Electronic supplementary information

A highly sensitive and selective fluorescent probe without quencher for Pb^{2+} ions detection based on ACQ phenomenon

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Synthesis of conjugate fluorophore

The synthesis route of conjugate fluorophore was shown in Fig. S1. It was based on previous reports[1-3].

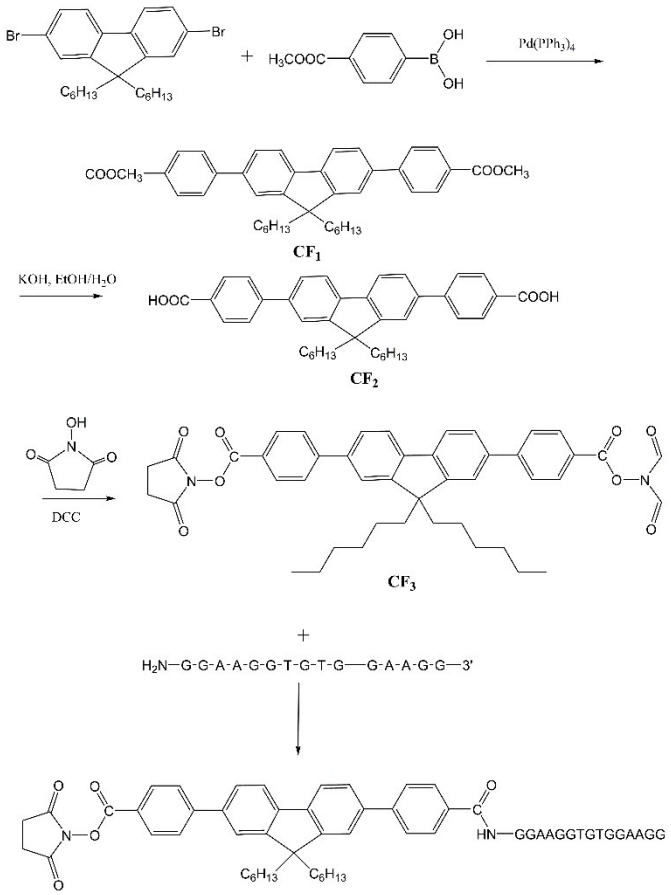

Fig. S1 Synthetic route for CF-DNA probe.

2,7-bis (4-phenylcarboxylic acid methyl ester)-9,9-di-n-octylfluorene (CF_1) was synthesized using a previously reported method via the Suzuki reaction. 2,7-Dibromo-9,9-di-n-octylfluorene (4.917 g, 10 mmol) , 4-methoxycarbonylphenylboronic acid (4.169 g，23.3 mmol) and K_2CO_3 solution (2 M，56 mL)，and Tetrakis(triphenylphosphine)palladium(0) (300 mg) and THF (60mL) were vigorously stirred at 80°C for 18 h under a nitrogen atmosphere. The reaction mixture was extracted into ethyl acetate (3×25 mL) and washed with brine (100 mL). After drying over anhydrous $MgSO_4$，the product was purified by silica-gel column chromatography (4.745g，78.8%) (Fig. S2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J*

= 8.3 Hz, 4H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 4H), 7.69 – 7.59 (m, 4H), 3.99 (s, 6H), 2.13 – 2.01 (m, 4H), 1.18 – 1.00 (m, 12H), 0.76 (dd, *J* = 16.1, 9.0 Hz, 10H).

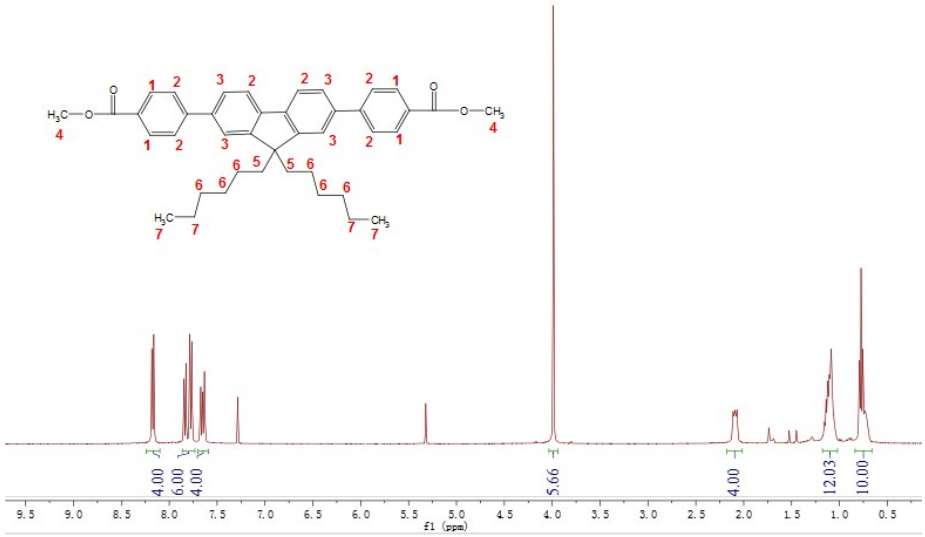

Fig. S2 The ^{1}H NMR of the CF_1 .

CF_1 (1.40g，2.33 mmol) was dissolved in 30 mL of THF/H_2O (2:1，v/v)，then KOH (1.60g，28 mmol) was added，and the mixture was reflux for 12h. Then 100 mL water was added into the solution，then acidified with HCl. The precipitated white solid was washed 3 times and vacuum-dried without further purification (1.359，100%) (Fig. S3). ^{1}H NMR (400 MHz, DMSO) δ 13.04 (s, 2H), 8.04 (s, 4H), 7.97 (s, 2H), 7.90 (s, 6H), 7.77 (d, *J* = 7.9 Hz, 2H), 2.19 – 2.09 (m, 4H), 1.24 – 0.67 (m, 22H).

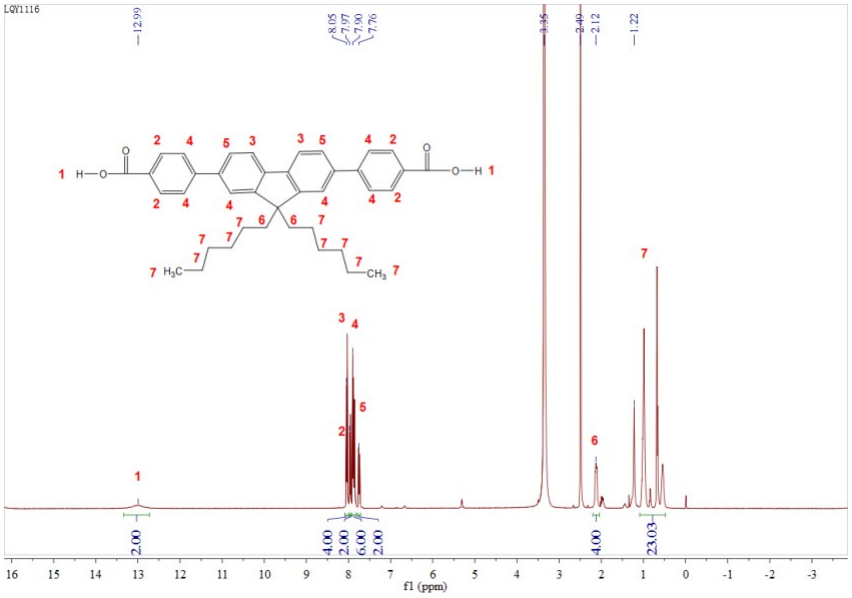

Fig. S3 The ^{1}H NMR of the CF_2.

CF_2 (808 mg，1.4 mmol) and N-hydroxysuccinimide (NHS，760 mg，6.25 mmol) were dissolved in dry N, N-Dimethylformamide (DMF) (8mL). DCC (180 mg，0.87 mmol) dissolved in DMF (7 mL) was added and stirred at room temperature for 48 h. The mixture was extracted with dichloromethane (30 mL) and then washed with plenty of water，then crude product was purified by silica-gel column chromatography (458 mg，56.7%) (Fig. S4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.2 Hz, 4H), 7.90 – 7.79 (m, 6H), 7.70 – 7.62 (m, 4H), 2.96 (s, 8H), 2.10 (s, 5H), 1.10 (s, 13H), 0.77 (d, J = 7.1 Hz, 12H).

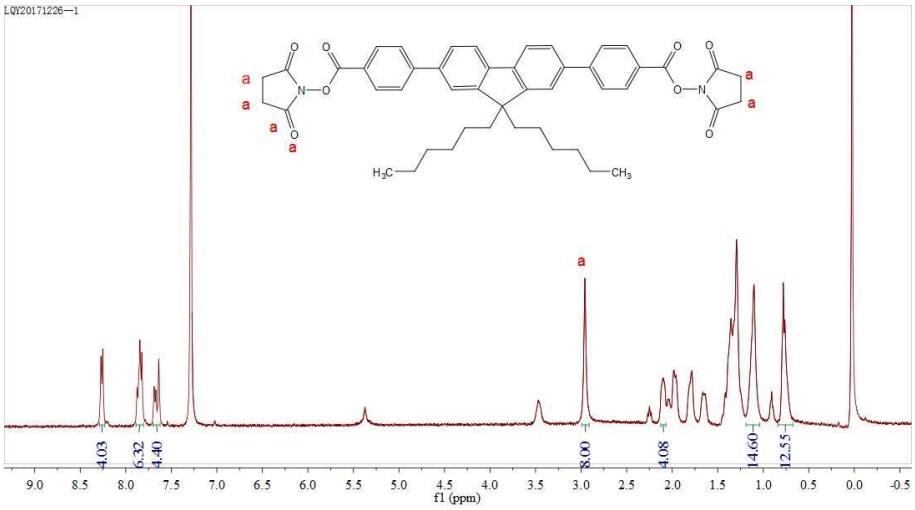

Fig. S4 The ^{1}H NMR of the CF_3

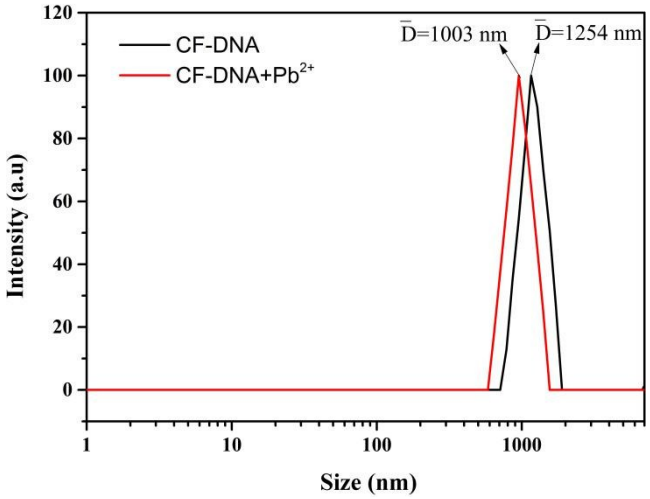

Fig. S5 Light scattering measurement of CF-DNA (5 μM) probe before and after the Pb^{2+} detection in PBS buffer.

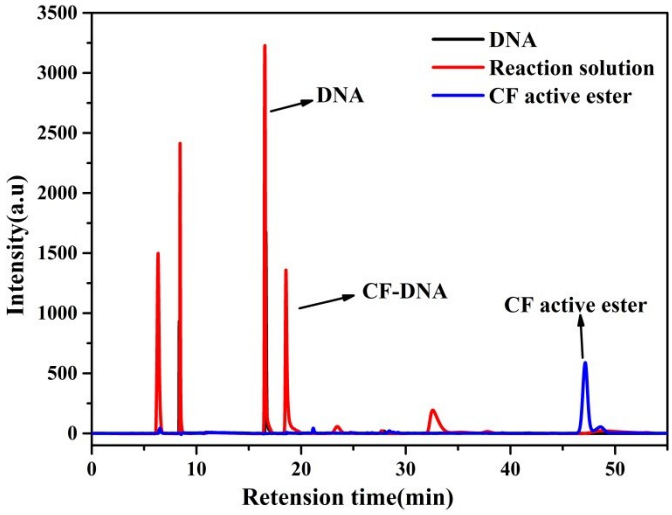

Fig. S6 The result of HPLC purification. The retention time of DNA (black line) was 16.5 min while the retention time of CF-DNA probe 18.65 min.

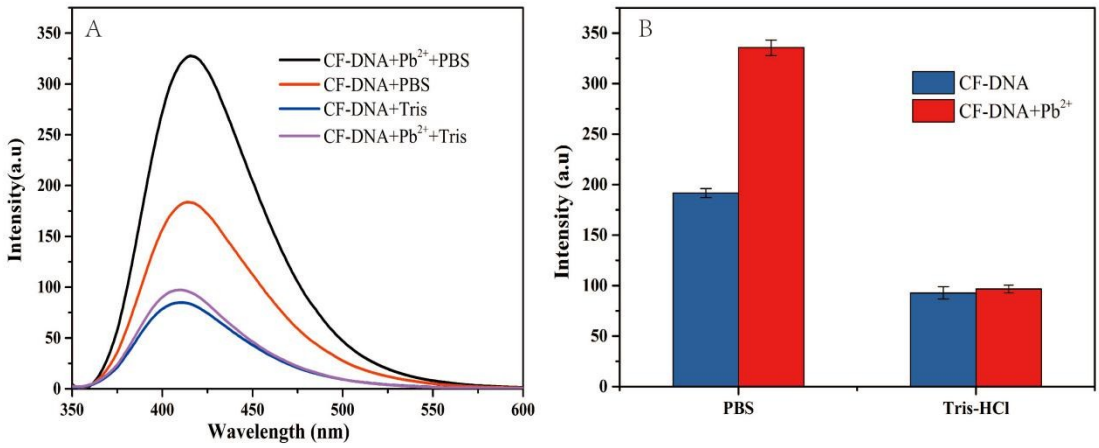

Fig. S7 The fluorescence intensity of CF-DNA probe in different buffer system

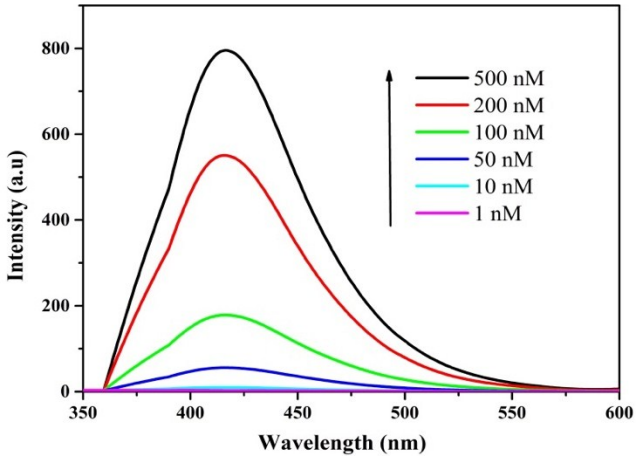

Fig. S8 The fluorescence spectra of different concentration of CF-DNA.

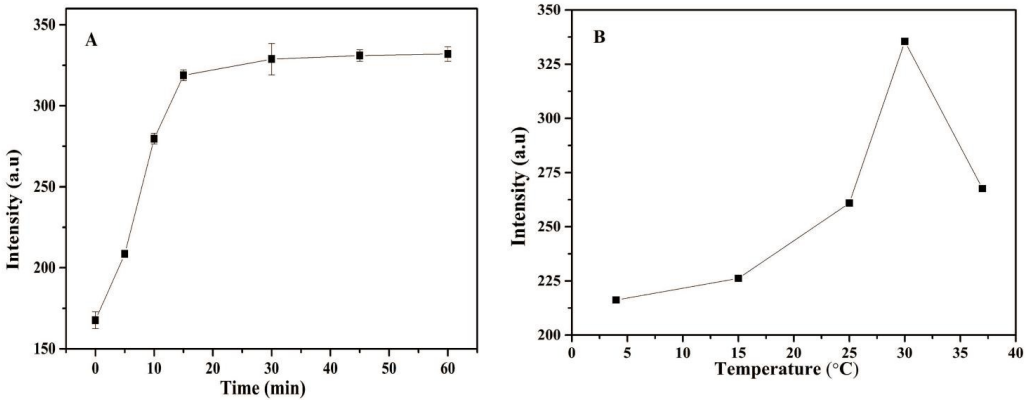

Fig. S9 The Optimization of conditions for Pb^{2+} detection. (A) Fluorescence intensity change for detecting Pb^{2+} with the increasing of time. (B) Fluorescence intensity change for detecting Pb^{2+} under different temperature.

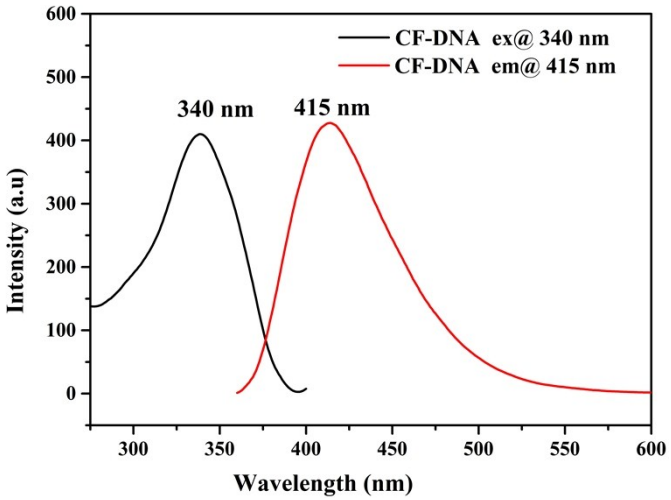

Fig. S10 The fluorescence spectra of CF-DNA probe.

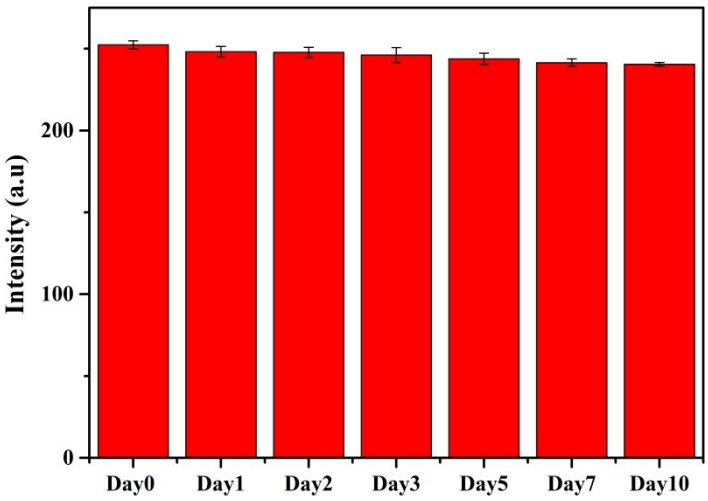

Fig. S11 Stability of the CF-DNA probe at 0-10d.

Table S1 Comparison of nucleic acid biosensors for the detection of Pb^{2+}.

Sensors	LOD	response times	Linear range(s)	selectivity	Reference
CF-DNA probe	0.36 nM	15 min	0-1 nM	good	this work
FAM-aptamer/AuNPs	10 nM	15 min	12.5-100 nM	good	4
T30695 aptamer/SYBR Green I	18 nM	25 min	0-480 nM	good	5
RNA aptamer	6 nM	15 min	5-500 nM	good	6
Cu QCs/BSA	2 nM	not reported	0-0.2 nM	good	7
DNA duplex-quadruplex	20 nM	2 h	20-1 μM	good	8
AuNPs/DNAzyme	20 nM	10 min	not reported	good	9
Electrochemical bisensor	0.5 nM	not reported	0.5-50 μM	good	10
NMM–G-quadruplex aptamer	1 nM	30 min	5 nM-1 μM	good	11
glutathione modified AuNDs	2 nM	2 h	5-5 μM	good	12
thrombin binding aptamer	0.9 nM	5 min	1-120 nM	moderate	13
single-stranded DNAzyme	3.1 nM	35 min	5–100 nM.	good	14

References

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