## **Supporting Information**

## Catalytic reduction of 4-nitrophenol with gold nanoparticles stabilized by large-ring cyclodextrins

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Figure S1. Photograph of Au\_LR-CD NP after reduction step in alkaline aqueous solution.



**Figure S2.** XPS spectra of Au NP stabilized by (a)  $\alpha$ -CD, (b)  $\beta$ -CD, (c)  $\gamma$ -CD, and (d) LR-CD.



**Figure S3.** Liquid UV-Vis spectra of (a)  $Au_{\alpha}$ -CD NP, (b)  $Au_{\beta}$ -CD NP, (c)  $Au_{\gamma}$ -CD NP, (d)  $Au_{LR}$ -CD NP and (e) superposition of all of the UV-Vis spectra.



Figure S4. Successive UV-Vis spectra of Au\_LR-CD NP at different time from 1h to 4h.



**Figure S5.** Size distribution in volume of (a) Au\_ $\alpha$ -CD NP, (b) Au\_ $\beta$ -CD NP, (c) Au\_ $\gamma$ -CD NP and (d) Au\_LR-CD NP obtained by Dynamic Light Scattering.



Figure S6. Scheme of the catalytic reduction of 4-nitrophenol into 4-aminophenol by Au NP in the presence of an excess of  $NaBH_4$ .



**Figure S7.** UV-Vis absorption spectra during the reaction of 4-nitrophenol with  $NaBH_4$  without any Au NP.



**Figure S8.** UV-Vis absorption spectra during the reduction of 4-nitrophenol with NaBH<sub>4</sub> by (a) Au\_ $\alpha$ -CD NP, (b) Au\_ $\beta$ -CD NP and (c) Au\_ $\gamma$ -CD NP.



Figure S9. Determination of the  $k_{app}$  values relating to 4-nitrophenol reduction catalyzed by Au\_ $\alpha$ -CD NP, Au\_ $\beta$ -CD NP, Au\_ $\gamma$ -CD NP and Au\_LR-CD NP



**Figure S10.** T-ROESY spectrum of 4-nitrophenol + LR-CD in  $D_2O$  considering [4-nitrophenol] = 6 mM, [LR-CD] = 6 mM and [NaBH<sub>4</sub>] = 0.26 M at 20 °C.