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Dual-Emitting Dyes-CDs@MOFs for Selective and Sensitive Identification of Antibiotics and MnO_4^- in Water

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Materials and Methods

All reagents and solvents were purchased from commercial sources and were used without further purification. Elemental analyses were carried out on a Perkin–Elmer 2400 automatic analyzer. FT–IR spectra data (4000–400 cm^{-1}) were collected by a Nicolet impact 410 FT–IR spectrometer. Scan electron microscope (SEM) images were recorded by Rili SU 8000HSD Series Hitachi New Generation Cold Field Emission SEM. The emission properties were recorded with Edinburgh FLS 920 fluorescence spectrometer equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube. An Edinburgh Xe900 450 W xenon arc lamp was used as an exciting light source. Thermal analysis was performed on a ZRY-2P thermogravimetric analysis from 30 to 700 °C with a heating rate of 10 °C·min^{-1} under a flow of air. Powder X-ray diffraction (PXRD) patterns were recorded in the 2θ range of 5 – 50° using Cu Kα radiation with a Shimadzu XRD-6000 X-ray diffractometer. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hν = 1253.6 eV).

Single-Crystal X-Ray Crystal Structure Determination

The X-ray diffraction data taken at room temperature for **1** was collected on a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0. 71073 Å). The structure of **1** was solved by direct methods and refined on F^2 by the full-matrix least squares using the SHELXTL-97 crystallographic software. Anisotropic thermal parameters are refined to all of the non-hydrogen atoms. The hydrogen atoms were held in calculated ideal positions on carbon atoms and nitrogen atoms in ligands and that were directly included in the molecular formula on water molecules. The chemical formulas were determined by the combination of single crystal data, TGA results and elemental analysis. The CCDC 1944353 contains the crystallographic data **1** of this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/ deposit. Crystal structure data and details of the data collection and the structure refinement are listed as Table S1, selected bond lengths and bond angles of **1** are listed as Table S2.

Table S1. Crystal data and structure refinement parameters of **1**

Identification code	1
Empirical formula	$C_{23}H_{16}Cu_2O_9$
CCDC	1944353
Formula mass	563.44
Crystal system	Monoclinic
Space group	C 2/c
a (Å)	18.0119(2)
b (Å)	25.5207(3)
c (Å)	5.78740(10)
α (˚)	90.00
β (˚)	98.9520(10)
γ (˚)	90.00
V (Å3)	2627.92(6)
Z	4
Dc/(g cm-3)	1.424
μ (Mo Kα)/mm-1	2.398
F(000)	1136
θ range (°)	3.03 –68.20
Limiting indices	$-21 \le h \le 21$
	$-30 \le k \le 30$
	$-6 \le l \le 5$
Data/Restraints/Parameters	2398 / 0 / 156
GOF on F2	1.142
R1a	0.0478
wR2b	0.1716
R1	0.0495
wR2	0.1754

[a] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$; [b] $wR_2 = [\sum[w (F_o^2 - F_c^2)^2] / \sum[w (F_o^2)^2]]^{1/2}$.

Table S2. Selected bond lengths (Å) and bond angles (°) for **1**

1			
Cu(1)-O(4)	1.9160(12)	Cu(1)-O(3)	1.9363(19)
Cu(1)-O(1)	1.944(2)	Cu(1)-O(2)	1.958(2)
O(4)-Cu(1)-O(3)	93.64(10)	O(4)-Cu(1)-O(1)	90.84(10)
O(3)-Cu(1)-O(1)	175.35(9)	O(4)-Cu(1)-O(2)	178.96(10)
O(3)-Cu(1)-O(2)	85.45(9)	O(1)-Cu(1)-O(2)	90.08(9)

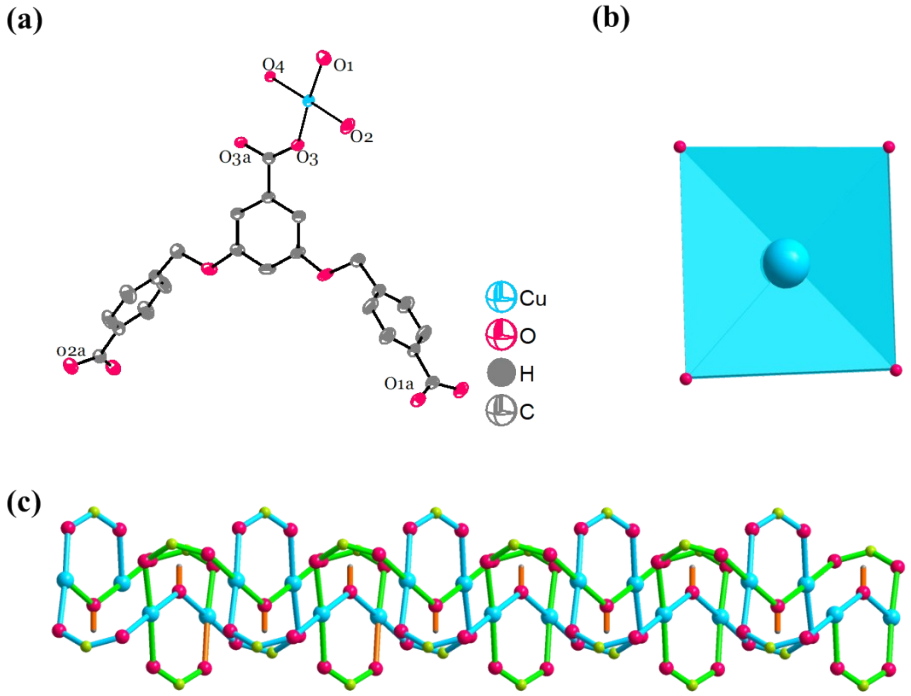

Fig. S1. (a) The structural unit of 1 with labeling scheme and 50% thermal ellipsoids (hydrogen atoms are omitted for clarity); (b) Twisted plane quadrilateral geometry of Cu^{2+} in 1. (c) The 1D copper (II) chains along the c axis

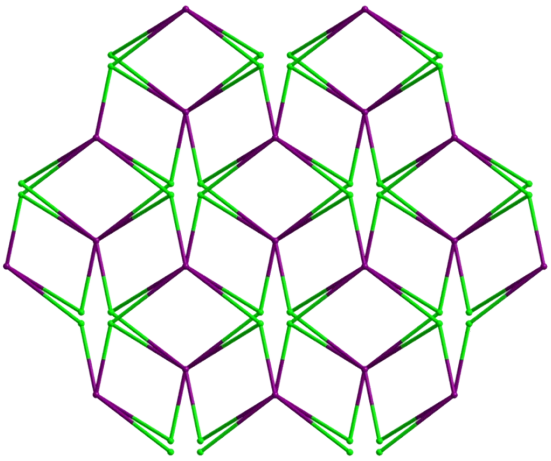

Fig S2. The *ant* network of 1

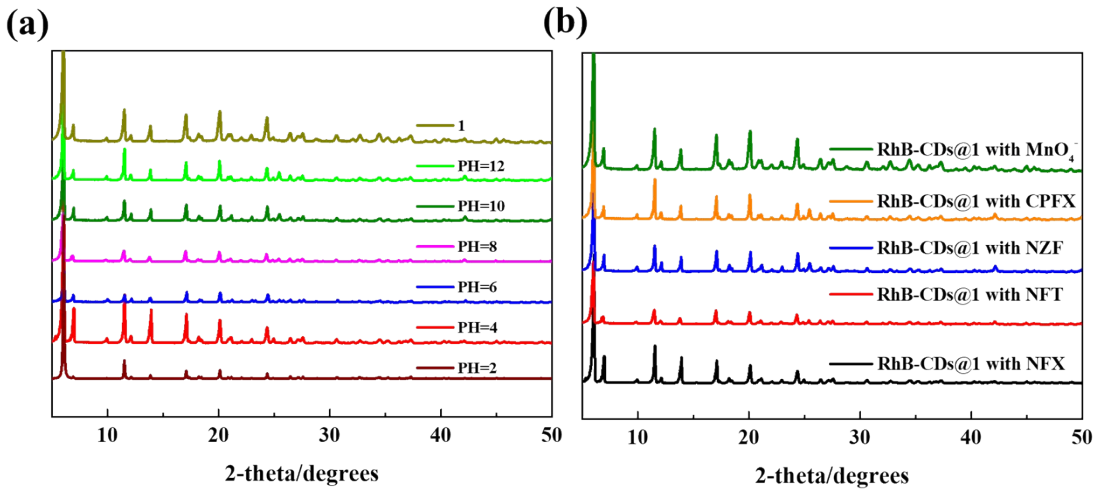

Fig. S3. PXRD patterns of (a) 1, 1 in aqueous solutions with the pH value ranging from 2 to 12 for one day and (b) PXRD patterns of **RhB-CDs@1** treated by various substances.

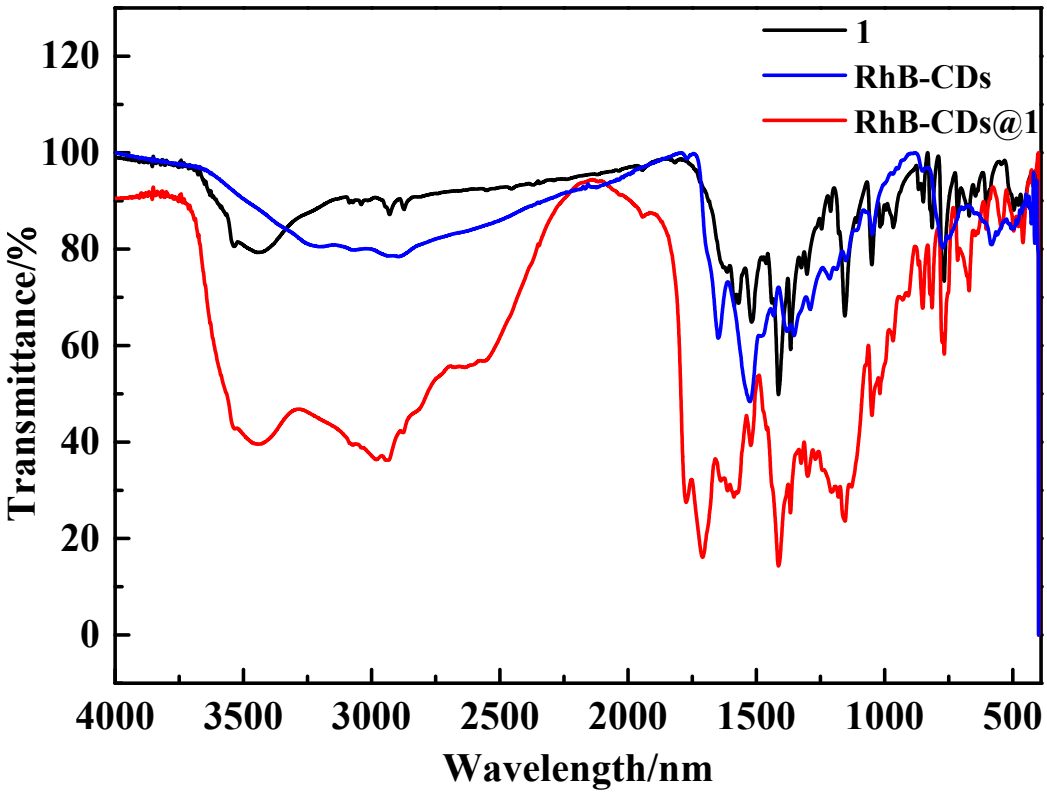

Fig. S4. FT-IR spectra of **1**, **RhB-CDs,** and **RhB-CDs@1**.

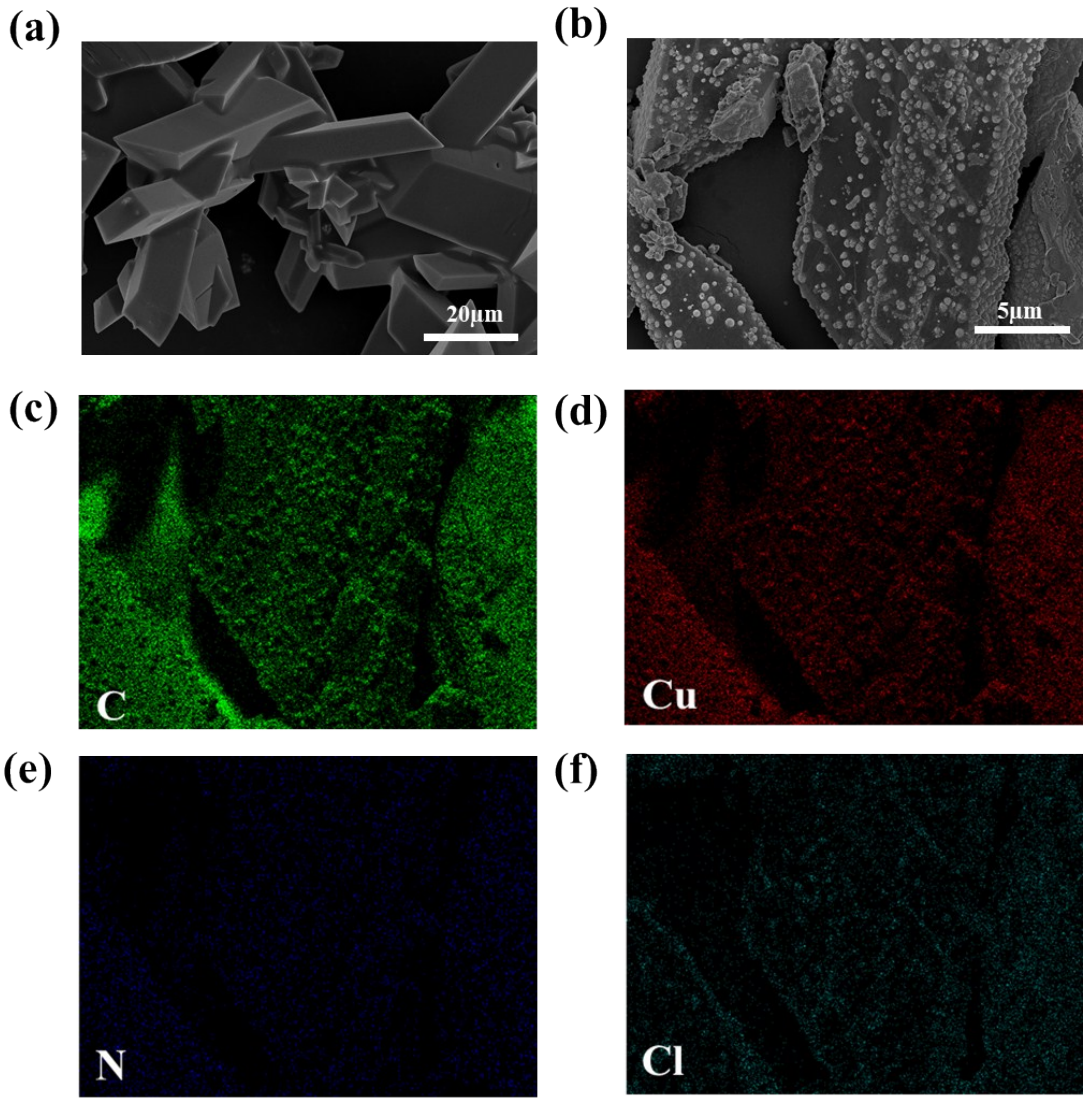

Fig. S5. SEM images for (a) **1** and (b) **RhB-CDs@1**, corresponding to the elemental mapping image of **RhB-CDs@1** for (c) the carbon element; (d) the copper element (e) the chlorine element and (f) the nitrogen element.

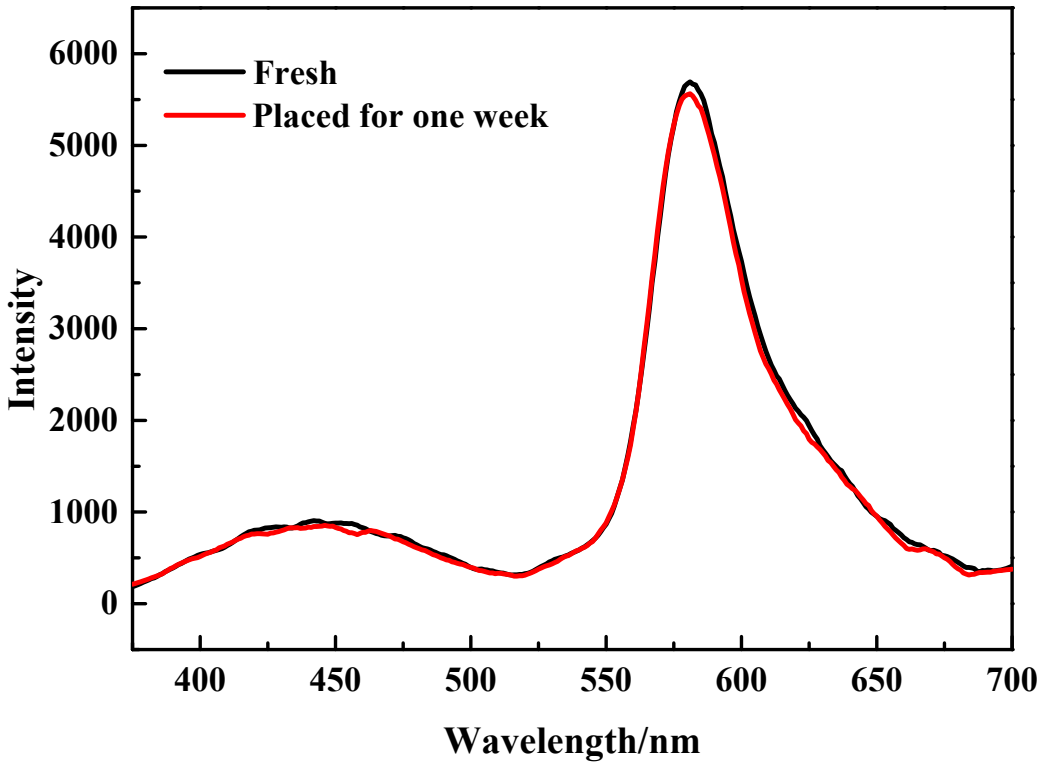

Fig. S6. Fluorescence emission spectrum of the **RhB-CDs@1** and placed for one week under excitation at 355 nm.

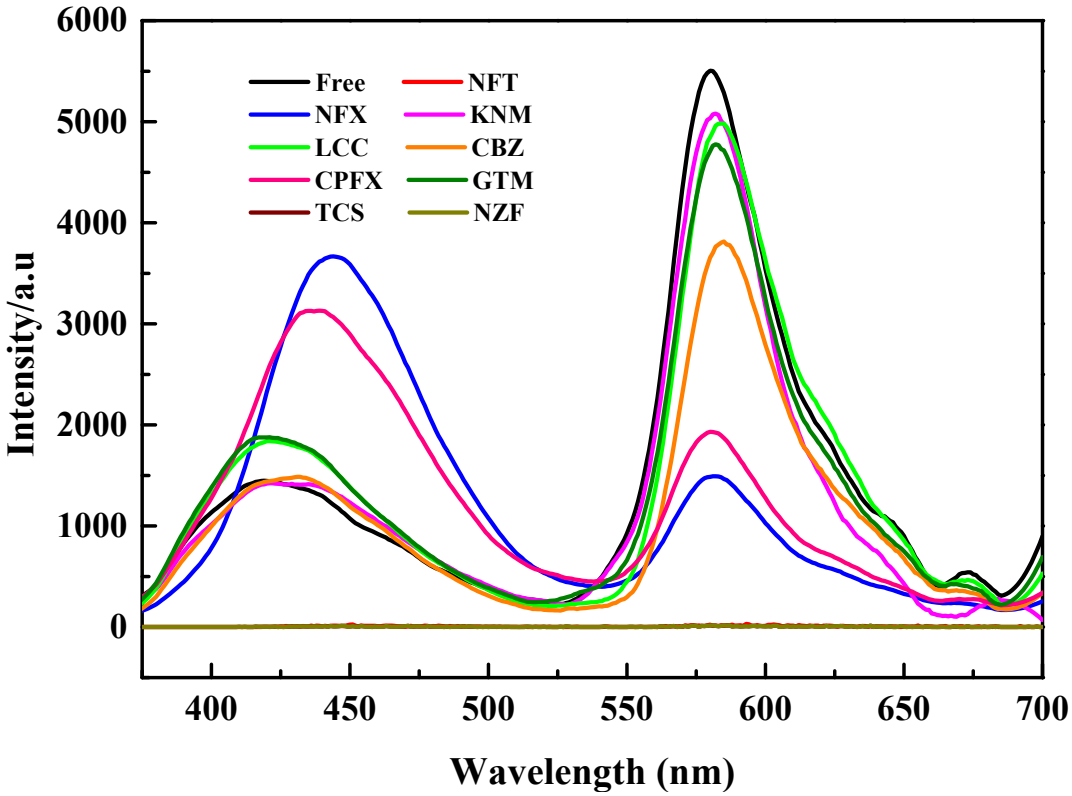

Fig. S7. Fluorescence response of **RhB-CDs@1** treated by different antibiotics (1 mM aqueous solution for 30 min) excited at 355 nm.

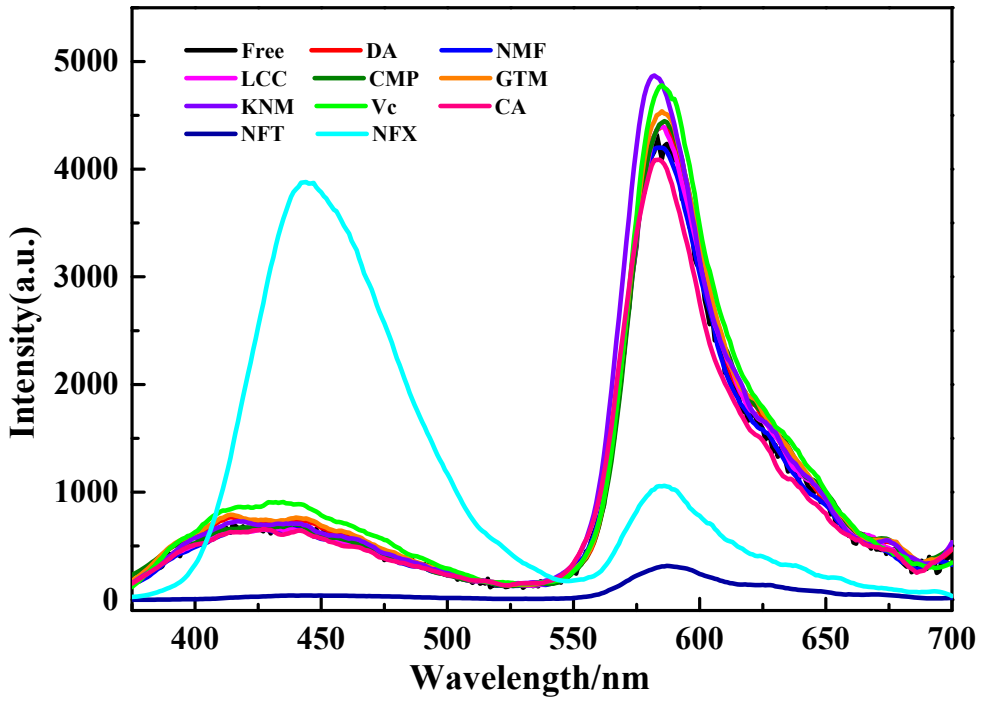

Fig. S8. Fluorescence response of **RhB-CDs@1** treated by different biomolecules (1 mM aqueous solution for 30 min) excited at 355 nm.

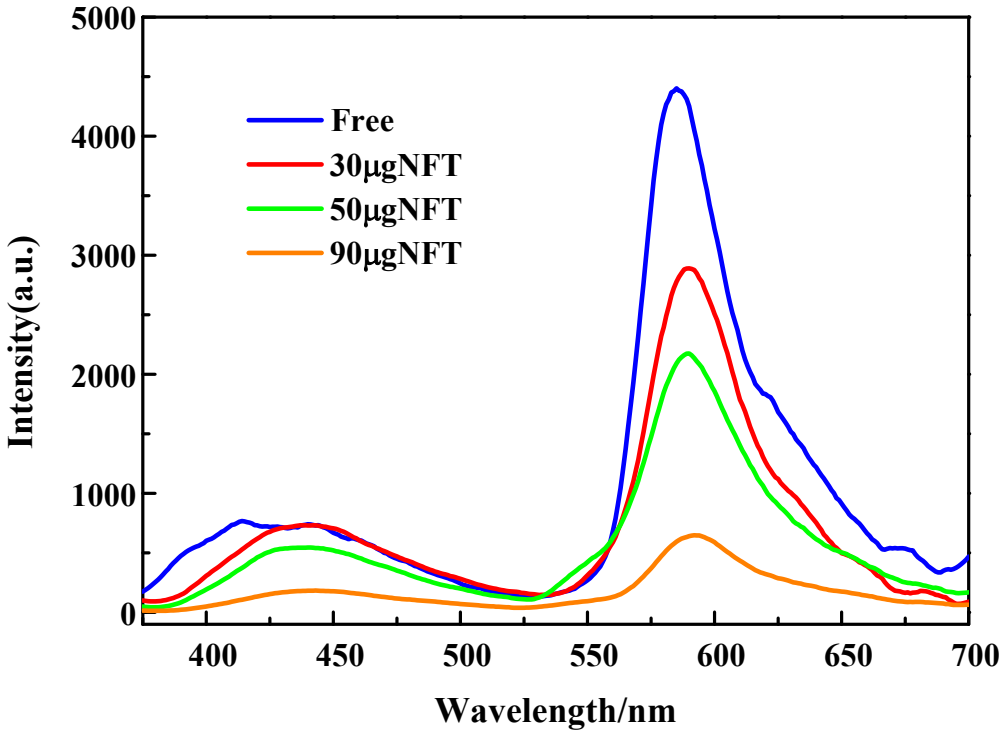

Fig. S9. Fluorescence response of **RhB-CDs@1** treated by different concentration of NFT.

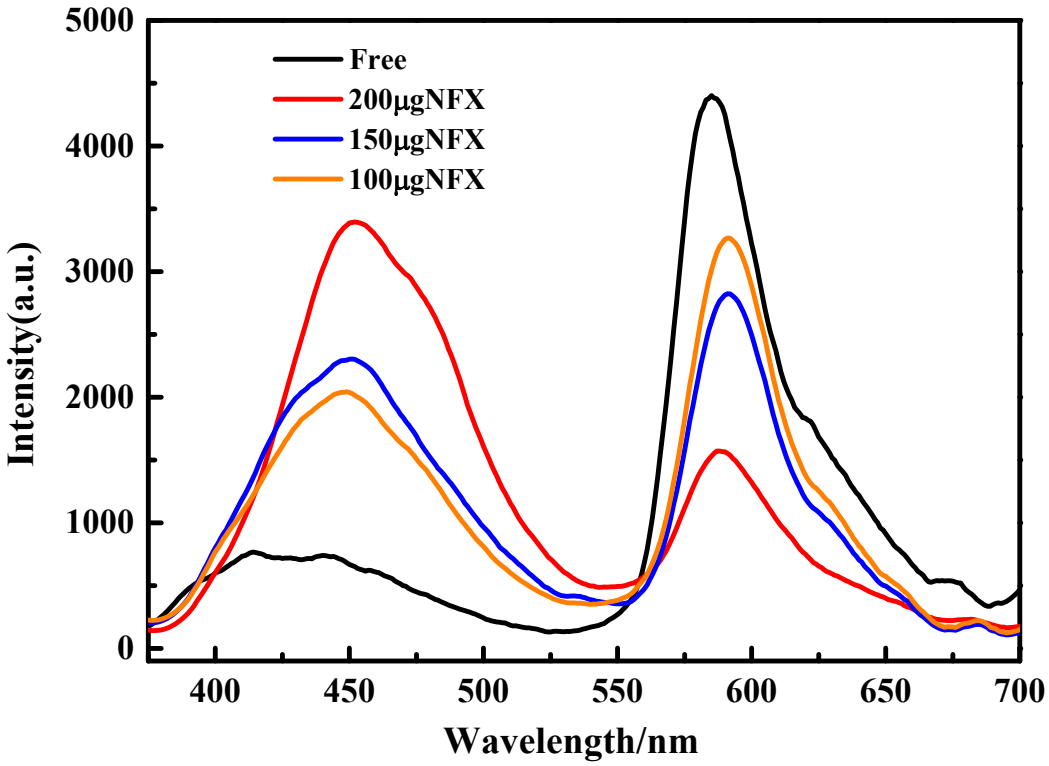

Fig. S10. Fluorescence response of **RhB-CDs@1** treated by different concentration of NFX.

Table S3. Determination of NFT and NFX in domestic water

Analytes	Samples	Added (μg)	Detected (μg)	Recovery (%)	RSD (n=3, %)
NFT	Water 1	30	30.18±0.26	100.06	0.87
	Water 2	50	48.81±0.15	97.62	0.30
	Water 3	90	90.82±2.19	100.92	2.43
NFX	Water 1	100	102.11±0.09	102.11	0.09
	Water 2	150	145.88±1.62	97.25	1.08
	Water 3	200	199.47±3.76	99.74	1.88

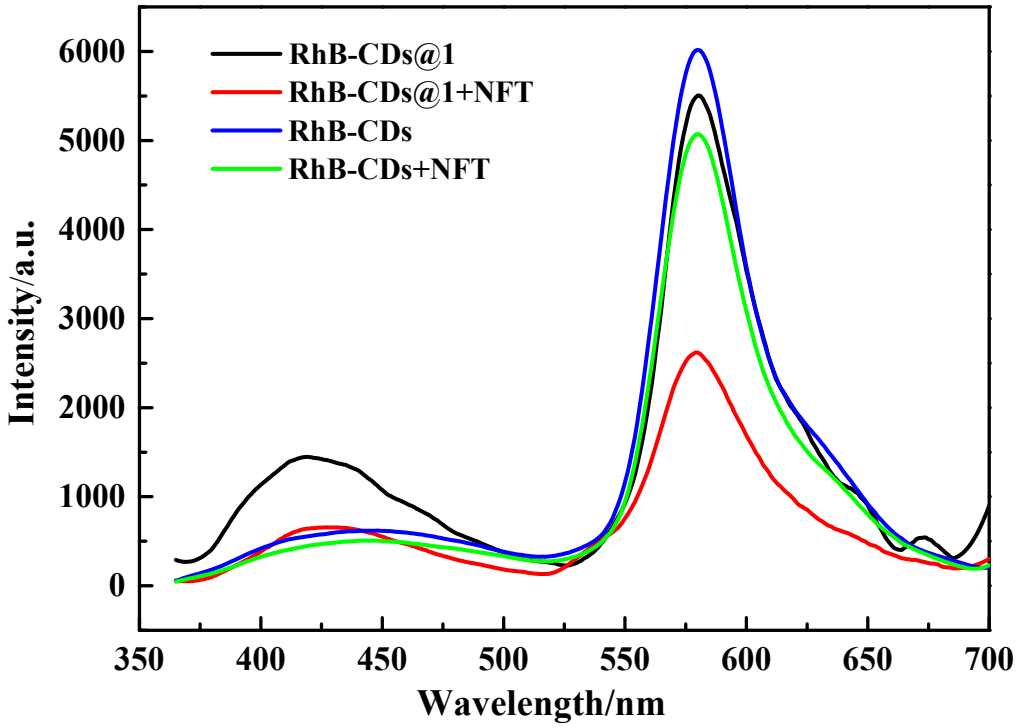

Fig. S11. Fluorescence spectra of RhB-CDs and RhB-CDs@1 in the presence and absence of 20μM of NFT.

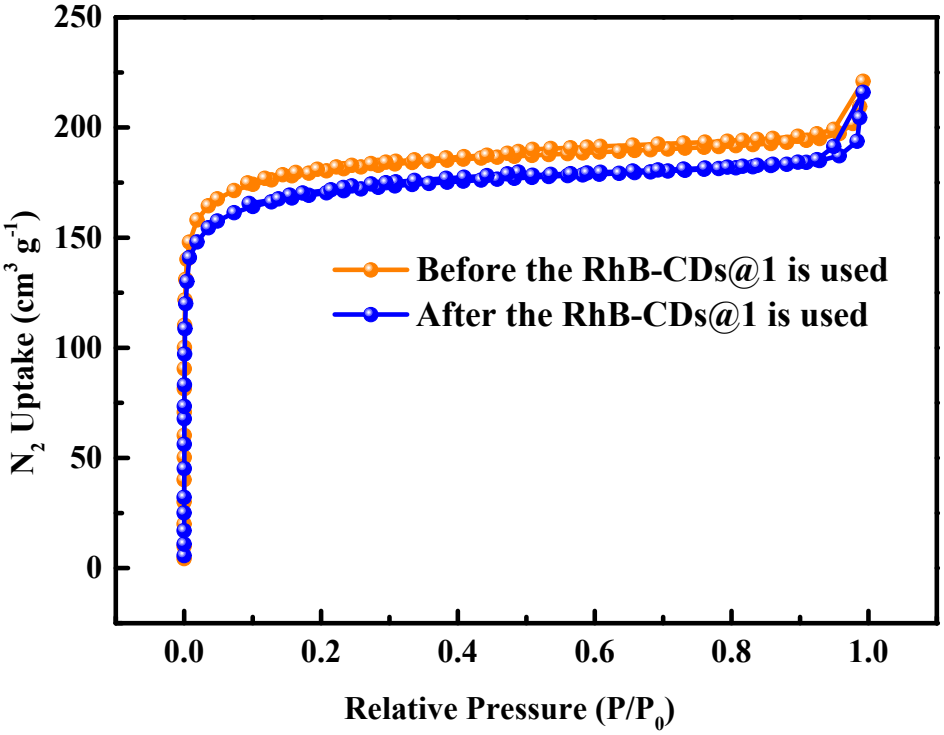

Fig. S12: N2 adsorption and desorption isotherms of RhB-CDs@1 that are used to detect the NFT before (orange) and later (blue).

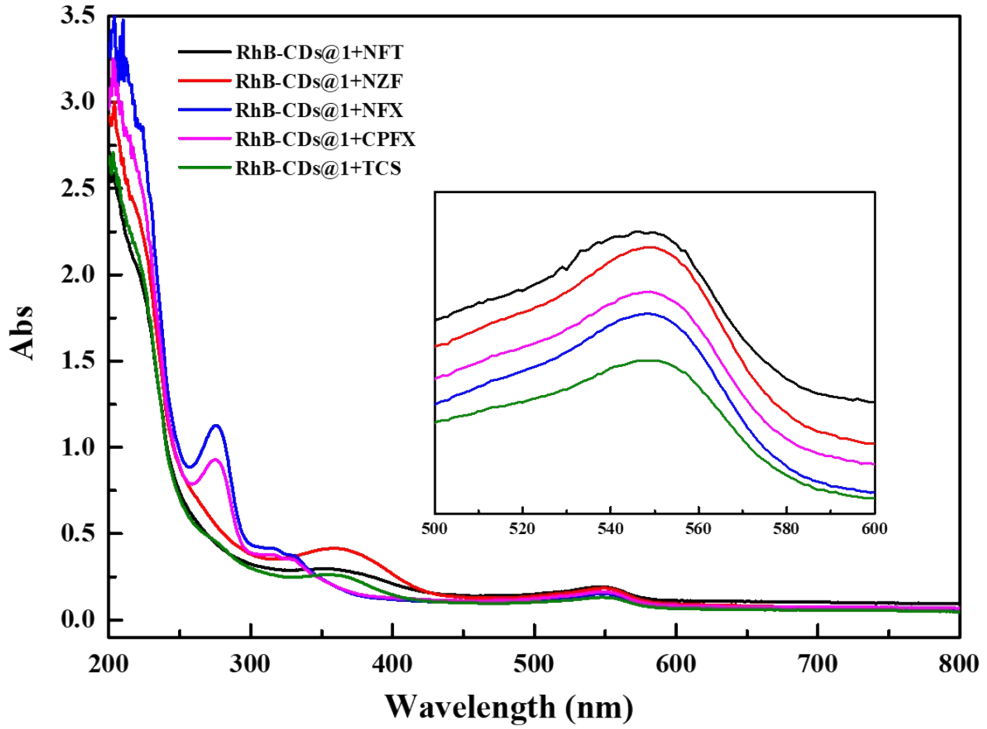

Fig. S13. the UV−vis absorption spectra of **RhB-CDs@1** aqueous suspension in the presence of analytes (NFT,NZF,NFX,CPFX,TCS).

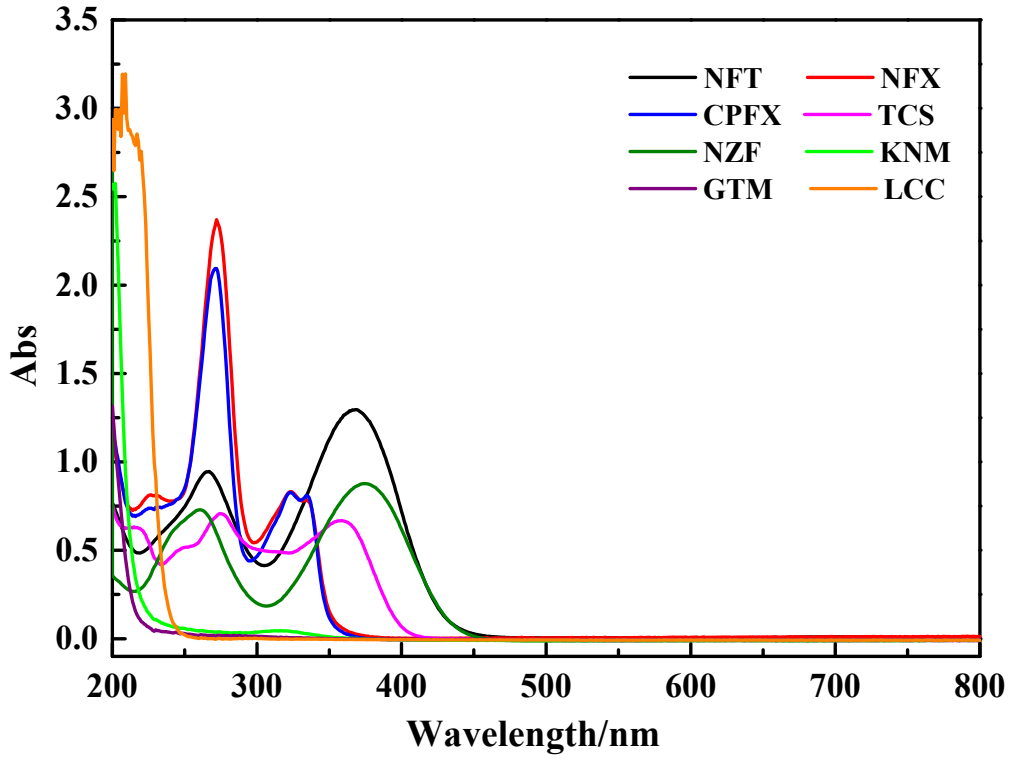

Fig. S14. UV−vis absorption spectra of each antibiotics.

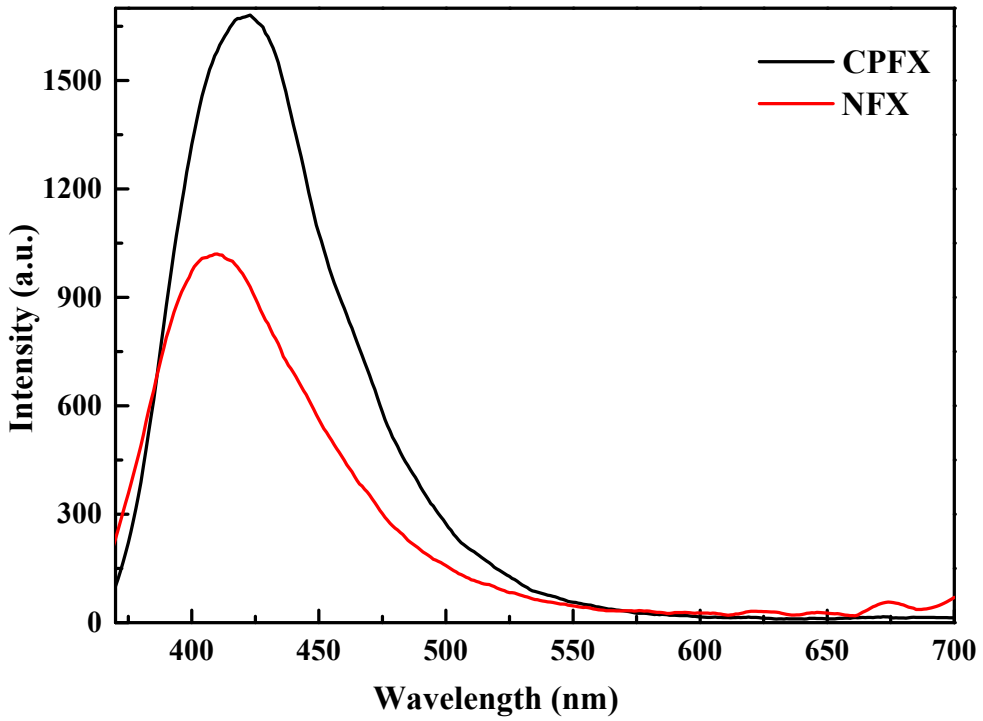

Fig. S15. Fluorescence emission spectrum of the CPFX and NFX at 355 nm.

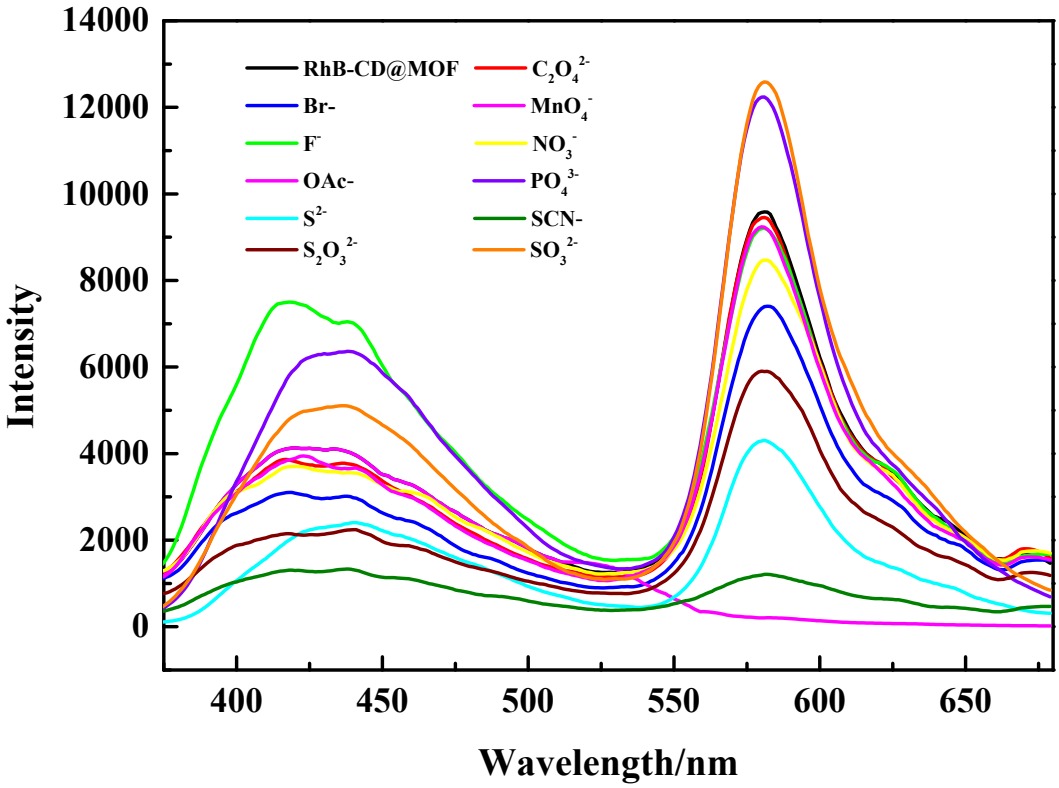

Fig. S16. Fluorescence response of RhB-CDs@1 treated by different anions (1 mM aqueous solution for 30 min) excited at 355 nm.

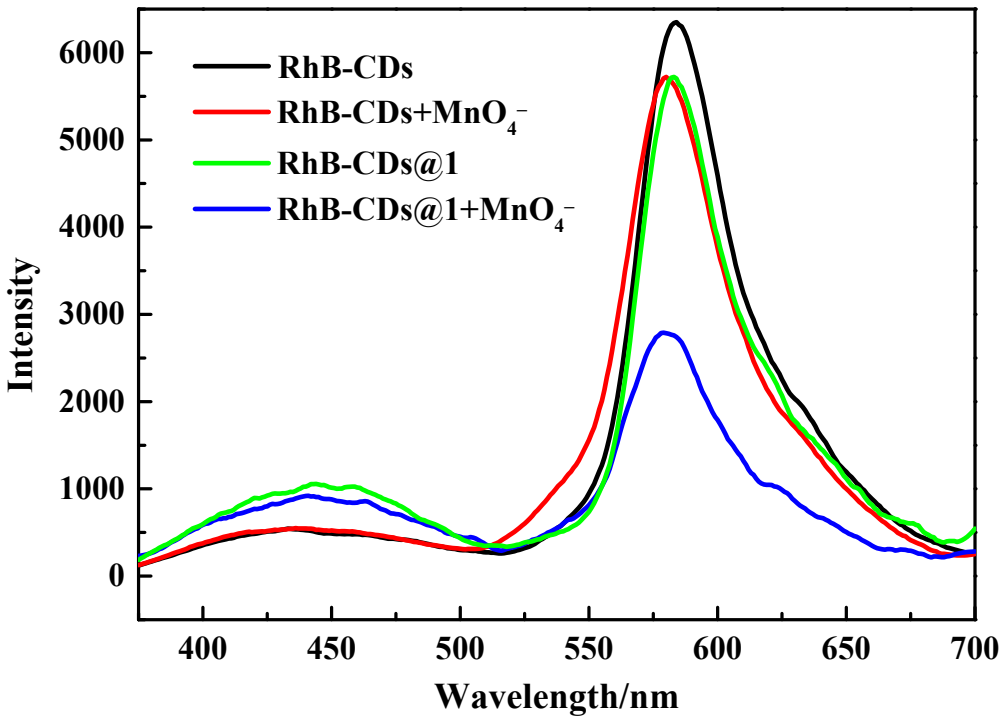

Fig. S17. Fluorescence spectra of RhB-CDs and RhB-CDs@1 in the presence and absence of 100μM of MnO_4^-.

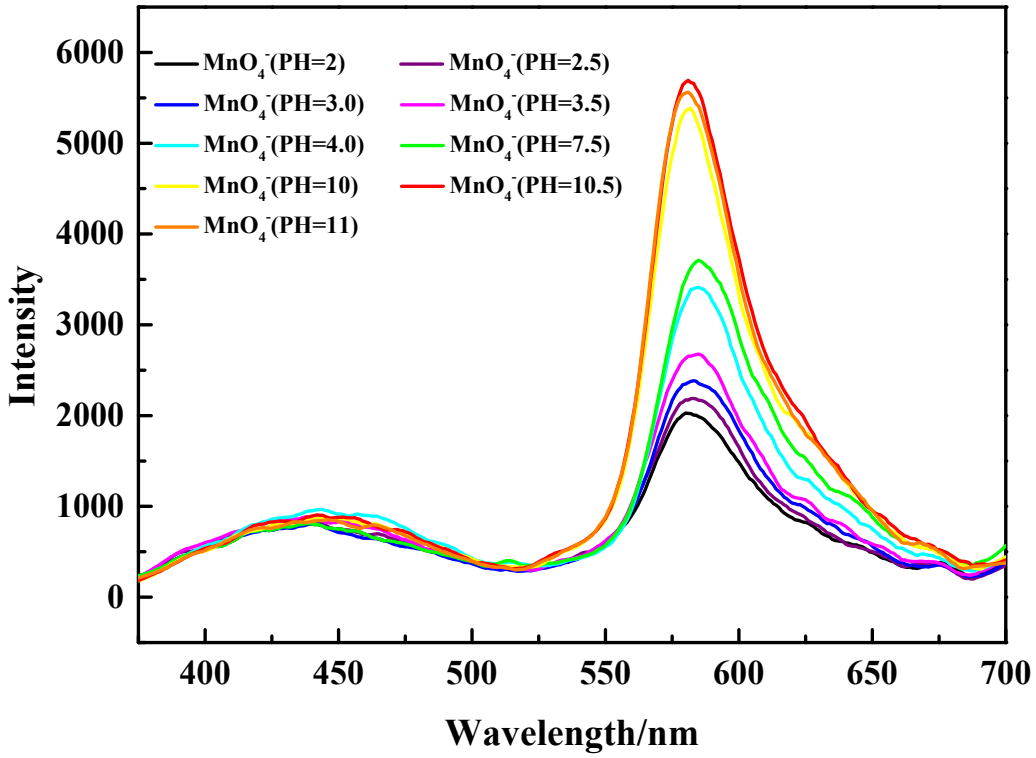

Fig. S18. Fluorescence spectra of the RhB-CDs@1 probe in the presence of several PH values of MnO_4^- (PH=2, 2.5, 3, 3.5, 4,7.5, 10, 10.5, 11).