Sonochemical synthesis of cyclodextrin-coated quantum dots for optical detection of pollutant phenols in water

Haibing Li[*] *and Cuiping Han*

Key Laboratory of Pesticide and Chemical Biology (CCNU), Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, PR China

Supporting Information

[*]Corresponding author. Tel.: +86-27-67866423
E-mail address: lhbing@mail.ccnu.edu.cn,

A) The TEM images of β-CD-QDs and γ-CD-QDs

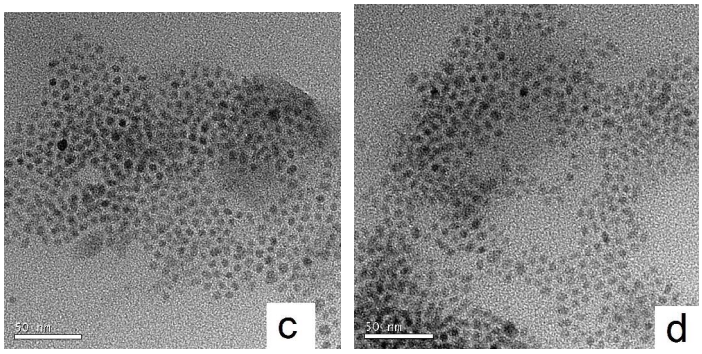


Figure S1. The TEM images of (c) β-CD-QDs and (d) γ-CD-QDs

B) ^{31}P NMR of β-CD-QDs and TOPO-QDs

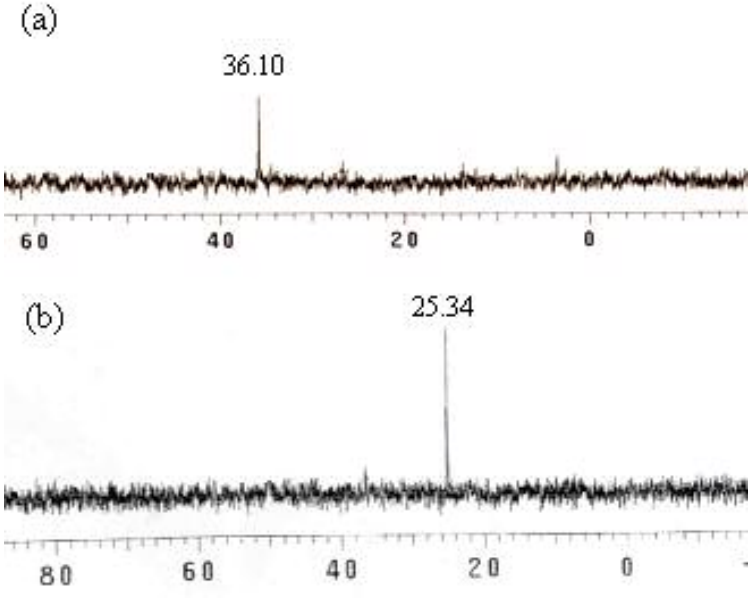


Figure S2. ^{31}P NMR of (a) β-CD-QDs and (b) TOPO-QDs.

C) Approximate the number of CD molecules on each quantum dot

In this study, we find that the emission intensity of resulting CD-QDs enhances as the CD dosage increases from 0.88 mM (for 1 mL of 0.5 mg/mL QDs solution, 0.88 μmol of CD is added. So is for the following CD concentration) to 5.29 mM (Figure S3a). Interestingly, the CD-concentration dependence of the FL intensity can be effectively described by a Langmuir-type binding isotherm. According to the literature, [1] the surface of QDs affords a finite number of binding sites. Each of the binding sites could absorb one CD molecule from the solution. The fraction of occupied sites, defined as Θ, is relate to the ratio between the signal obtains at given CD concentration I and the maximum intensity $I_{max.}$

$$\Theta = I / I_{max}$$

And an expression that related the CD concentration, C, to the signal intensity can be written as:

$$C / I = (1 / BI_{max}) + (1 / I_{max})C$$

The dependence of C/I as function of C according to the data is shown in Figure S3 b. A relative linearity is observed over the concentration of CD range from 0.88□5.29 mM, with a correlation coefficient $r = 0.992$. The maximum intensity I_{max} is estimated from the slope. And the number of CD molecules per quantum dots at given CD concentration can be calculated using 100 binding sites per nanocrystal.[2] Approximately 20 CD molecules per QDs at CD concentration of 0.88 mM, and the number of CD molecules is 65 per QDs when the CD concentration increased to 5.29 mM.

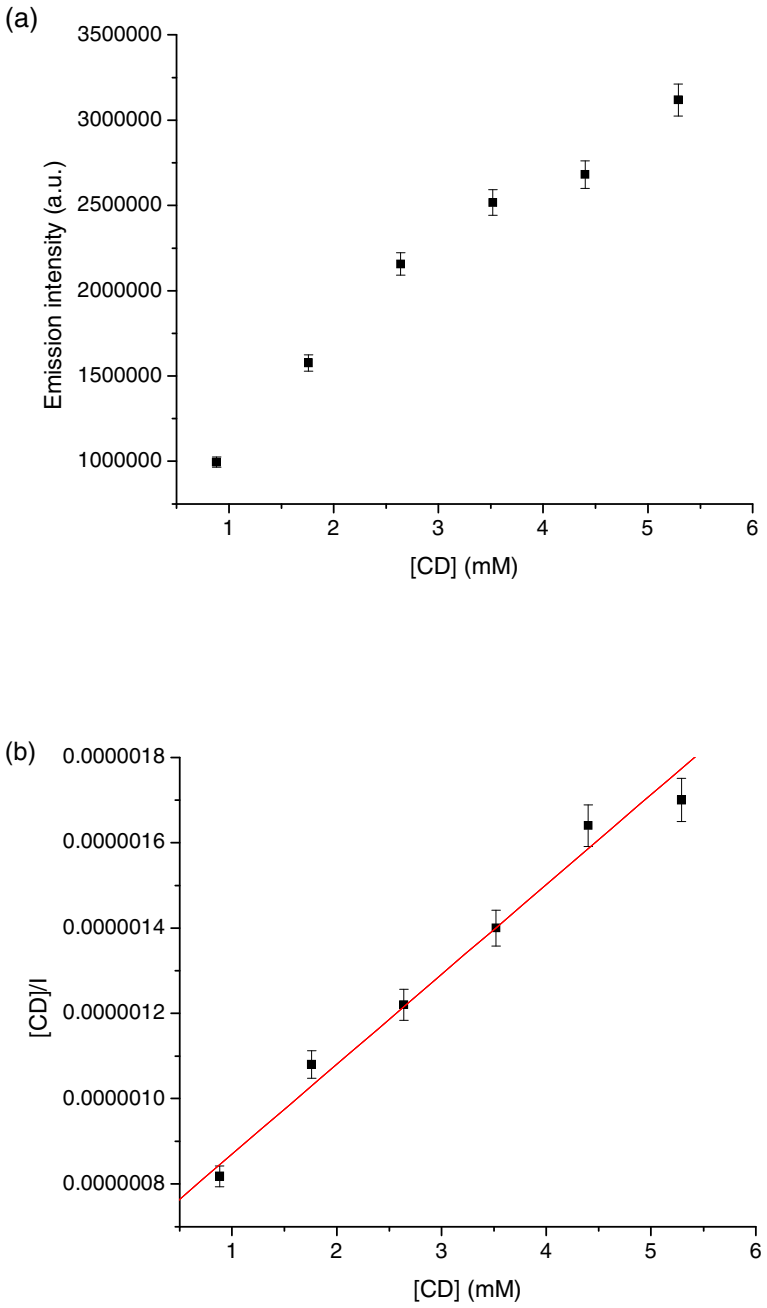


Figure S3. (a) Emission intensity *vs* totally added β-CD concentration for TOPO-capped QDs at a concentration of 0.5 mg/mL. (b) Langmuir binding isotherm description of the data showing a linear fit over the concentration range from 0.88□ 5.29 mM.

D) Synthesis of water-soluble CdSe QDs with different sizes using β-CD as surface coating agents by sonochemical route

Figure S4 shows the fluorescence spectra of CdSe QDs with different sizes after the surface coating with β-CD via ultrasonic irradiation for 30 min. It is found that the sonochemical method is general due to CdSe QDs with different size could be transferred into water in the presence of CD *via* the sonochemical process.

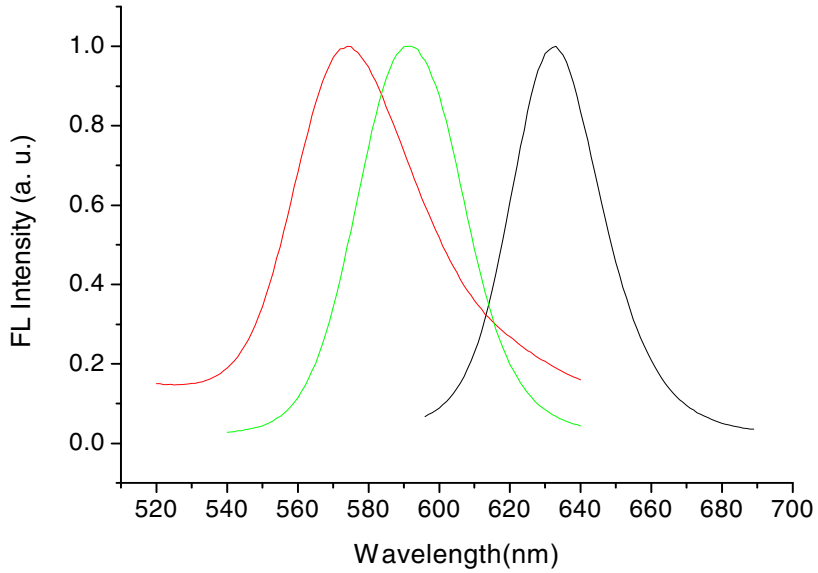


Figure S4. Fluorescence spectra of β-CD-coated CdSe QDs in water. The QDs are prepared from TOPO capped CdSe QDs with emission peaks at 575, 590, and 625 nm (Ex: 400nm, 450nm, and 480nm).

E) photostability of CD-QDs

The stability of CD-QDs in water is estimated by emission intensity and quantum yield as a function of time at 5 ºC, as shown in Figure S5. The emission intensity increases dramatically in first day and becomes constant in the following eight days. The spectral widths and emission wavelengths are almost constant over time. The QY increases gradually in five days and decreases the next four days.

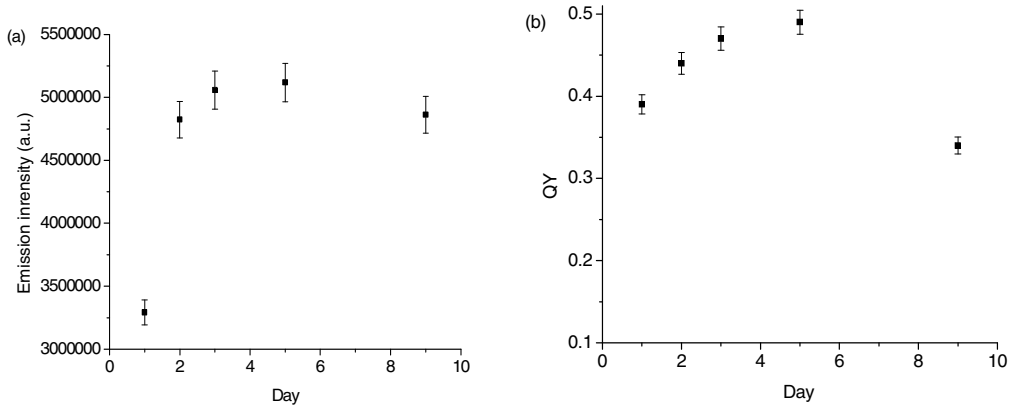


Figure S5. (a) Emission and (b) quantum yield (QY) stabilization of CD-QDs.

F) Effect of pH on the luminescence response of α-CD/CdSe/ZnS, β-CD/CdSe/ZnS, and γ-CD/CdSe/ZnS QDs

The effect of pH in a range between 1 and 13 on the FL of CD-QDs is studied. As can be seen from Figure S6, the FL intensity of n-CD-QDs in the interval 6.0–9.0 is considerably stable. The luminescence emission obviously decreases in a pH medium below 6. It is clear that at low pH, the ZnS shell is being dissolved and creating surface defects. As pH is increased from 10 to 13, the FL intensity is increased quickly, because CD can be ionized at high pH, [3] coulomb repulsion between the modified nanocrystals with the same charges prevent aggregation in water.

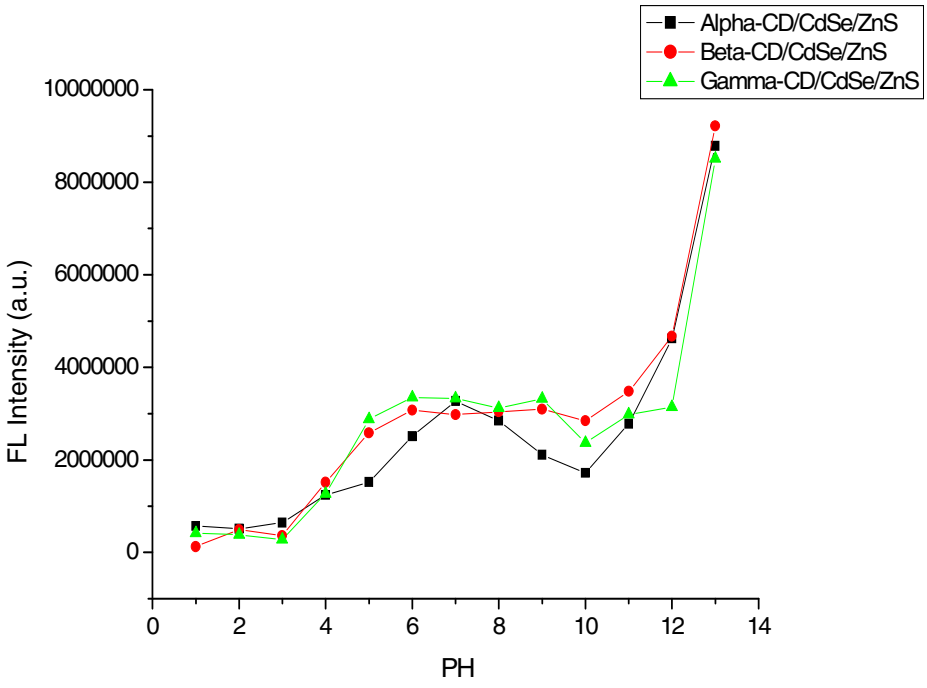
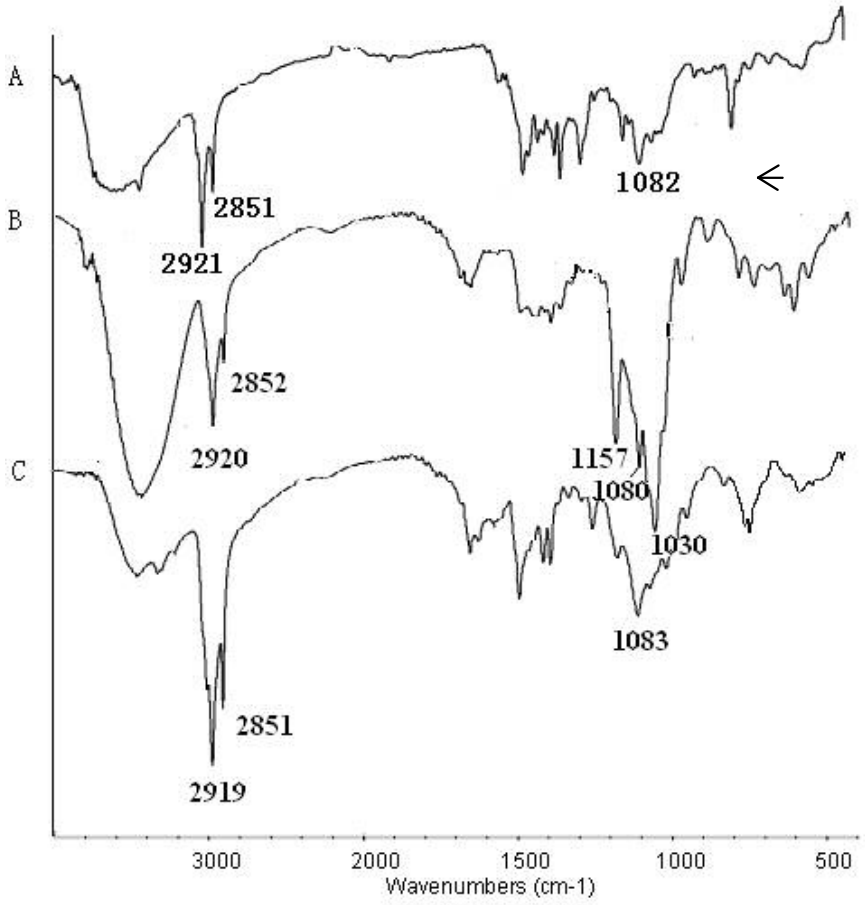


Figure S6. Effect of pH on luminescence response of the CD coated CdSe/ZnS QDs.

G)


A
B
C
2851
2921
1082
2852
2920
1157
1080
1030
1083
2851
2919
3000
2000
1500
1000
500
Wavenumbers (cm-1)

```
ERROR: invalidaccess
OFFENDING COMMAND: --filter--

STACK:

/LZWDecode
-filestream-
[64 0 0 -180 0 180 ]
true
180
64
-savelevel-
```