

Highly Selective and Sensitive Colorimetric Probes for Yb³⁺ Ions Based on Supramolecular Aggregates Assembled from β -Cyclodextrin/4, 4'-Dipyridine Inclusion Complex Modified Silver Nanoparticles

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Supplementary Information

Experimental Section

All chemicals and solvents unless otherwise specified were analytical grade, and triply distilled water was used throughout. AgNO₃ and KBH₄ were purchase from Shanghai Chemical Factory, China. RE ions (La(NO₃)₃, Ce(NO₃)₃, Pr(NO₃)₃, Nd(NO₃)₃, Sm(NO₃)₃, Eu(NO₃)₃ and Yb(NO₃)₃) were obtained from Beijing Chemical Corp. (Beijing, China). All REs standards were dissolved in triply distilled water and stored at room temperature.

UV-vis absorption spectra were acquired on a S-3100 UV-vis spectrometer. IR spectra were measured with a NEXUS FT-IR spectrometer (Thermo Nicolet Co.). Transmission electron micrograph (TEM) was recorded by a JEOL-JEM 2010 electron microscope operating at 200 kV. The samples are dropped onto a small copper mesh and left at room temperature so that the samples precipitate homogeneously on the carbon films among the tiny pores of the copper mesh.

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1. Preparation of β -cyclodextrin/4, 4'-dipyridine complexe (β -CD/4-DPD)

A mixture of β -cyclodextrin (1 mmol) and 4,4'-dipyridine (4-DPD, 1 mmol) was allowed to react in aqueous solution (60 mL) with stirring at 30 °C for 5 h. The precipitate formed was filtrated to give a white powder. The crude product was then dissolved in hot water to make a saturated solution, which was cooled to room temperature. After removing the precipitates by filtration, a small amount of water was added to the filtrate. The resultant solution was kept at room temperature for a week and the colorless crystal of β -CD/4-DPD complexe was formed. The analysis dates were consistent with those in literature.^[12b] FTIR (KBr): $\nu = 3384, 2926, 1597, 1534, 1411, 1369, 1336, 1299, 1246, 1157, 1081, 1030, 943, 850, 805, 756, 611, 578, 528 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, D_2O , tetramethylsilane (TMS)): $\delta = 3.37\text{--}3.69$ (m, 42H), 4.88–4.90 (d, 7H), 7.53–7.55 (d, 4H), 8.52– 8.54 ppm (d, 4H); elemental analysis calcd for $\text{C}_{52}\text{H}_{78}\text{O}_{35}\text{N}_2 \cdot 7\text{H}_2\text{O}$: C 44.07, H 6.54; N 1.98%; found: C 43.74, H 6.03, N 2.37%.

2. Preparation of β -CD/4-DPD-modifided Ag NPs

Ag nanoparticles were prepared by borohydride reduction of Ag (I). Briefly, 9 mg of KBH_4 was added to 100 mL of 10^{-4} M AgNO_3 solution with stirring for 5 min to form metallic silver nuclei. And then, 1 mL of 10^{-3} M β -CD/4-DPD aqueous solution was added. The mixture was continually stirred for 5 h at room temperature. The bright yellow silver colloids were finally obtained. The β -CD/4-PDP-Ag NPs were used in the following experiments without further purification. The finally concentration of β -CD/4-DPD-Ag NPs was 1.6 nM. According to the elemental analysis and TG-DTA results, the proportion of β -CD/4-DPD complexes in β -CD/4-DPD-Ag NPs: ca. 46% by elemental

analysis, ca. 42% by TG-DTA. The average content of the complex is 44%.

3. Preparation of 4-DPD-modified Ag NPs

9 mg of KBH_4 was added to 100 mL of 10^{-4} M AgNO_3 solution with stirring for 5 min to form metallic silver nuclei. And then, 1 mL of 10^{-3} M 4-DPD aqueous solution was added. The mixture was continually stirred for 5 h at room temperature. The bright yellow silver colloids were finally obtained. The 4-DPD-modified Ag NPs were used in the following experiments without further purification.

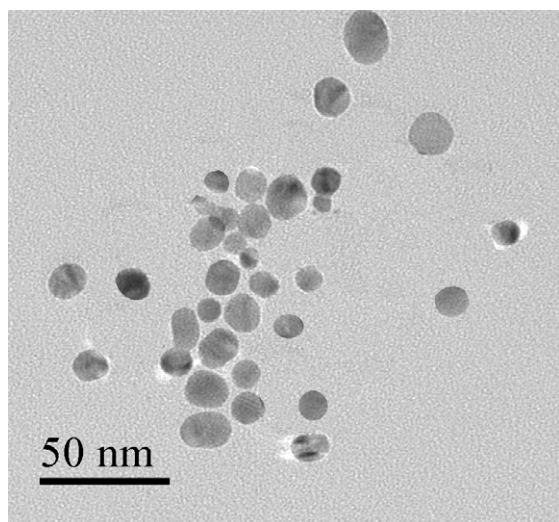


Figure S1. TEM images of 4-DPD-Ag NPs.

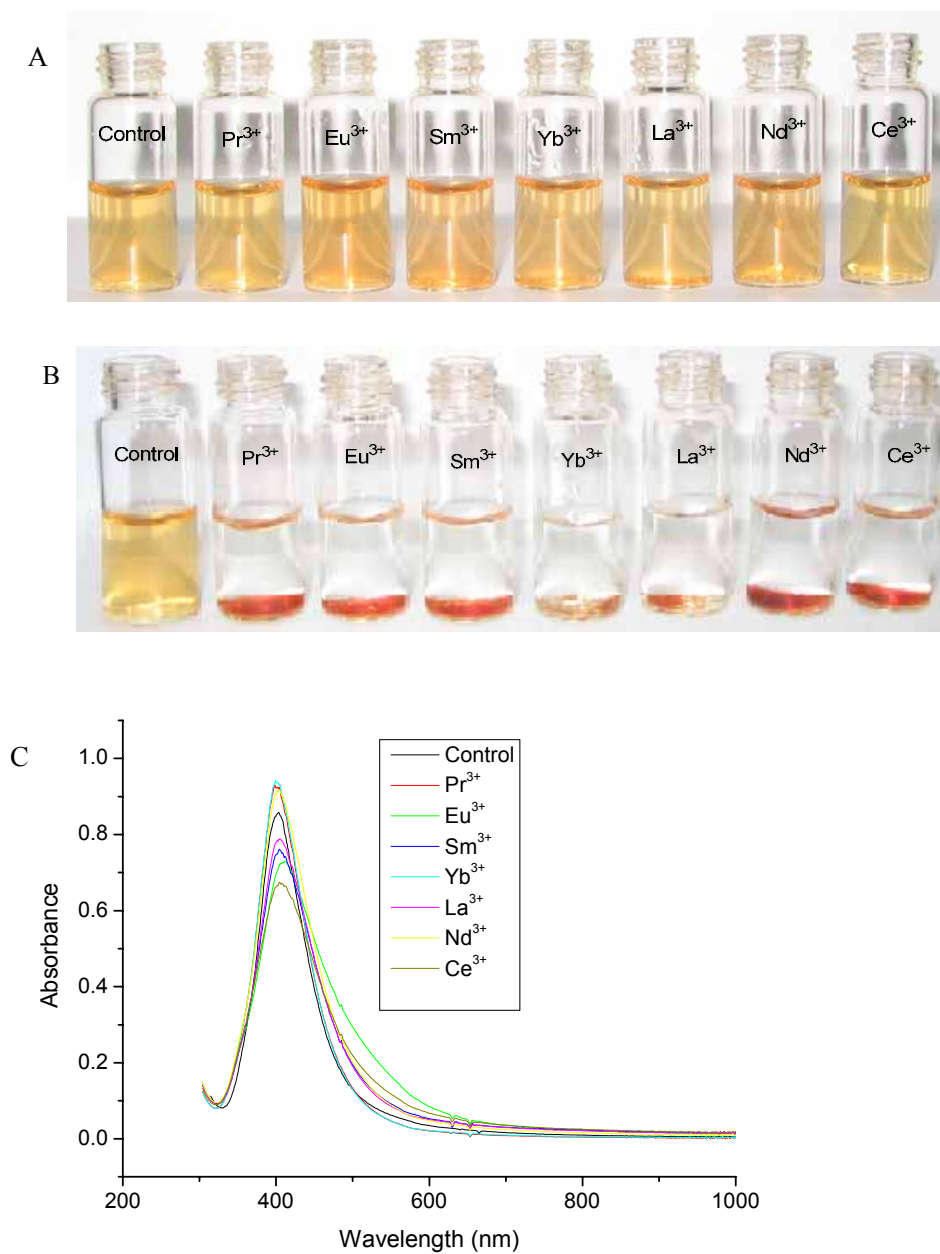


Figure S2. Photographic images and absorption spectra of 4-DPD-modified Ag NPs solution in the presence of 0.2 mM different RE ions. RE ions were added to Ag NPs samples (A) five minutes and (B) ten minutes after monitoring was started. (C) The corresponding absorption spectra of (A).

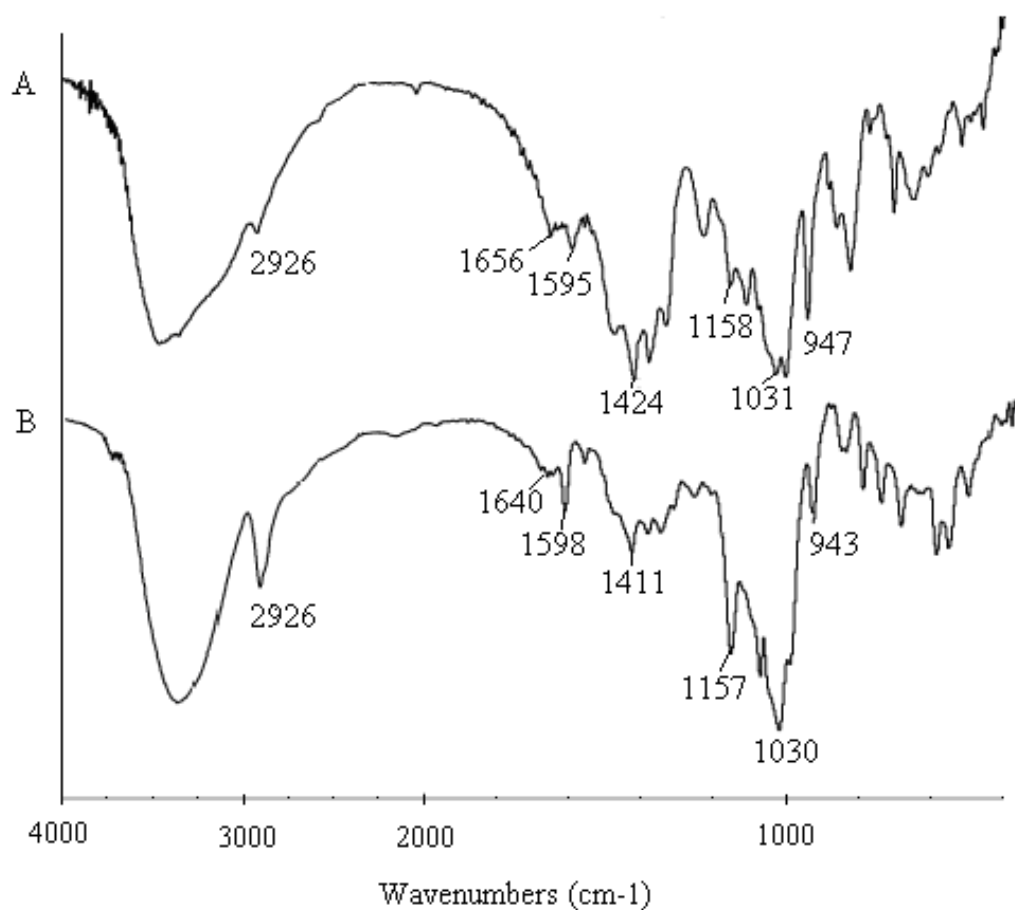


Figure S3. FT-IR spectra of (a) β -CD/4-DPD-Ag NPs and (B) β -CD/4-DPD samples.

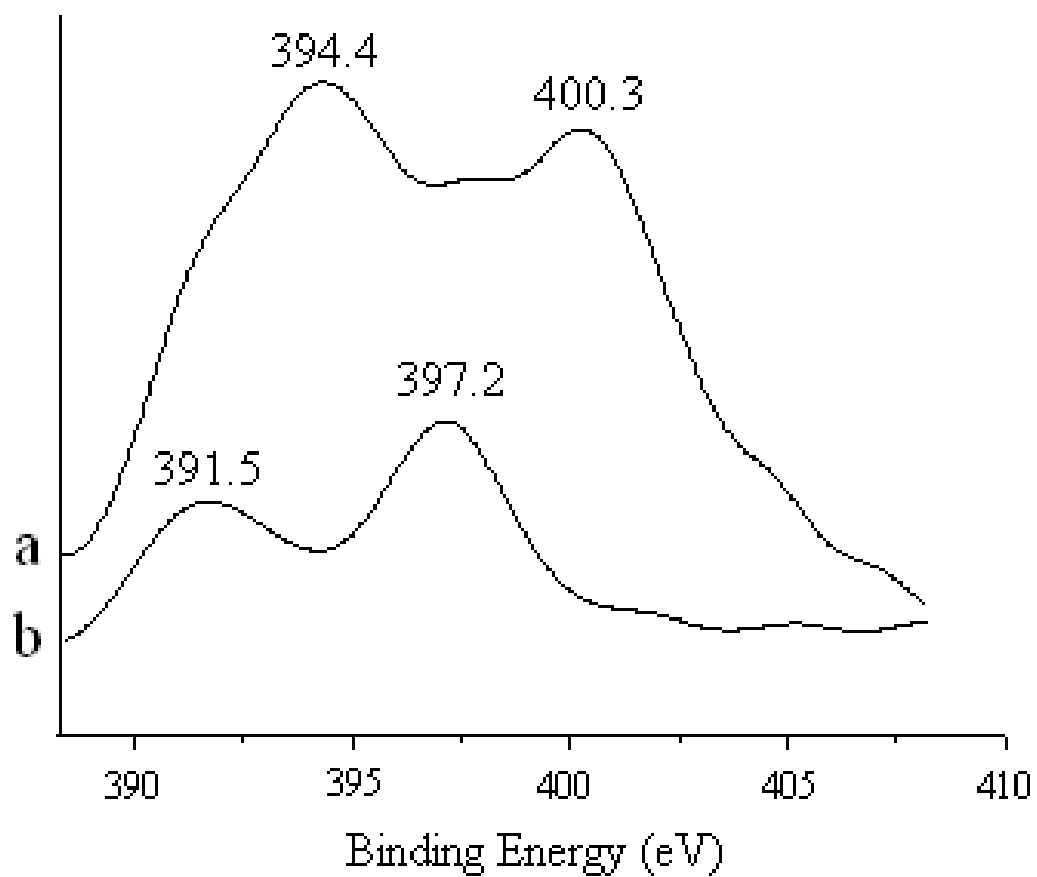


Figure S4. XPS spectra of N1s of (a) β -CD/4-DPD-Ag NPs and (b) β -CD/4-DPD.

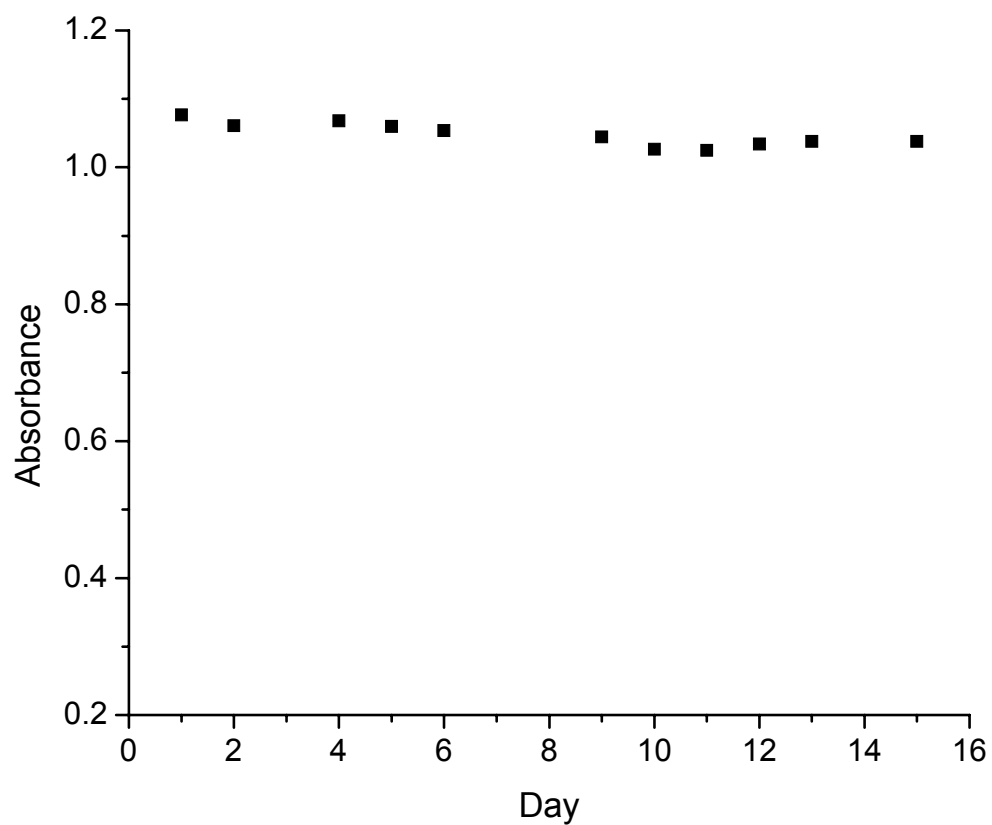


Figure S5. Absorption intensities of β -CD/4-DPD-Ag NPs at 401 nm which recorded at different time. The stability of β -CD/4-DPD-Ag NPs in water is estimated by UV-vis measurements. There was no obvious change in the shape, position and symmetry of the absorption peak after 15 days storage at room temperature.

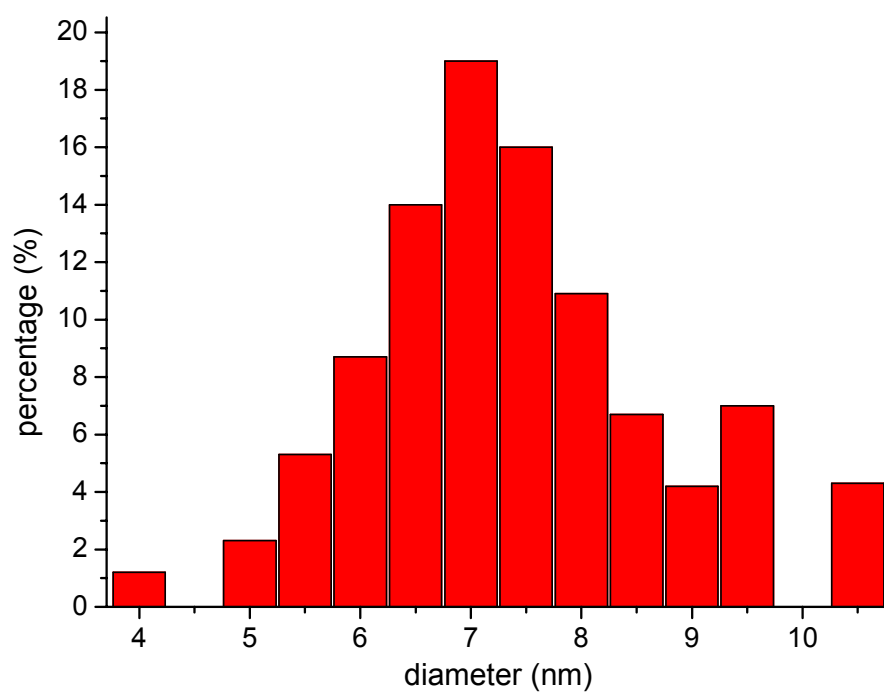


Figure S6. The size distribution of β -CD/4-DPD-Ag NPs. 300 particles are measured to get the size distribution.

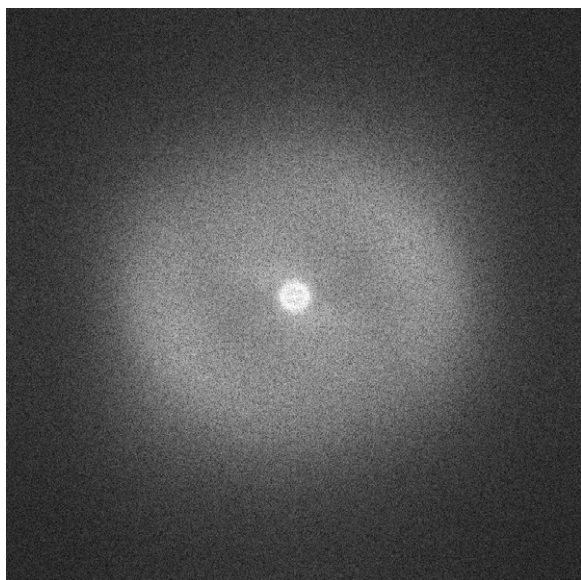


Figure S7. The corresponding electron diffraction pattern for shaded areas in Fig. 2C and D.

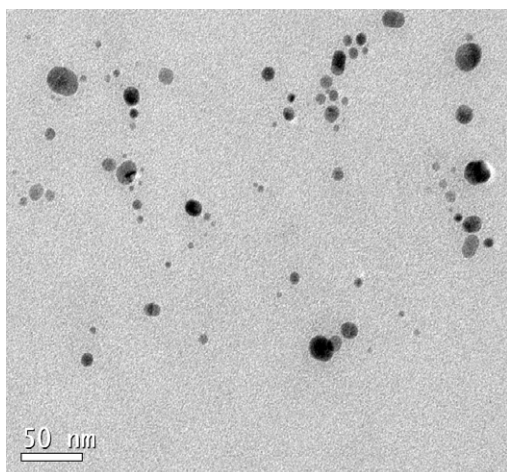


Figure S8. Typical TEM image of β -CD/4-DPD-Ag NPs in the presence of 0.2 mM La^{3+} ions.

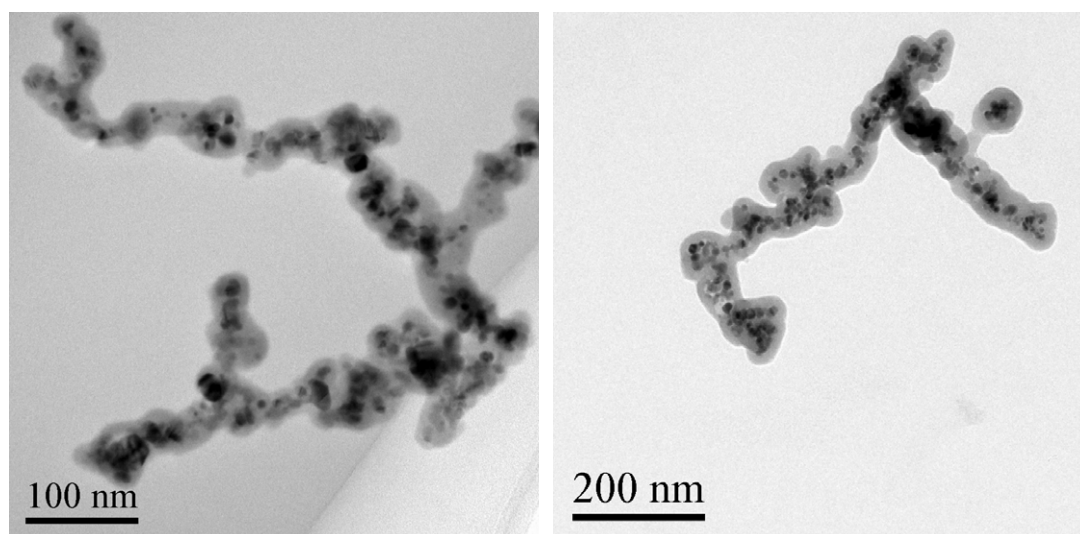


Figure S9. Typical TEM images of β -CD/4-DPD-Ag NPs in the presence of 0.2 mM Yb^{3+} ions.