Electronic Supplementary Information

A FRET fluorescent nanosensor based on carbon dot for ratiometric detection of Fe^{3+} in aqueous solution

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Experimental Section

Materials

Rhodamine 6G and diethylenetriamine were purchased from Sigma-Aldrich and used as received. Citric acid, ethylenediamine, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl), N-hydroxysulfosuccinimide (NHS) were purchased from Aladdin Industrial Inc. Chloride salts (K^+, Ca^{2+}, Ag^+, Na^+, Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Hg^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}) were used for experiments. Double distilled water from a Millipore Milli-Q purication system was used throughout the work.

Synthesis of the rhodamine 6G probe

Rhodamine 6G (1.0 g) and diethylenetriamine (2.0 g) were dissolved in methanol (10 mL) and refluxed for 12 h under nitrogen. After cooling to room temperature, the solvent was evaporated in vacuo. Then, CH_2Cl_2 (100 mL) and water (200 mL) were added and the organic layer separated. The CH_2Cl_2 layer was washed twice with water and dried over anhydrous Na_2SO_4. After filtration of Na_2SO_4, removal of the solvent in vacuo gave 0.8 g yellow solid (The ^{1}H NMR spectrum of 1 was shown in Fig. S1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, J = 6.1 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.10 – 7.05 (m, 1H), 6.37 (s, 2H), 6.25 (s, 2H), 3.53 (t, J = 4.9 Hz, 2H), 3.31 – 3.19 (m, 6H), 2.63 (d, J = 8.4 Hz, 3H), 2.43 (dt, J = 12.9, 6.2 Hz, 4H), 1.93 (s, 6H), 1.35 (t, J = 7.1 Hz, 6H) ppm.

Preparation of carbon dots (CDs)

CDs were prepared according to a reported method (Chem. Commun., 2012, 48, 7955–7957). In summary, citric acid (1.0g) and ethylenediamine (0.384 mL) were dissolved in double distilled water under vigorous stirring to form a clear solution. Then, the clear transparent solution was put into a domestic microwave oven (700 W) and heated for 2min to obtain red-brown viscous CD solution. Finally, the CDs were precipitated by centrifugation and rinsed with anhydrous ethanol twice. The carboxyl-coated CDs solution was dried to obtain a powder for further use.

Preparation of the R6G-CD nanosensor

The R6G-CD nanosensor was prepared as follows: the carboxylcoated CDs (20 mg) were dissolved in water (2 mL). EDC·HCl (10 mg) and NHS (3 mg) were added to the solution under a N_2 atmosphere. After the mixture being stirred for 1 h at room temperature, the probe (10 mg) in the solution of DMSO (2 mL) was added dropwise to the mixture and stirred for 48 h. Finally, the reaction solution was dialyzed against pure water through a dialysis membrane (MWCO of 500) for 3 days and then the

R6G-CD nanosensor was dried under vacuum.

Determination of fluorescence quantum yield for the CDs

The quantum yield of the CDs was measured referenced to quinine sulfate in sulfuric acid aqueous solution (Φ_{fr} = 0.546) and calculated according to the following equation:

$$\Phi_{fs} = \Phi_{fr} \times \frac{1 - 10^{-A_r L_r}}{1 - 10^{-A_s L_s}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}$$

where Φ_{fs} is the radiative quantum yield of the CDs; Φ_{fr} is the radiative quantum yield of the standard; A_s and A_r are the absorbance of the CDs and standard at the excitation wavelength, respectively; D_s and D_r are the integrated areas of the emission for the CDs and standard, respectively; L_s and L_r are the lengths of the absorption cells for the CDs and standard test; and N_s and N_r are the indexes of refraction of the CDs and standard solutions respectively.

Determination of detection limit

The limit of detection (DL) of the R6G-CD nanosensor for Fe^{3+} was calculated based on the fluorescence titration and determined from the following equation:

$$DL = 3\sigma/K$$

where σ is the standard deviation of the blank solution; K is the slope of the calibration curve.

Preparation of the test paper of the R6G-CD nanosensor and its sensing test

The filter paper was cutting into a strip and immersed in the aqueous solution of the R6G-CD nanosensor (1 mg/mL). A few minutes later, the filter paper was removed from the solution and dried. Then, the test paper was dropped with various metal cations aqueous solution (2 mM). The changes in the color and fluorescence of the test paper were investigated with a digital camera. The test paper was was written by a brush pen with the Fe^{3+} aqueous solution (2 mM). The fluorescence photographs were taken under 365 nm lamp.

Measurements

Absorption spectra were taken on a Shimadzu 3100 UV-VIS-NIR recording spectrophotometer. Fluorescence spectra were measured on a Shimadzu RF-5301PC spectrofluorophotometer. ^{1}H NMR (TMS) were recorded on a Bruker UltraShield 500 MHz spectrometer. FTIR spectra were recorded on a Bruker Optics VERTEX 80v Fourier transform infrared spectrometer, equipped with a DTGS detector in pressed

KBr pellets. Atomic-force microscopy (AFM) was performed on a DI Veeco Multimode V atomic force microscope operated in the contact mode.

Figure captions:

Scheme S1 Synthesis route for the R6G-CD nanosensor.

Fig. S1 AFM topography image of CDs with height profile along line AB in the image.

Fig. S2 Relative fluorescence intensity at 455 nm (λ_{ex} = 360 nm) of the CDs (0.02 mg/mL) in the presence of 50 μM various metal cations in aqueous solution.

Fig. S3 ^{1}H NMR spectra in $CDCl_3$ of the rhodamine 6G probe.

Fig. S4 (a) The fluorescence spectra of and (b) relative fluorescence intensity at 550 nm (λ_{ex} = 500 nm) of the rhodamine 6G probe (10 μM) in the presence of 50 μM various metal cations in aqueous solution containing 0.1% ethanol.

Fig. S5 ^{1}H NMR spectra (in D_2O) of (a) the plain CDs and (b) the R6G-CD nanosensor.

Fig. S6 FTIR spectra of the plain CDs (black) and the R6G-CD nanosensor (red).

Fig. S7 The fluorescence spectra of (a) the CDs and (b) the R6G-CD nanosensor in pH 3-10 Britton–Robinson buffer solution (40 mM).

Fig. S8 Absorption spectra of R6G-CD nanosensor (0.02 mg/mL) in aqueous solution before and after addition of Fe^{3+}.

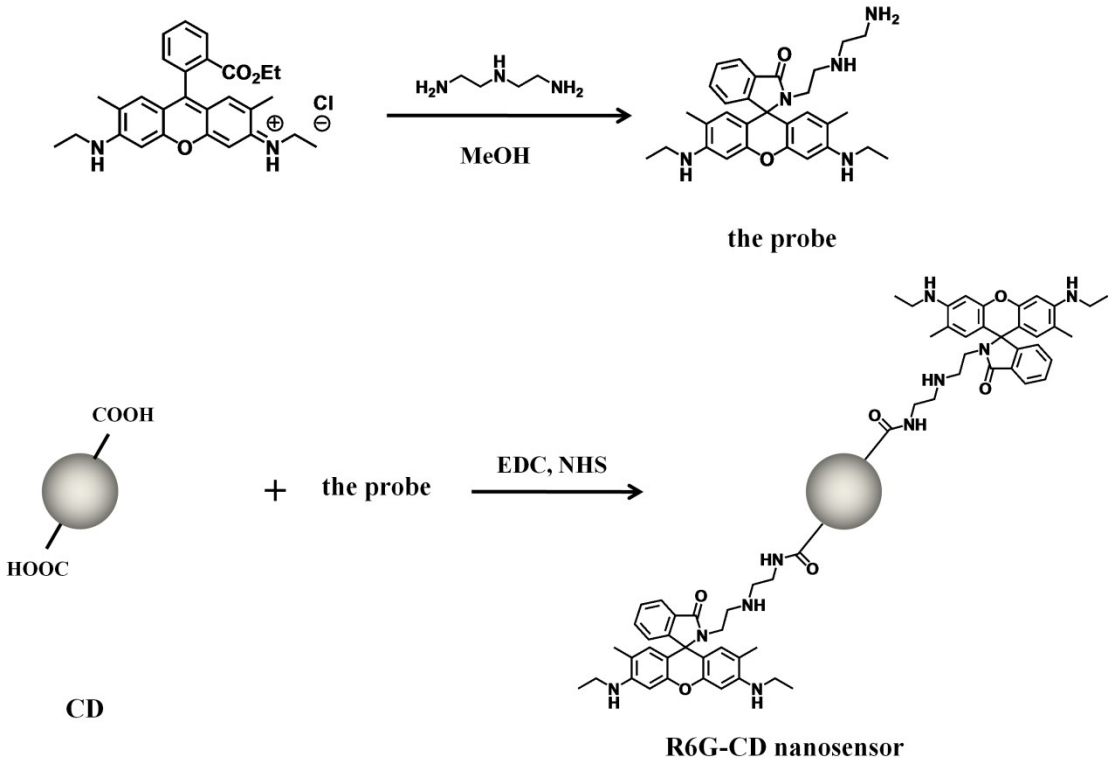
Fig. S9 The photograpghs of the R6G-CD nanosensor in the absence of Fe^{3+} and upon addition of Fe^{3+} in aqueous solution.

Fig. S10 Fluorescent intensity ratio (I_{550}/I_{455}) of the R6G-CD nanosensor (0.02 mg/mL) in the presence of different amounts of Fe^{3+} in aqueous solution (λ_{ex} = 360 nm).

Fig. S11 Fluorescence intensity (I_{550}) of the R6G-CD nanosensor (0.02 mg /mL) upon addition of 200 μM Fe^{3+} in water.

Fig. S12 The fluorescence spectra of the R6G-CD nanosensor (0.02 mg/mL) (a) in the absence or in the presence of 200 μM (b) Fe^{3+}, (c) Hg^{2+} and (d) Fe^{3+} + Hg^{2+} in aqueous solution (λ_{ex} = 360 nm).

Fig. S13 Fluorescence intensity ratio (I_{550}/I_{455}) of the R6G-CD nanosensor (0.02 mg /mL) in the presence of 200 μM various various Fe^{3+} salts (Cl^-, ClO_3^-, SO_4^{2-}, NO_3^-, CH_3COO^-), respectively.



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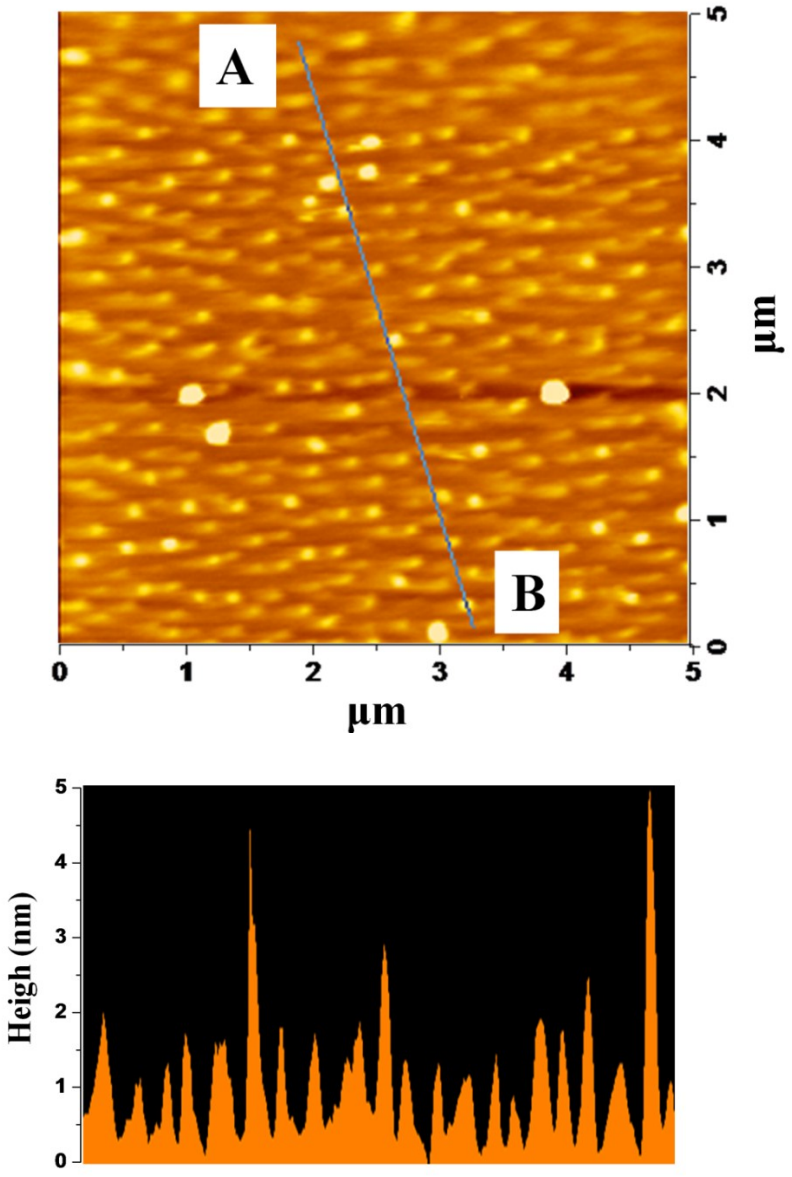

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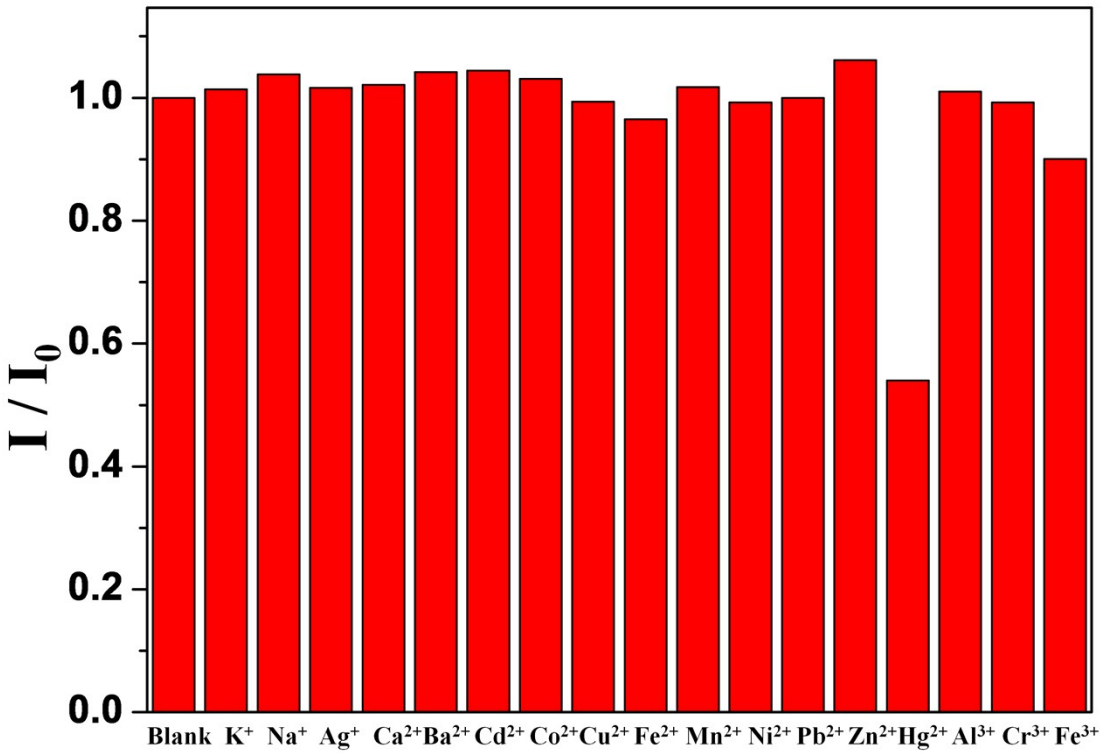
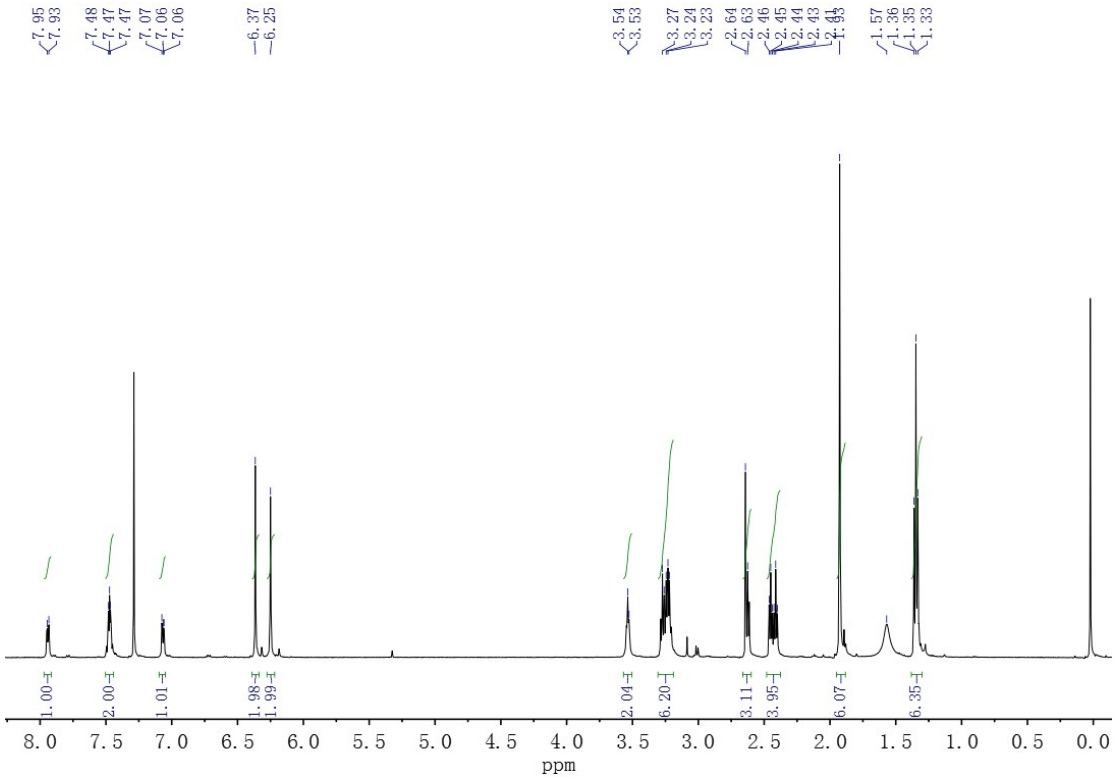


Fig. S2 Relative fluorescence intensity at 455 nm (λ_{ex} = 360 nm) of the CDs (0.02 mg/mL) in the presence of 50 μM various metal ions in aqueous solution.



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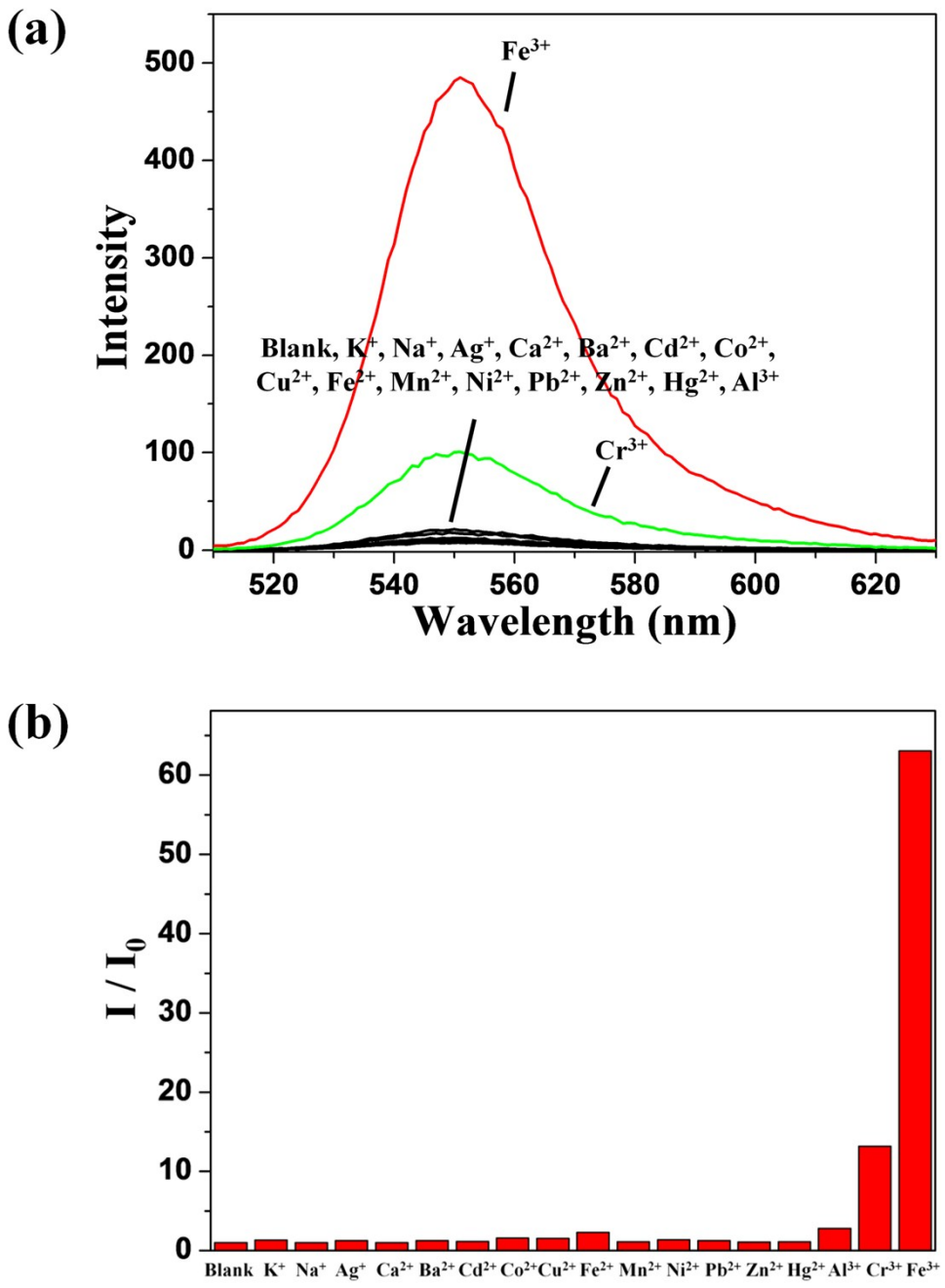

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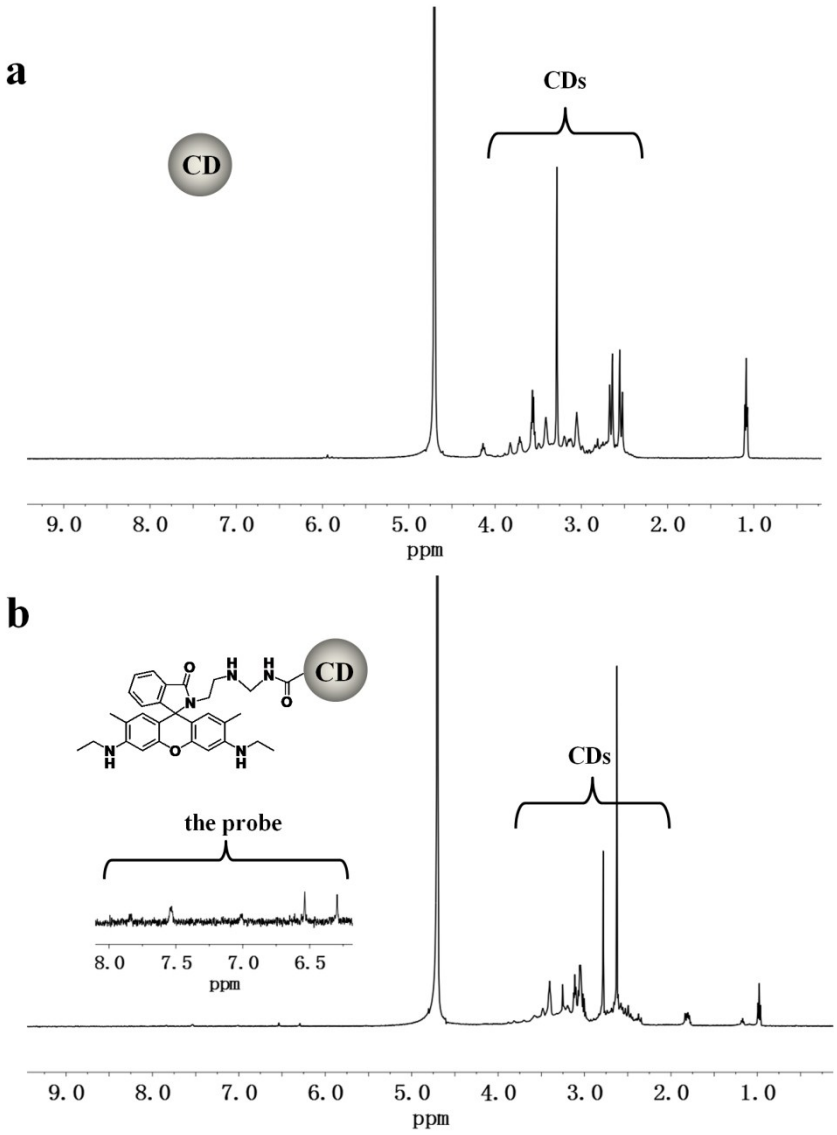

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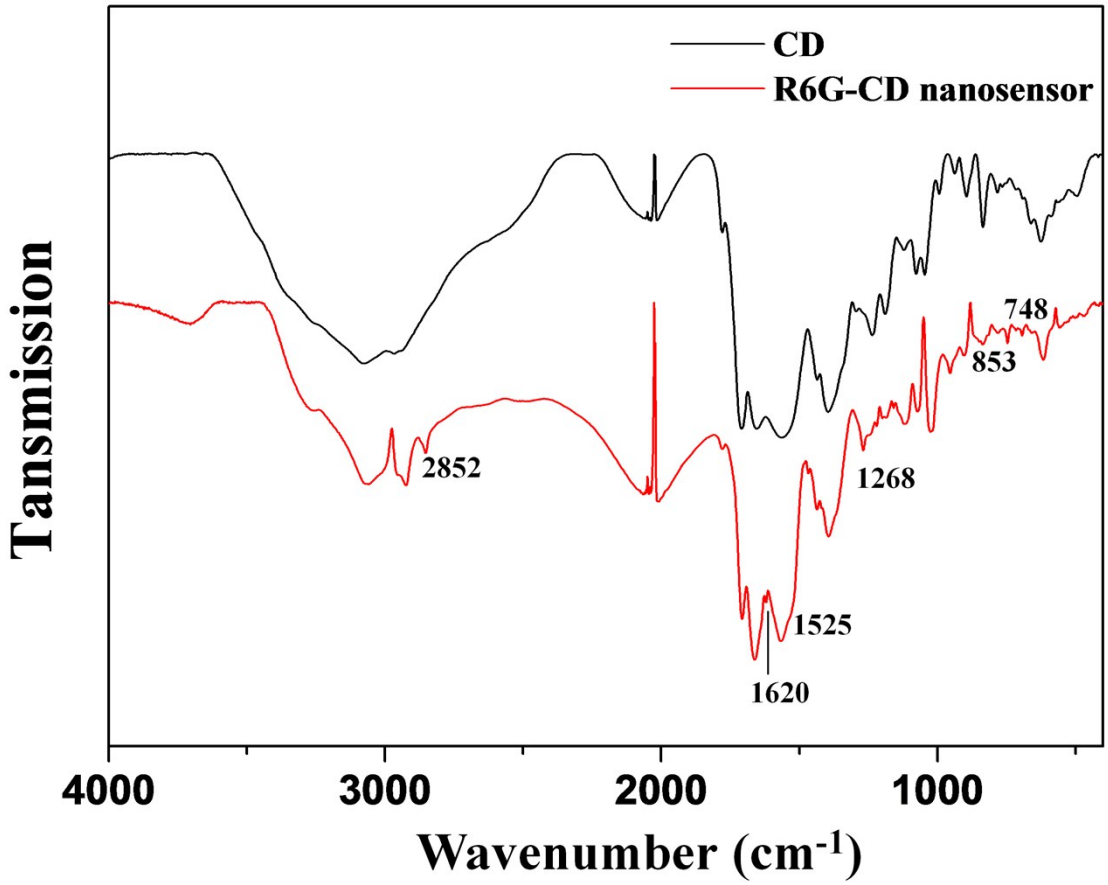


Fig. S6 FTIR spectra of the plain CDs (black) and the R6G-CD nanosensor (red).

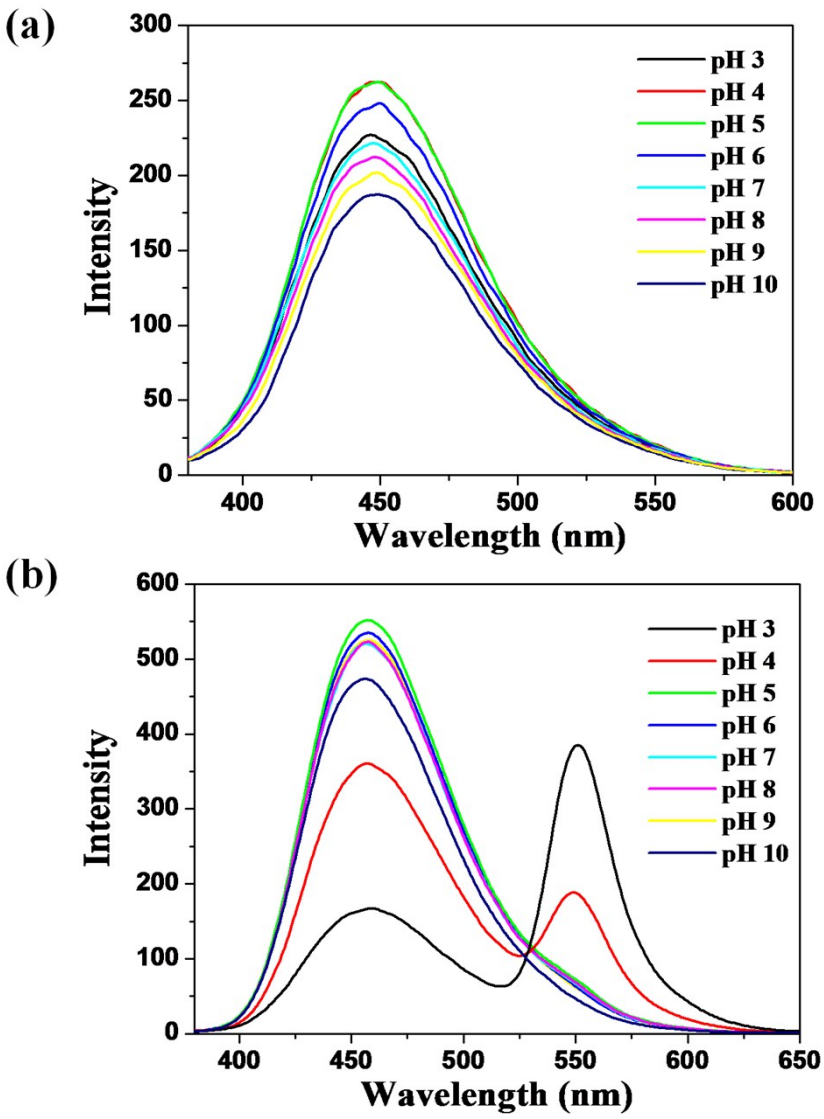


Fig. S7 The fluorescence spectra of (a) the CDs (0.01 mg /mL) and (b) the R6G-CD nanosensor (0.02 mg /mL) in pH 3-10 Britton–Robinson buffer solution (40 mM) (λ_{ex} = 360 nm).

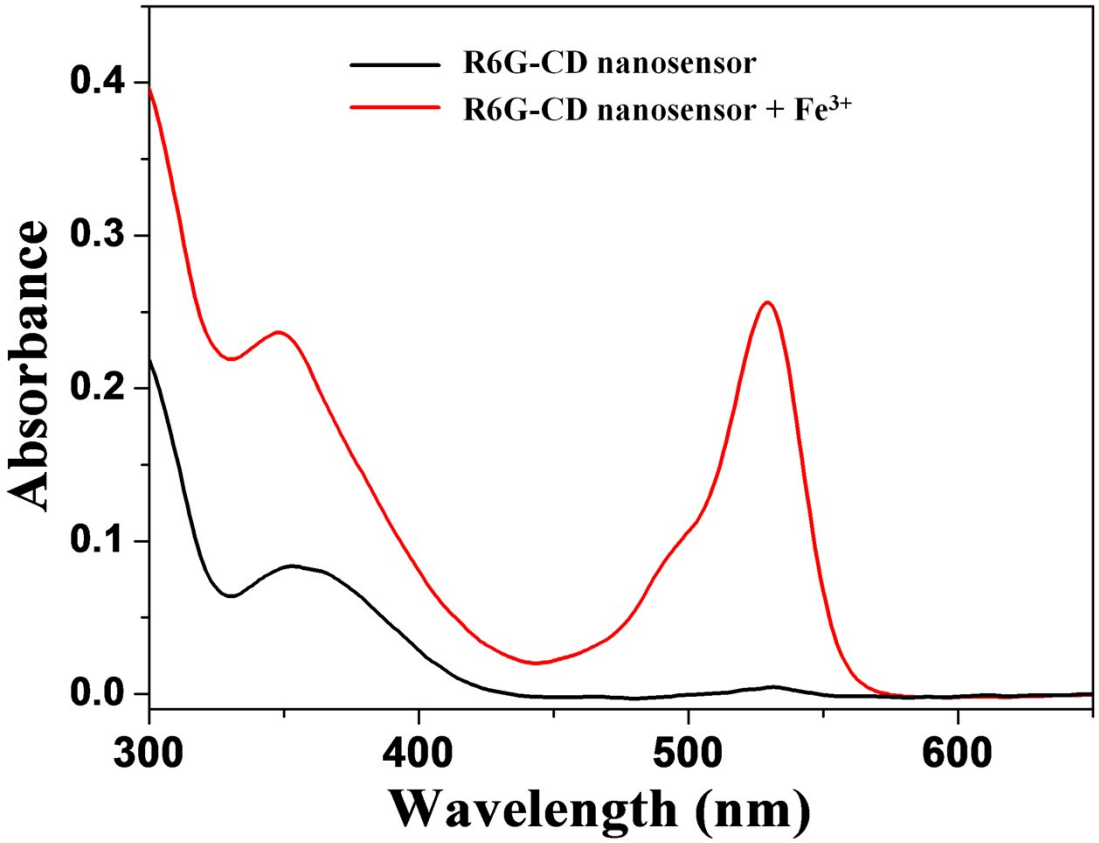
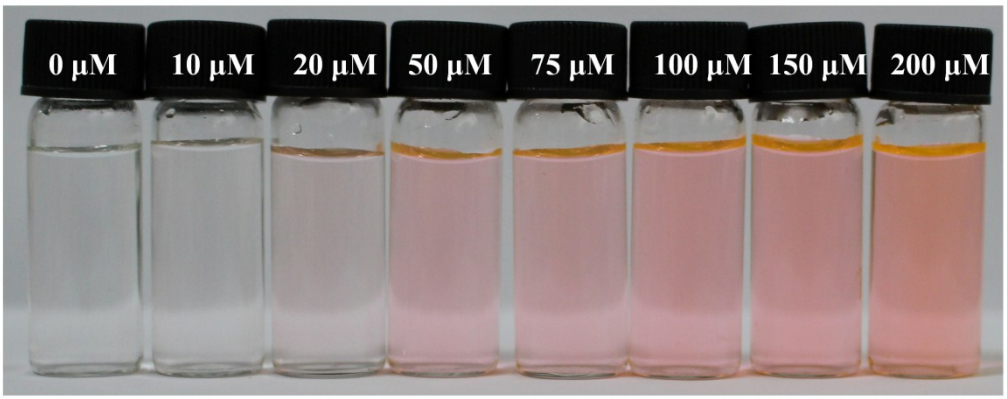


Fig. S8 Absorption spectra of R6G-CD nanosensor (0.02 mg/mL) in aqueous solution before and after addition of Fe^{3+}.



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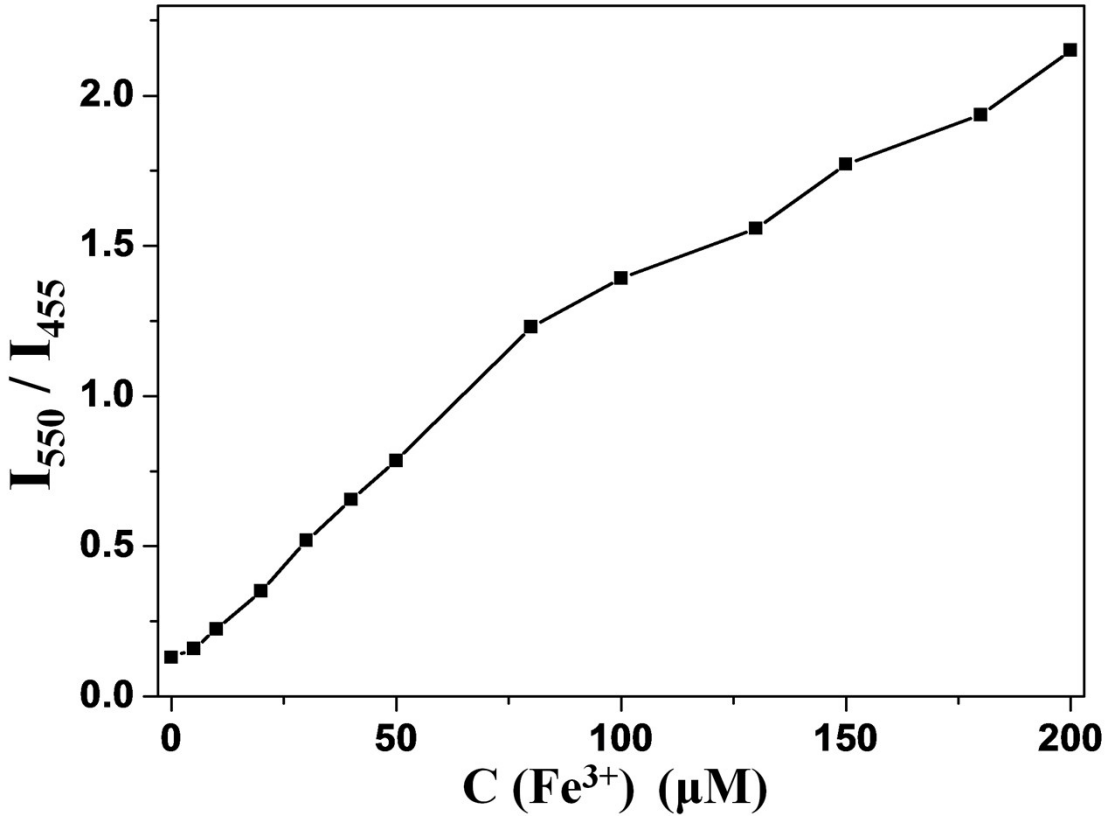


Fig. S10 Fluorescent intensity ratio (I_{550}/I_{455}) of the R6G-CD nanosensor (0.02 mg/mL) in the presence of different amounts of Fe^{3+} in aqueous solution (λ_{ex} = 360 nm).

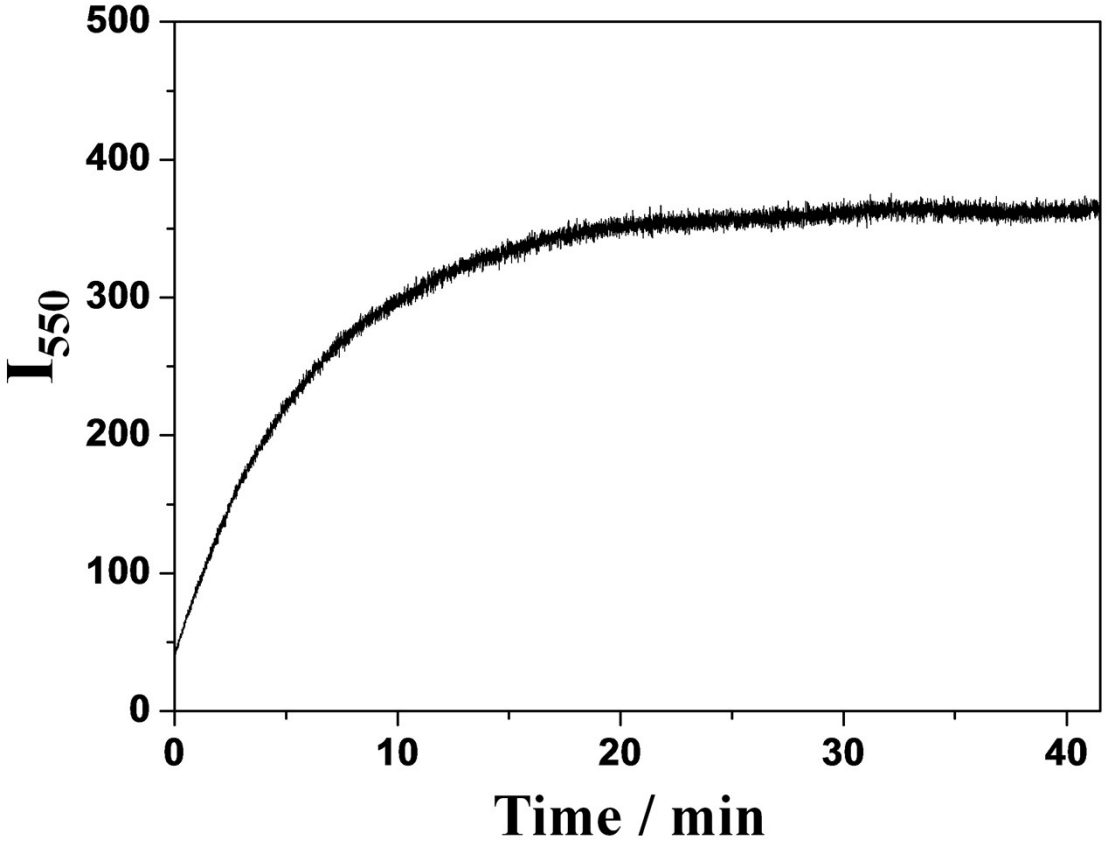


Fig. S11 Fluorescence intensity (I_{550}) of the R6G-CD nanosensor (0.02 mg /mL) upon addition of 200 μM Fe^{3+} in water.

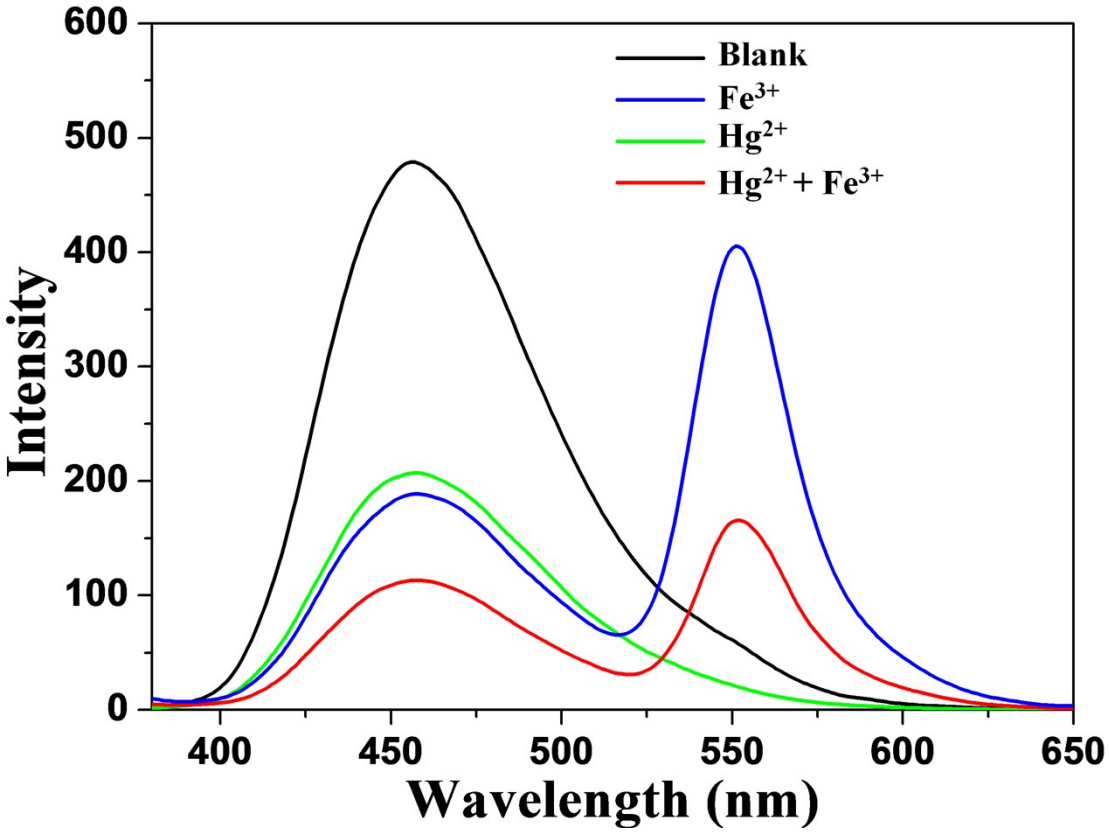
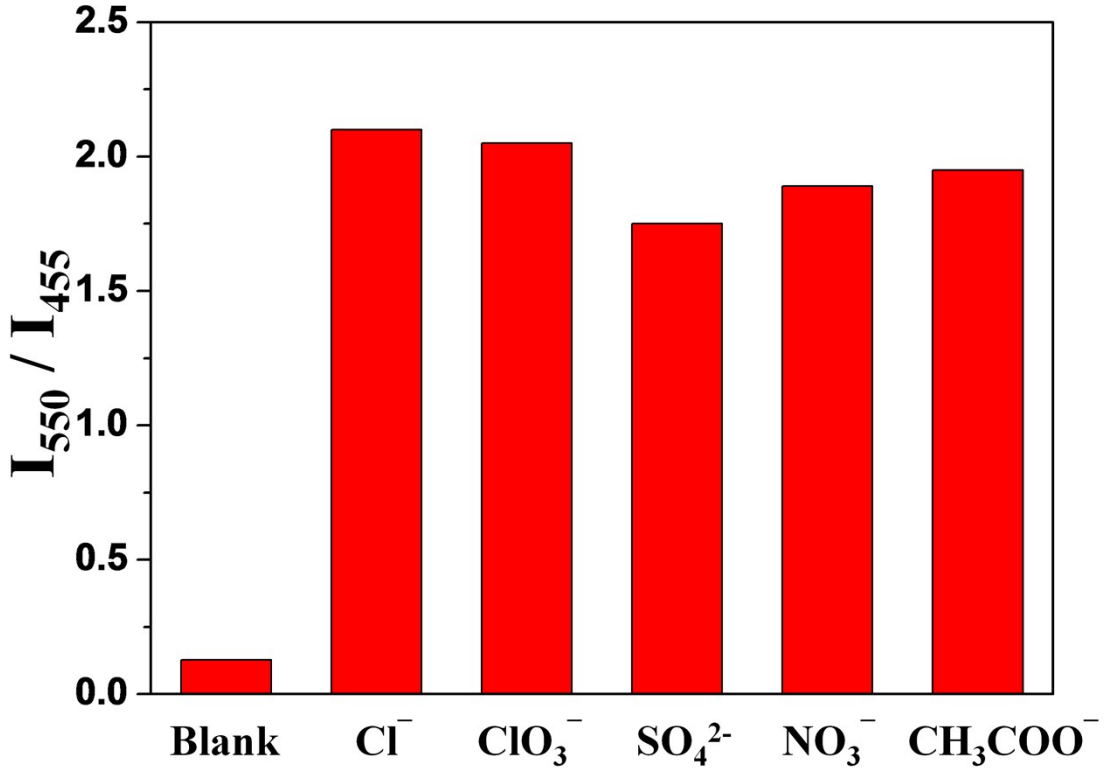


Fig. S12 The fluorescence spectra of the R6G-CD nanosensor (0.02 mg/mL) (a) in the absence or in the presence of 200 μM (b) Fe^{3+}, (c) Hg^{2+} and (d) Fe^{3+} + Hg^{2+} in aqueous solution (λ_{ex} = 360 nm).



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