Supplementary Material

A quadruple-channel fluorescence sensors array based on label-free carbon dots for sensitive detection of tetracyclines

Dengying Long, Jingdong Peng*, Huanjun Peng, Hong Xian, Shiyu Li, Xiang Wang, Jun Chen, Zhongying Zhang and Ranxi Ni

School of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400700, P. R. China.

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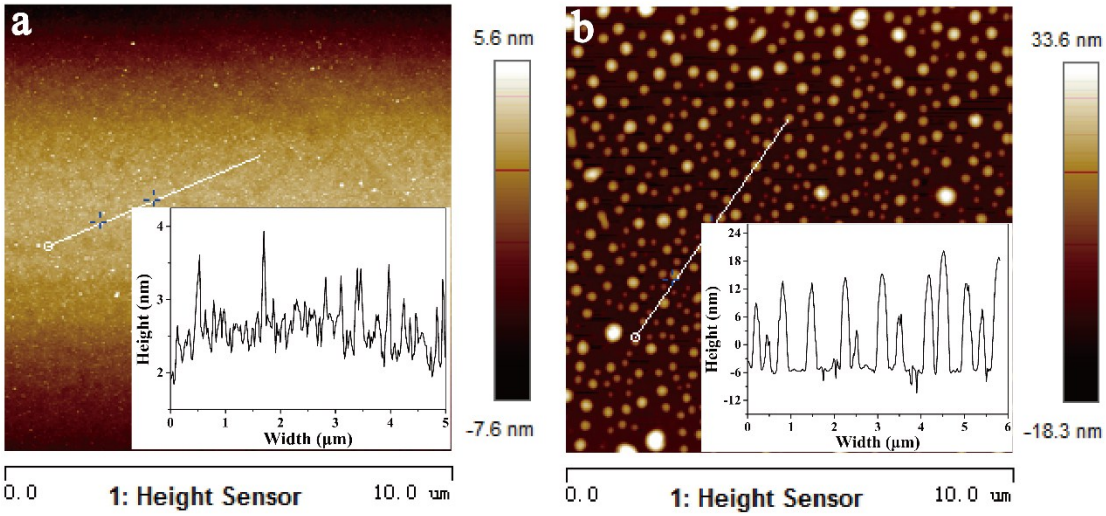


Fig. S1 AFM of (a) B-CDs and (b) G-CDs on a silicon substrat, respectively. (insets: height profiles follow the marked lines in the AFM images)

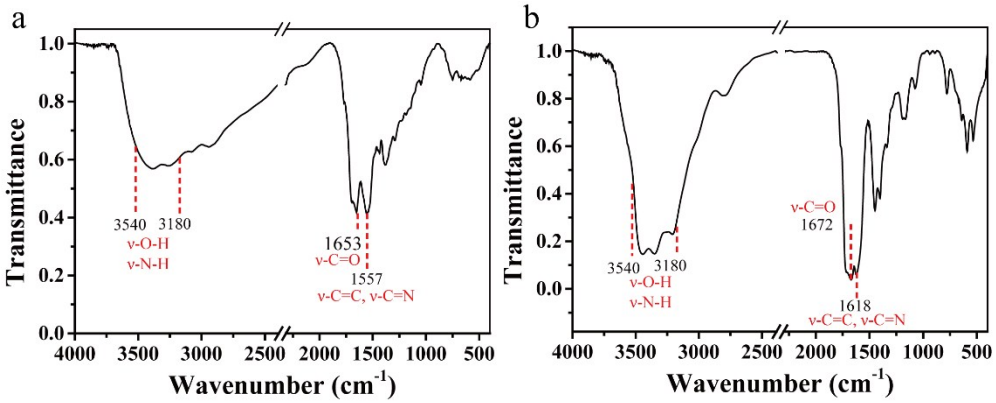


Fig. S2 FT-IR spectra of (a) B-CDs and (b) G-CDs in the dry state, respectively.

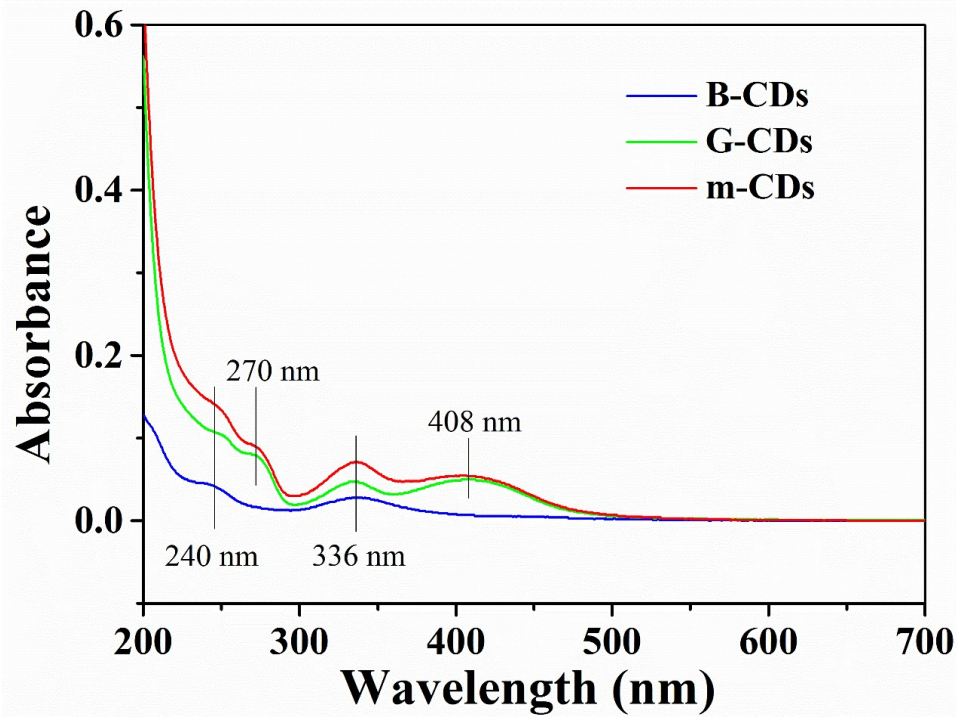


Fig. S3 UV–vis absorption spectra of B-CDs, G-CDs and m-CDs in aqueous solutions, respectively.

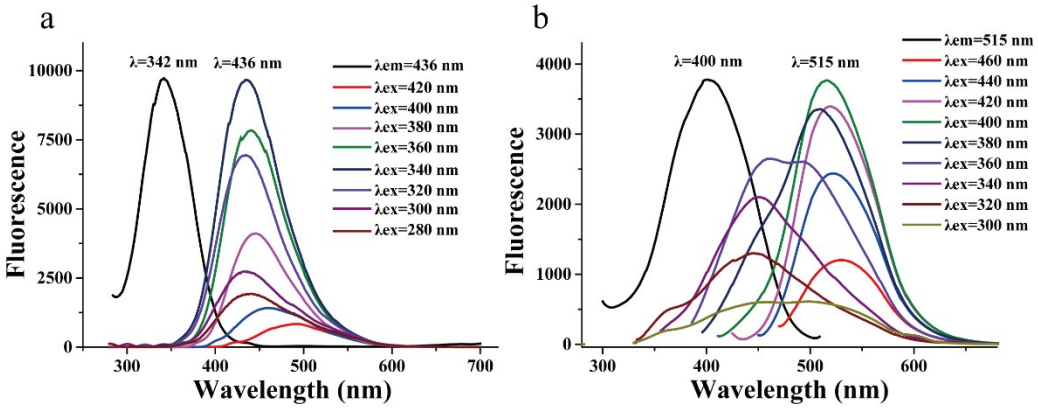


Fig. S4 Fluorescence excitation and emission spectra of (a) B-CDs and (b) G-CDs in aqueous solutions, respectively.

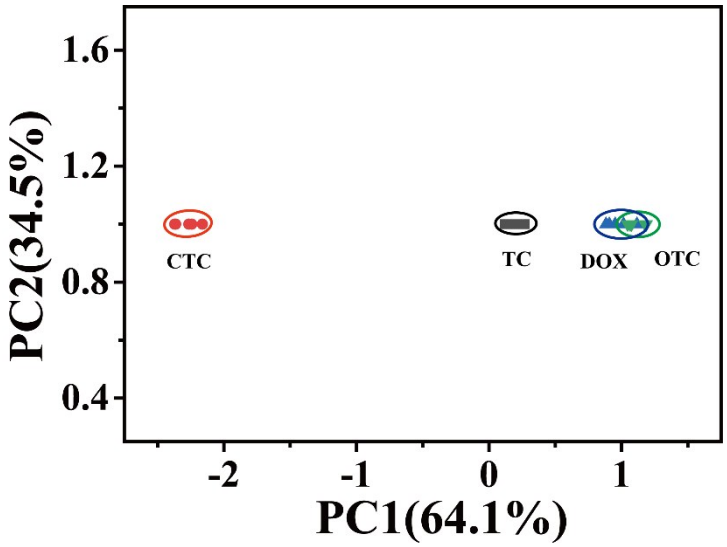
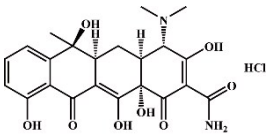
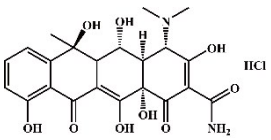
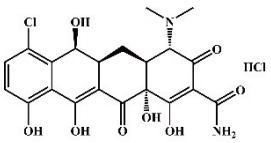
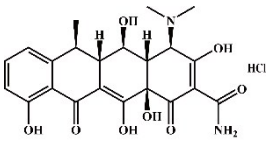


Fig. S5 Two-dimensional PCA score plot of the double-channel fluorescence sensor array for discrimination of TCs. The concentration is 15 μM.

Table S1 Basic information of the four selected tetracyclines antibiotics.

Antibiotics	Abbreviation	Molecular weight	Structure
Tetracycline hydrochloride	TC	480.90	
Oxytetracycline hydrochloride	OTC	496.89	
Chlortetracycline hydrochloride	CTC	515.34	
Doxycycline hydrochloride	DOX	462.45	

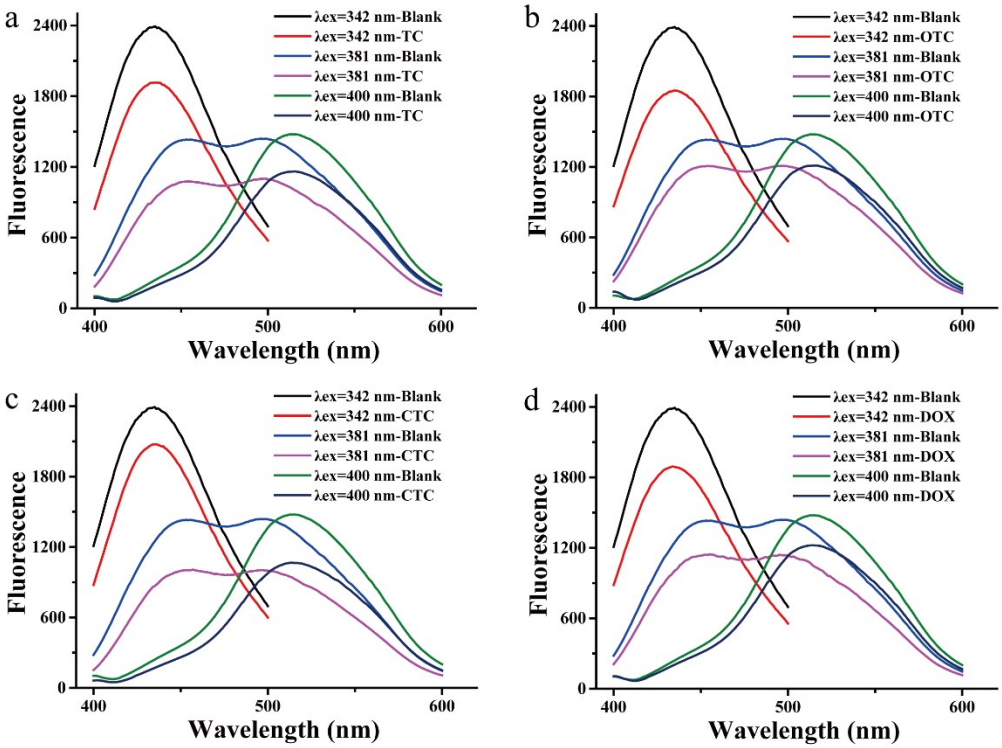


Fig. S6 The fluorescence emission spectra of the B-CDs, m-CDs and G-CDs in the absence and presence of (a) TC, (b) OTC, (c) CTC and (d) DOX at 15 μM in B-R solution (pH=7.4), separately.

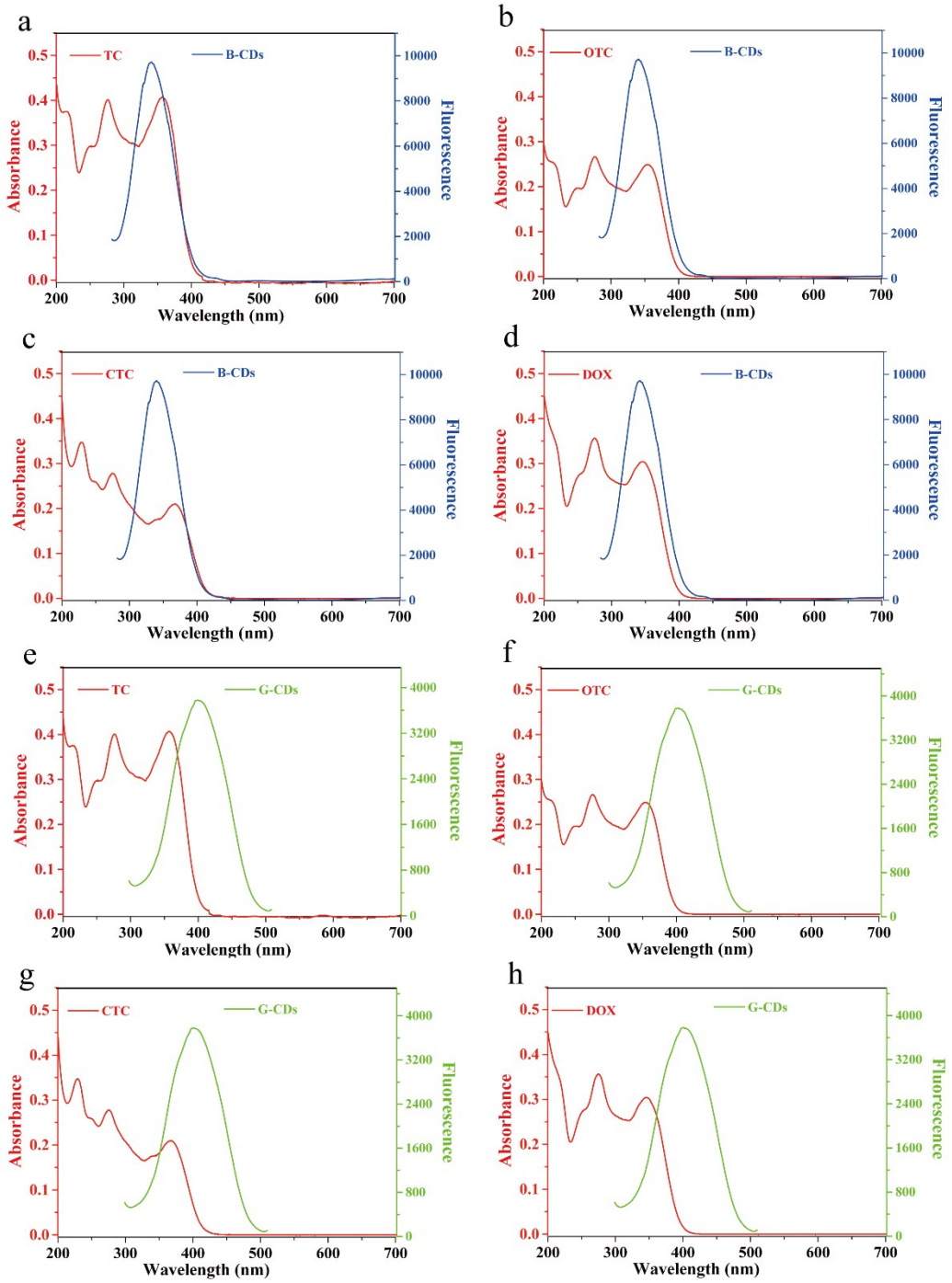


Fig. S7 The different assemblages by combining UV–vis absorption spectrum of TCs (red line) with fluorescence excitation spectrum of B-CDs at λem=436 nm (blue line) and G-CDs at λem=515 nm (green line), respectively.

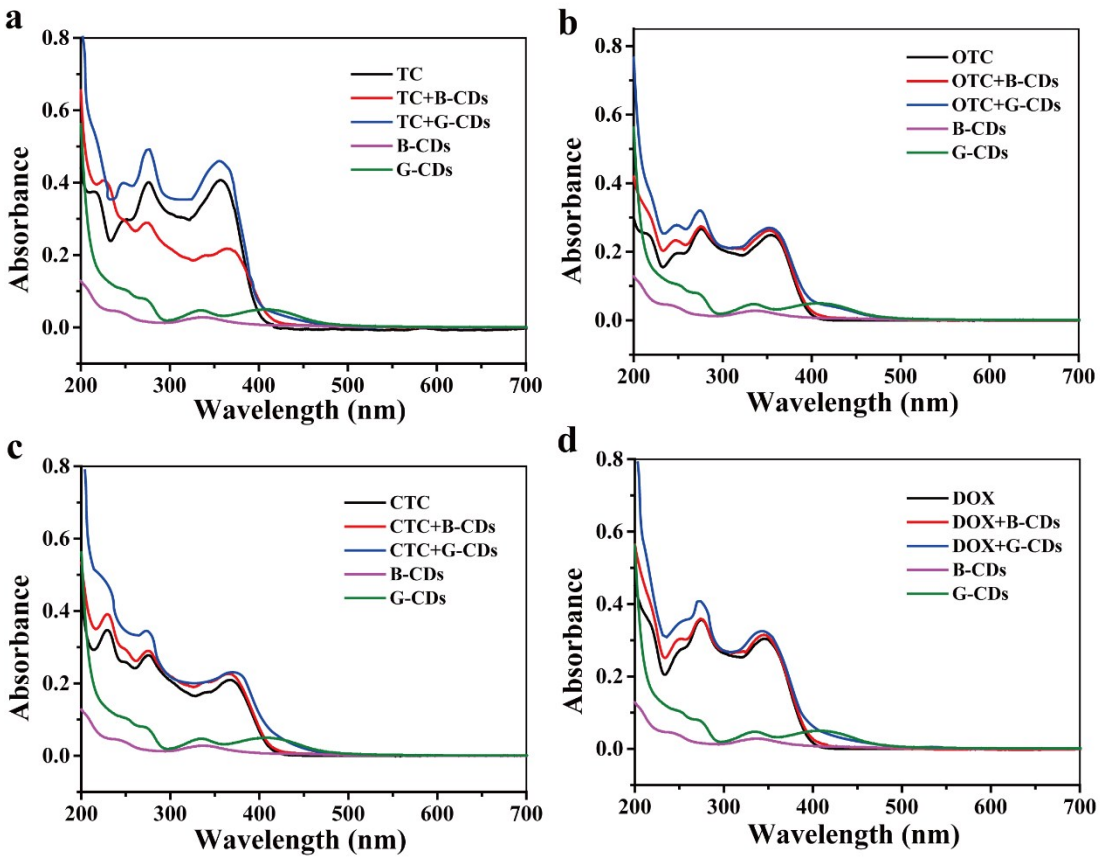


Fig. S8 The UV-vis absorption spectra of TCs, B-CDs, G-CDs, B-CDs+TCs and G-CDs+TCs.

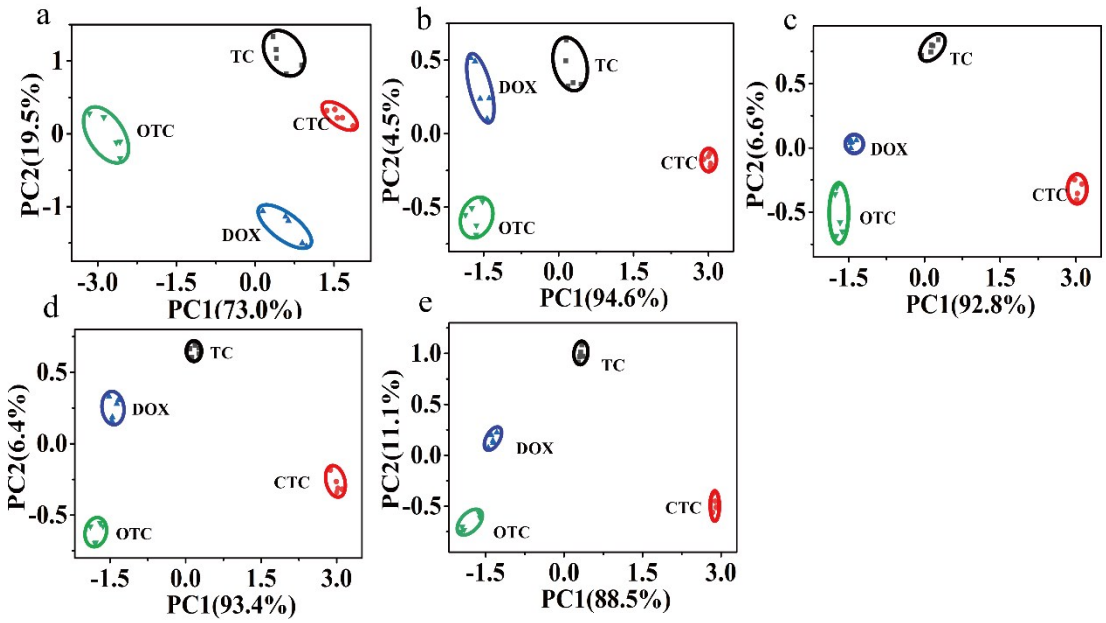


Fig. S9 Two-dimensional PCA score plot of the flourescence sensors array for discrimination of TC, CTC, DOX and OTC at same concentration. (a) 1 μM, (b) 35 μM, (c) 45 μM, (d) 100 μM, and (e) 300 μM.

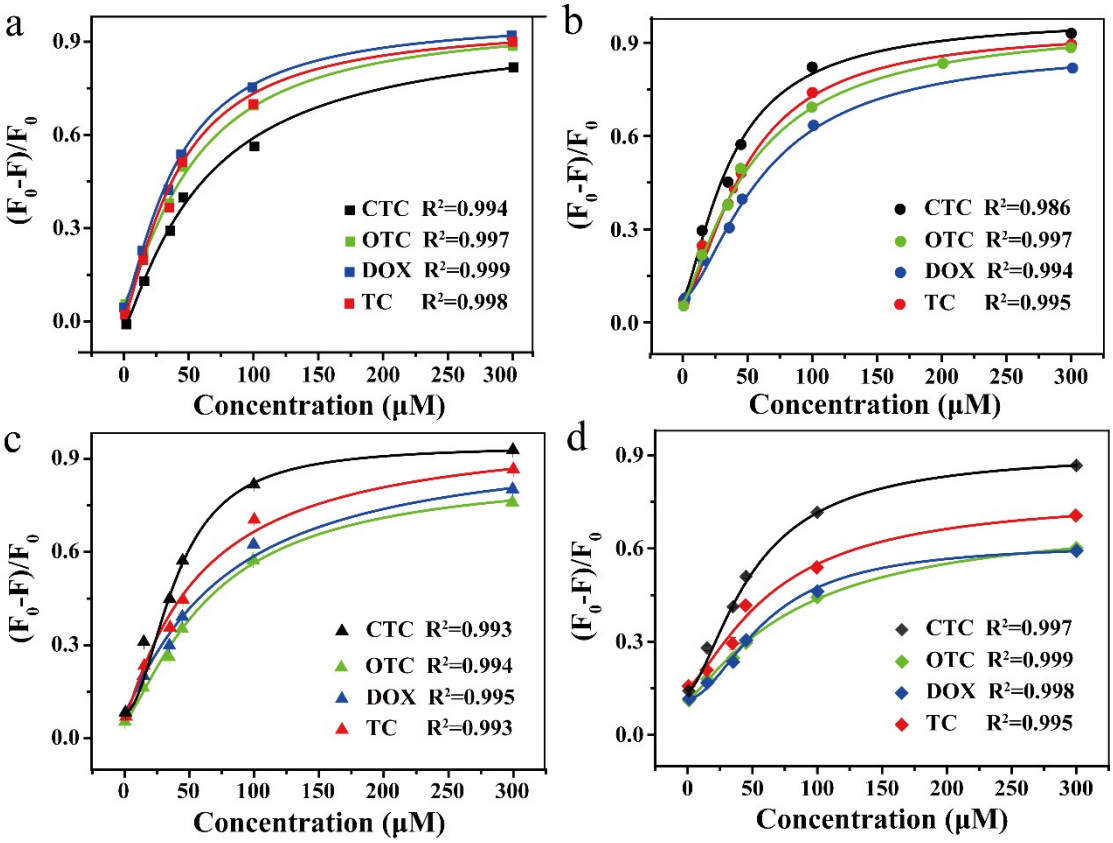


Fig. S10 The fluorescence response in (a) S1, (b) S2, (c) S3 and (d) S4 to TC, OTC, CTC, and DOX with the concentration range of 1−300 μM, respectively.

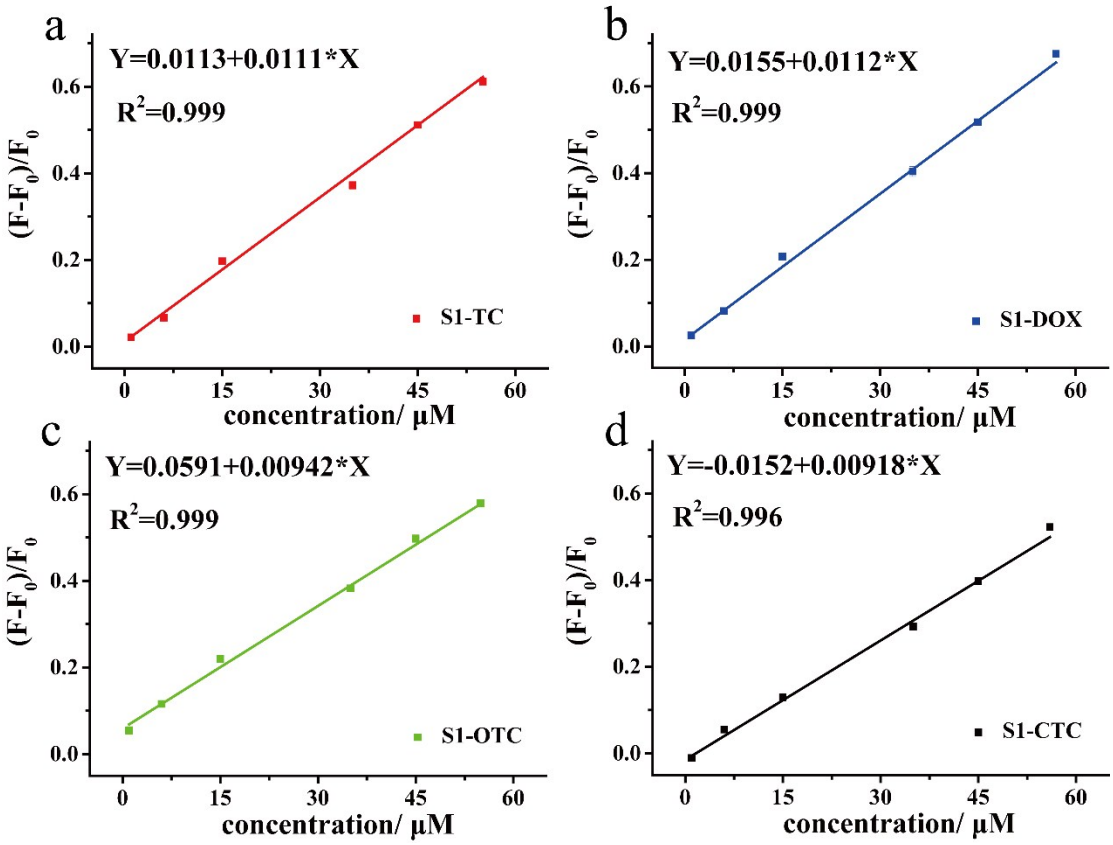


Fig. S11 The linear relationship between the fluorescence intensity variation $(F_0\text{-}F)/F_0$ in S1 and the concentrations of four TCs in range from 1 to 55 μM.

Table S2 Training matrix of the response patterns against TCs at 15μM.

antibiotics	$(F_0-F)/F_0$-S1	$(F_0-F)/F_0$-S2	$(F_0-F)/F_0$-S3	$(F_0-F)/F_0$-S4
TC	0.2063	0.2523	0.2660	0.1207
TC	0.2140	0.2539	0.2675	0.1078
TC	0.2042	0.2578	0.2682	0.1134
TC	0.2054	0.2609	0.2675	0.1038
TC	0.2071	0.2616	0.2682	0.1271
CTC	0.0872	0.2158	0.2333	0.1850
CTC	0.0923	0.2267	0.2378	0.1842
CTC	0.0978	0.2345	0.2401	0.1842
CTC	0.0991	0.2407	0.2416	0.1842
CTC	0.0808	0.2430	0.2424	0.1842
DOX	0.2463	0.2019	0.2234	0.0740
DOX	0.2535	0.2042	0.2249	0.0700
DOX	0.2561	0.2065	0.2264	0.0692
DOX	0.2620	0.2089	0.2249	0.0676
DOX	0.2480	0.2104	0.2264	0.0684
OTC	0.1765	0.1102	0.1322	0.0603
OTC	0.1808	0.1126	0.1330	0.0563
OTC	0.1795	0.1165	0.1322	0.0628
OTC	0.1786	0.1180	0.1345	0.0595
OTC	0.1799	0.1211	0.1353	0.0628

Table S3 Detection and identification of unknown TCs at 15 μM.

Sample no.	$(F_0-F)/F_0$ -S1	$(F_0-F)/F_0$ -S2	$(F_0-F)/F_0$ -S3	$(F_0-F)/F_0$ -S4	Identification	Verification
1	0.2071	0.2508	0.2667	0.1207	TC	Yes
2	0.0915	0.2174	0.2348	0.1850	CTC	Yes
3	0.1761	0.1095	0.1307	0.0555	OTC	Yes
4	0.2118	0.2547	0.2667	0.1102	TC	Yes
5	0.2459	0.2042	0.2249	0.0724	DOX	Yes
6	0.2144	0.2570	0.2682	0.1070	TC	Yes
7	0.0880	0.2213	0.2356	0.1842	CTC	Yes
8	0.2522	0.2011	0.2242	0.0708	DOX	Yes
9	0.2071	0.2593	0.2675	0.1054	TC	Yes
10	0.0953	0.2290	0.2378	0.1850	CTC	Yes
11	0.1791	0.1118	0.1315	0.0547	OTC	Yes
12	0.2544	0.2050	0.2264	0.0684	DOX	Yes
13	0.0991	0.2430	0.2485	0.1866	CTC	Yes
14	0.2042	0.2624	0.2690	0.1287	TC	Yes
15	0.1795	0.1134	0.1315	0.0636	OTC	Yes
16	0.2569	0.2065	0.2264	0.0668	DOX	Yes
17	0.1808	0.1180	0.1337	0.0619	OTC	Yes
18	0.0868	0.2430	0.2401	0.1826	CTC	Yes
19	0.1808	0.1203	0.1337	0.0611	OTC	Yes
20	0.2616	0.2096	0.2257	0.0676	DOX	Yes

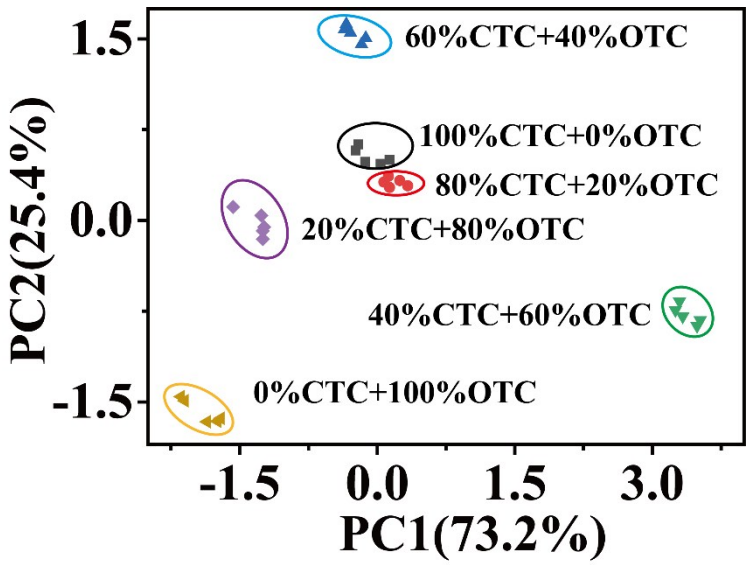


Fig. S12 Two-dimensional PCA score plot of the flourescence sensor array for discrimination of the mixtures of CTC and OTC at different molar ratios (total concentration at 6 μM).

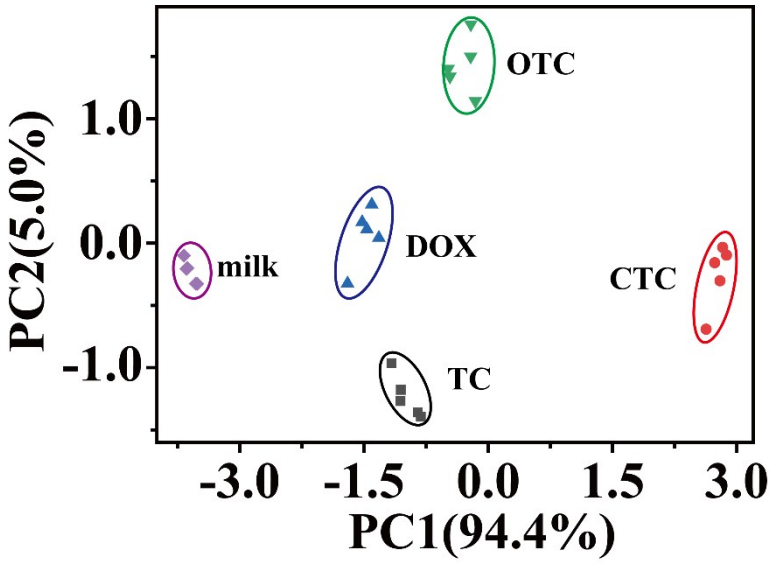


Fig. S13 Two-dimensional PCA score plot the discrimination of four TCs with the same concentration at 10 μM in the milk samples.