

Electronic Supplementary Information

Multiple amplified detection of microRNA based on host-guest interaction between β - cyclodextrin polymer and pyrene

Xiaochen Guo,^a Xiaohai Yang,^{*a} Pei Liu,^b Kemin Wang,^{*a} Qing Wang,^a Qiuping Guo,^a Jin Huang,^a Wenshan Li,^a Fengzhou Xu^a and Chunxia Song^a

^a State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Key Laboratory for Bio-Nanotechnology and Molecular Engineering of Hunan Province, Hunan University, Changsha 410082, China.

^b Hunan Province Environmental Monitoring Centre, Changsha 410014, China.

*To whom correspondence should be addressed:

Phone: +86-731-88821566.

Fax: +86-731-88821566.

E-mail: kmwang@hnu.edu.cn, yangxiaohai@hnu.edu.cn.

Table S1. All the sequences are listed as below (from 5' to 3')

Name	Sequence (5'-3')
mono-pyrene-labeled molecular beacon	(Phosphorylated)AAGCTGAGGTCTTGGACATCAACATCAGT CTGATAAGCTATGTCCAAGA(Pyrene)
primer	TCTTGGAC
miRNA-21	UAGCUUAUCAGACUGAUGUUGA
smRNA	UAGCUUAUCAG <i>UCUGAUGUUGA</i>
tmRNA	<i>UCGCUUAUCGGACUGAUCUUGA</i>
Random RNA	AAUAUAUCUGCUGAGGAUCAGA

Nucleotide mismatches were marked in red and indicated as italic letters.

Characterization of β -CDP

The structure of β -CDP was confirmed by FTIR spectra and ^1H NMR spectra (Fig. S1). The molecular weight of β -CDP ($M_n \sim 94,400$) was measured by using gel permeation chromatography (GPC, waters-515). As shown in Fig. S1 A, the FTIR spectra showed that most absorption bands of β -CD were still present in spectrum of β -CDP. Due to the cross-linking reaction of β -CD, the absorption bands of stretching vibration of C-O-C at $1070 \sim 1160 \text{ cm}^{-1}$ were broadened as shown in the spectrum of β -CDP. The ^1H NMR spectra showed that most bands of β -CD at 4.0-3.4 ppm were broadened in the spectrum of β -CDP (Fig. S1 B).

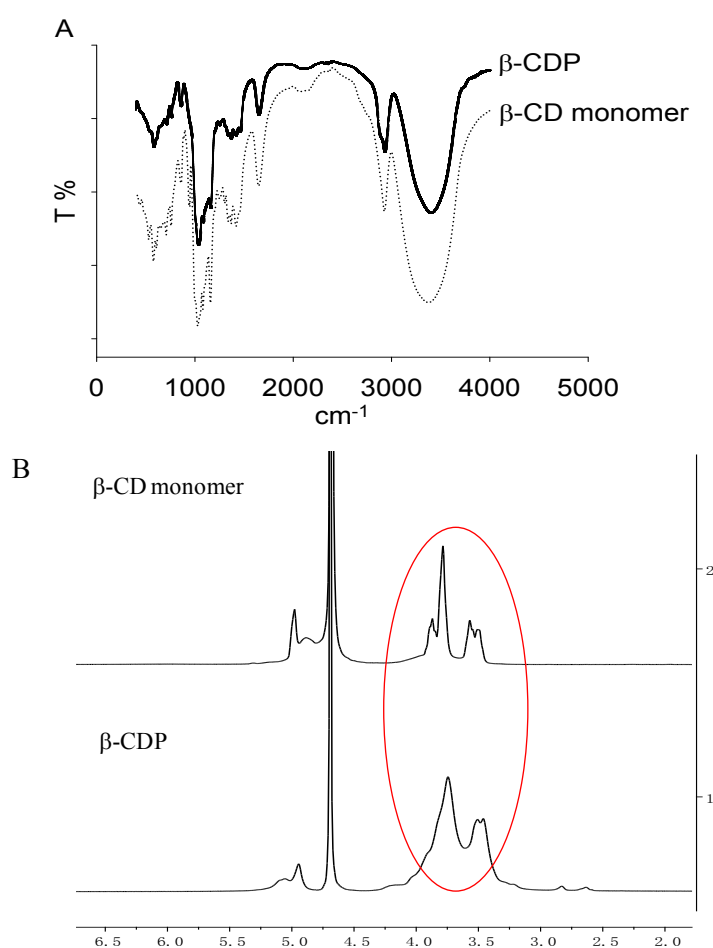


Fig. S1 (A) FTIR spectra of β -CD monomer and β -CDP. (B) ^1H NMR spectra of β -CD monomer and β -CDP.

Optimization of experimental conditions

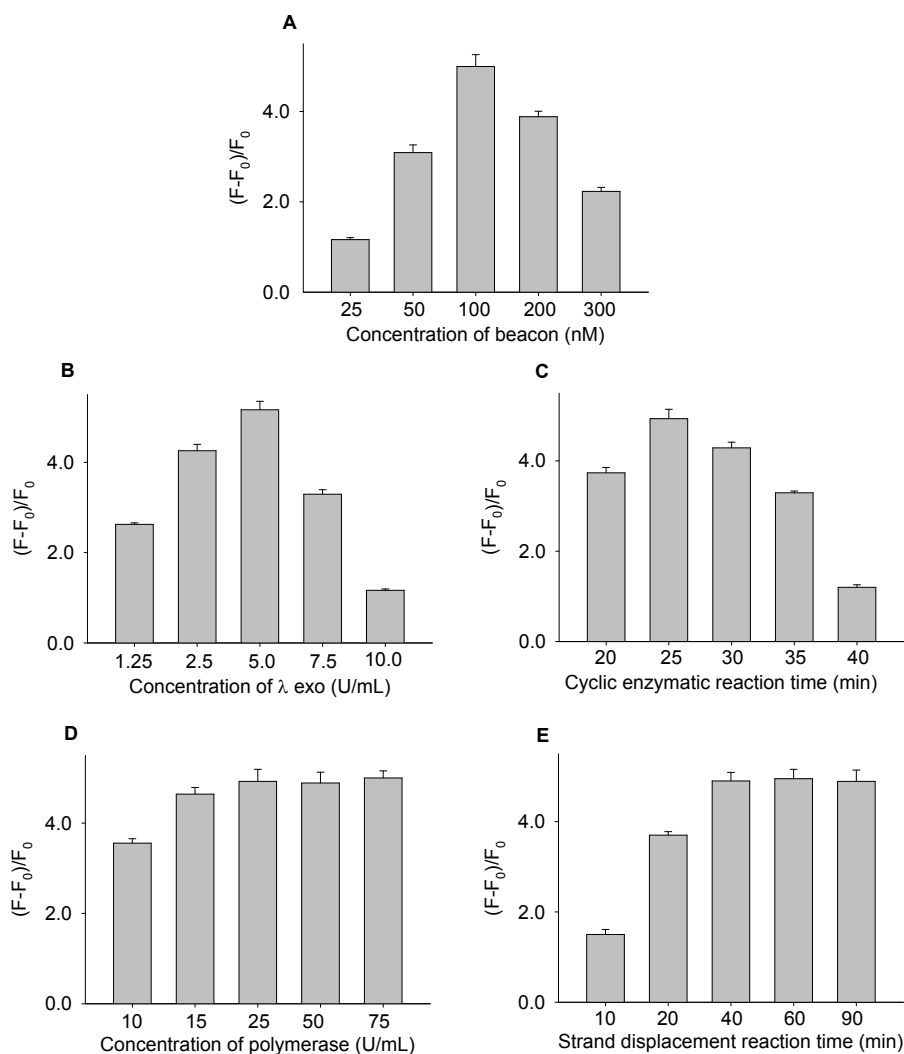


Fig. S2 The effect of different condition for detection of miRNA-21 based on host-guest interaction between β -CDP and pyrene. (A) Different concentrations of mono-pyrene-labeled molecular beacon, the concentrations of miRNA-21, primer, polymerase, λ exo and β -CDP were 0.5 nM, 200 nM, 25 U mL⁻¹, 5 U mL⁻¹ and 1.5 mg mL⁻¹, respectively; (B) Different concentrations of λ exo, the concentrations of miRNA-21, beacon, primer, polymerase and β -CDP were 0.5 nM, 100 nM, 200 nM, 25 U mL⁻¹ and 1.5 mg mL⁻¹, respectively; (C) Different cyclic enzymatic reaction time, the concentrations of miRNA-21, beacon, primer, polymerase, λ exo and β -CDP were 0.5 nM, 100 nM, 200 nM, 25 U mL⁻¹, 5 U mL⁻¹ and 1.5 mg mL⁻¹, respectively; the strand displacement reaction time is 40 min; (D) Different concentrations of polymerase, the concentrations of miRNA-21, beacon, primer, λ exo and β -CDP were 0.5 nM, 100 nM, 200 nM, 5 U mL⁻¹ and 1.5 mg mL⁻¹, respectively; (E) Different strand displacement reaction time, the concentrations of miRNA-21, beacon, primer, polymerase, λ exo and β -CDP were 0.5 nM, 100 nM, 200 nM, 25 U mL⁻¹, 5 U mL⁻¹ and 1.5 mg mL⁻¹, respectively; the cyclic enzymatic reaction

time is 25 min; The excitation/emission wavelength was set at 345 nm/380 nm. Error bars indicated the standard deviations of three experiments.

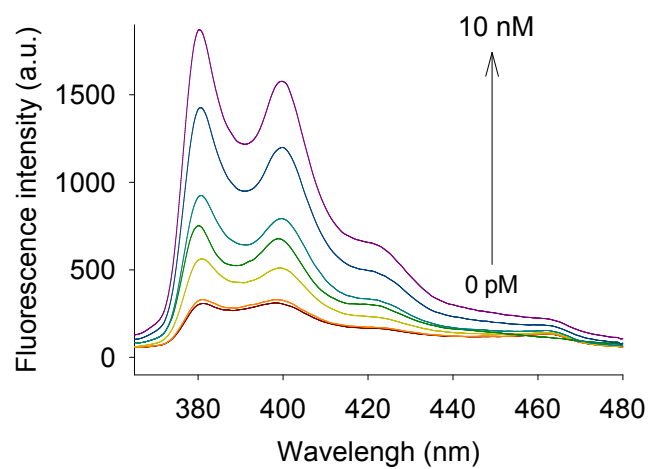


Fig. S3 Fluorescence spectra of the multiple amplified fluorescent method in serum samples over a range of miRNA-21 concentrations. The concentrations of beacon, primer, polymerase, λ exo and β -CDP were 100 nM, 200 nM, 25 U mL⁻¹, 5 U mL⁻¹ and 1.5 mg mL⁻¹, respectively. Error bars indicated the standard deviations of three experiments.

Table S2. Comparison of the proposed method with other amplification strategies.

Style	Detection limit	Response time	References
Catalytic Recycling	0.4 fM	4 h	S1
Magnetic beads-assisted assay	0.1 pM	4 h	S2
DNase I-assisted target recycling	2.3 pM	90 min	S3
Graphene oxide-assisted enzymatic amplification	9 pM	4 h	S4
Gold nanoparticle	5-8 pM	5 h	S5
WS ₂ nanosheet mediated assay	0.3 pM	40 min	S6
Copper nanoparticles strategy	10 pM	16 h	S7
This method	0.3 pM	65 min	

References

- S1 P. Miao, B. Wang, X. Chen, X. Li and Y. Tang, *Appl. Mater. Interfaces.*, 2015, **7**, 6238.
- S2 W. Shen, K. H. Yeo and Z. Gao, *Analyst*, 2015, **140**, 1932.
- S3 Y. Xie, X. Lin, Y. Huang, R. Pan, Z. Zhu, L. Zhou and C. J. Yang, *Chem. Commun.*, 2015, **51**, 2156.
- S4 L. Cui, X. Lin, N. Lin, Y. Song, Z. Zhu, X. Chen and C. J. Yang, *Chem. Commun.*, 2012, **48**, 194.
- S5 F. Degliangeli, P. Kshirsagar, V. Brunetti, P. P. Pompa and R. Fiammengo, *J. Am. Chem. Soc.*, 2014, **136**, 2264.
- S6 Q. Xi, D. Zhou, Y. Kan, J. Ge, Z. Wu, R. Yu and J. Jiang, *Anal. Chem.*, 2014, **86**, 1361.
- S7 F. Xu, H. Shi, X. He, K. Wang, D. He, Q. Guo, Z. Qing, L. Yan, X. Ye, D. Li and J. Tang, *Anal. Chem.*, 2014, **86**, 6976.