Supplementary Information for

Sensitive fluorescent assay for copper (II) determination in aqueous solution using quercetin-cyclodextrin system

Captions:

Table S3 The performance of probes on recognition of Cu^{2+}

The ^{1}H NMR spectra of **CD**, **Q** and **Q-CD** were showed as Fig.S1-Fig.S3. The chemical shifts of H from **CD** and **Q** moved, and the chemical shifts of H from **Q** changed obviously. Thus, the chemical shifts of H from **Q** were studied before and after the **Q-CD** system formed.

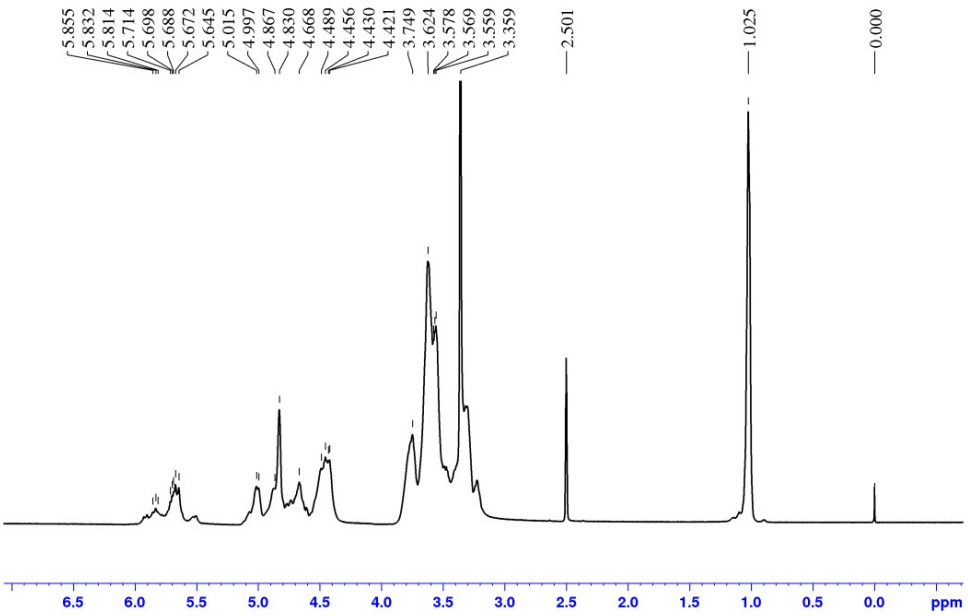


Fig.S1 The ^{1}H NMR spectrum of **CD**

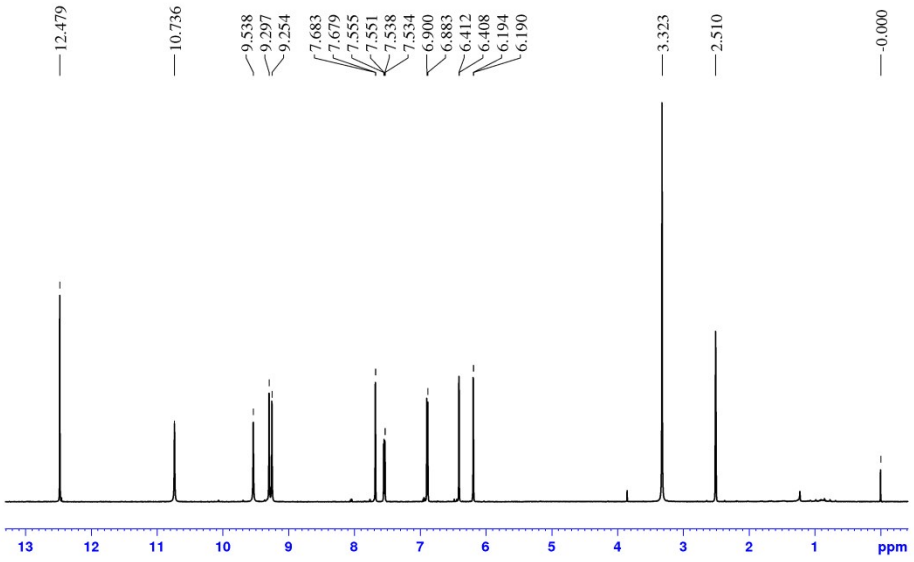


Fig.S2 The ^{1}H NMR spectrum of **Q**

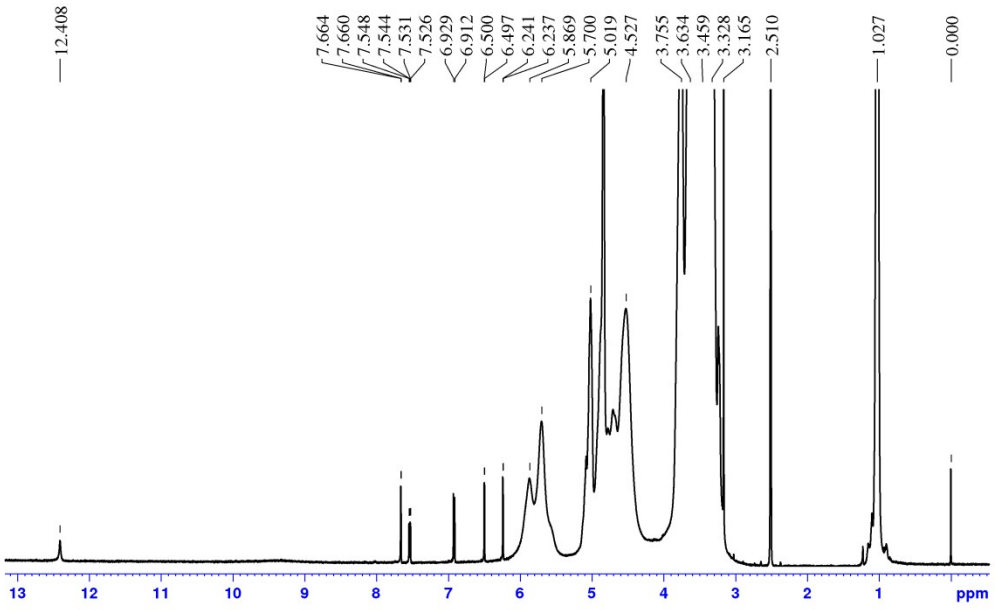


Fig.S3 The ^{1}H NMR spectrum of **Q-CD** system

The FT-IR spectrum of **CD**, **Q** and **Q-CD** were showed in Fig. S4 and Fig..S5. The band at 1667cm^{-1} for Q, due to carbonyl, disappeared in **Q-CD,** which implied that **Q** had got into CD's cavity.

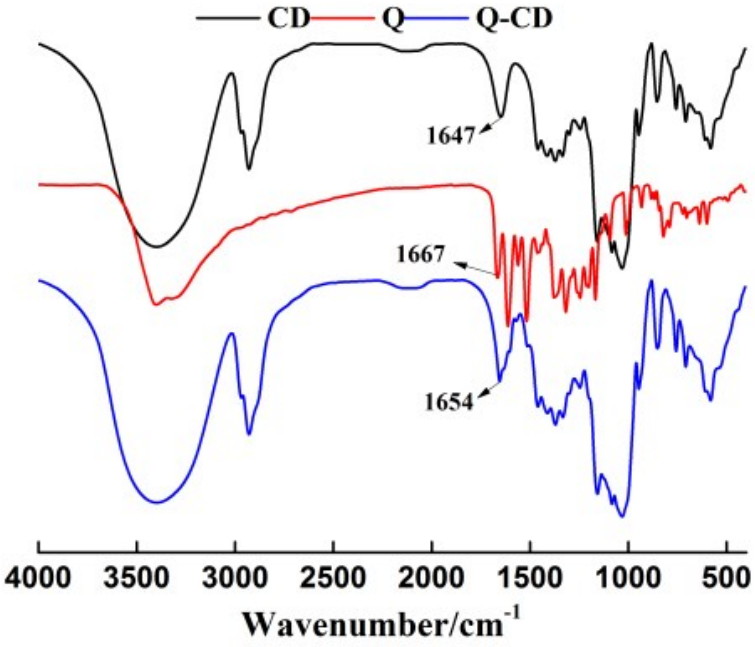


Fig.S4 The FT-IR spectra of **CD**, **Q** and **Q-CD** system.

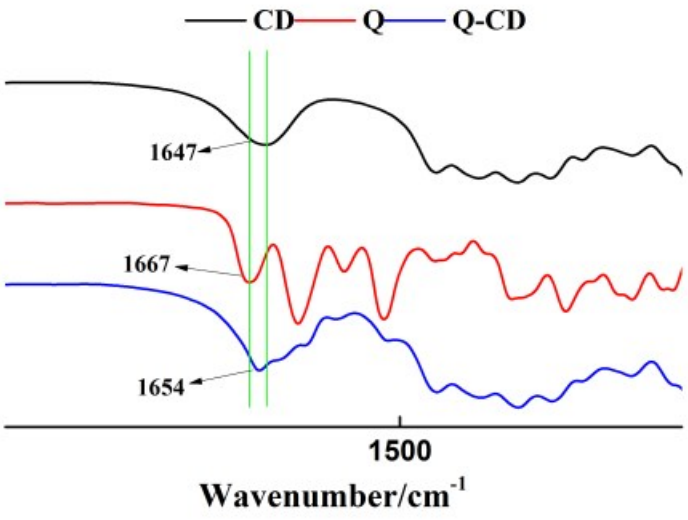
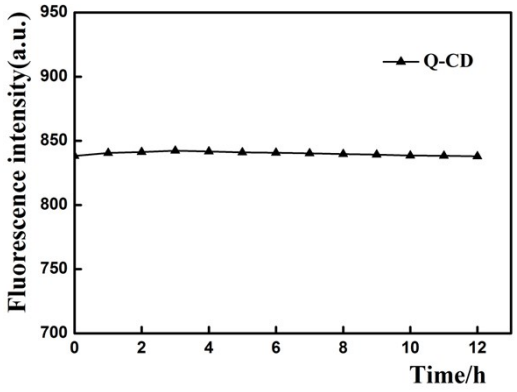
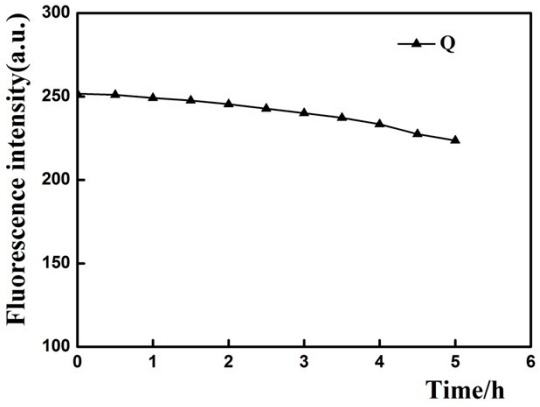


Fig.S5 The magnification of FT-IR spectra of **CD**, **Q** and **Q-CD** system.

To study the stability of **Q** and **Q-CD** system, the fluorescence emission intensity of **Q** was recorded every half hour, and the fluorescence emission intensity of **Q-CD** system was recorded each hour. The fluorescence emission intensity of **Q-CD** system showed almost no change within 12 h, however that of **Q** changed obviously within 5 h (Fig. S6), which indicated the stability of **Q-CD** system was higher than that of **Q**.



(a)



(b)

Fig. S6 The effect of time on the fluorescence intensity of Q-CD system (a) and Q (b)

Fe^{2+} induced interference for **Q** as probe to recognize Cu^{2+}, while for the **Q-CD** system, Fe^{2+} did not affect the sensing process (Fig. S7), which indicated **Q-CD** system could recognize Cu^{2+} with better selectivity than Q.

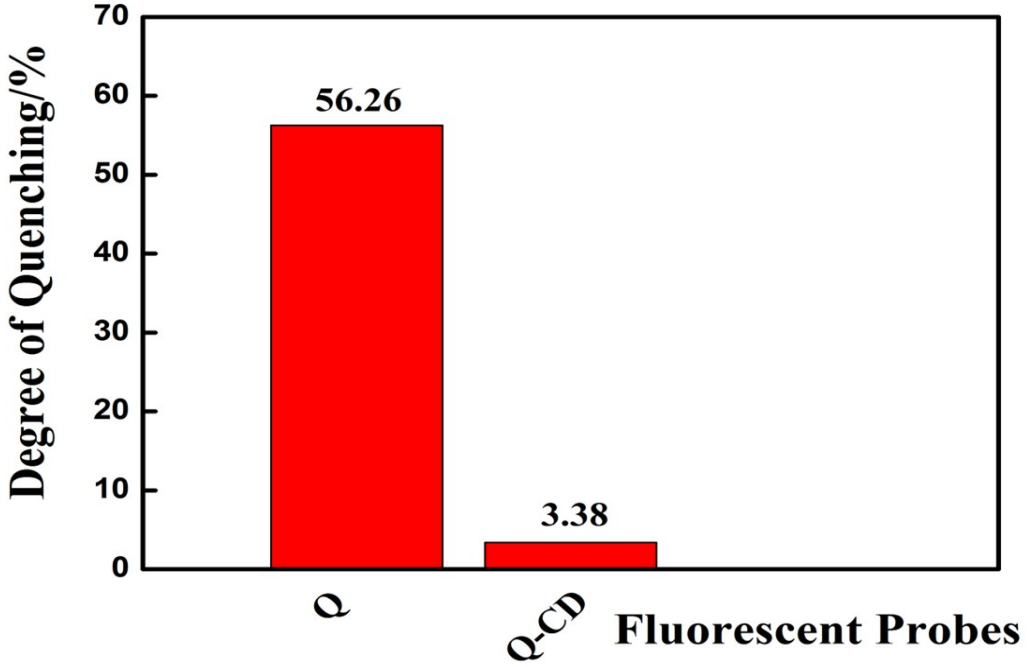


Fig.S7 The degree of fluorescence quenching caused by Fe^{2+}

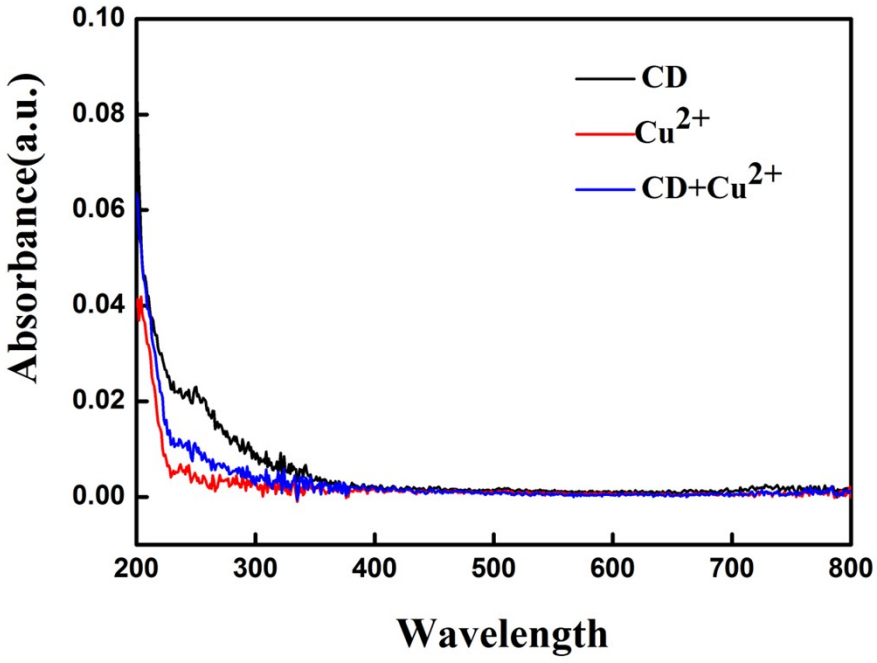


Fig.S8 The influence of Cu^{2+} on UV/Vis absorption spectrum of **CD**

There is no obvious change in colour during formation of **Q-CD** complex, and the colour was changed to dark yellow obviously during coordination of Cu in **Q-CD-Cu(II)** complex. The images were showed as below.

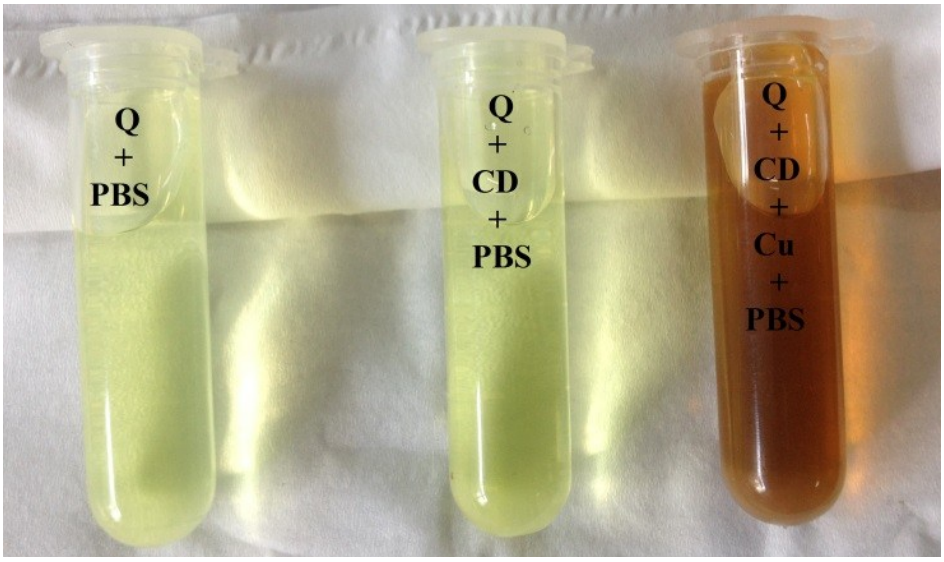


Fig.S9 The colour of **Q-CD** and **Q-CD-Cu(II)**

The UV-visible spectra of Q-CD system added metal ions were shown in Fig. S10. When cu^{2+} added, band I was shifted to 430 nm, which was a characteristic of the formation of the **Q-CD-Cu(II)** complex. While adding the other ions, the UV-visible absorption spectra of **Q-CD** system had no obvious change, the UV-visible spectra were similar.

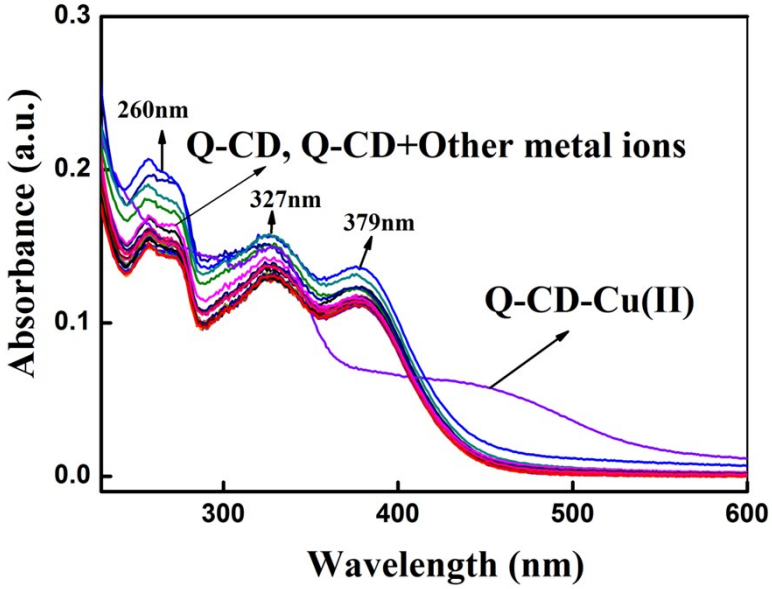


Fig.S10 The influence of different cations on UV/Vis absorption spectra of Q-CD system in CH_3OH-PBS buffer solution(1:99, V/V, pH = 7.40).

The FT-IR spectra of **Q-CD** and **Q-CD-Cu(II)** were studied in Fig.S11 and Fig.S12. The main change in the spectra was the shift of C=O. The C=O stretching mode of **Q-CD** system was 1654 cm^{-1},when adding Cu^{2+} into the **Q-CD** system, the $\nu_{C=O}$ was shifted to 1639 cm^{-1}, which was a characteristic of the formation of **Q-CD-Cu(II)** complex.

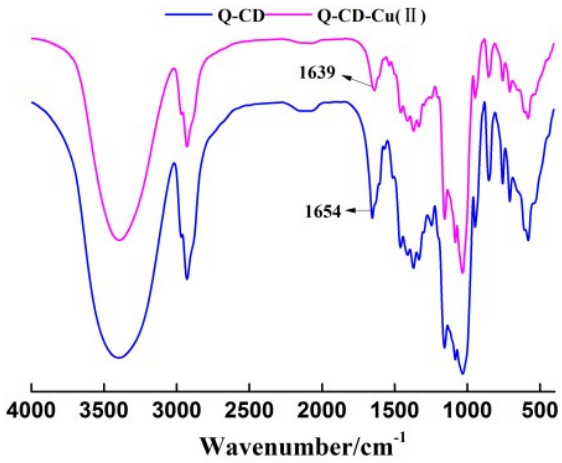


Fig.S11 The FT-IR spectra of **Q-CD** and **Q-CD-Cu(II).**

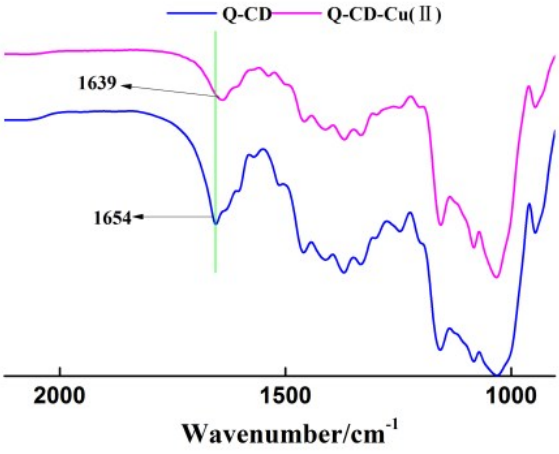


Fig.S12 The magnification of FT-IR spectra of **Q-CD** and **Q-CD-Cu(II).**

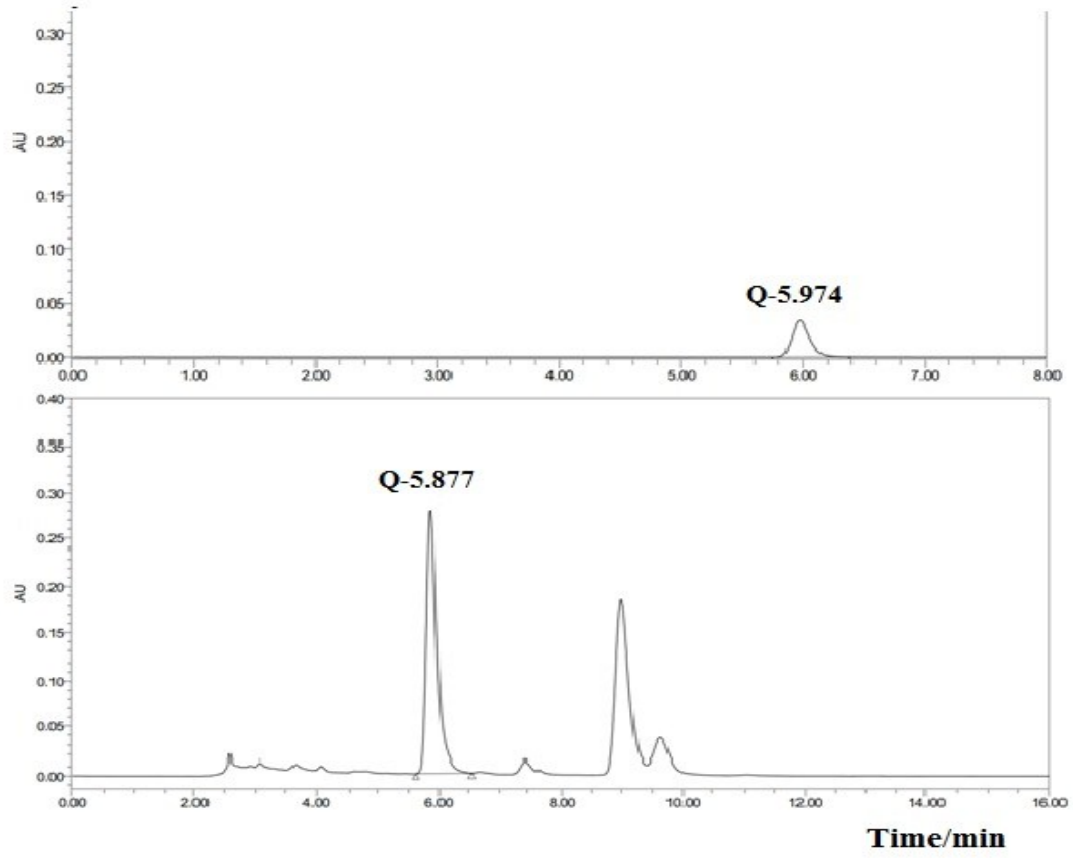


Fig.S13 The chromatogram of **Q**

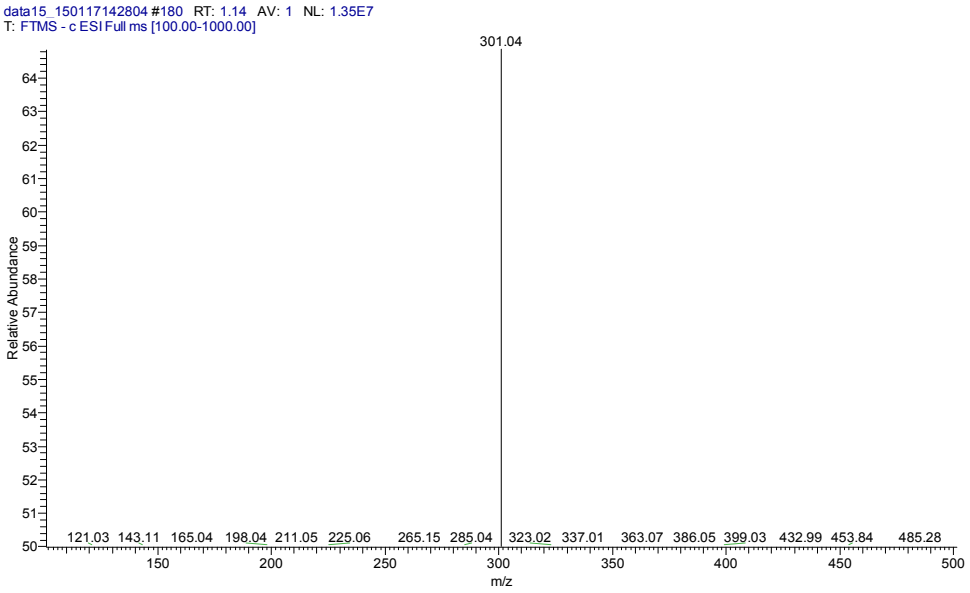


Fig.S14 The mass sepcturm of **Q**

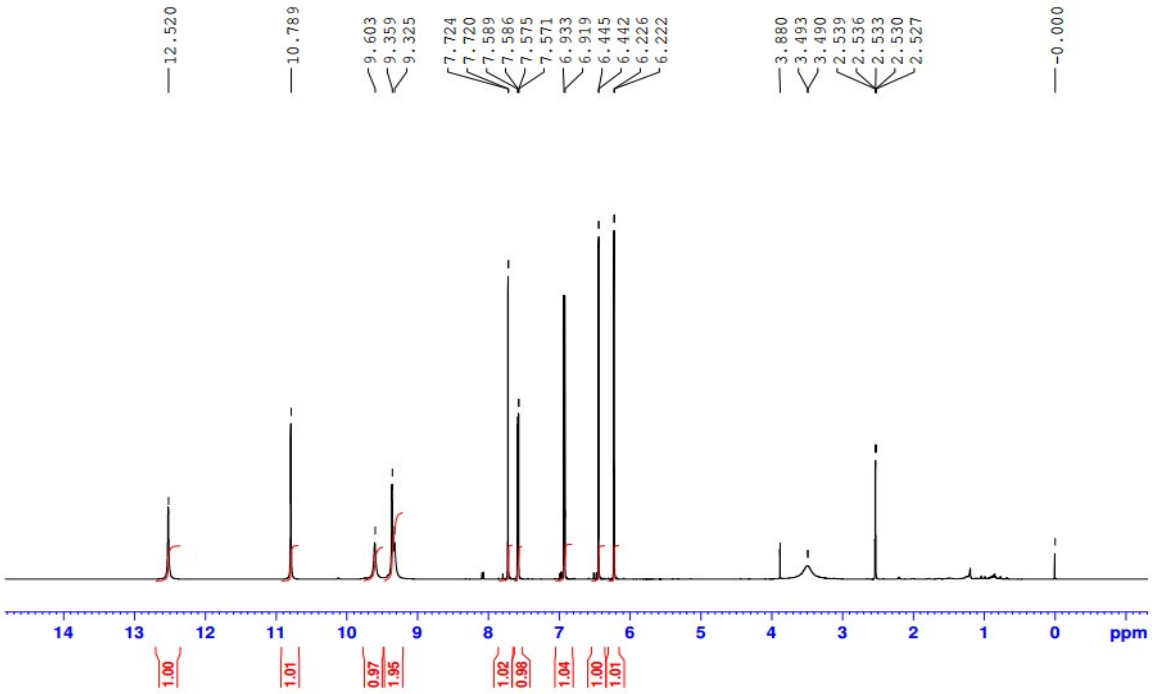


Fig.S15 The ^{1}H NMR of Q

The chemical shifts of **Q** and **Q-CD** are showed in Table S1.

Table S1 The chemical shifts of Q and Q-CD

Q	5-OH	7-OH	3-OH	4'-OH	3'-OH	2'-H	6'-H	5'-H	8-H	6-H
δ(ppm)	12.479	10.736	9.538	9.297	9.254	7.681	7.545	6.892	6.410	6.192
Q-CD	5-OH	7-OH	3-OH	4'-OH	3'-OH	2'-H	6'-H	5'-H	8-H	6-H
δ(ppm)	12.408	---	---	---	---	7.662	7.537	6.921	6.499	6.239

The detection limits for Cu^{2+} using **Q-CD** system and other materials were listed in the following table. It is easy to find the detection limit of **Q-CD** system is not the lowest, but it is lower than that of most materials. And the linearity range of **Q-CD** system is outstanding.

Table S2 The performance of probes on recognition of Cu^{2+}

Probes	Range(μM)	Detection Limit(nM)	Ref.
Q-CD	0.050-8.3	23	This Work
Cys-CdS QDs	2-10	1500	[1]
P1P2P3/SA-SiO_2	0.050-2.0	17.8	[2]
CdTe(S)@PAI QDs	0.05 -1.6	24	[3]
Ag_{20} nanoclusters	0.0167-7.2	4	[4]
BnA	2-100	1000	[5]
C-DA	0.015-10	3.0	[6]
HMC1	0-10	640	[7]
Probe 1	0.2-5	54	[8]
MAST	0.2-1	16.9	[9]
PC	0-6	3.49	[10]
B, N-carbon dots	1-25	300	[11]
CDs	0.01-2	6.7	[12]
C-dots	1-10	40	[13]
DPBT	0.45-3.6	170	[14]

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To study the reproducibility of the **Q-CD** system, each sample was analyzed at

least three times at three different concentrations (22.0×10^{-7} to 52.0×10^{-7} mol·L^{-1}), which was shown in Table S3. The change in fluorescence intensity was very less. That is, the reproducibility of the probe was good and the standard curve with good linearity could be used to quantify.

Table S3 The reproducibility of **Q-CD** system as fluorescent probe to detect copper ions

Probe	**[Cu^{2+}] /mol·L^{-1}**	**Fluorescence Intensity/a.u.**	**Average/a.u.**	**RSD (%)**
Q-CD	22.0×10^{-7}	642.94, 644.33, 640.13	642.47	0.33
	32.0×10^{-7}	546.72, 546.08, 547.36	546.72	0.12
	42.0×10^{-7}	456.12, 453.37, 451.88	453.79	0.47
	52.0×10^{-7}	362.70, 634.52, 365.33	364.18	0.37