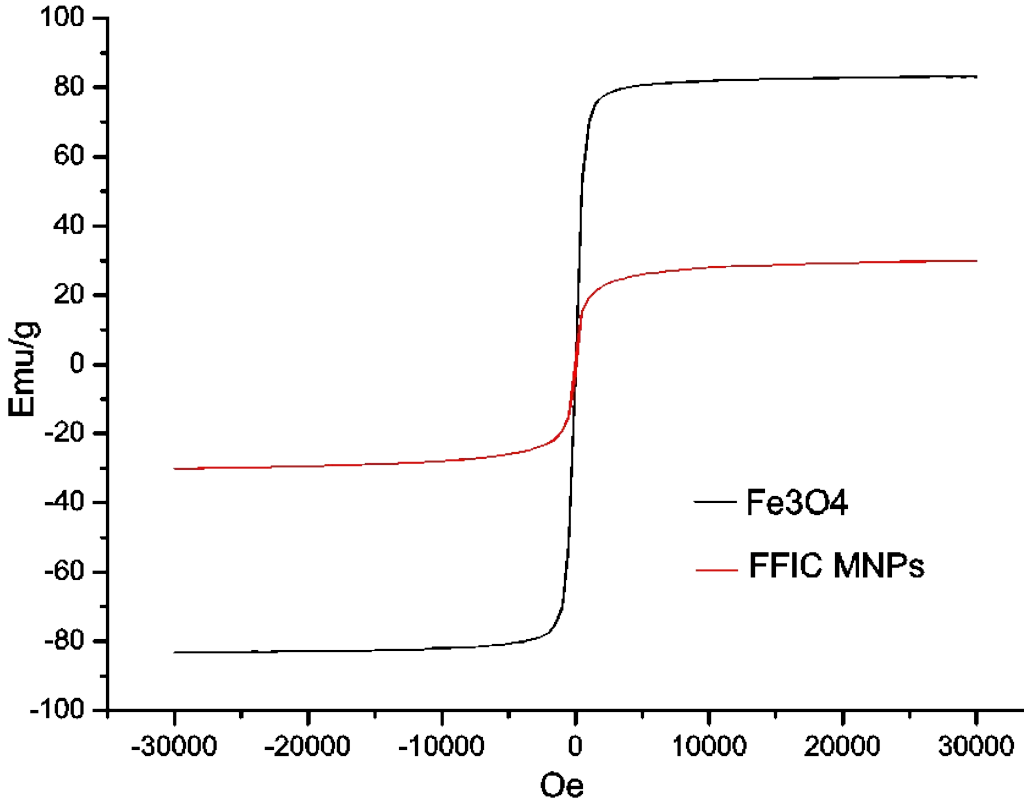

Fig.S2b

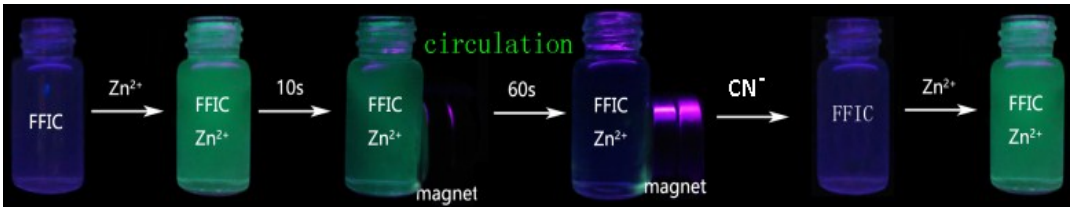

Fig.S3a

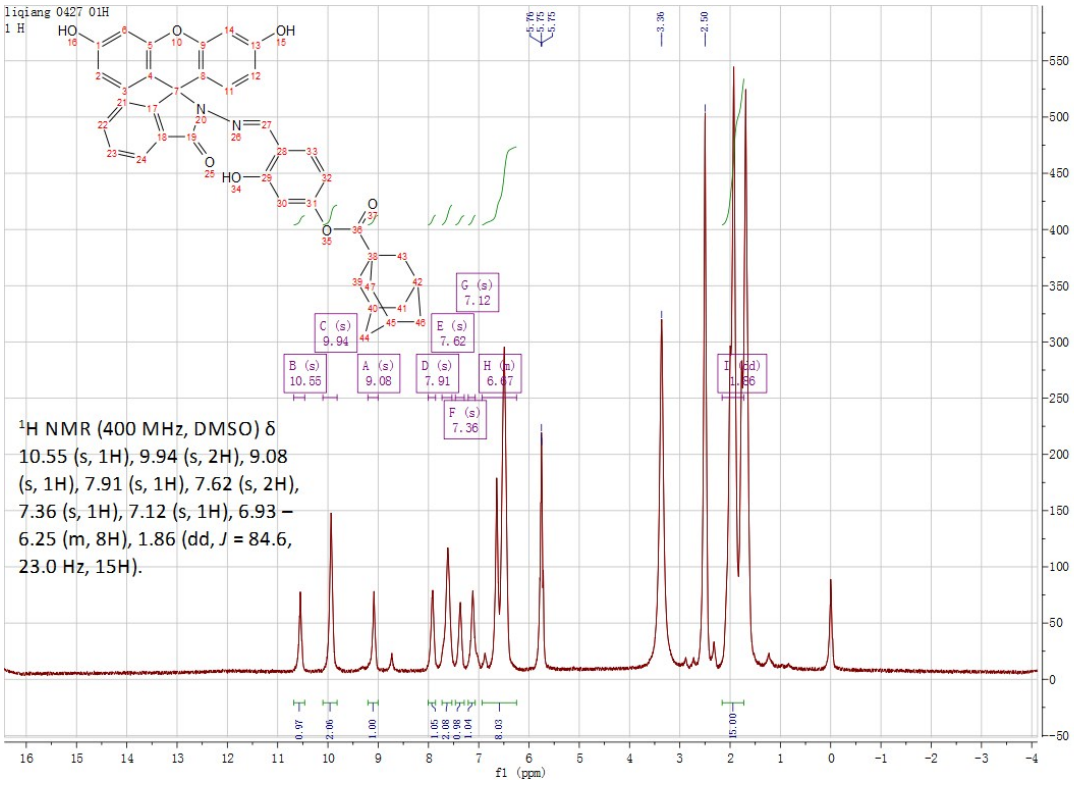

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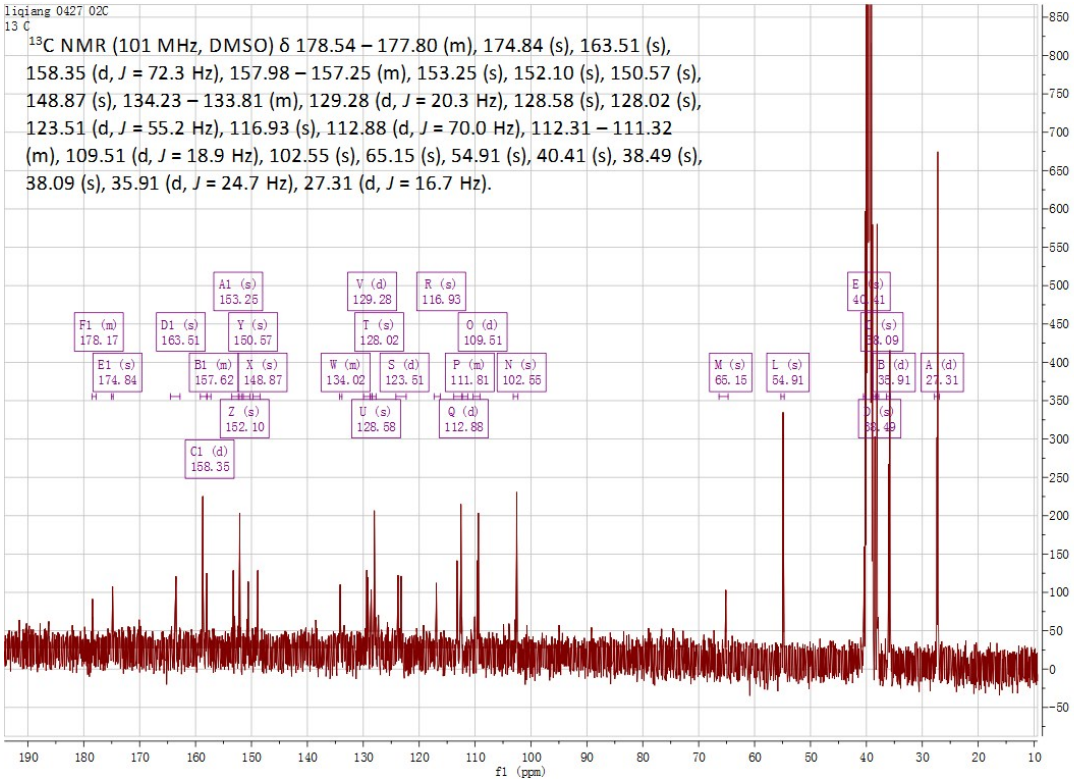
Fig.S3b


liqiang 0427 02C
13 C
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A1 (s) 163.25
V (d) 129.28
R (s) 116.93
F1 (m) 178.17
D1 (s) 163.51
Y (s) 150.57
T (s) 128.02
O (d) 109.51
E1 (s) 174.84
B1 (m) 157.62
X (s) 148.87
W (m) 134.02
S (d) 123.51
P (m) 111.81
N (s) 102.55
M (s) 65.15
L (s) 54.91
B (d) 35.91
A (d) 27.31
Z (s) 152.10
U (s) 128.58
Q (d) 112.88
C1 (d) 158.35
f1 (ppm)

Fig.S4

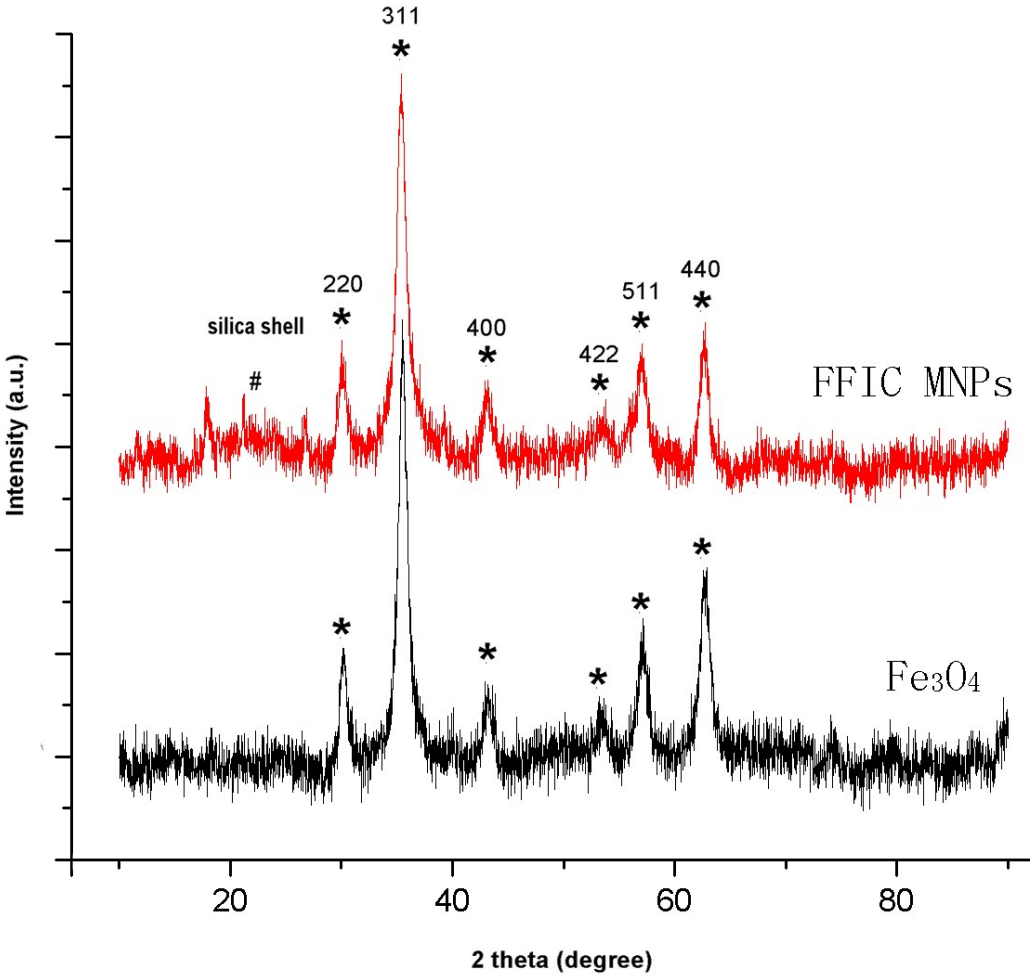

311
220
silica shell
#
400
422
511
440
FFIC MNPs
Fe3O4
Intensity (a.u.)
20
40
60
80
2 theta (degree)

Fig.S5

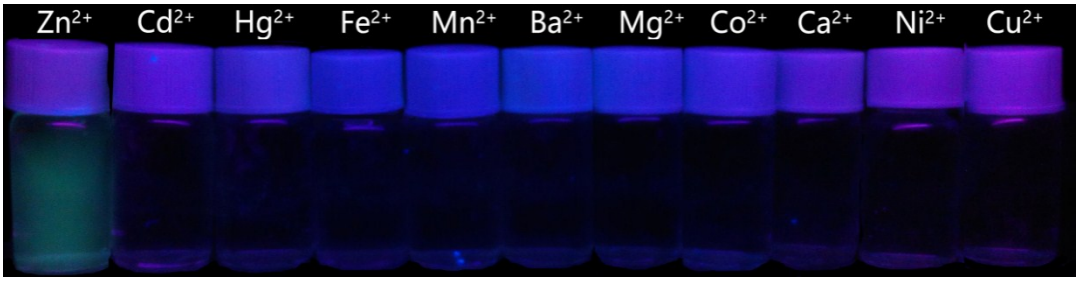

Zn2+
Cd2+
Hg2+
Fe2+
Mn2+
Ba2+
Mg2+
Co2+
Ca2+
Ni2+
Cu2+

Fig.S6

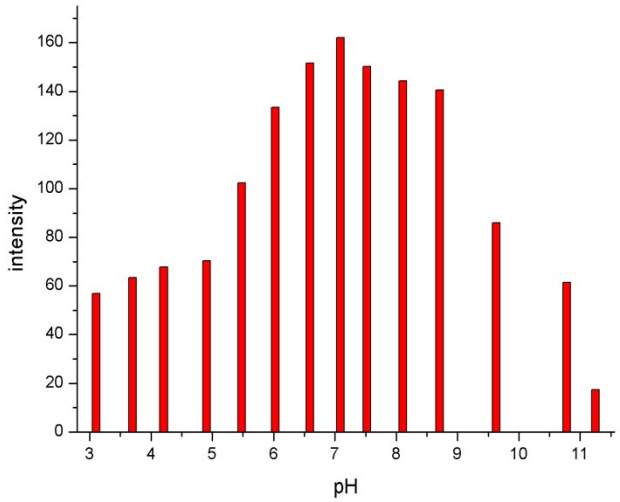


Fig.S7

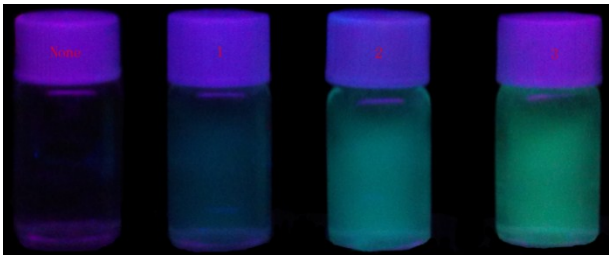


Fig.S8

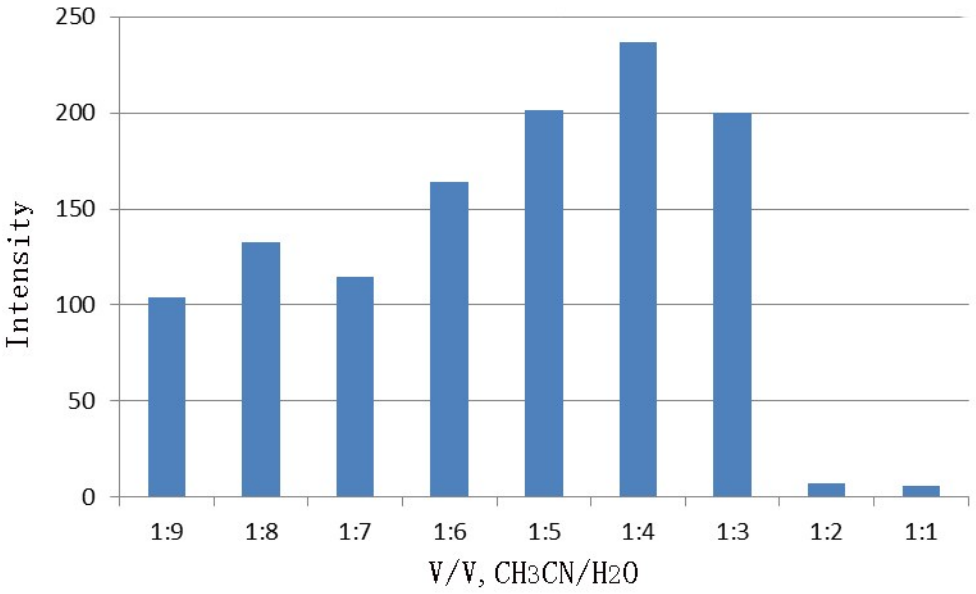

250
200
150
100
50
0
Intensity
1:9
1:8
1:7
1:6
1:5
1:4
1:3
1:2
1:1
V/V, CH3CN/H2O

Fig.S9

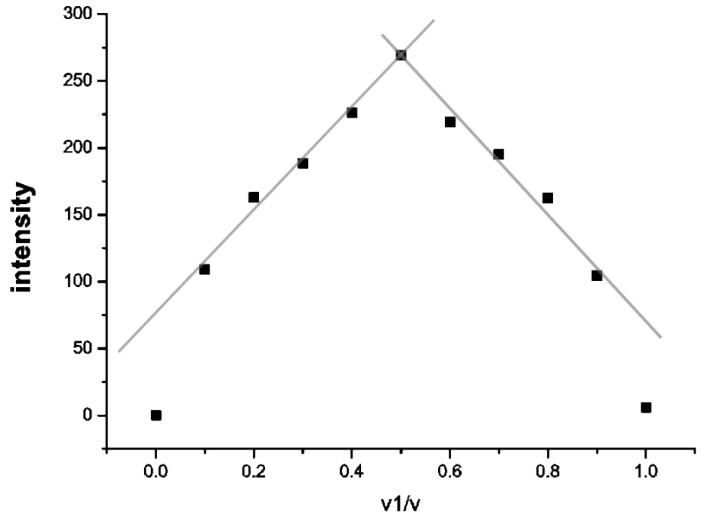

300
250
200
150
100
50
0
intensity
0.0
0.2
0.4
0.6
0.8
1.0
v1/v

Fig.S10

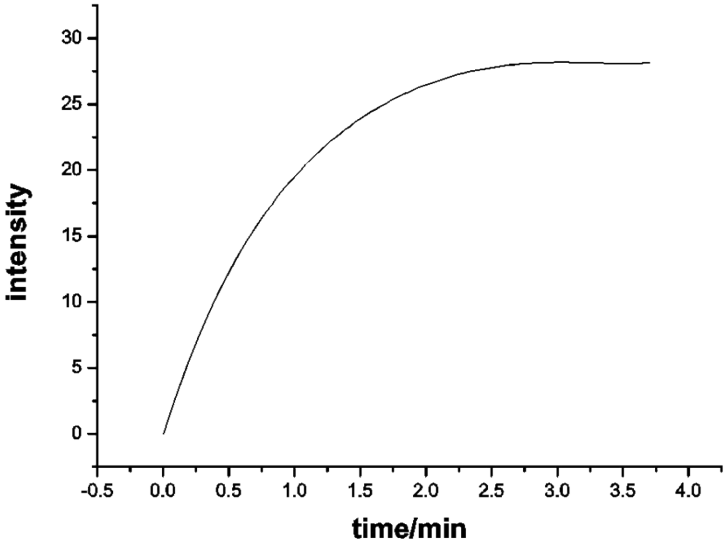


Fig.S11

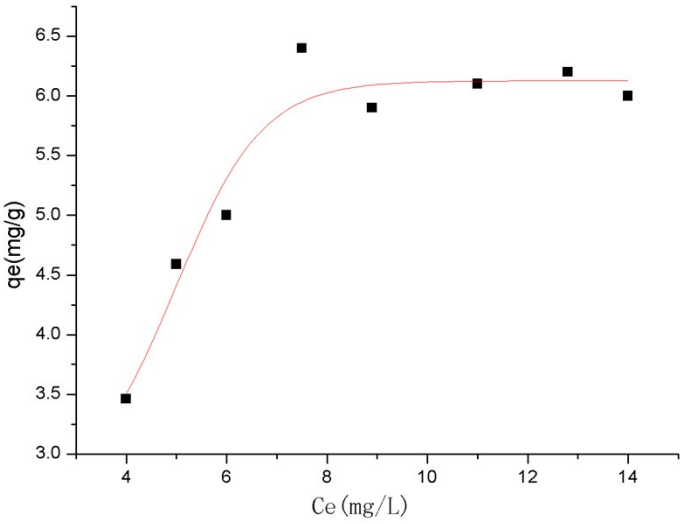
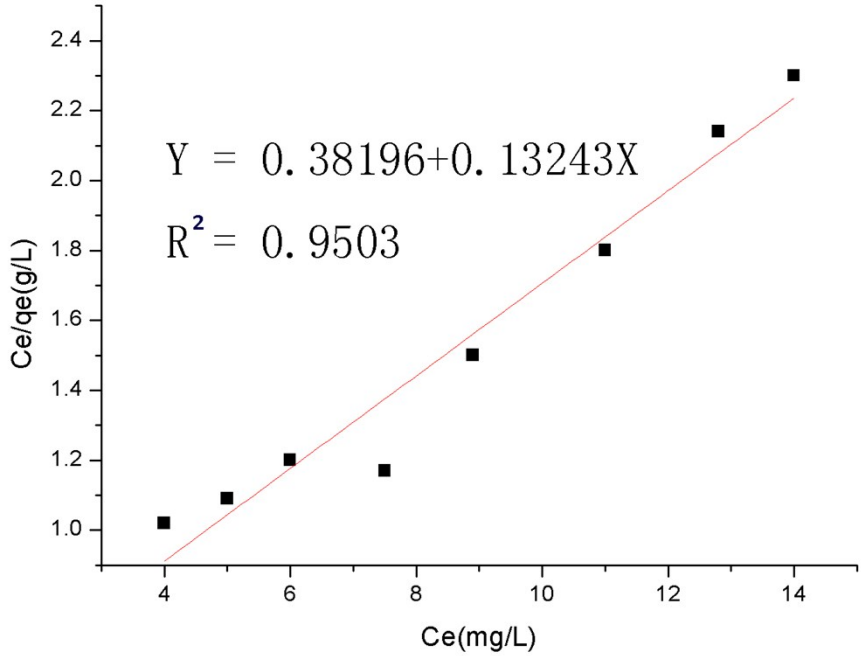
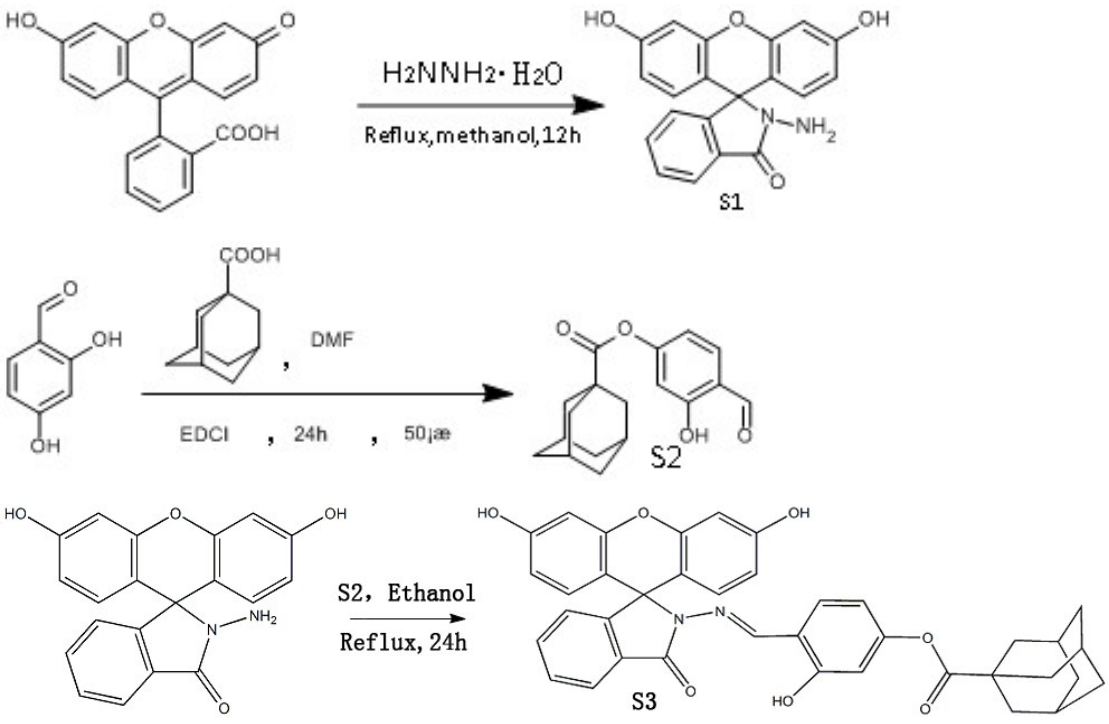


Fig.S12



Scheme S1



Scheme S2