Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

A dendritically amplified fluorescence signal probe on SiO_2 microspheres for ultrasensitive detection of mercury ions

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Experimental section

Apparatus

Transmission electron microscopy (TEM) images were recorded using a JEM-2000EXinstrument (Hitachi). Field-emission scanning electron microscopy (FE-SEM) was carried out on a JEOL JSM-6700F instrument. Photoluminescence (PL) spectra were obtained on a F-4500 spectrophotometer (Shimadzu). Absorption measurements were carried out using a Varian Cary 300 UV-vis spectrophotometer.All optical measurements were carried out at room temperature under ambient conditions.

Reagents

1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC), N-Hydroxysuccinimide (NHS), Hydrogentetrachloroaurate ($HAuCl_4 \cdot 4H_2O$, 99.9%), mercury perchlorate trihydrate ($Hg(ClO_4)_2 \cdot 3H_2O$) and Tris(2-carboxyethyl) phosphinehydrochloride (TCEP) were obtainedfrom Aladdin (Shanghai, China). Terminal deoxynucleotidyl transferase (TdT), the nicking endonuclease (Nt.BbvCI), phi29 DNApolymerase and 10×phi29 DNA polymerase reaction buffer were purchased fromThermo Fisher Scientific, Inc. deoxyguanosine triphosphate (dGTP), deoxythymidine 5′-triphosphate (dTTP) , deoxyribonucleoside triphosphate (dNTPs) werepurchased fromSangon biotech Co., Ltd. (Shanghai, China). SiO_2 microsphere was provided by Tianjin BaseLine ChromTech Research Centre (Tianjin, China). Other reagents were obtained from Aladdin (Shanghai, China). NEB buffer (pH 7.9) was obtained by using 50 mM NaCl, 10 mM Tris-HCl, 10mM $MgCl_2$, and 1 mM dithiothreitol. The DNA probes in our study (Table-1) were synthesized and purified by Sangon Biotech Co., Ltd. (Shanghai, China).

Table S1. Sequences of the DNA

Name	Sequence（5'---3'）
M (Machine) DNA	CGTCTAGACGTAGCTGAGGTTCCCCAGATTCTTTCTTCCCTTGTTTGTTTCTG
Capture probe 1	GTCTAGACGTAGCTGA-NH_2
Capture probe 2	CCCCCCCCCCCCCCCCCCAGAAGA-SH
Reporter probe	SH-ACAAGCAAGGACAGCT
Signal probe	Cy5-AAAAAAAAAAAA

Results and discussions

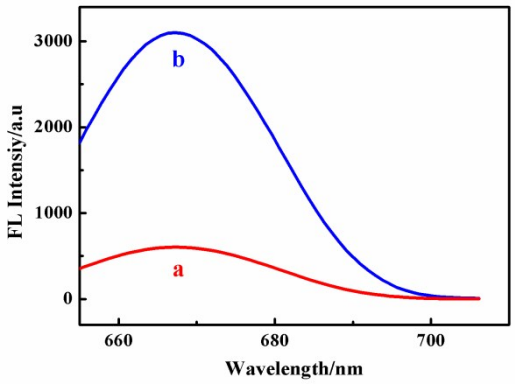

Figure S1. Feasibility of the dendritically amplified fluorescence sensing system: (a) blank; (b) 0.1 fM Hg^{2+}.

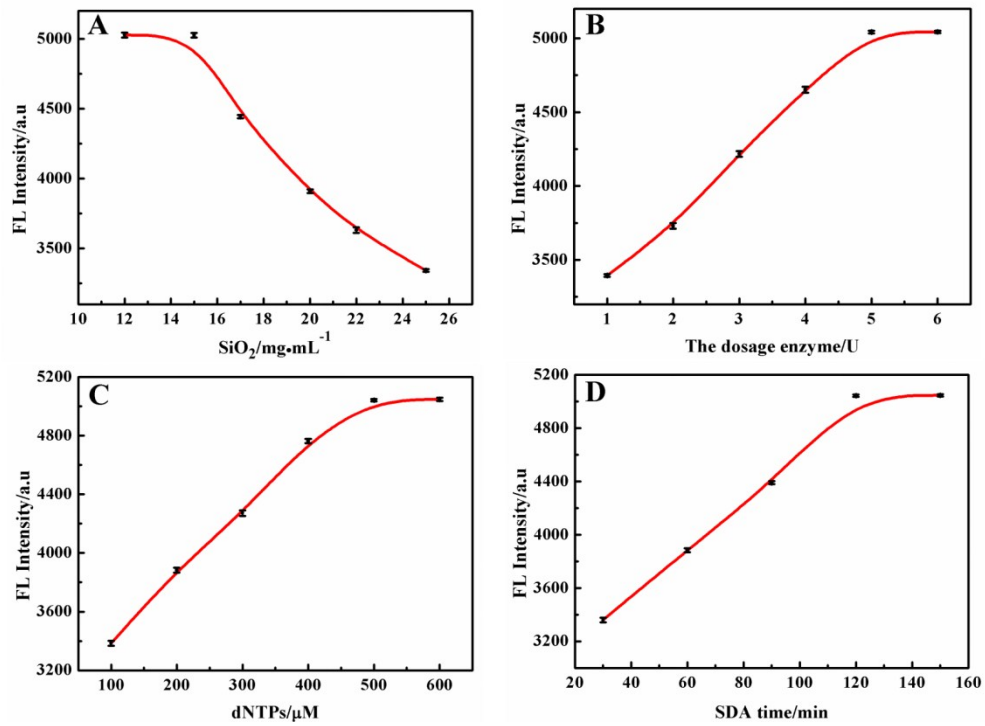

Figure S2. Effects of (A) SiO_2 microsphereconcentration; (B) phi29 polymerase and Nt.BbvCI amount; (C) dNTPs concentration; (D) SDA reaction time on FL signal for detection. (concentrations of target Hg^{2+}:1.0 pM)

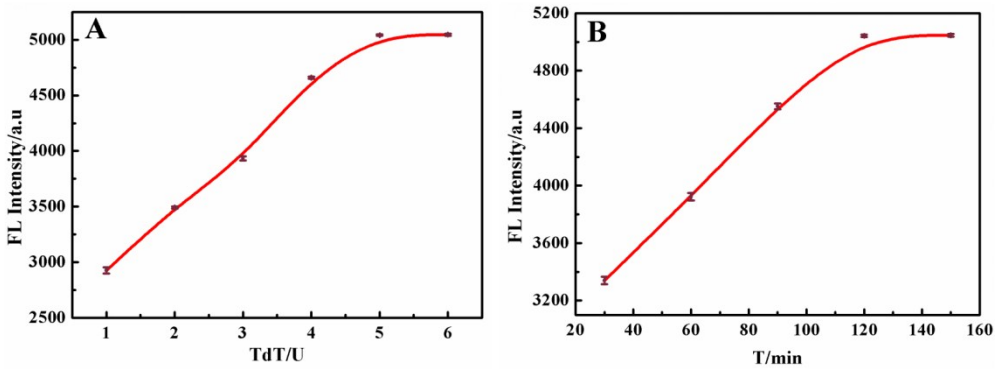

Figure S3. Effects of (A) TdT amount; (B) TdT extension time on FL signal for detection. (concentrations of target Hg^{2+}:1.0 pM)

Table S2. Comparison of Different Methods for Assay of Hg^{2+}

methods	detection limit	dynamic range	ref
fluorescence	1.0 aM	1 aM to 10 pM	This work
fluorescence	0.92 nM	1nM to 50 nM	1
fluorescence	2 nM	2 nM to 60 nM	2
SERS	1 pM	1 pM to 1 μM	3
ECL	2 fM	5 fM to 100 pM	4
ECL	0.33 fM	1 fM to 100 pM	5
electrochemistry	0.001 aM	1.0 aM to 100 nM	6

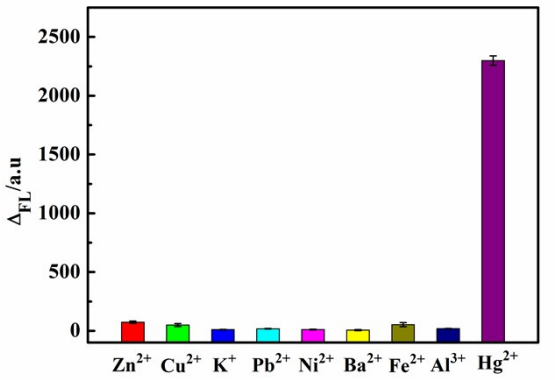

Figure S4 Selectivity of the fluorescence strategy for detecting Hg^{2+} in the presence of other metal ions (The concentration of Hg^{2+} was 0.1 fM, the concentrations of interfering ions were all 100 fM).

Table S3. Recovery in Different Water Samples (n=3) with the Proposed Method

sample	Added/fM	obtain /fM	recovery/%	RSD/%
	1	0.978	99.13	1.23
drinking	10	10.034	100.5	1.77
pure	100	100.32	102.8	2.71
water	1000	994.28	97.6	1.48
	1	1.008	100.03	1.63
tap	10	10.108	103.13	1.92
water	100	96.72	96.99	2.95
	1000	973.28	97.94	1.44
	1	1.024	102.7	2.31
underground	10	9.685	96.31	1.69
water	100	98.02	98.44	1.94
	1000	1002.7	103.5	3.17
	1	0.958	95.92	2.75
surface	10	10.42	104.7	3.41
water	100	101.25	102.4	2.39
	1000	973.7	97.86	1.71
	1	1.035	103.9	2.16
water with	10	9.729	97.42	2.85
high mineral	100	103.22	102.3	3.26
content	1000	958.8	95.68	1.89

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