

## Endowing Light-Inert Aqueous Surfactant Two-Phase System with Photo Responsiveness by Introducing a Trojan Horse

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8 **with Photo Responsiveness by Introducing a Trojan Horse**  
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42 **KEYWORDS:** Photo-Responsive, Aqueous surfactant two-phase system,  
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45 Azobenzene, Host-Guest Interaction, Cyclodextrin, Trojan horse  
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## ABSTRACT

The ability to modulate the phase behavior of aqueous surfactant two-phase (ASTP) system reversibly with light is of great importance in both fundamental and applied science. Thus far, most of the light-responsive ASTP systems are based on covalent-modification of the component molecules. In this article, we for the first time achieve photo-responsiveness in a light-inert ASTP system by physically introducing a photo-trigger with the aid of an Trojan Horse. The ATPS system formed with sodium laurate (SL) and dodecyl tributyl ammonium (DBAB) doesn't show light responsiveness by physically mixing a light responsive azobenzene compound, 2-(4-(phenyldiazenyl)phenoxy)acetate sodium (Azo). However, in the presence of the host-guest complex SL@ $\beta$ -CD formed with  $\beta$ -CD and sodium laurate (SL), the ASTP turns quickly into a homogenous suspension under visible light, which recovers to the original ASTP state again under 365 nm UV irradiation. Because the SL@ $\beta$ -CD complex exists harmonically with the ASTP, it can be viewed as a "Trojan horse" that becomes fatal only when the encapsulated SL is triggered to release. In the presence of the Trojan horse, the photo-responsiveness of the ASTP can be manipulated reversibly by alternatively exerting UV and visible light. Using this strategy, we are able to collect trace amount of oily components from water. The current strategy points out that it is possible to achieve light-responsiveness in light-inert systems with physical method, which may have profound impact both on the fundamental and

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## 17 **1. INTRODUCTION**

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23 Aqueous two-phase systems (ASTP) which consist of two immiscible aqueous  
24 phases have attracted great attention for their unique properties such as good  
25 biocompatibility, low interfacial tension<sup>1</sup> and their wide application in separation of  
26 various biomaterials<sup>2-3</sup>, carbon nanotubes<sup>4-6</sup> and small molecules<sup>7</sup>. More recently,  
27 ASTP was also used as template in material synthesis<sup>8</sup> and medium for cell printing  
28 <sup>9-10</sup>. It is expected that the application area can be further expanded and the existing  
29 properties can be further enhanced if stimuli responsiveness was introduced into the  
30 ASTP.  
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44 Among various stimuli responsive triggers (heat<sup>11</sup>, light<sup>12</sup>, magnetic field<sup>13</sup>, pH<sup>14</sup>,  
45 metal ion<sup>15</sup>, etc.), light has attracted considerable attention because it works rapidly,  
46 reversibly, and remotely, without generating any undesired substances. Moreover, the  
47 system can also be regulated more accurately at spatio-temporal scale through  
48 controlling the intensity, wavelength, waveform, spot size of the incident light.  
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50 However, there are few successful cases for light controlled ASTP. Generally, people  
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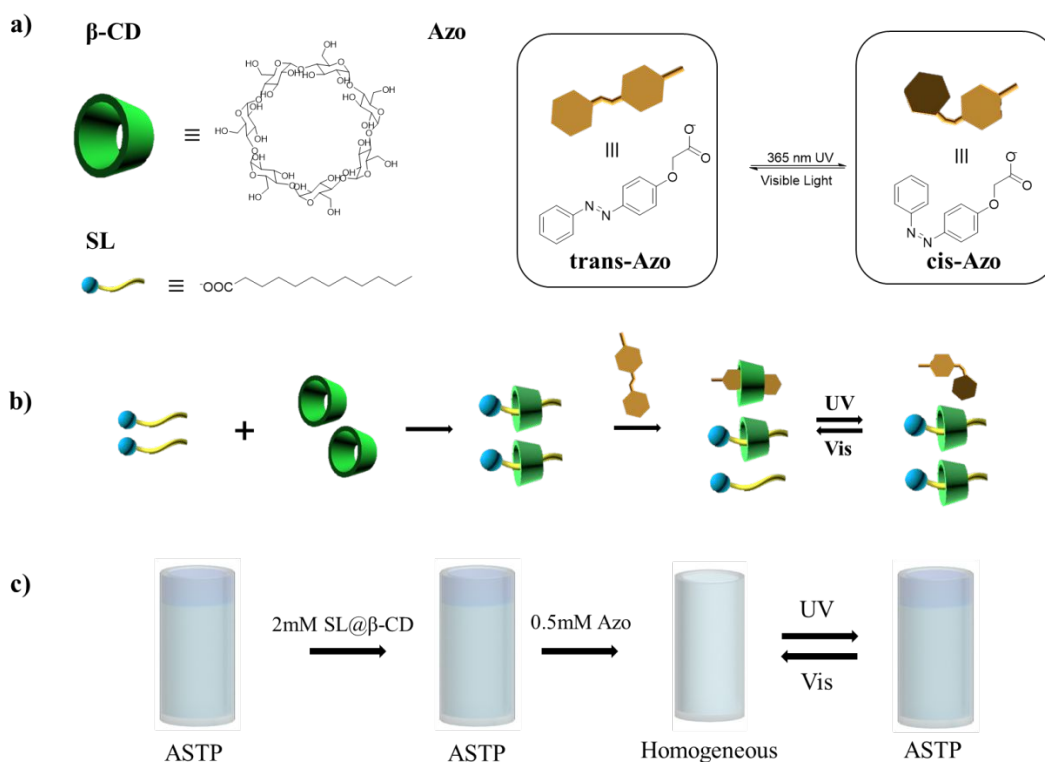
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4 fabricate a photo-responsive system by introducing a photo-responsive group  
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6 covalently into a polymer<sup>16-19</sup>, which requires tedious organic synthesis. For instance,  
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8 a reversible light-controlled ASTP had been achieved by introducing a light  
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10 responsive spiropyran group to the side chain of dextrin<sup>19</sup> or copolymerizing  
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12 chlorophyll into the main chain of a polymer through covalent bond<sup>20</sup>. However, the  
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14 ASTP formation process is often drastically affected with these approaches, because  
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16 ASTP is very sensitive to changes in molecular structures. For this reason, most of the  
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18 reported ASTP are light-inert<sup>21-22</sup>. It is still challenging to find a simple and general  
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20 method to introduce light-responsiveness into various light-inert ASTP.  
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28 In this work, we report a physical strategy to generate photo-responsiveness  
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30 physically in ASTP formed with a pair of cationic and anionic surfactants. It is  
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32 well-known that at molar ratios approaching to 1:1, some cationic and anionic  
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34 surfactants can form ASTP<sup>23</sup>. The ASTP is very sensitive to the molar ratio between  
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36 the cationic and anionic surfactants, and slight variation of the components will result  
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38 in transition from an ASTP to a single homogeneous aqueous phase<sup>24-26</sup>. This inspires  
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40 that if we are able to manipulate the composition of the ASTP system formed by the  
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42 mixture of cationic and anionic surfactants with photo, a photo-responsive ASTP can  
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44 be created.  
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51 To this goal, we introduced a “Trojan horse” composed of the host-guest complex  
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53 of a surfactant and  $\beta$ -CD into the ASTP system. CDs are well-known to form  
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55 host-guest complex with surfactants, where the alkyl chain of the surfactant is  
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57 sheltered in the cavity of CD via hydrophobic interaction<sup>27-29</sup>. However, the binding  
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4 constant between CD and a surfactant is not very large<sup>30</sup>, so that the guest surfactant  
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6 can be replaced by other guests with stronger binding ability. Azo compounds are a  
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8 family such stronger guests<sup>31</sup>. Azos may undergo *trans*-to-*cis* transition under UV  
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10 light, whereas a reverse transition occurs under visible light<sup>32</sup>. Only the *trans*-Azos  
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12 have stronger binding ability with CD, and the *cis* one do not bind to CD<sup>31</sup>. The  
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14 drastic binding affinity difference of *trans* and *cis* Azos with CD makes the Azos an  
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16 ideal photo trigger in a ASTP system with the assistance of Trojan horse.  
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22 In the following, we report that addition of Azos to the ASTP system without  
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24 Trojan horse does not lead to photo-responsive ASTP. However, the ASTP system  
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26 immediately gains light-responsiveness in the presence of a Trojan horse composed of  
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28 the host-guest complex of SL@CD (Scheme 1), which releases excess SL to shift the  
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30 equilibrium as a result of the stronger binding affinity of Azos with CD. We show that  
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32 using this strategy, we are able to collect oily components in water with light.  
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**Scheme 1.** Illustration of light-controlled aqueous surfactant two-phase systems. a) Molecular structures of  $\beta$ -CD, SL and Azo. b) Schematic illustrations of the construction a photo-responsive self-assembly using Azo@ $\beta$ -CD. c) Schematic illustrations of the photo-responsive ASTP system.

## 2. EXPERIMENTAL SECTION

### 2.1 Reagents and Materials

Dodecyltributylammonium bromide (DBAB) was prepared by recrystallizing five times from ethanol/acetone. Sodium laurate (SL) was purchased from Sigma-Aldrich.  $\beta$ -CD was purchased from Sinopharm Chemical Reagent Co., with a water content of 14%. D<sub>2</sub>O (99.9%) was purchased from Cambridge Isotope Laboratories. Inc.

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4 Aqueous solutions were prepared using Milli-Q water of 18 M $\Omega$ . Other reagents were  
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6 purchased from Beijing Chemical Reagents (Beijing, China). All reagents were used  
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8 as received, and the solvents were purified according to general procedures used  
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10 before. The synthesis of 2-(4-(phenyldiazenyl)phenoxy)actate sodium (Azo) was  
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12 published elsewhere<sup>33</sup>. All the molecular structures are shown in Figure S1.  
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## 16 17 **2.2 Sample preparations**

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19 All the concentrations mentioned in this article are final concentrations.

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21 Construction of Trojan photo-trigger: A Trojan photo-trigger was a mixture of  
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23 4mM SL and 4mM  $\beta$ -CD which forming SL@ $\beta$ -CD.  
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27 Construction of photo-responsive ASTP: 500 uL SL/DBAB (8 mM /8 mM) and  
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29 250 uL photo-trigger and 250 uL H<sub>2</sub>O were mix together forming a new ASTP with  
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31 final concentration of SL/DBAB/SL@ $\beta$ -CD/Azo=4 mM/4 mM/2 mM./ 0.5 mM.  
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35 The electrostatic control system: A mixture of SL/DBAB solution and Azo with  
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37 final concentration of SL/DBAB/Azo=4 mM/ 4 mM/ 0.5 mM .  
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41 All solutions were then thermostatically incubated at 25°C for 48h to allow the  
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43 formation of stable aggregates. The pH of SL, DBAB,  $\beta$ -CD and Azo mixed system  
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45 was fixed to 9.2 (10 mM Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>•10H<sub>2</sub>O) to control the hydrolysis of SL and Azo.  
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47 The structural formulas of all compounds are given in Figure S1. The UV light was  
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49 generated using a model FC-100/F long-wave UV (365 nm, 230V, 50Hz, and 0.9 A).  
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51 The duration of irradiation was 4h.  
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55 **Transmission Electron Microscopy (TEM).** Samples for TEM were prepared by  
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57 directly dipping an ultrathin carbon-coated copper grid into the sample, which was  
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4 then allowed to dry in ambient air at room temperature (RT). The samples were  
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6 observed by Jeol JEM 100CX, 80 kV.  
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9 **UV-vis spectrum.** UV-vis measurements were carried out on a  
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11 computer-manipulated spectrometer (TU-1810 UV-vis). All spectral measurements  
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13 were recorded at RT. The samples were exposed to UV light for 4h.  
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17 **Dynamic Light Scattering (DLS).** A commercialized spectrometer (Brookhaven  
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19 Instruments Corporation, Holtsville, NY) equipped with a 100 mW solid-state laser  
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21 (GXC-III, CNI, Changchun, China) operating at 532 nm was used to conduct dynamic  
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23 light scattering (DLS) experiments. Photon correlation measurements in self-beating  
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25 mode were carried out at multiple scattering angles using a BI-Turbo Co digital  
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27 correlator. The temperature was held at RT.  
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33 **Zeta-Potential Measurement.** Zeta-Potentials were measured using a  
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35 temperature-controlled zeta sizer 2000 (Malvern Instruments Ltd.).  
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39 **<sup>1</sup>H Nuclear Magnetic Resonance (<sup>1</sup>H-NMR).** <sup>1</sup>H-NMR experiments were performed  
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41 on a Bruker ARX 500 MHz spectrometer with D<sub>2</sub>O as the solvent.  
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### 46 **3. RESULTS AND DISCUSSION**

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48 The ASTP is constructed in the aqueous mixed system of SL and DBAB at  
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50 equimolar condition. The phase diagram suggests that the ASTP phases exist in a  
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52 narrow range with SL/DBAB ratio close to 1:1 at various concentrations (Figure 1).  
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54 In the following work, the ASTP with composition of 4 mM SL/4 mM DBAB was  
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56 used for study. Initially, a turbid solution is formed upon mixing the two solutions  
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(Table S1). Stable ASTP is formed after equilibrating for 24 hours (Figure 2a) at 25 °C. TEM results reveal the presence of large vesicles with an average radius of 3  $\mu\text{m}$  in the upper phase (Figure 2d), whereas smaller vesicles about 300 nm are observed in the lower phase (Figure 2e), which is consistent with the result of DLS (Figure S2). This ASTP system is light inert, even in the presence of physically introduced photo active component Azo. Figure 2 shows that addition of Azo doesn't affect the ASTP, regardless under visible (Figure 2b) or UV (Figure 2c) light, although UV light has triggered *trans* to *cis* transition of Azo (Figure S3). This means both the *trans* and the *cis* Azo have very weak interaction with SL and DBAB.

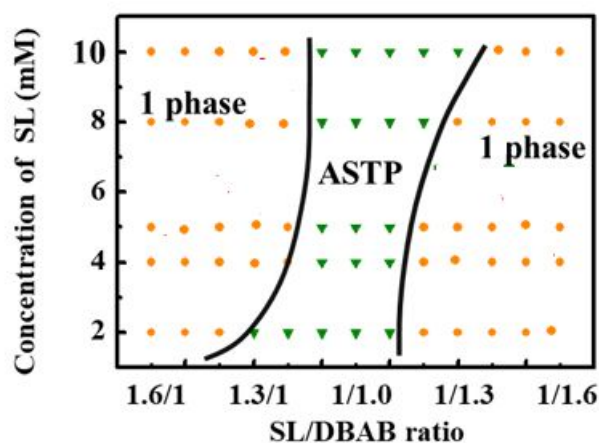
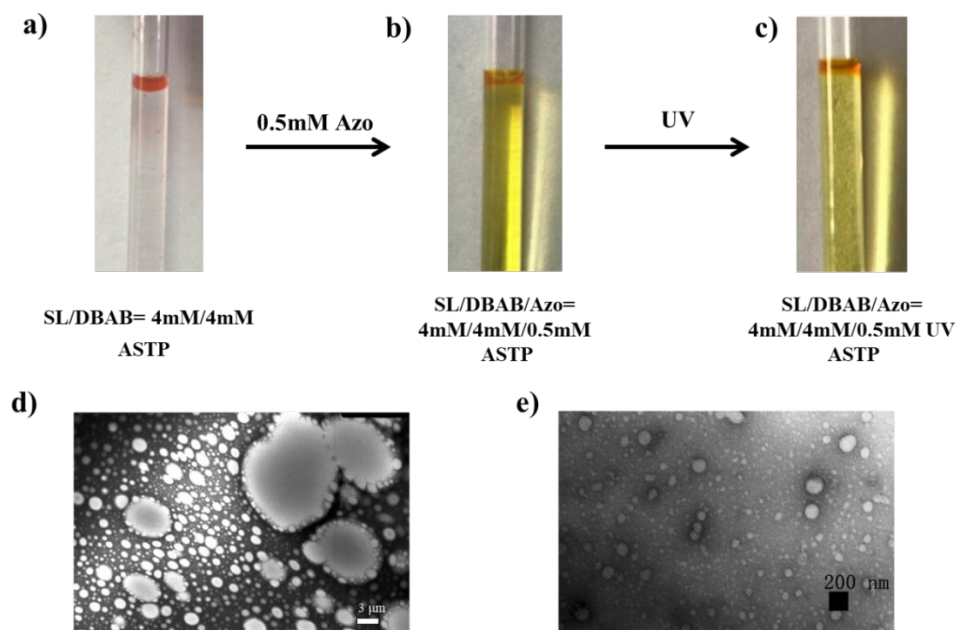


Figure 1. Phase diagram of SL/DBAB aqueous system at 25°C. Yellow dots: samples of single phase; green triangles: samples in ASTP state.

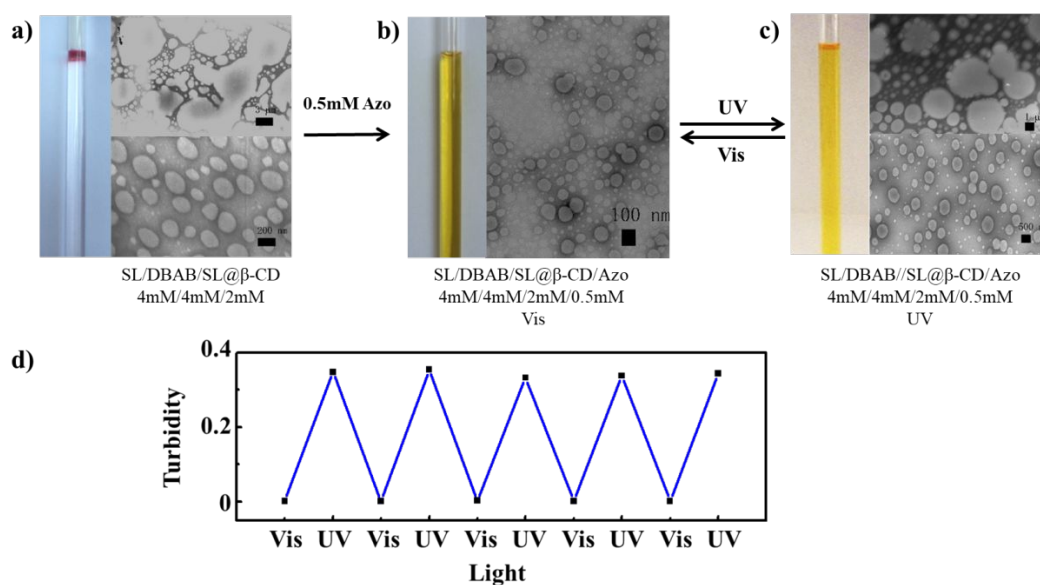


**Figure 2.** Photographs of a) SL/DBAB = 4 mM/4 mM ASTP. b) SL/DBAB/Azo = 4 mM/4 mM/0.5 mM systems and c) after UV irradiation. TEM images of the d) upper phase and e) of SL/DBAB = 4 mM/4 mM ASTP.

In order to endow the photo-inert ASTP with light-responsiveness, we decide to introduce a Trojan horse composed of 2 mM SL@ $\beta$ -CD, into the ASTP system of SL/DBAB. This design utilizes the stronger binding ability of Azo with  $\beta$ -CD than SL. We expect that in the presence of the Trojan horse SL@ $\beta$ -CD, addition of the photo active Azo will leads to release of extra free SL into the ASTP system. Because the ASTP is very sensitive to the molar ratio between SL and DBAB, this extra SL will shift the equilibrium in the original ASTP system, resulting in transition from ASTP to a homogenous single phase.

First of all, we examined the impact of the Trojan horse on the ASTP system of SL/DBAB. Figure 3a reveals that both the phase volume and the morphology and size of the vesicles in the two phases are not affected, indicating the Trojan horse does not

participate the aggregates formation. Figure S4 validates that the SL has been threaded into the cavity of  $\beta$ -CD, and the SL@ $\beta$ -CD complex does not self-assemble into hierarchical structures. However, after adding a small amount of Azo (0.5 mM) into the SL/DBAB ASTP system in the presence of the Trojan horse SL@ $\beta$ -CD, the ASTP is transformed into a homogenous phase and only separated vesicles with radius of 200 nm were found in the system (Figure 3b). Under 365 nm UV irradiation, the homogenous phase transforms back to ASTP. The radius of the aggregates in the upper phase is about 3  $\mu$ m while in the lower phase is about 300 nm (Figure 3c). As this ASTP is subjected to visible light, it transforms into a single phase again. It is worth noting that the photo-stimuli process could be repeated several times by alternating UV and visible light irradiations (Figure 3d).

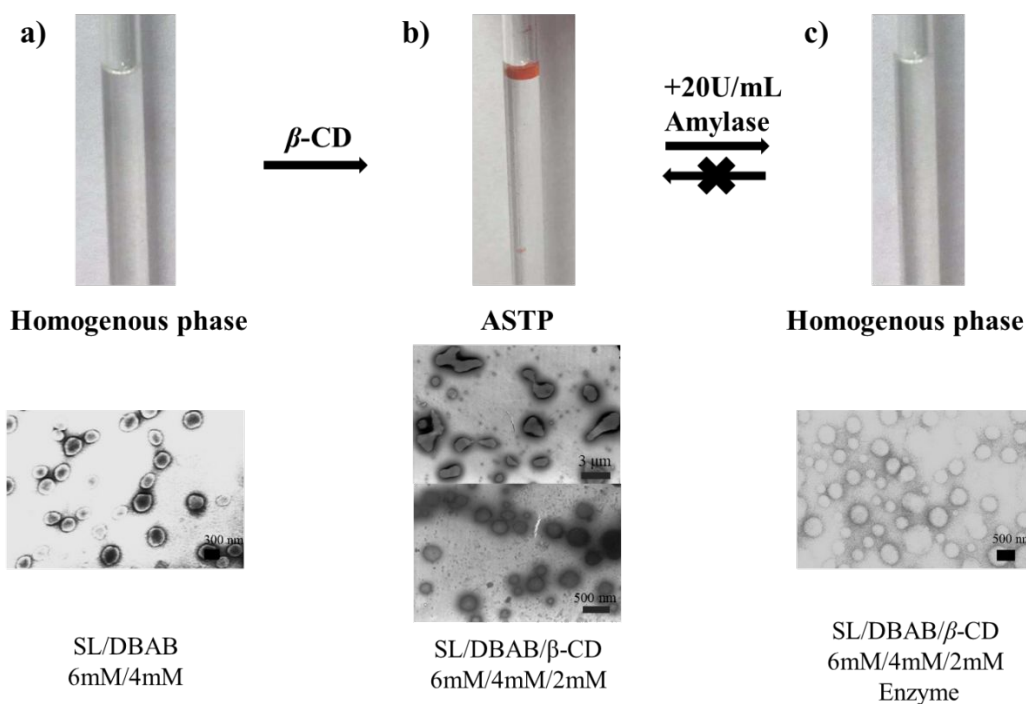


**Figure 3.** Photographs and TEM images of a) SL/DBAB/SL@ $\beta$ -CD(4 mM/4 mM/2 mM) systems. b) SL/DBAB/SL@ $\beta$ -CD/Azo (4 mM/4 mM/2 mM/0.5 mM) under visible light. c)

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4 SL/DBAB/SL@ $\beta$ -CD/Azo (4 mM/4 mM/2 mM/0.5 mM) under 365nm UV light irradiation. d)

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6 Phase transformation after alternating UV and visible light irradiations.  
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11 To investigate the physical insight of the role of the Trojan horse and Azo in the  
12 photo responsive ASTP system, we designed a contrast experiment. 6 mM SL and 4  
13 mM DBAB were mixed together to form a homogenous phase. TEM observation  
14 reveals the formation of vesicles with average radius of 200 nm (Figure 4a). These  
15 vesicles are negatively charge indicated by a negative  $\zeta$  potential value (Table 1),  
16 indicating the presence of excessive SL than DBAB in the vesicle membrane.  
17 However, after addition of 2 mM  $\beta$ -CD, the single phase of vesicle suspension is  
18 transformed into an ASTP with the formation of 3  $\mu$ m aggregated vesicles in the  
19 upper phase and 300 nm vesicles in the lower phase (Figure 4b).  $\zeta$  potential  
20 measurements reveal that the particles in both the upper and lower phase are nearly  
21 zero-charged (Table 1), indicating the excessive negatively charged SL has been  
22 removed from the vesicles. This is in line with our previous study that  $\beta$ -CD will bind  
23 the excess component<sup>34</sup> to form hydrophilic host-guest complex. This complex then  
24 leaves the vesicles and enters into bulk water, which shifts the molar ratio between the  
25 positive and negative surfactant to nearly 1:1 in the vesicles. To further confirm this  
26 scenario, 20 U/ml  $\alpha$ -amylase was added into the ASTP to decompose the  $\beta$ -CD. As  
27 expected, a homogenous phase was obtained again (Figure 4c), validating the role of  
28  $\beta$ -CD in shifting the ASTP phases.  
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28 **Figure 4.** Photograph and TEM images of a) SL/DBAB=6 mM/4 mM, b) SL/DBAB/β-CD=6  
29 mM/4 mM/4 mM which ASTP formed. c) After adding 20 U/ml Amylase, β-CD was hydrolyzed  
30 and ASTP transformed into homogenous phase.  
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35 **Table 1:** Zeta-potential of SL/ DBAB = 6mM/ 4mM and related system  
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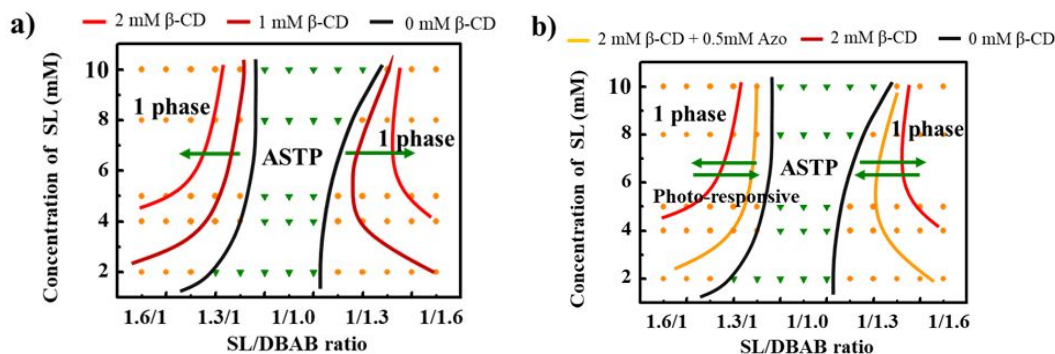
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SL/DBAB/β-CD(mM)	6/4/0	6/4/2	6/4/2
Phase	Single	Two	Single
Enzyme	-	-	Amylase
Zeta potential(mV)	Upper phase	-3.78	-21.72
	Lower phase	-23.15	-5.23

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The above results unambiguously confirm that the phase changes in the SL/DBAB system is caused the by changes in the molar ratio between SL and DBAB. Therefore, we believe that similar molar ratio change has been produced by alternatively exerting

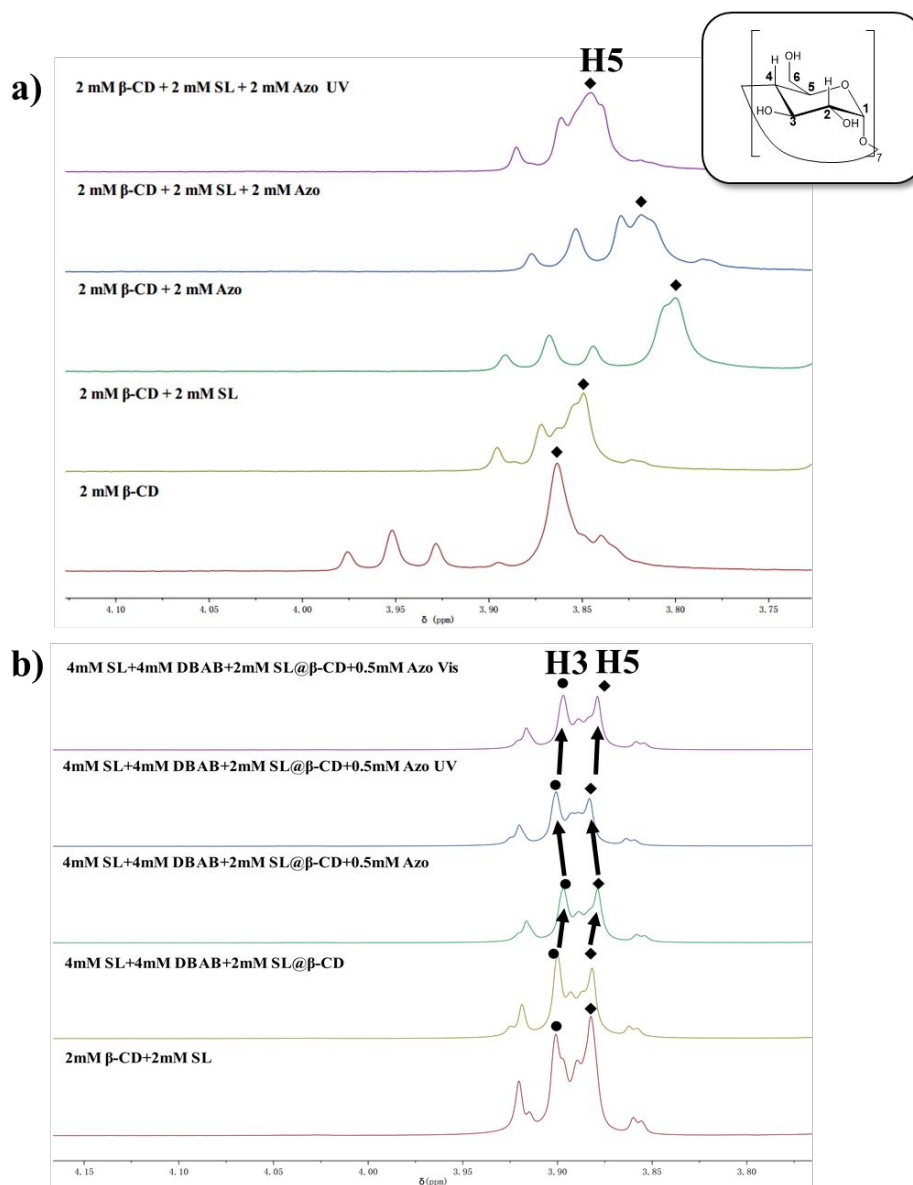
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4 visible and UV light to the ASTP system containing the Trojan horse SL@ $\beta$ -CD  
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6 (Scheme 2). Obviously,  $\beta$ -CD prefers most to bind with the *trans*-Azo under visible  
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8 light, which causes release of extra SL into the ASTP system. As a result, the  
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10 effective molar ratio between SL and DBAB in surfactant mixtures is shifted (bias  
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12 1:1), which leads to the formation of a homogeneous single phase. In contrast, under  
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14 365 nm UV irradiation, the *trans* Azo is changed into the *cis* isomer, which does not  
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16 form host-guest complex with  $\beta$ -CD. Therefore, the excess SL in the surfactant  
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18 mixtures enters into the cavity of  $\beta$ -CD again, which removes the excessive SL from  
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20 the vesicle membrane thus leading to recovery of the ASTP. Such a scenario can be  
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22 proved by the variation of the phase boundary of the ASTP of SL/DBAB in the  
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24 presence of  $\beta$ -CD (Figure 5a). Owing to the hosting of SL into the cavity of  $\beta$ -CD, the  
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26 effective concentration of SL in solution is reduced, so that the ASTP occurs at molar  
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28 ratios farther bias from 1:1. In contrast, if Azo was added, it would replace SL in the  
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30 cavity of  $\beta$ -CD, which results in switch back of the phase boundary, and the variation  
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32 of phase boundary can be reversibly manipulated by alternatively exerting to UV and  
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34 visible light(Figure 5b). Further details about the Azo triggered release of SL can be  
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36 obtained with  $^1\text{H-NMR}$  measurements. As shown in Figure 6, the signal of SL  
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38 appears gradually as Azo is added to the SL@ $\beta$ -CD system. Upon UV irradiation, the  
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40 signal of SL vanishes again, indicating the binding strength of  $\beta$ -CD with *trans,cis*  
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42 Azo and SL follows the sequence of *trans*-Azo > SL > *cis*-Azo. Therefore, we can  
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44 conclude that SL@ $\beta$ -CD indeed behaves as a Trojan horse that brings  
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46 photo-responsiveness to the light-inert ASTP of SL/DBAB.  
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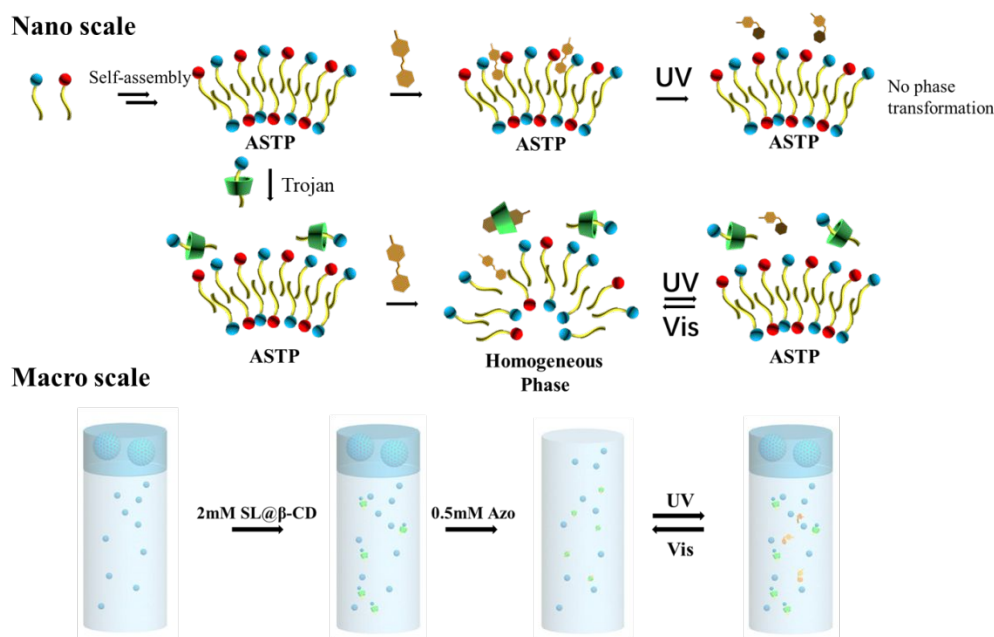
**Figure 5.** Variation of the phase boundary of the ASTP system of SL/DBAB in the presence of  $\beta$ -CD (a) and the Trojan horse SL@ $\beta$ -CD (b). It is clear that with increasing the concentration of  $\beta$ -CD, the phase ASTP phase region is broadened, while the phase boundary can be reversibly switched in the presence of both  $\beta$ -CD and Azo. Yellow dots: samples of single phase; green triangles: samples in ASTP state.

It is worth noting from Figure 5a that addition of  $\beta$ -CD to the DBAB rich side also results in shifting of the phase boundary of the ASTP. This is because  $\beta$ -CD can bind surfactants regardless their charging state.<sup>35-42</sup> In our previous work we have reported that  $\beta$ -CD act as stoichiometry modifier in the cationic surfactant systems.<sup>34</sup> Namely,  $\beta$ -CD always bind the excess one in the mixed systems formed with oppositely charged surfactants.<sup>34,39</sup> This means that the host-guest complex of DBAB@ $\beta$ -CD can also serve as the Trojan horse, which is clearly identified in Figure 5b, where addition of Azo to the DBAB rich side in the presence of  $\beta$ -CD causes phase boundary shift, too. This unambiguously manifests that the Trojan horse strategy could be a general approach to endow the light-inert ASTP system with light responsiveness.





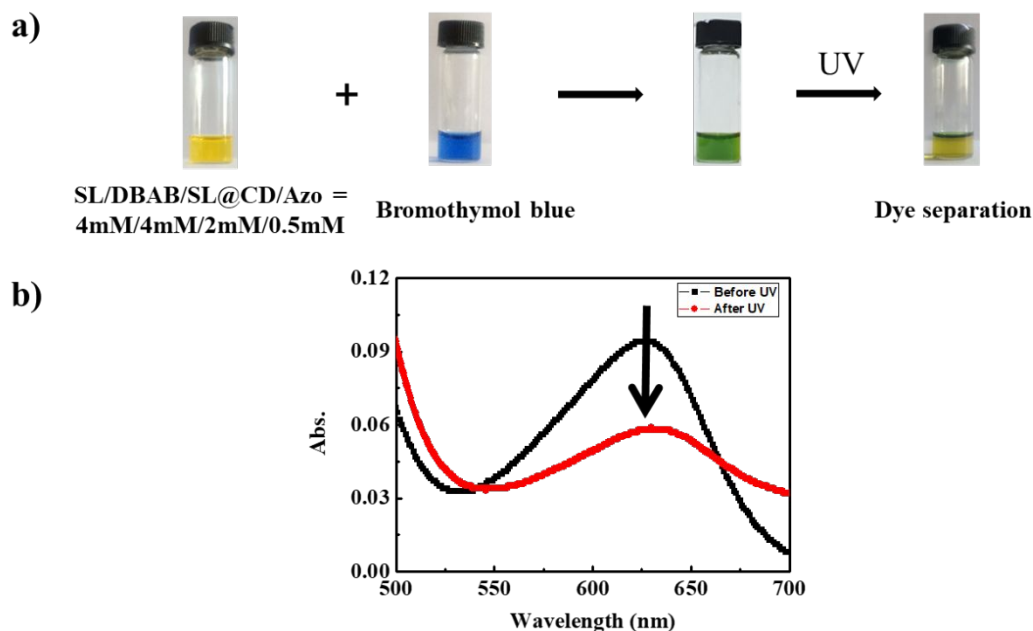
**Figure 6.** a) <sup>1</sup>H-NMR spectra of β-CD, SL@β-CD, *trans*-Azo@β-CD and the host-guest competition before and after UV. [β-CD] = 2mM in all spectra. b) <sup>1</sup>H-NMR spectra of SL/DBAB/SL@β-CD = 4 mM/ 4mM/ 2mM ASTP and light responsive ASTP. Circle and rhombus represent to H3 and H5 in β-CD. To avoid the generation of heat, a UV lamp of 6 W was used. Daylight was the source of visible light.



25 **Scheme 2.** Representative scheme of photo-responsive mechanism of the transformation between  
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28 ASTP at multiscale level.

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33 Next, the photo-responsive ASTP system was employed to practice photo-driven  
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35 separation. Hydrophobic dyes, such as bromothymol blue and eriochrome black T  
36  
37 (The chemical structures of bromothymol blue and eriochrome black T were shown in  
38  
39 the Figure S6), were added into the single phase containing the Trojan horse. It can be  
40  
41 observed in Figure 7 a that bromothymol blue diffuse uniformly in the homogeneous  
42  
43 phase. However, it is enriched in the upper phase within 30 minutes upon UV  
44  
45 irradiation, and the lower phase becomes yellow. UV-vis spectroscopy (Figure 7 b)  
46  
47 reveals that the concentration of bromothymol blue in the lower phase decreases  
48  
49 sharply upon UV irradiation. Similar photo triggered separation of the hydrophobic  
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51 dye of eriochrome black T is shown in Figure S7. Control experiments demonstrate  
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that the absorption of both dyes in water do not change under UV irradiation, eliminating the possibility of degradation of dye upon UV irradiation (Figure S8).



**Figure 7.** a) Dye separation application based on photo-responsive ASTP. b) UV-vis spectrum for dye separation process.

#### 4. CONCLUSIONS

In summary, we proposed a simple and effective approach to construct photo-responsive ASTP by physically introducing a photo-trigger in the presence of a Trojan horse. In principle, this strategy can be applied to many other aqueous two-phase systems, and to regulate other phase behaviors, for instance, emulsion. We expect the current strategy is very facile to introduce photo-responsiveness to a large variety of light-inert systems, which opens a new vista in the construction and application of smart materials.

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4 **Supplementary information.** <sup>1</sup>H-NMR, DLS, TEM, MS and UV-vis measurements  
5  
6 are listed in supporting information. This material is available free of charge via the  
7  
8 Internet at <http://pubs.acs.org>  
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