

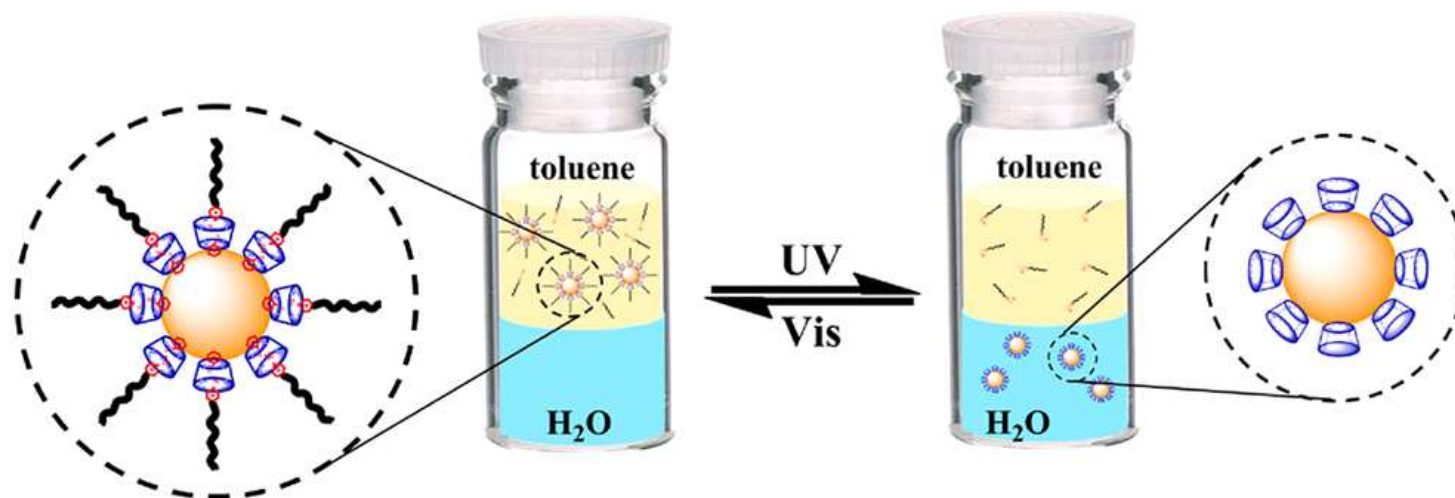
# Reversible Phase Transfer of Nanoparticles Based on Photoswitchable Host-Guest Chemistry

Lu Peng, Mingxu You, CuichenWu, Da Han, Ismail Oc-soy, Tao Chen, Zhuo Chen, Weihong Tan

Department of Chemistry and Department of Physiology and Functional Genomics, Center for Research at Bio/nano Interface, Shands Cancer Center, University of Florida, Gainesville, Florida 32611-7200, United States.

Molecular Sciences and Biomedicine Laboratory, State Key Laboratory for Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering and College of Biology, Collaborative Innovation Center for Chemistry and Molecular Medicine, Hunan University, Changsha, Hunan, 410082 China.

*ACS Nano*, Article ASAP



Manju C.K.  
15.03.14

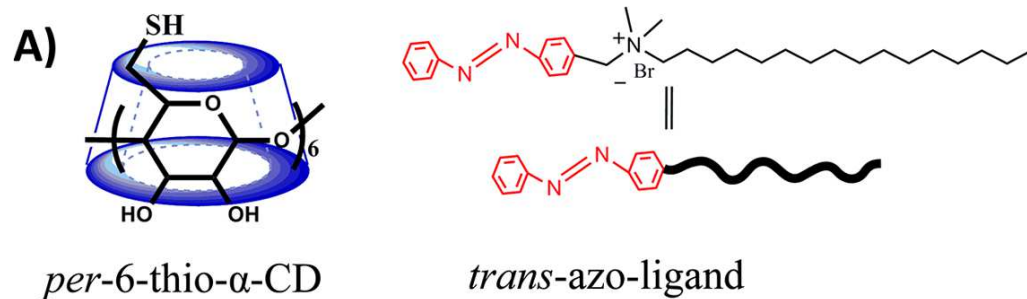
## Introduction

- Because of their unique optical, electrical, and chemical properties, nanoparticles (NPs) have attracted considerable interest in diverse research areas, including catalysis, sensing, electronics, biomedicine, and optics.
- The rapid growth in applications of NPs has been accompanied by the development of synthetic methods resulting in NPs with well defined properties, such as shape, size, composition and surface modification.
- However, many of these synthetic strategies are realized with the aid of specific hydrophobic or hydrophilic ligands in their respective organic or aqueous solvents, while synthesized NPs possess distinct solubility in media with different polarities
- Therefore, additional steps for phase transfer are usually required, especially between water and organic solvents, for specific applications.

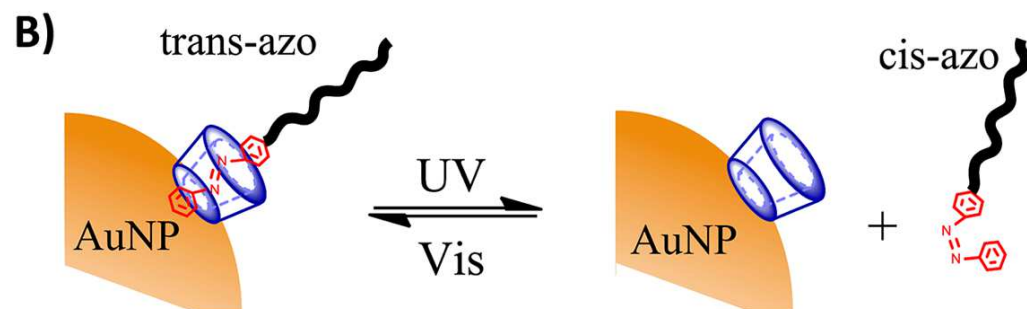
- Reversible phase transfer of NPs between two immiscible phases still remains challenging and complicated.
- Moreover, none of the reported reversible phase transfer strategies has been used for practical applications.
- Smart materials based on photoresponsive systems have emerged as a dynamic research area, where the properties of matter can be reversibly modulated with light.

In this paper

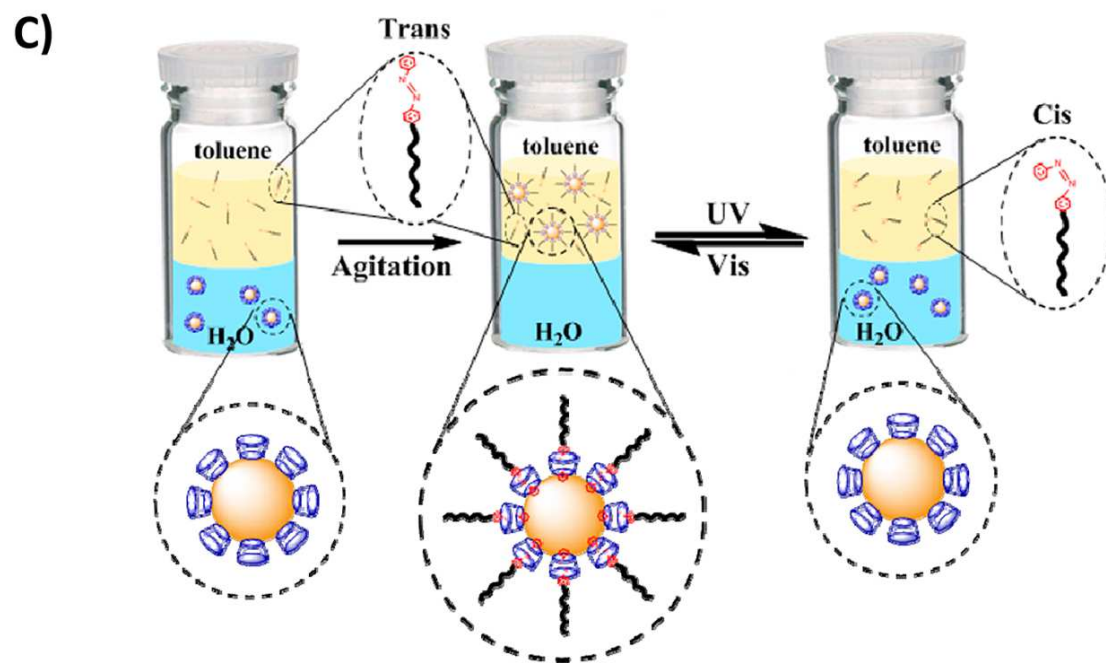
- The photoswitchable host-guest interaction between  $\alpha$ -CD and azobenzene is used as a trigger to induce the reversible phase transfer of the AuNPs between water and toluene.
- Furthermore, the phase transfer scheme was applied for the quenching of a reaction catalyzed by gold nanoparticles, as well as the recovery and recycling of the gold nanoparticles.



(A) Structures of host per-6-thio- $\alpha$ -CD and guest azobenzene-containing ligand (azo-ligand).



(B) Photoreversible inclusion of azo-ligand in  $\alpha$ -CD-coated AuNPs.



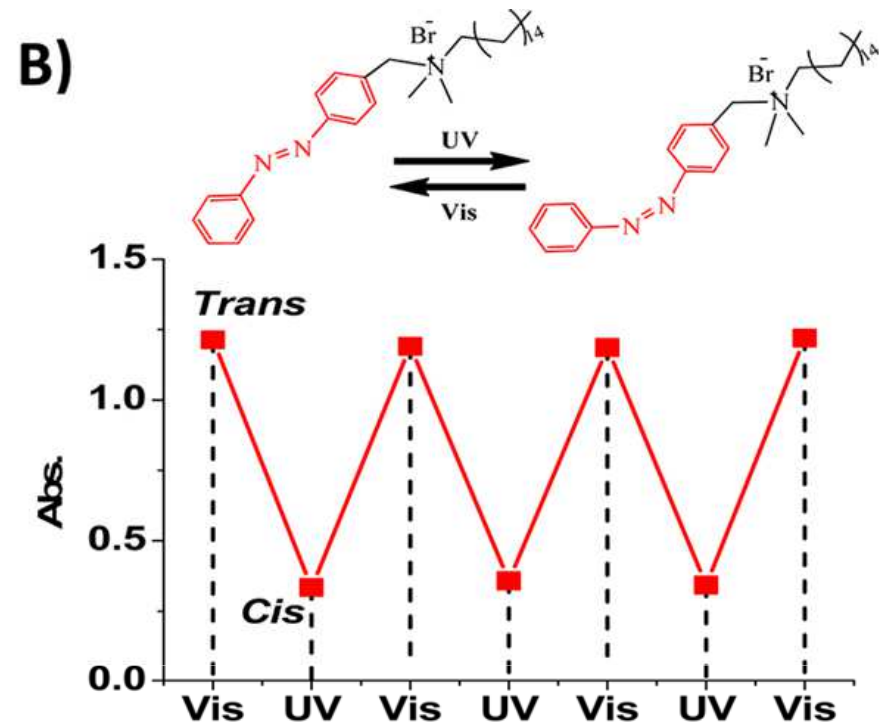
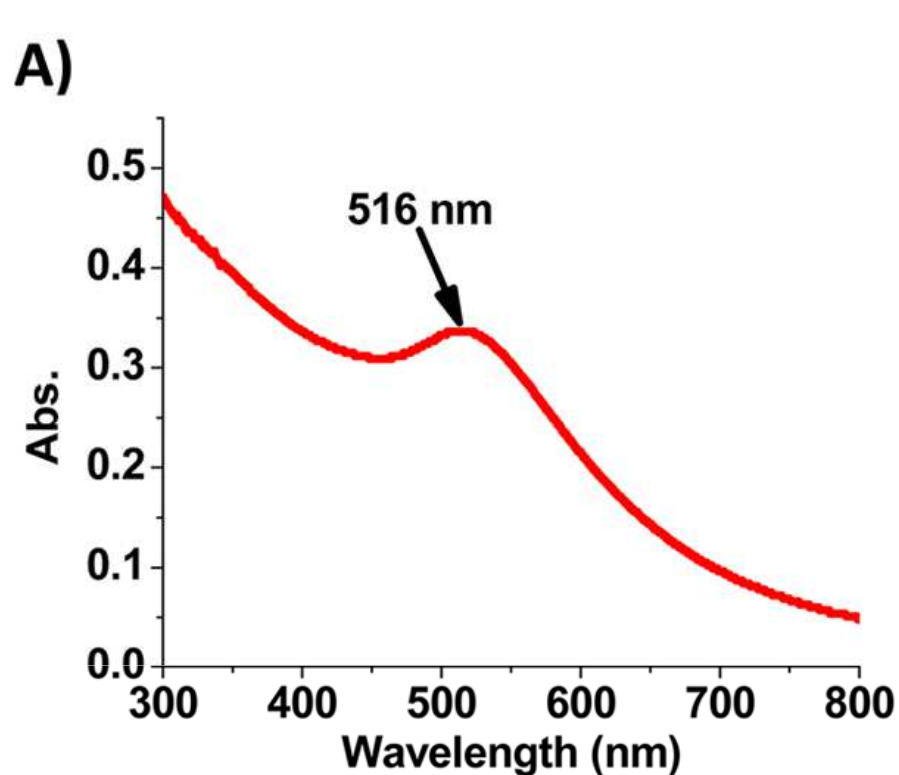
(C) Light-responsive phase transfer of  $\alpha$ -CD-capped AuNPs by azo-ligands between the water and toluene phases.

- This photoresponsive supramolecular system consists of azobenzene containing surfactant (azo-ligand) and a thiolated  $\alpha$ -CD.

- Innovation of this approach is the light induced modification of azo-ligand.

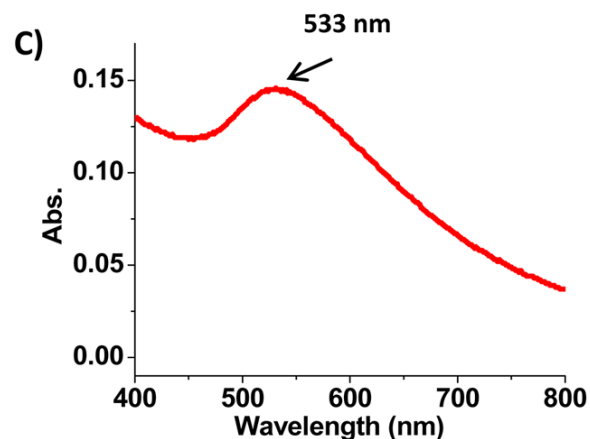
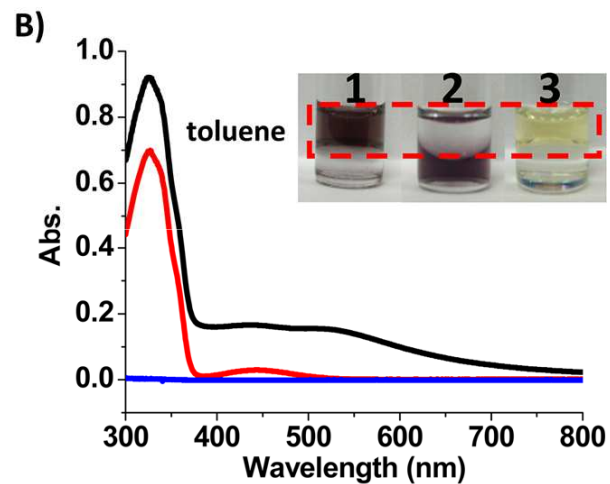
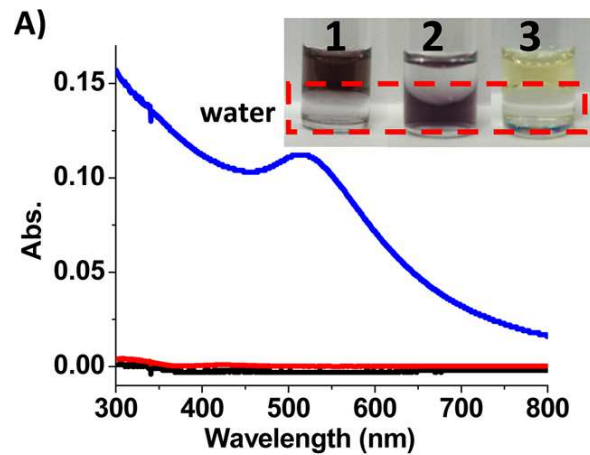
- Reversible trans- to- cis isomerization.

- Only trans isomer can form inclusion complex.



(A) Absorption spectrum of thiolated  $\alpha$ -CD-coated AuNPs (3.6 nm) in water. (B) Reversible photoisomerization of azo-ligand (absorbance at 326 nm) in toluene upon alternating irradiation with UV and visible light.

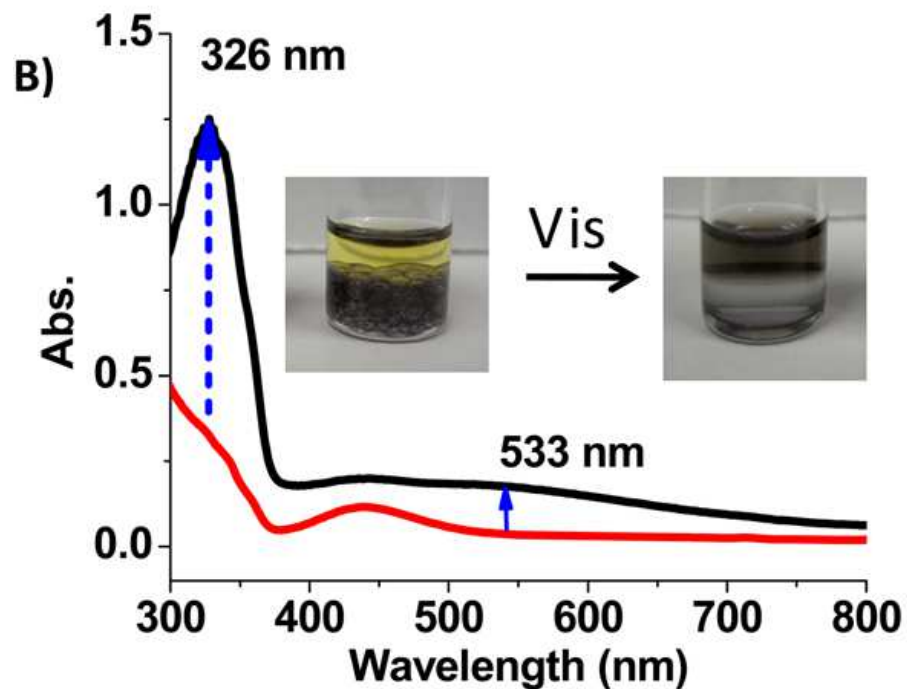
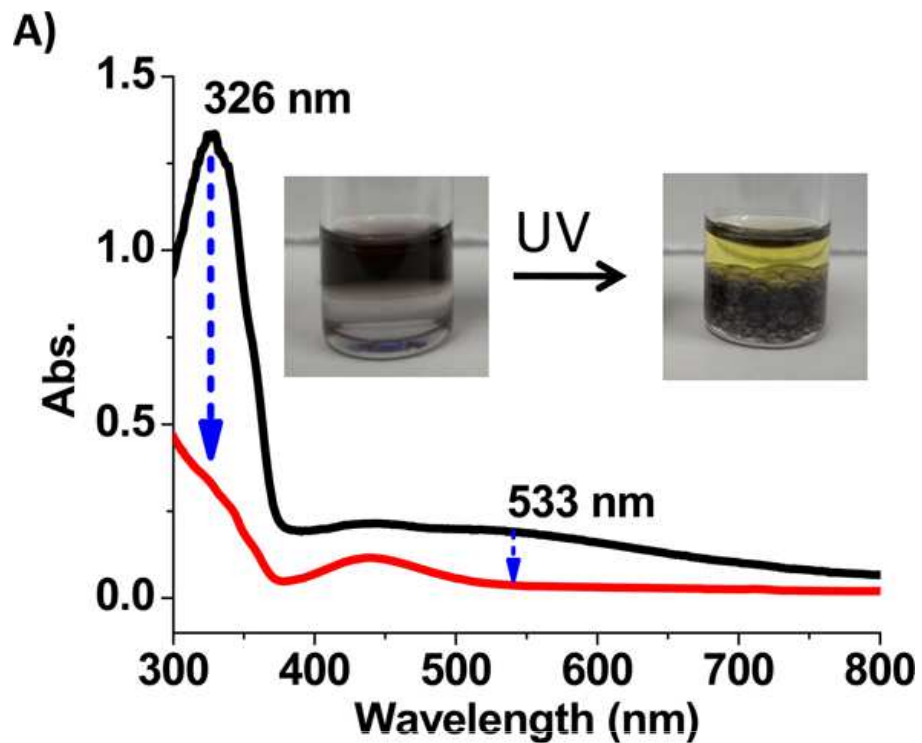
- The azo-ligand synthesized in the trans state show a characteristic peak at 326 nm.
- Upon UV light irradiation at 365 nm, the intensity of this peak decreases dramatically, indicating photoisomerization of the azo-ligand from the trans to the cis state.
- When visible light is applied afterward, the peak intensity at 326 nm recovers as the azo-ligand undergoes cis-to-trans isomerization



Phase transfer of AuNPs from water to toluene phase by trans-azo-ligands (vial 1). Vial 2 has no azo-ligands in the toluene phase, and vial 3 has no AuNPs in the water phase.

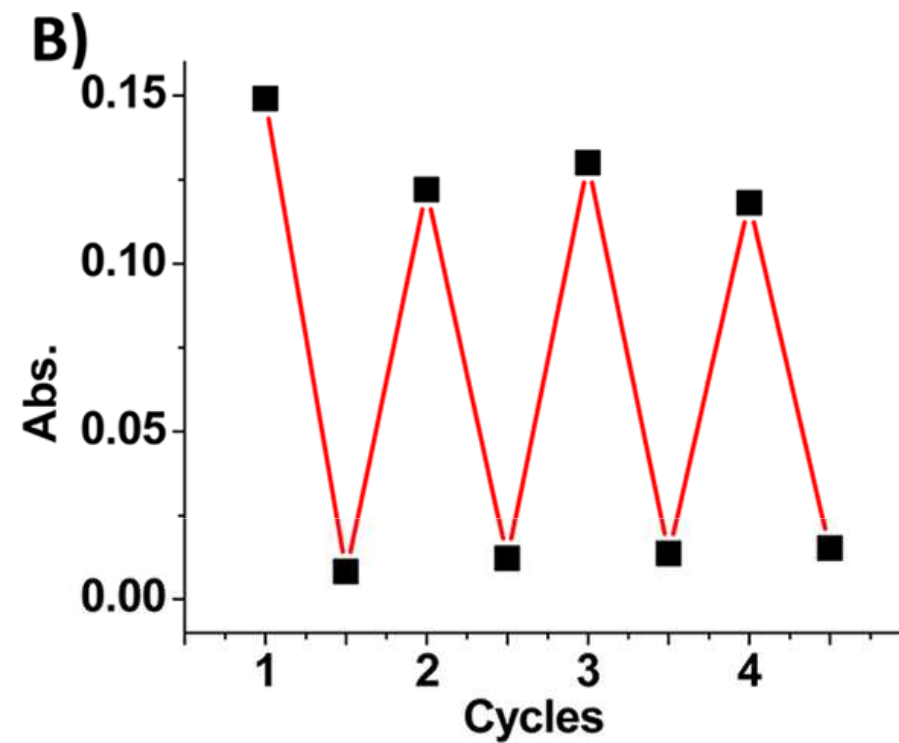
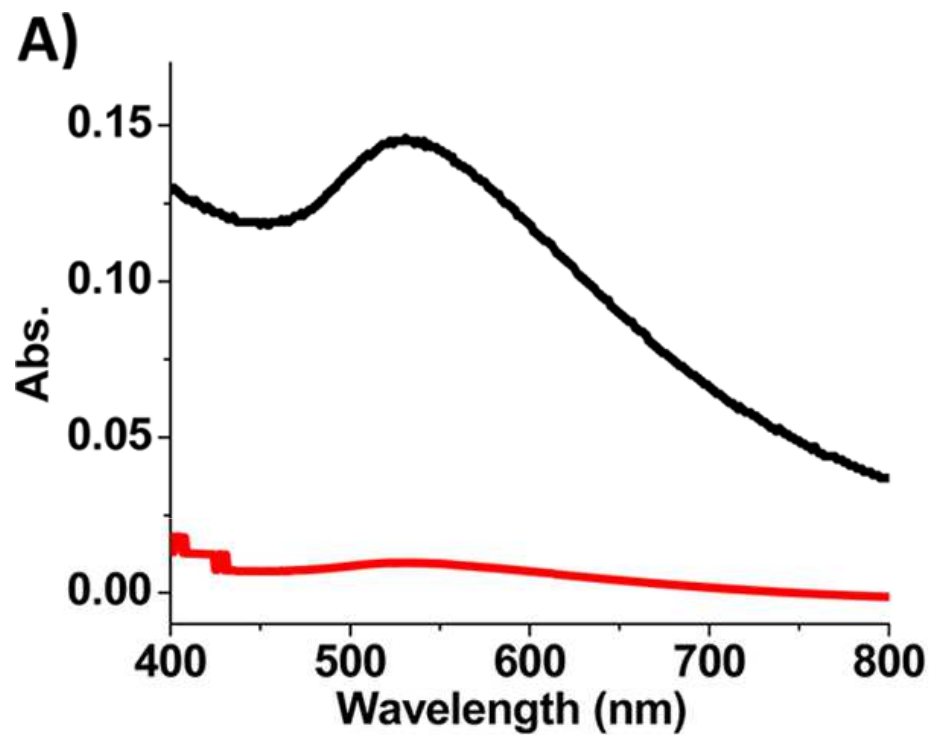
The absorption spectra show absorbance of (A) water phase and (B) toluene phase in vial 1 (black), vial 2 (blue) and vial 3 (red). (C) Absorption spectrum of AuNPs in the toluene phase is achieved by subtraction of the red line from the black line in panel B.

- Concentration of nanoparticles transferred increase with increase in initial azo-ligand concentration



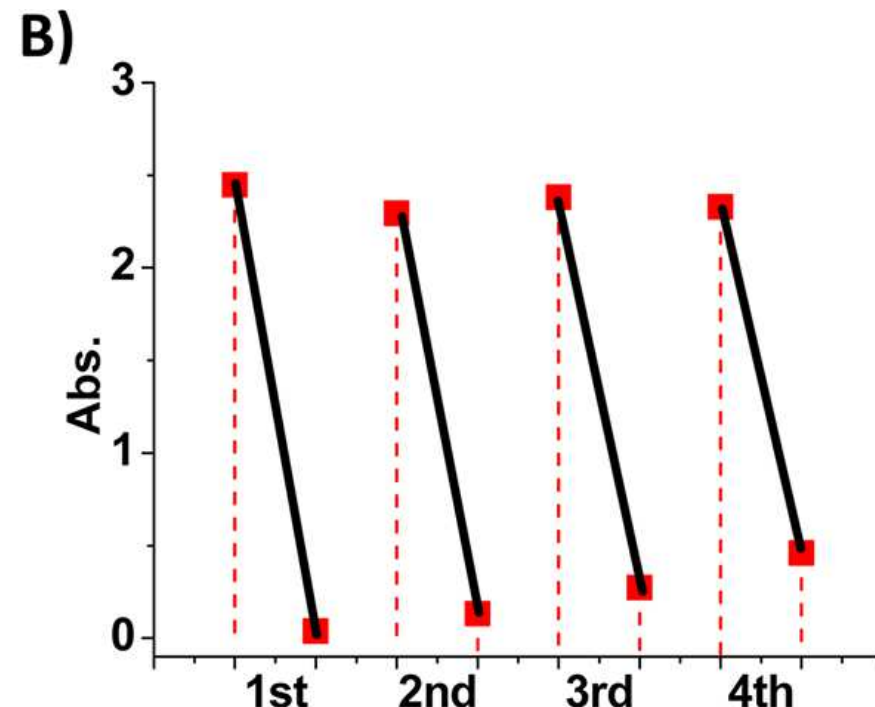
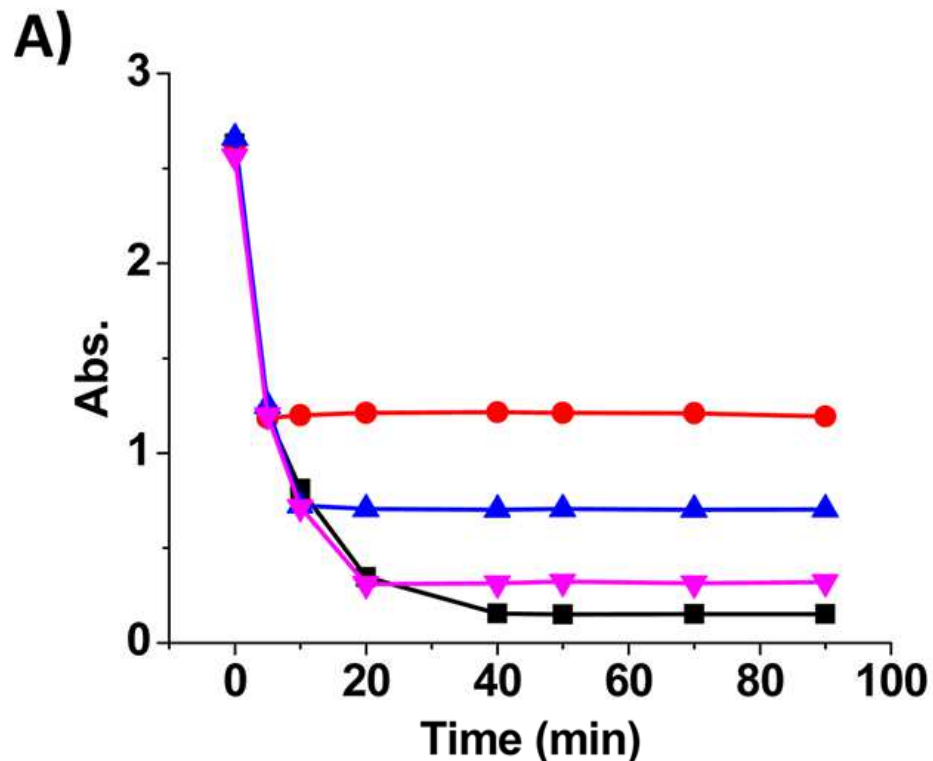
Absorption spectra of toluene phase during the light-responsive phase transfer of AuNPs. (A) Phase transfer of  $\alpha$ -CD-coated AuNPs from toluene to water phase by irradiation with UV light. (B) Phase transfer of  $\alpha$ -CD-coated AuNPs from water to toluene phase by irradiation with visible light.





(A) Absorption spectra of toluene phase upon irradiation with UV (red) and visible (black) light during reversible phase transfer. (B) Reversible phase transfer of AuNPs (absorbance at 533 nm in toluene phase) between water and toluene phase.





(A) Absorbance (400 nm in water) during the reduction of 4-NP (0.3 mM) in the presence of NaBH<sub>4</sub> (15 mM) and  $\alpha$ -CD-capped AuNPs (6.7  $\mu$ g/mL): reaction not quenched (black) and quenched by phase transfer of AuNPs from the addition of toluene containing azo-ligands at 5 min (red), 10 min (blue), and 20 min (pink). (B) Multicycle reduction of 4-NP (absorbance at 400 nm) catalyzed by AuNPs recovered and recycled through photoreversible phase transfer.

- It has been reported that CD-capped-AuNPs can catalyze the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in the presence of sodium borohydride (NaBH<sub>4</sub>) in aqueous solution.

## Conclusions

- Photoreversible phase transfer of AuNPs by photoswitchable host-guest interaction between  $\alpha$ -CD and azobenzene have been demonstrated.
- The basic principle relies on the reversible surface modification of the  $\alpha$ -CD-capped hydrophilic AuNPs with an azobenzene-containing surfactant ligand.
- Reversible phase transfer can be performed for multiple cycles as monitored by absorption spectra.
- By the alternating irradiation of UV and visible light, the same batch of  $\alpha$ -CD-capped hydrophilic AuNPs can be recycled to catalyze multiple rounds of 4-NP reduction.

- Using the phase transfer strategy based on the host-guest interaction, it was able to quench the catalytic reaction by removal of the catalytic AuNPs.
- The method of reversible phase transfer based on photoswitchable molecular recognition could bring more insight to nanoparticle surface engineering, thus improving and augmenting applications in different research areas.