Supporting information

A fluorescence on-off sensor for Cu^{2+} and its resultant complex as off-on sensor for Cr^{3+} in aqueous media

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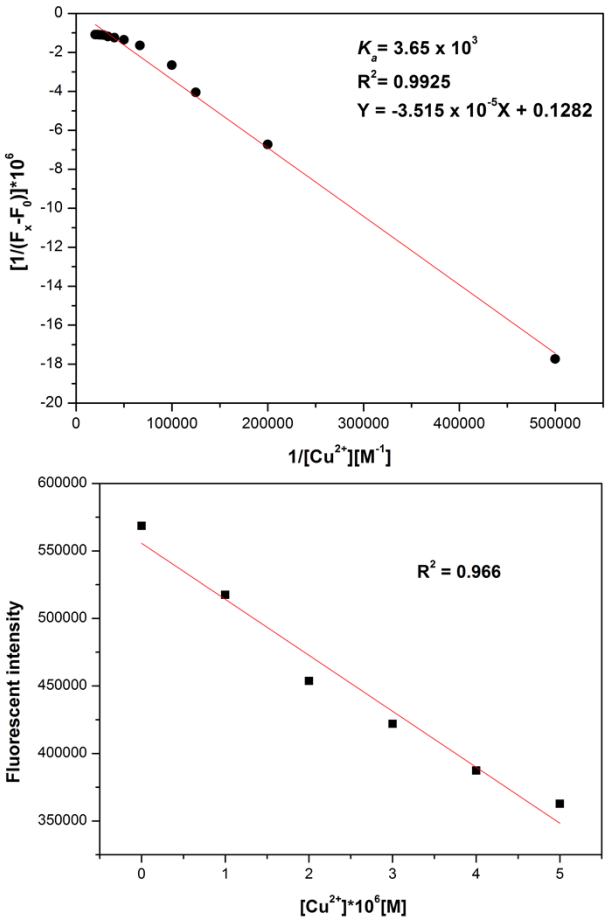


Fig. S1. Benesi-Hildebrand plot of the sensor **1** and Cu^{2+} (top) and the linear fitting of the fluorescence intensity of the sensor **1** toward the concentration of Cu^{2+} (bottom).

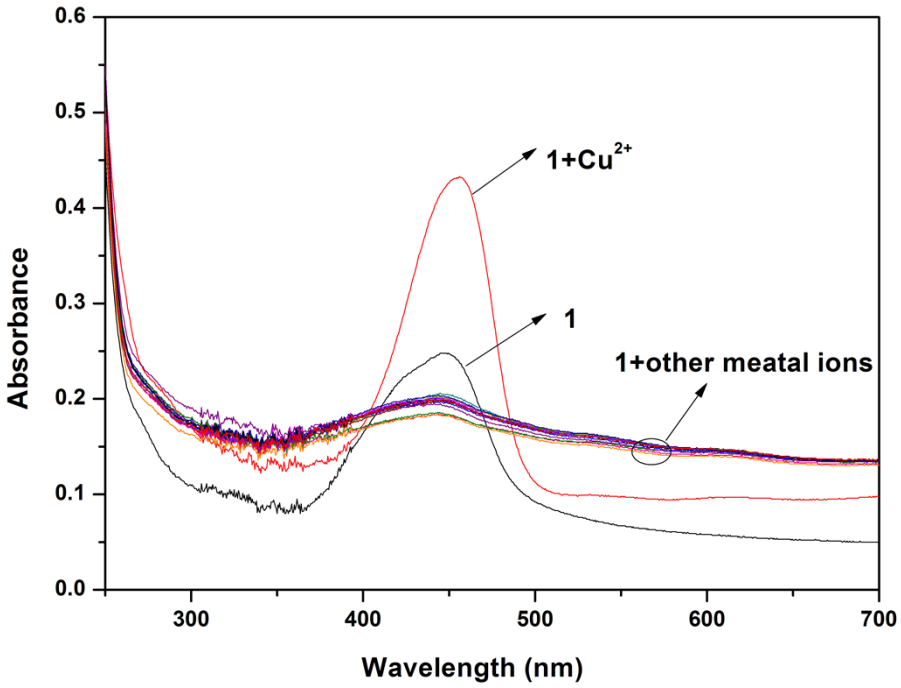


Fig. S2. Absorption changes of the sensor **1** (10 μM) upon addition of 3.0 equiv. of individual metal ions in 0.1 M HEPES-DMSO (9:1, v/v, pH = 7.2) solution.

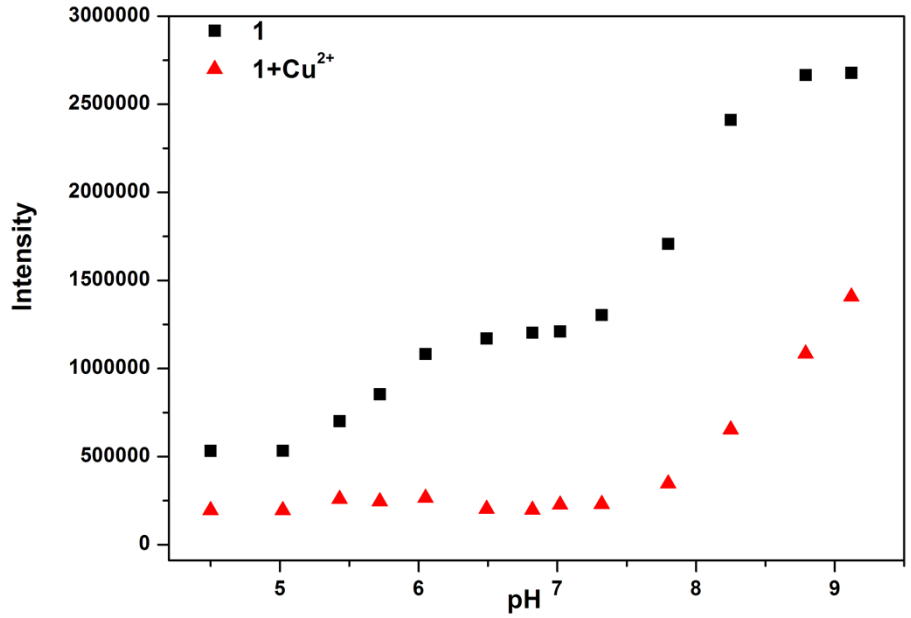


Fig. S3. Influences of pH on the fluorescence intensity of the sensor **1** (10 μM) and the sensor **1** plus Cu^{2+} (30 μM) in 0.1 M HEPES-DMSO (9:1, v/v, pH = 7.2) solution.

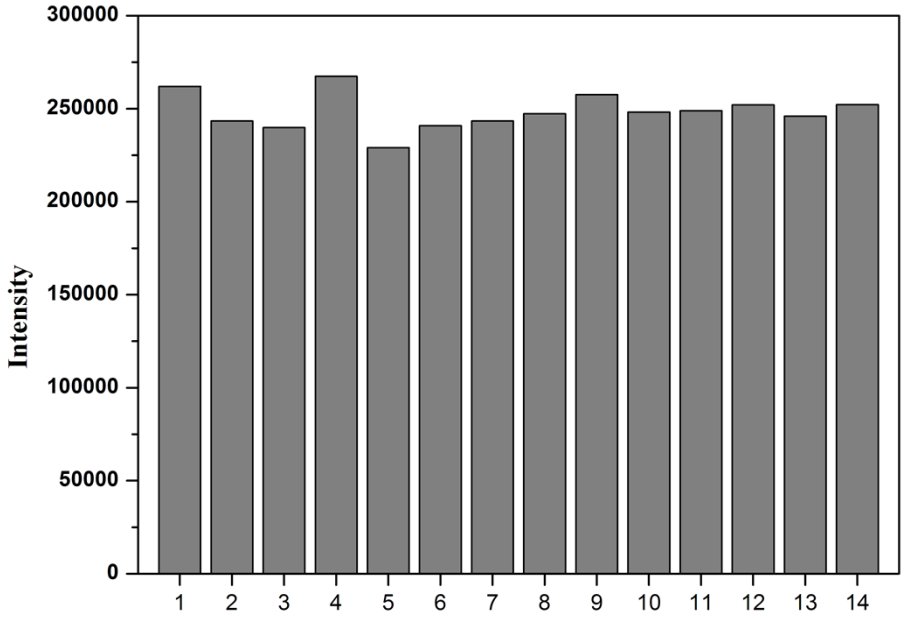


Fig. S4. Fluorescence response of the sensor **1** (10 μM) and Cu^{2+} (30 μM) in the presence of other different metal ions (30 μM) in 0.1 M HEPES-DMSO (9:1, v/v, pH = 7.2) solution. 1: Cu^{2+}, 2: Zn^{2+}, 3: Al^{3+}, 4: Na^{+}, 5: Fe^{3+}, 6: Ca^{2+}, 7: Ag^{+}, 8: Cd^{2+}, 9: K^{+}, 10: Mg^{2+}, 11: Ni^{2+}, 12: Co^{2+}, 13:Pb^{2+}, 14: Hg^{2+}.

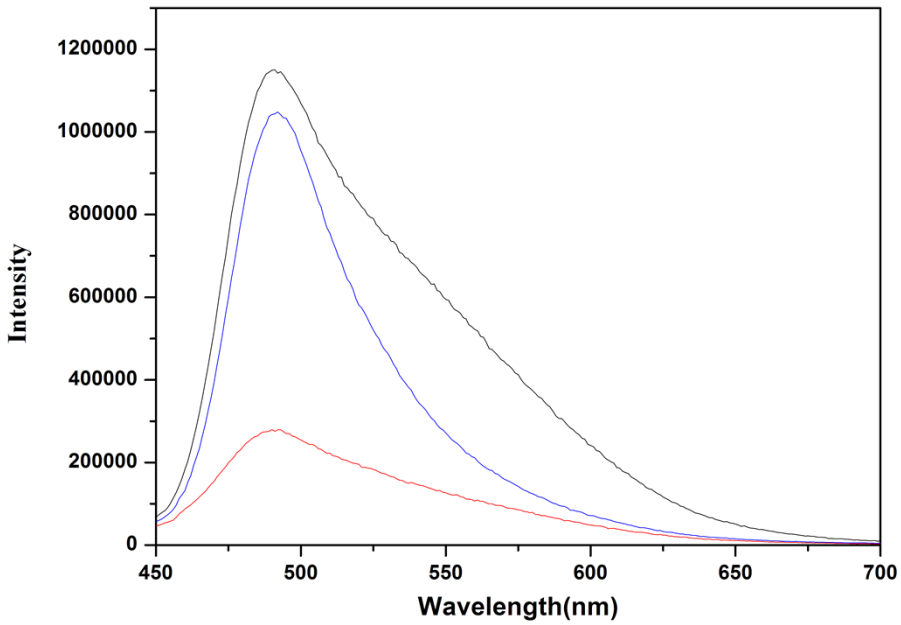


Fig. S5. Fluorescence changes of the sensor **1** (10 μM) upon sequential addition of 3.0 equiv. of Cu^{2+} and 3.0 equiv. of Cr^{3+} in 0.1 M HEPES-DMSO (9:1, v/v, pH = 7.2) solution (dark line for the sensor **1**, red line for 1+Cu^{2+}, blue line for 1+Cu^{2+}+Cr^{3+}).

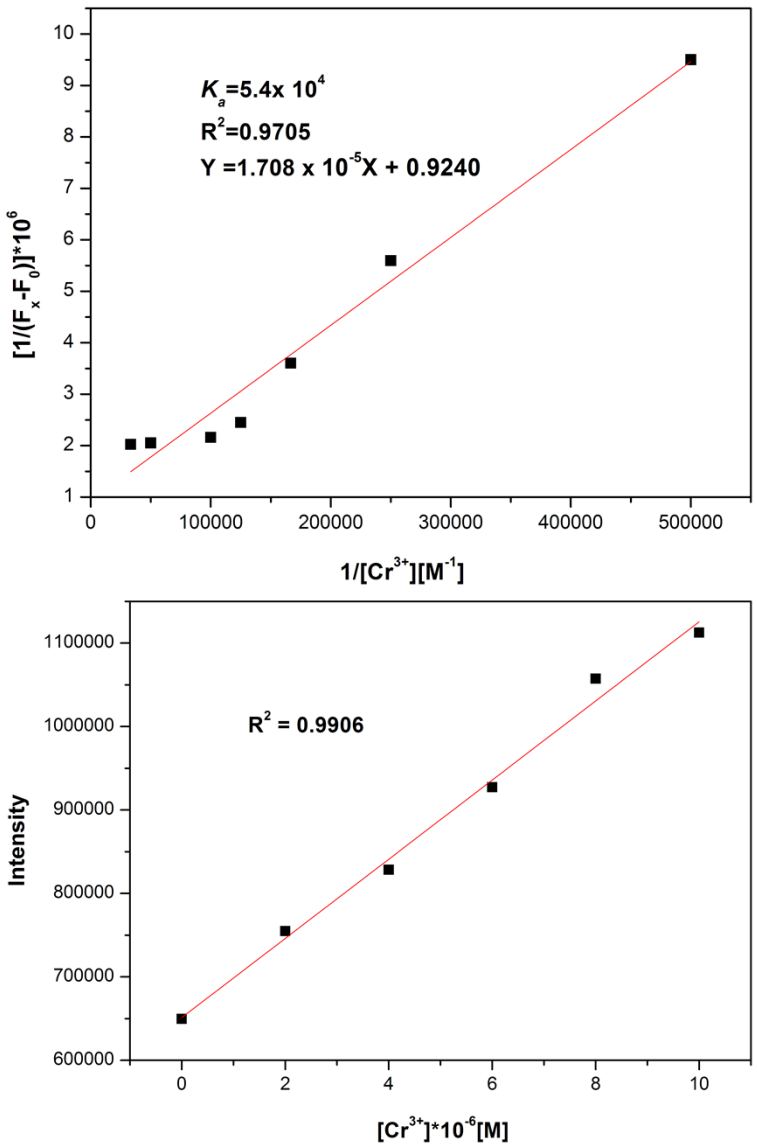


Fig. S6. Benesi-Hildebrand plot of **1**-Cu^{2+} with Cr^{3+} (top) and the linear fitting of the fluorescence intensity of **1**-Cu^{2+} toward the concentration of Cr^{3+} (bottom).

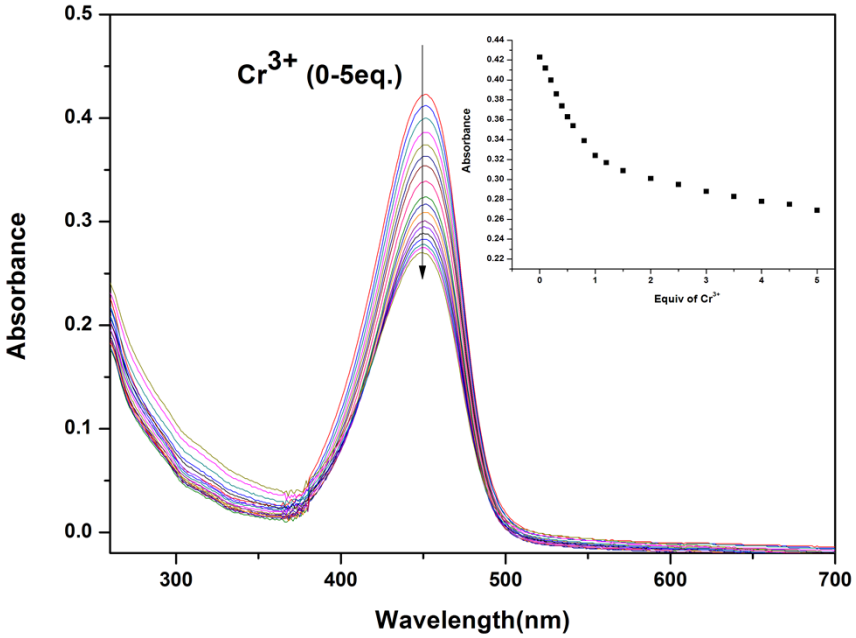


Fig. S7. Absorption changes of **1**-Cu^{2+} (13 μM) upon addition of different equivalents of Cr^{3+} (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0, 1.2, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 equiv.) in 0.1 M HEPES-DMSO (9:1, v/v, pH = 7.2) solution. Inset: a plot of the maximum absorption change at 451 nm against different equivalents of Cr^{3+}.

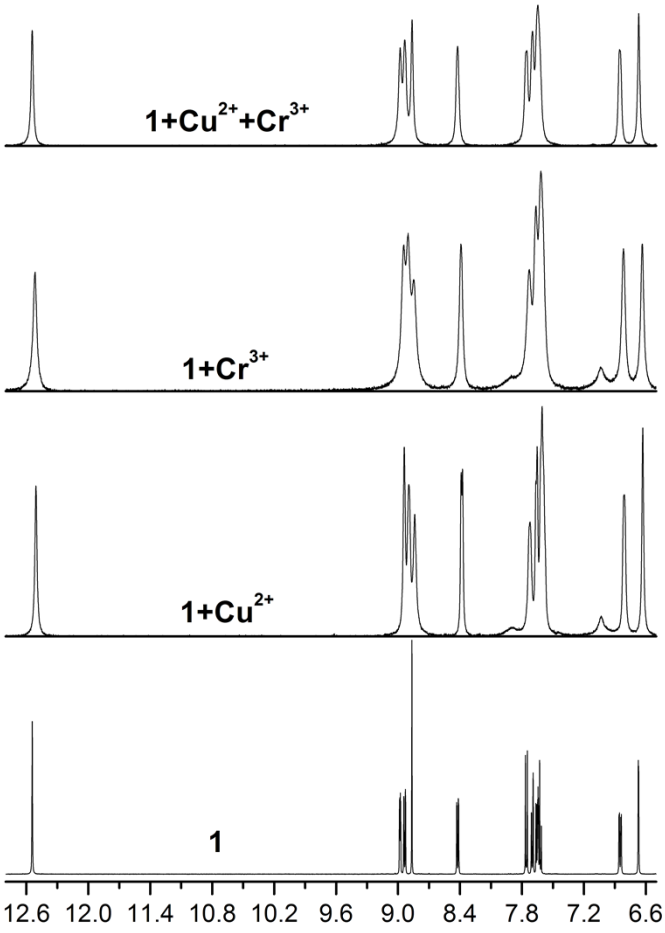


Fig. S8. ^{1}H NMR spectra of the sensor **1** in the presence of Cu^{2+} and Cr^{3+} in DMSO-d_6.

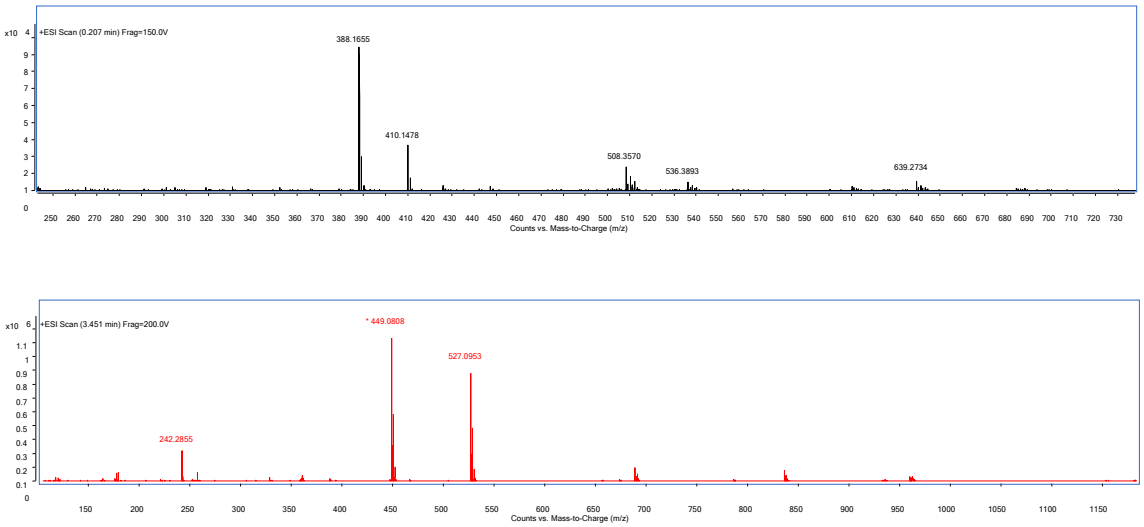


Fig. S9. HRMS for the sensor **1** (top) and **1**-Cu^{2+} complex (bottom).

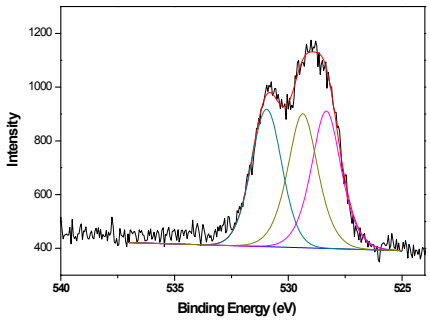
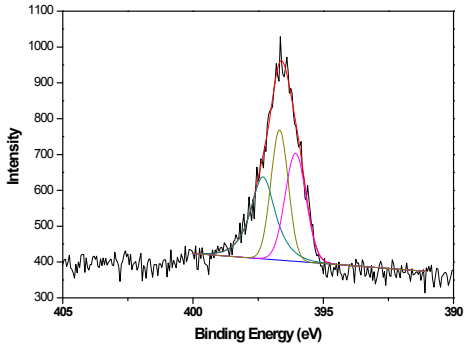
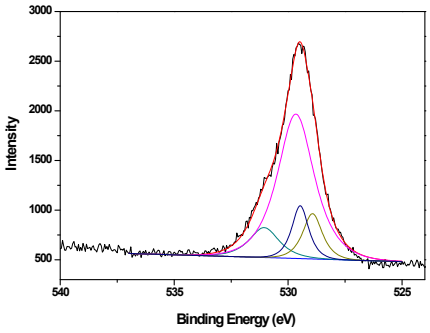
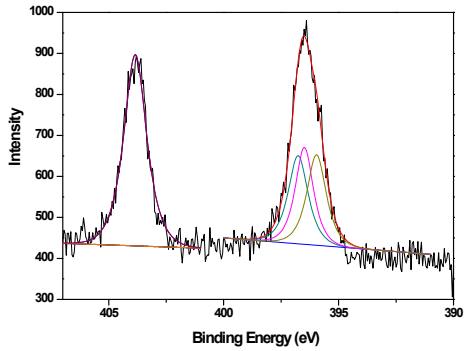
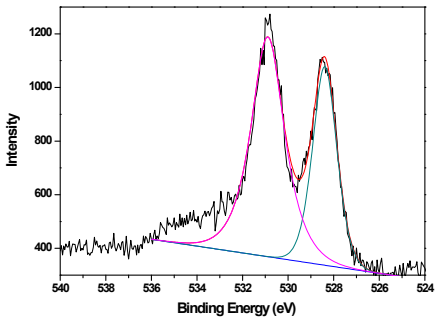
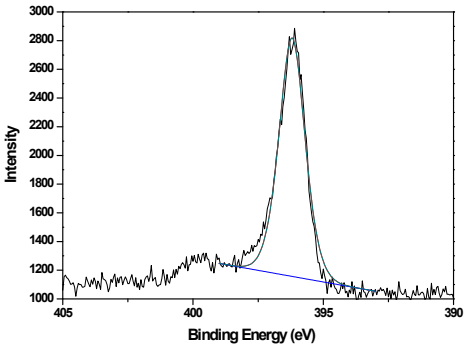
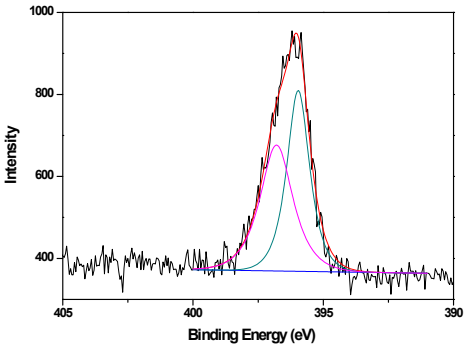
	O1s	N1s
1		
1-Cu^{2+}		
Coumarin 120		
8-amino quinoline		

Fig. S10. XPS spectra of O1s and N1s of the sensor **1** and **1**-Cu^{2+}.

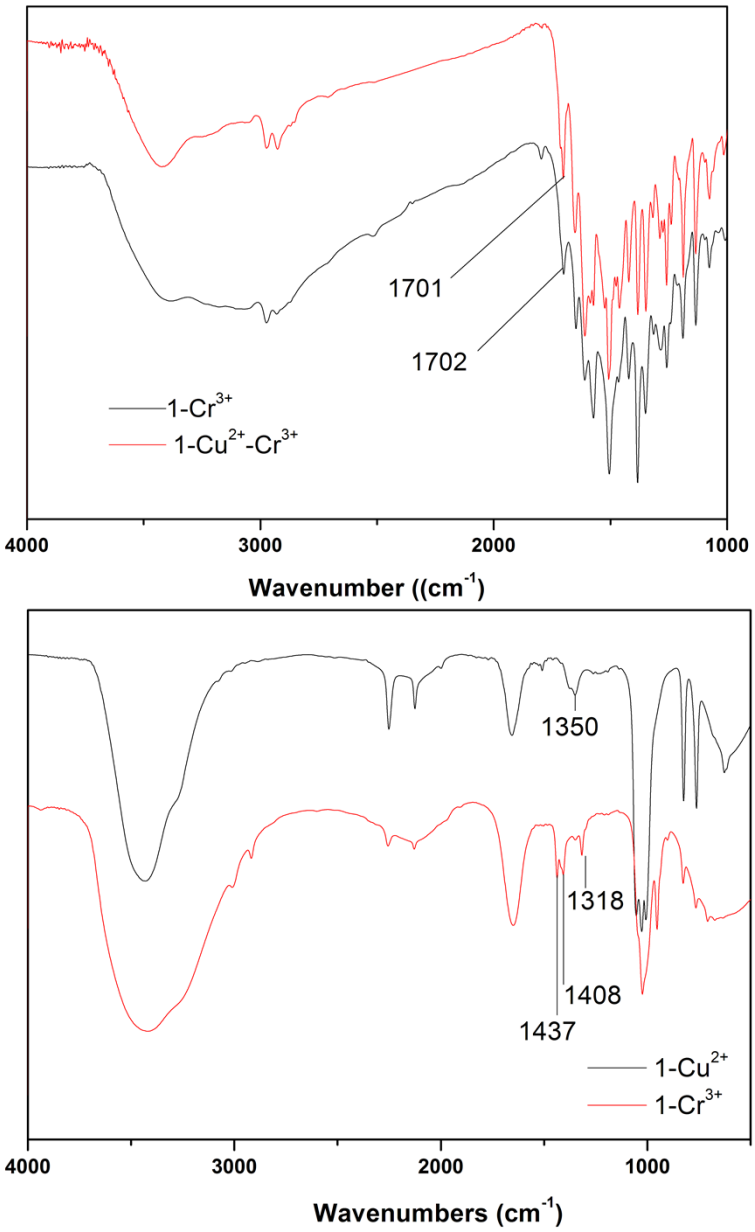
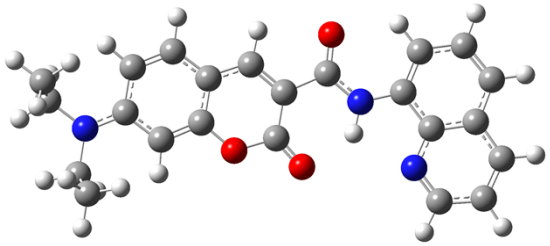


Fig. S11. FT-IR spectra of 1-Cu^{2+} with Cr^{3+} and 1-Cr^{3+} using the KBR compression method (top); FT-IR spectra of 1-Cu^{2+} and 1-Cr^{3+} in DMSO (bottom).

DFT-optimized structure of the sensor **1**



Cartesian coordinate:

C	4.55318900	-1.50332600	-0.21714800
C	3.27519300	-2.00768900	-0.15992600
C	2.14686700	-1.16411900	-0.15175500
C	2.38765400	0.22133600	-0.20055000
C	3.66394200	0.75434900	-0.25696100
C	4.79034600	-0.09662600	-0.28136300
H	0.56650000	-2.65882400	-0.04796200
H	5.38119800	-2.19581800	-0.21057400
H	3.12506000	-3.08089800	-0.11596800
C	0.79973400	-1.60006400	-0.08937200
H	3.74971600	1.82972800	-0.27873300
C	0.00721800	0.70831200	-0.13168500
C	-0.25014600	-0.72579500	-0.07925500
N	6.06579900	0.40873200	-0.37573500
C	7.23689800	-0.47135700	-0.38772100
H	8.04385100	0.07894100	-0.87616900
H	7.03195300	-1.33155800	-1.03063600
C	6.30308700	1.85367200	-0.43068800
H	7.27099400	2.00138600	-0.91450400
H	5.56377100	2.30946800	-1.09492100
O	-0.80433300	1.60255200	-0.13141200
C	-1.63061300	-1.32202200	-0.01089900
O	-1.76087000	-2.53992400	0.03729500
O	1.34793300	1.09912700	-0.18794600
N	-2.67460600	-0.43871900	-0.00717500
H	-2.45733600	0.55898000	-0.05229400
C	-4.03666800	-0.74111900	0.05334300
C	-4.92425300	0.39015700	0.03689800
C	-4.57290200	-2.01581500	0.12694400
C	-6.33388500	0.18120400	0.09756500
C	-5.97183800	-2.19902300	0.18586200
H	-3.90826300	-2.86462600	0.13865200
C	-5.16911000	2.67336800	-0.05260100
C	-7.15322600	1.33602500	0.07816600

C	-6.84373500	-1.13871600	0.17264500
H	-6.35455900	-3.21204700	0.24289600
C	-6.57798900	2.58035000	0.00351400
H	-4.68795700	3.64622300	-0.11239100
H	-8.23146000	1.22071300	0.12259700
H	-7.91616900	-1.29364900	0.21829800
H	-7.17998200	3.48110800	-0.01314700
N	-4.37216400	1.62730100	-0.03673800
C	6.29773500	2.56240200	0.92966000
H	7.09538300	2.18654500	1.57411300
H	6.45280900	3.63629000	0.79126500
H	5.34888400	2.42246500	1.45118900
C	7.70572300	-0.94404800	0.99428500
H	8.56630800	-1.61120300	0.88921000
H	8.00704600	-0.10046400	1.61882900
H	6.91788100	-1.48674800	1.52054600