

Supplementary Information for

**Ratiometric captopril assay based on the recovery of the Bi (III)-quenched
yellow fluorescence of dually emitting carbon nanodots**

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Materials

Ascorbic acid (AA), ethylene glycol, CH_3COOH , CH_3COONa , AgNO_3 , NaCl , KCl , CoCl_2 , $\text{Sr}(\text{NO}_3)_2$, NiCl_2 , BaCl_2 , MgSO_4 , MnSO_4 , $\text{Pb}(\text{NO}_3)_2$, ZnCl_2 , CuCl_2 , $\text{Hg}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3$, $\text{Bi}(\text{NO}_3)_3$, CAP, glucose, methionine, cysteine, norvaline, threonine, histidine, and arginine were purchased from Aladdin (Shanghai, China). DNA oligonucleotides used in this work were synthesized by Sangon Biotechnology Co., Ltd. (Shanghai, China). CAP tablets and human blood were purchased from a local pharmacy. All of the chemicals were used as received without further purification. Ultrapure water was used throughout all of the experiments.

Apparatus

A Hitachi F-7000 fluorescence spectrophotometer (Tokyo, Japan) was used for recording fluorescence spectra with the slits (Ex/Em) of 10.0/10.0 nm. The photomultiplier tube (PMT) voltage was set at 400 V.

The calculation of limit of detection (LOD) of CAP

All experiments were repeated at least 3 times, and the standard deviation (SD) of experimental data was controlled within 0.25%. The limit of detection (LOD) was defined as the concentration of analyte that corresponds to three times the signal-to-noise ratio ($S/N=3$). Here, LOD was calculated according to the expression $\text{LOD}=3\sigma/K$, where σ was the standard deviation for the blank solution ($n=10$), and K was the slope of the calibration curve. In this paper, 3σ was about 0.0043; the corresponding linear regression equation was $I_{530}/I_{410}=0.354C+0.366$, and C was the concentration of p-NP, so the $\text{LOD}=0.0043/0.354=12\text{ nM}$.

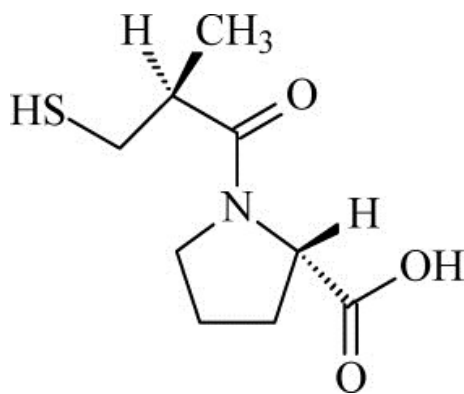


Fig. S1 Structure of captopril.

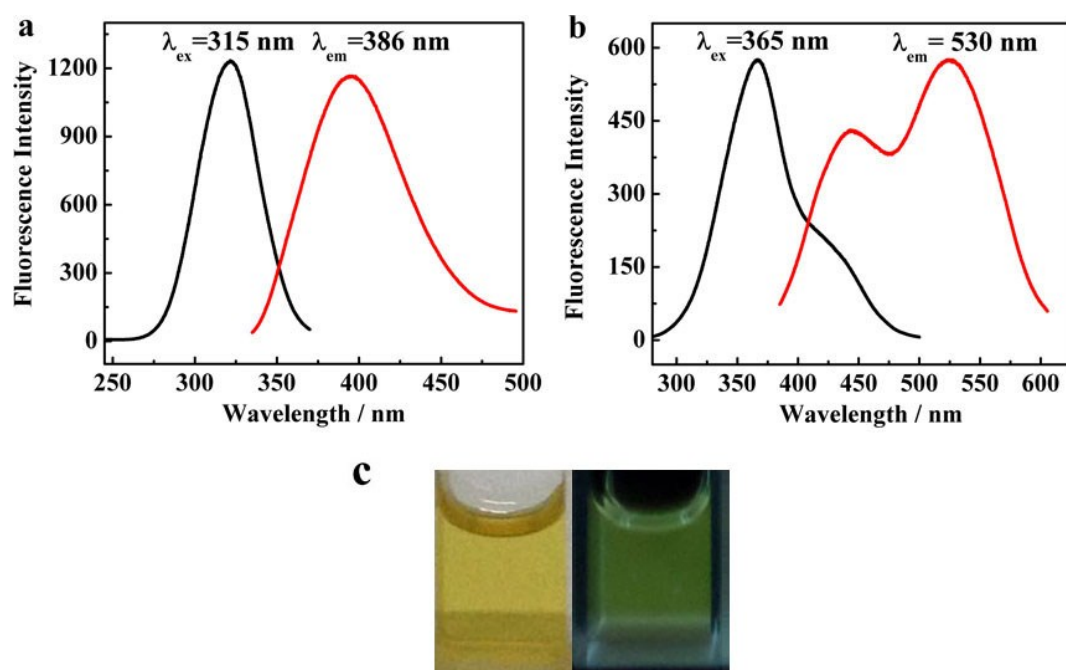


Fig. S2 Fluorescence spectra of blue emitters (a) and yellow emitters (b). The photographs of de-CDs under visible and UV light at 365 nm (c).

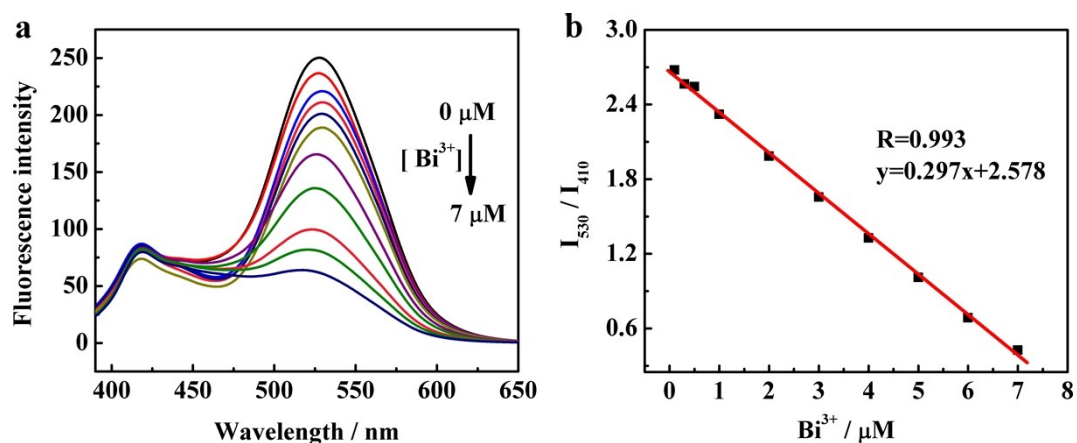


Fig. S3 Fluorescence responses to different concentrations of Bi^{3+} (a) and corresponding linear range (b). The concentrations of Bi^{3+} were 0.05, 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7 μM , respectively.

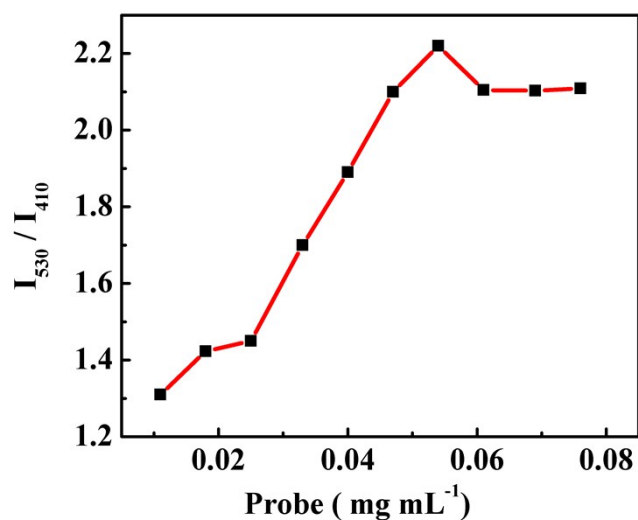


Fig. S4 Effect of probe concentration on the sensing assay for CAP. The concentrations of Bi^{3+} and CAP were 7 and 10 μM , respectively.

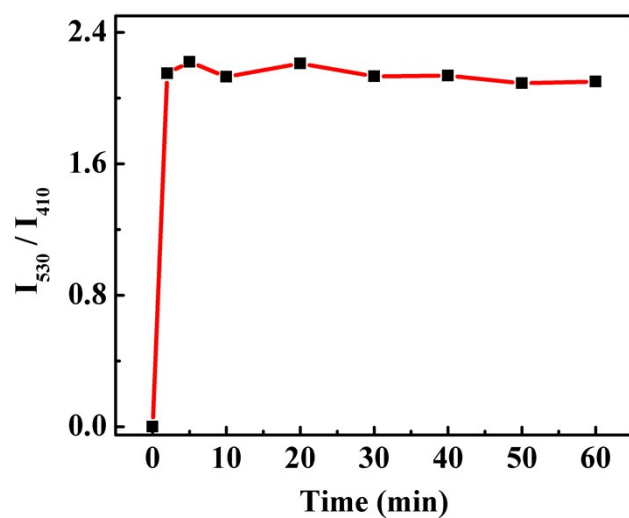


Fig. S5 Influence of reaction time on the detection of CAP. The concentrations of de-CDs, Bi^{3+} and CAP were 0.054 mg mL^{-1} , $7 \text{ }\mu\text{M}$ and $10 \text{ }\mu\text{M}$, respectively.

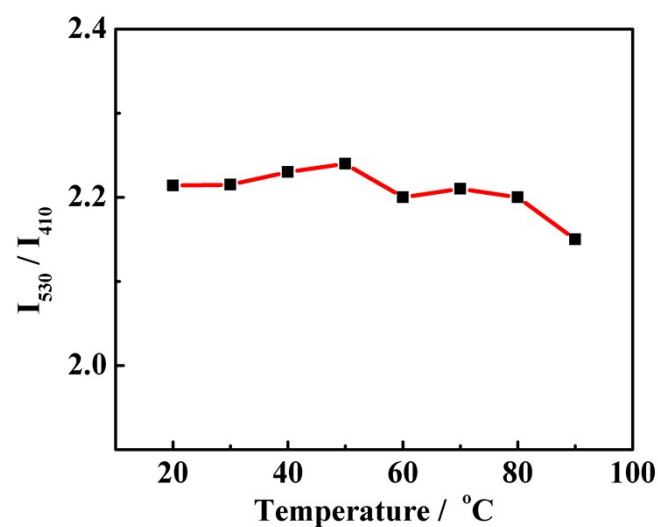


Fig. S6 Effect of reaction temperature on the determination of CAP. The concentrations of de-CDs, Bi^{3+} and CAP were 0.054 mg mL^{-1} , $7 \text{ }\mu\text{M}$ and $10 \text{ }\mu\text{M}$, respectively.

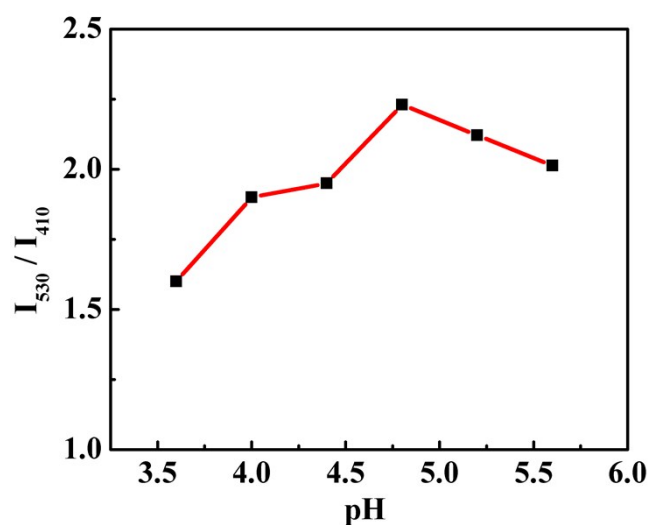


Fig. S7 Effect of pH on the determination of CAP. The different pH values (pH 3.6, 4.0, 4.4 4.8, 5.2, 5.6) were adjusted by adding 0.2 M $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$. The concentrations of de-CDs, Bi^{3+} and CAP were 0.054 mg mL^{-1} , $7 \text{ }\mu\text{M}$ and $10 \text{ }\mu\text{M}$, respectively.

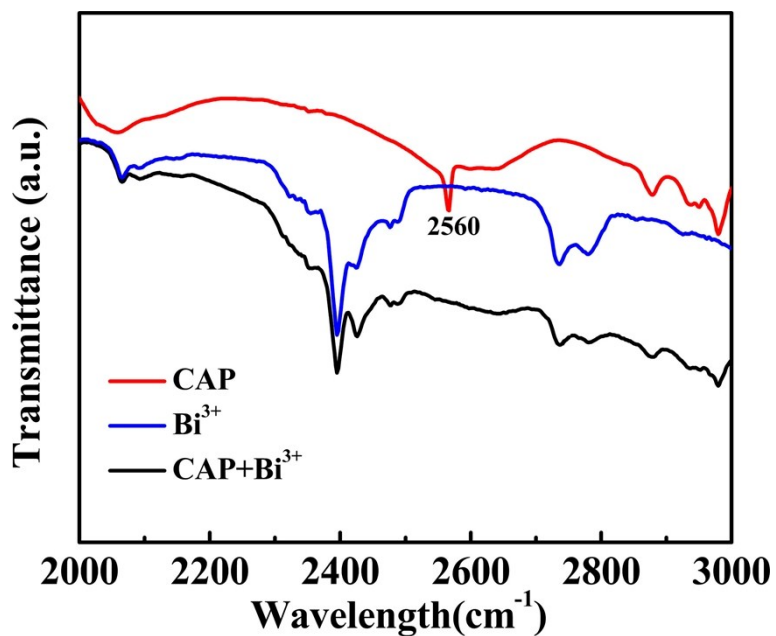


Fig. S8 FT-IR spectra of CAP (red line), Bi^{3+} (blue line), and CAP in the presence of Bi^{3+} (black line).

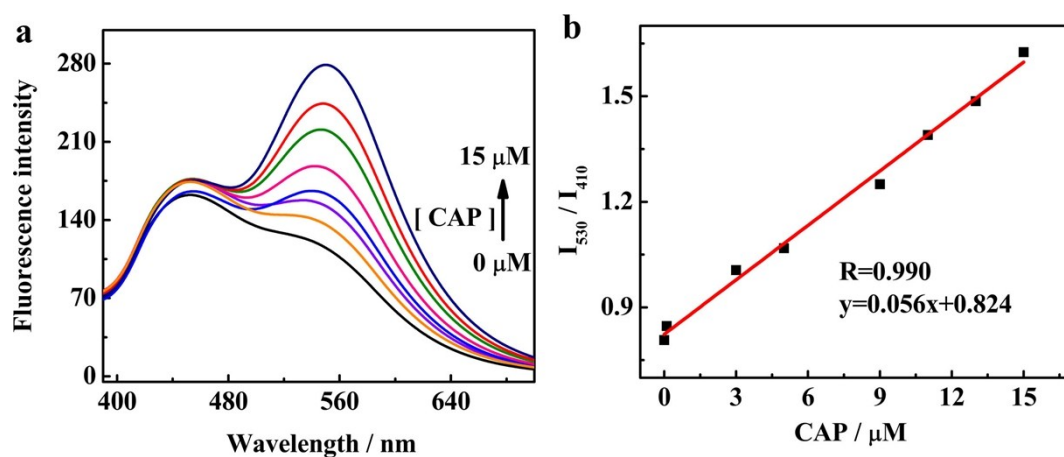


Fig. S9 (a) Fluorescence spectra of de-CDs-Bi³⁺ with the addition of different concentrations of CAP (from bottom to top: 0, 0.1, 3, 7, 9, 11, 13, 15 μ M) in the human plasma and the corresponding linear range (b).

Table S1. Determination of CAP in tablets.

Number	Labeled amount (μ M)	Found amount (μ M)	Recovery (n = 3, %)
1	5	5.03	100.6
2	5	4.85	97.0
3	5	4.79	95.8

Table S2. Determination of CAP in human plasma and urine.

Samples	Found amount (μM)	Standard added (μM)	Found value (μM)	Recovery (n = 3, %)
plasma	NF	0.2	0.195	97.5
	NF	3	2.90	96.7
	NF	10	10.05	100.5
urine	NF	0.1	0.095	95.0
	NF	3	3.12	104.0
	NF	10	10.21	102.1

NF: not found

References

1. D. Y. Liu, F. Qu, X. E. Zhao and J. M. You, **J. Phys. Chem. C**, 2015, **119**, 17979-17987.