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Visible light-controlled inversion of Pickering emulsions stabilized by functional silica microspheres

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ABSTRACT: A new class of donor-acceptor Stenhouse adducts (DASAs) functionalized silica microspheres (SM) is designed and described to formulate Pickering emulsions with inversion property and large polarity change under visible light irradiation. By tuning the hydrophilicity of the functional SM particles with visible light, these Pickering emulsions can easily perform

inversion from w/o to o/w. The inversion performance of the emulsions is ascribed to DASAs photoisomerization from an extended, hydrophobic, and intensely purple colored triene to a compact, zwitterionic, and colorless cyclopentenone upon irradiation with visible light. This unique inversion behavior has been applied to control encapsulation and release of fluorescein sodium salt.

INTRODUCTION

Pickering emulsions, which are stabilized solely by colloidal particles, have been known for more than a century.^{1,2} Due to the adsorption of colloid particles at the interface of two immiscible liquids such as oil and water, such emulsions are very stable compared with those stabilized by surfactants.³ Moreover, after removal of the resolved oil layer, the remnant emulsion still exhibits good stability without any coalescence.^{4,5} Studies on Pickering emulsions are therefore of critical importance in both understanding the fundamentals and developing potential applications.^{6,7}

In some practical applications, such as biocatalysis, fossil fuel production, oil transport, and emulsion polymerization, emulsions need to be temporarily stabilized and subsequently demulsified or inversed. For instance, stimulus-responsive Pickering emulsions stabilized by switchable surface-active colloid particles have shown the ability to allow on-demand demulsification or phase inversion.^{8,9} In this case, switchable Pickering emulsions are desirable and have received considerable attention in recent years.^{10,11}

In this context, the colloid particles used as stabilizers at a range of fluid interfaces should be convertible between hydrophilicity and hydrophobicity to response environmental triggers.^{12–14} Nevertheless, the design and synthesis of the functional particles are in general complicated.

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Recently, much effort has been made to develop intelligent Pickering emulsions stabilized by surface active particles that respond to a specific trigger such as pH,^{15–17} temperature,^{18–20} magnetic field,^{21,22} CO₂²³⁻²⁵ or specific ion concentration.^{26,27} In contrast, light is an excellent trigger without the need to add chemicals, and the wavelength, polarization direction and intensity of the light can be easily controlled. For example, Binks et al.²⁸ reported a dual stimuliresponsive oil in water Pickering emulsion with light and CO₂/N₂ triggers. Negatively charged silica nanoparticles in combination with a trace amount of dual switchable surfactant were used as stabilizers. Ou et al.²⁹ synthesized silica coated upconversion nanoparticles followed by grafing photochromic spiropyrans on them by amido bond. These nanoparticles were used to achieve the reversible inversion of a light-triggered Pickering emulsion for biphasic enantioselective biocatalysis. Meng et al.³⁰ prepared stable water in oil emulsions by UV-induced tailored wettability of TiO₂ nanoparticles anchoring at the interface. Such emulsions were used for controlled encapsulation and release of cargos using light trigger. Yang et al.³¹ reported a light-triggered reversible phase transfer of composite colloids. These composite colloids could transfer reversibly between hydrophobic and hydrophilic phases upon irradiation with different wavelengths of light. UV responsive Pickering emulsions stabilized by titanium dioxide nanoparticles for photocatalytic degradation of nitrobenzene³² and Rhodamine B³³ were also developed. Nevertheless, either multistep synthesis or UV light is inevitable. Although some visible light responsive compounds,^{34,35} near-Infrared photoswitchable azobenzenes³⁶ and lightcontrolled colloid assembly^{37,38} were also reported, hydrophilicity/hydrophobicity of the surface was not suitable to form emulsions. Therefore, developing more convenient approaches to tune particle surfaces is necessary.³⁹

Recently, donor–acceptor Stenhouse adducts (DASAs) has attracted a lot of attention.^{40,41} These compounds can be synthesized easily in two steps from commercially available starting materials, and undergo reversible isomerization in some organic solvents upon irradiation with visible light. The primary process is the conversion from an extended, hydrophobic, and intensely purple colored triene to a compact, zwitterionic, and colorless cyclopentenone upon irradiation with visible light.^{42,43} However, to the best of our knowledge, reports on visible light controlled surface switch of particles modified by DASAs in Pickering emulsions have not been found in literature so far.

Scheme 1. Schematic illustration for the synthesis of DASAs-functionalized SM particles SM- C_xD (x=6, 7 and 9), where x refers to the number of carbons connected to the nitrogen atom



In this work, we propose a conceptually new approach for the first time: a series of new photochromic DASAs have been used to functionalize silica microspheres (SM) with covalent

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linkage (Scheme 1). Upon irradiation with a visible light, DASAs photoisomerize from a colored neutral linear form (a) to a colorless zwitterionic cyclic form (b). Such a transformation makes the hydrophilicity/hydrophobicity of the surface of colloidal emulsifiers switchable, thus leading to the inversion of Pickering emulsions from w/o to o/w. In particular, this unique inversion behavior has been applied to control encapsulation and release of fluorescein sodium salt. Thus a highly efficient process is achieved by using DASAs-functionalized SM particles as the emulsifier and visible light as a smart trigger.

EXPERIMENTAL SECTION

Materials. Tetraethyl orthosilicate (TEOS, 99%), N-ethylaminoisobutyltrimethoxysilane (98%), N-(n-butyl)-3-aminopropyltrimethoxysilane and N-cyclohexyl-3-aminopropyl-trimethoxysilane were purchased from Aladdin Co. Ltd. Meldrum's acid (98%), ammonia (NH₃·H₂O, 25 wt%) and furfural (99%) were obtained from Alfa and used as received. Toluene (99.5%) was from Aldrich, and trace of water was removed with sodium before use. ethyl formate (99.5%), methyl acetate (99.5%), ethyl acetate (99.5%), dichloromethane (99.5%), trichloromethane (99%), tetrachloromethane (99.5%), ethanol (95%), n-pentanol (99.5%) and n-hexanol (99%) were purchased from Alfa and used as received unless stated otherwise. Deionized water was used in this study.

Synthesis of 5-(Furan-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione. 5-(Furan-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione was prepared according to the procedures described in the recent literature.⁴² The typical procedure was as follows: 2,2-dimethyl-1,3-dioxane-4,6-dione (1.51 g, 10.5 mmol) and 2-furaldehyde (0.83 mL, 10 mmol) were mixed with water (30 mL) at 30°C under N₂ atmosphere. The obtained mixture was heated to 45 °C and reacted for 2h. After completion of the reaction (as monitored by TLC, hexane : ethyl acetate =

3:1), the mixture was cooled to room temperature. The precipitated solid was collected by vacuum filtration and washed twice with 30 mL of cold water. The resulted solid was dissolved in dichloromethane, washed sequentially with 30 mL of aqueous saturated NaHSO₃, 30 mL of water, 30 mL of aqueous saturated NaHCO₃ and 30 mL of brine. The organic layer was dried over MgSO₄, filtered and the solvent was removed by rotary evaporation to give 2.10 g (95%) of the product as a bright yellow powder. ¹H NMR (600 MHz, CDCl₃): δ = 8.47 (d, 1H, *CH*), 8.36 (s, 1H, *CH*), 7.85 (d, 1H, *CH*), 6.76 (ddd, 1H, *CH*), 1.77 (s, 6H; 2*CH*₃) ppm.

Synthesis of SiO₂ **microspheres.** SiO₂ microspheres were synthesized according to the well established Stöber method.⁴⁴ For this purpose, 200 mL of 95% ethanol, 50 mL of deionized water and 11.2 mL of 25 wt% aqueous NH₃ were mixed to form a uniform system. After stirring for 30 min at room temperature, 8.32 g of tetraethyl orthosilicate was added dropwise into this solution under stirring. After stirring for 12 h, the precipitation was isolated by centrifugation, washed with deionized water, and then dried under air at 100 °C for 2 h to give SiO₂ microspheres.

Synthesis of secondary amine-modified silica microspheres. 1.0 g of the synthesized SiO₂ microspheres (dried at 125 °C for 4 h) was dispersed into 100 mL of toluene, and 1.6 mL of organosilane was added into this suspension. After refluxing at 60°C for 1 h and then reaction at 110 °C for 24 h under N₂ atmosphere, the material was isolated by centrifugation, washed five times with toluene. After being dried at 40 °C for 12 h under vacuum, secondary amine-functionalized SiO₂ microsphere was afforded (noted as SM-C_X particles, x refers to the carbon number of the secondary amine silane, x=6, 7, 9, respectively).

Synthesis of DASAs-modified silica microspheres. Typically, 5-(furan-2-ylmethylene)-2,2dimethyl-1,3-dioxane-4,6-dione (0.6 gram, 2.7 mmol) was dissolved in 7 ml of tetrahydrofuran.

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0.61 gram of SM-C₉ (0.06 mmol of secondary amine was grafted on the surface, as assessed by TGA^{45,46}) was added to this solution. After being stirred at 23 °C for 10 min, the solution was cooled to 0 °C and further stirred for 10 min, and then filtered to collect the precipitated solid. This solid was washed with cold diethyl ether three times, and dried under vacuum to afford the DASAs-modified silica microspheres as a pink solid (noted as SM-C₉D particles). For the preparation of SM-C₆D and SM-C₇D, the procedures were the same as the SM-C₉D.

Preparation of Pickering emulsion. 2 mL of deionized water was first added into a vial containing 0.024 g of the functionalized silica microspheres. Then, 2 mL of an organic solvent (toluene in most of the cases) was added into the vial. After vigorously stirring with a magnetic bar at 800 rpm for 3 min, SM-C_xD particles-stabilized emulsion was obtained.

Characterization. Scanning electron microscope (SEM) images were obtained on a HITACHI UHR FE-SEM (SU8010, Japan). Thermogravimetric analysis (TGA) was performed with a NETZSCHTG analyzer (STA449C, Germany) under nitrogen atmosphere from room temperature to 900°C with a heating rate of 10 °C/min. X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific ESCALAB (250Xi, America). Photographs of each emulsion were observed on an optical microscope (DYP-990, Shanghai, China). A drop of each emulsion was mounted on a glass slide and was observed with a digital camera. Water contact angles (water-solid-air) were measured on a KRUSS Drop Shape Analyzer (DSA25, Germany).

RESULTS AND DISCUSSION

Synthesis and characterization of DASAs-modified silica microspheres. A series of photochromic DASAs-functionalized SM particles (Figure. 1a) were designed and synthesized. The Si-OH groups on SiO_2 microspheres were reactive and could be selectively modified by silanes. Thus, the DASAs-modified silica microspheres were obtained by introducing functional

secondary amine groups on SiO₂ microspheres. The successful grafting of DASAs onto SiO₂ microspheres was confirmed by FTIR spectroscopy (Figure. 2). The typical carbon-nitrogen bond vibration (at 1190 cm⁻¹), conjugated olefin double bond stretching (at 1600 cm⁻¹), carbon-hydrogen bond stretching (at 2954 cm⁻¹, 2856 cm⁻¹, 1460 cm⁻¹) and gem-dimethyl carbon-hydrogen bond stretching (at 1383 cm⁻¹, 1365 cm⁻¹) indicate that DASAs were really introduced on the surface of SiO₂ microspheres. To obtain a desired surface chemistry, the carbon number of secondary amine silane was varied from 6 to 7 and 9. The resultant silica microspheres were denoted as SM-C_xD (x=6, 7, 9). It was found that the particles were well dispersed after modification, and SM-C_xD was spherical in morphology and its diameter was in the range of 250–350 nm (Figure. 1b). According to the XPS results (Figure 1c and Figures S1-3), the atom ratio of carbon to nitrogen gradually increased from SM-C₆D to SM-C₉D. Thermogravimetric analysis results (Figure. S4) indicate that DASAs loadings on these SM particles were, respectively, 3.84, 2.29 and 3.55 wt%.

As a representative example, the UV-vis absorption spectrum of SM-C₉D composite colloids dispersed in toluene–water mixture was determined, and the results were reported in Figure S5. It can be seen that before irradiation with visible light, there was a strong absorption peak at around 515 nm in the upper toluene phase, which corresponds to the triene form of SM-C₉D. However, the characteristic peak became very weak after visible light irradiation by a Crystal Clear 200 bulb (200 watt, 3780 lumens) for 1h. Meanwhile, two absorption peaks at around 515 nm and 268 nm appeared in the bottom water layer. This means that photoisomerization of DASA took place from triene to cyclopentenone isomers. Because of the stronger hydrophilicity of cyclopentenone isomer, most of the colloids were transferred into the aqueous phase. These

results suggest that the surface chemistry can be influenced by the carbon chain length of the organosilane and polarity change of the functional groups.⁴⁷



Figure 1. (a) The structural description for DASAs functionalized silica microspheres; (b) SEM image of SM-C₇D, scale bar: 100nm; (c) Three types of functional SM particles with different loadings of DASAs elements.



Figure 2. FTIR spectra of SM, SM-C₆D, SM-C₇D and SM-C₉D.

The photoreaction dynamic of the composite colloids was also investigated by UV-vis absorption spectroscopy³¹ with THF (Tetrahydrofuran) as a dispersion media since both triene and cyclopentenone forms of SM-C₉D were dispersible in THF. It is apparent from Figure 3a that exposure of SM-C₉D composite colloids under a standard incandescent bulb resulted in a remarkable decrease in the absorption at around 515 nm over the irradiation course of 1h. A concomitant increase in the absorption at around 268 nm was also observed for the cyclopentenone form (Figure 3a and 3b). After irradiation of 1h, saturation absorption (isomerization equilibrium) was observed.



Figure 3. (a) Absorption spectra of the SM-C₉D composite colloids dispersed in THF (0.1 mg/mL) irradiated by visible light as a function of time; (b) Expanded view of absorption spectra of the SM-C₉D composite colloids between 250 and 280 nm.

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Characteristics of the Pickering emulsions stabilized by different functionalized silica **microspheres.** We examined the interfacial activity and the remote controlled inversion of the synthesized samples. Typically, after the mixture of the functionalized silica microspheres, toluene and water was stirred in the dark for 3 min (800 rpm) at ambient conditions, different phenomena could be observed for these samples. Bare silica microspheres precipitated in the bottom water layer (Figure. S6) and emulsion droplets were not found under optical microscope. Different from the bare silica microspheres, SM-C₆D and SM-C₆ led to a Pickering emulsion in the upper toluene layer since droplets were observed (Figure, 4 and Figure, S6). The drop test confirmed that it was an o/w emulsion. On the contrary, SM-C₇D, SM-C₉D, SM-C₇ or SM-C₉ was well dispersed in the bottom water layer. Optical microscopy result confirmed that it was also a Pickering emulsion because spherical droplets were clearly observed (Figure. 4 and Figure, S6). The drop test indicates that it was a w/o Pickering emulsion. Upon irradiation with visible light and homogenization, only SM-C₇D and SM-C₉D transferred to the upper toluene layer where o/w emulsions were formed. However, no inversion was found for the systems with SM-C₆, SM-C₇ and SM-C₉ because of the absence of a visible light sensitive moiety. As assumed in theory, we did not observe any other changes either (Figure, S6). Interestingly, the SM-C₆D stabilized Pickering emulsion was demulsified upon irradiation with visible light, as observed from the optical micrographs (Figure 4). In addition, we investigated the stability of the Pickering emulsions before and after visible light irradiation. As a representative example, the $SM-C_9D$ stabilized emulsion was found to be well dispersed in the bottom water layer (w/o) before visible light irradiation. After irradiation with visible light by a Crystal Clear 200 bulb (200 watt, 3780 lumens) for 50 min followed by agitation, o/w Pickering emulsions were formed in the top toluene layer. The two types of emulsions could be stable against sedimentation at least 12 days (Figure, S7).



Figure 4. Appearance of emulsions with different functional silica microspheres in toluene-water mixture (photographs taken after standing for 30min). Every vial contains 2 mL of toluene, 2 mL of water, and 0.024 g of functional silica microspheres. State 1: before visible light irradiation; State 2: after visible light irradiation. Scale bar is 200 μm.

The difference in the emulsion inversion is related to the visible light responsive surface chemistry. As shown in Figure. 5a, the conductivity variation in the continuous phase of Pickering emulsions demonstrated the inversion processes. As a representative example, the conductivity of the emulsions stabilized by SM-C₉D particles was measured to be approximately 0 before visible light irradiation. After exposed to visible light for 1h, it increased to 1235 µscm⁻¹, and accompanied by unidirectional conversion of the colored triene to its colorless zwitterionic cyclopentenone isomer. In contrast, the conductivity always maintained at 1328 µscm⁻¹ for the bare silica microspheres during irradiation with visible light. The difference between these

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Figure 5. a) Conductivity of Pickering emulsions of toluene and 0.01 M aqueous NaCl (1:1) stabilized by SM- C_XD particles before and after visible light irradiation; b) Water contact angles of SM- C_XD before and after visible light irradiation.

The visible light triggered phase inversion was further supported by water contact angle measurements (Figure. 5b and Figure. S8). The water contact angle of the freshly prepared SM-C₉D was measured to be 116.8°, which decreased to 58.2° after irradiation with visible light, confirming the increase of hydrophilic property. Similar trend was observed for the contact angle of SM-C₇D. As anticipated, such changes drove the inversion of SM-C₉D stabilized emulsions from w/o to o/w. In contrast, the wettability of the bare silica microspheres, SM-C₆, SM-C₇ and SM-C₉ was almost unaffected by visible light because of the absence of a visible light sensitive moiety. SM-C₆D is relatively hydrophilic and its surface is more hydrophilic after visible light irradiation, resulting in demulsification. The surface silanol group (SiOH) made the silica surface more hydrophilic, whereas the photochromic DASAs on the silica surface rendered the particles

surface partially hydrophobic. These changes in the surface wettability of the particles are the origin of the switching between triene and cyclopentenone isomers.

Besides water/toluene system, SM-C₇D and SM-C₉D were also good emulsifiers for water/ethyl formate, methyl acetate, ethyl acetate, dichloromethane, trichloromethane, tetrachloromethane, n-pentanol and n-hexanol systems (Figures. S9-11). However, SM-C₆D formed w/o emulsions only in water/ dichloromethane and water/trichloromethane systems. In other systems (not including water/ethyl formate), o/w emulsions were observed. In these systems, except for water/n-pentanol and water/n-hexanol, all w/o emulsions could be inverted easily to o/w emulsions by just exposing to visible light. After exposed to visible light, the surface of SM-C₆D became too hydrophilic to stabilize the emulsions, leading to the demulsification in the case of water/tetrachloromethane, methyl acetate and ethyl acetate systems.

Usually, emulsion type (o/w or w/o) is believed to be determined in some way by the particle wettability, expressed in terms of the contact angle θ . Here θ is the three-phase contact angle between the colloidal particle, the oil phase, and the water phase at the interface. In fact, the strength with which a particle is held at an oil/water interface is related not only to θ but also to the interfacial tension, γ_{ow} .⁴⁸⁻⁵⁰ It is well established that a colloidal particle crossing an oil/water interface needs to overcome an energy obstacle, which can be calculated according to the equation: ⁴⁸⁻⁵⁰

$$E = \pi R^2 \gamma_{ow} \left(1 \pm \cos \theta \right)^2 \tag{1}$$

where R is the particle radius. Apparently, the energy obstacle depends on the particle size, the interfacial tension and the three-phase contact angle. The interfacial tension values of water / organic solvents used in this work are quite different. The γ_{ow} values of water / ethyl acetate,

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water / toluene and water / tetrachloromethane are, respectively, 19.8, 36.1 and 43.7 mN m⁻¹ at 25 °C.^{51,52} From the above equation, it is easy to see that *E* increased with the increase of γ_{ow} at a given contact angle. For example, if R of 150 nm and γ_{ow} of 43.7 mN m⁻¹ are considered for SM- C_9D / water / tetrachloromethane system, E is estimated to be as high as $10^6 k_BT$ (where k_B is the Boltzmann constant and T the temperature) at $\theta = 90^{\circ}$. This can lead to the greater difficulty for the particles in crossing the phase interface compared with the other two systems. In the experiments, we found that although SM-C₉D particles formed w/o Pickering emulsions in water / ethyl acetate, water / toluene and water / tetrachloromethane systems and all the emulsions inversed from w/o to o/w after irradiation with visible light, the required time of irradiation was quite different from 30 min, 50 min to 120 min for the three different systems. This is consistent with theoretical estimation. All these results indicate surface the that both hydrophilic/hydrophobic transitions and interfacial tension are critically important to this inversion process.

Additionally, the emulsion inversion was also observed in the presence of different mass fractions of SM-C₇D and SM-C₉D using toluene as oil phase. Taking SM-C₉D as an example, the average droplet diameter decreased from 711 to 150 µm when the content of the colloidal emulsifier was increased from 0.8 to 1.5 wt% (Figure. S12). Also, the polydispersity of the emulsion droplets increased simultaneously. More interestingly, after removing the resolved oil layer or water layer, the remnant emulsion still exhibited good stability without any coalescence, disproportionation or water drainage.

Encapsulation and release of fluorescein sodium salt. To visually illustrate the emulsion inversion process and simulate encapsulation and release of cargos, fluorescein sodium salt was encapsulated into the droplets investigated by fluorescence microscopy. As shown in Figure. 6,

initially, green emission of fluorescein sodium salt was observed in the droplets of the w/o Pickering emulsions. Upon irradiation with visible light, the functionalized SM particles, such as SM-C₉D, became relatively hydrophilic. Following homogenization, o/w emulsions were formed and the fluorescein sodium salt was released into the water layer which exhibited green fluorescence. These results are closely consistent with the isomerization of SM-C₉D structure caused by the visible light induced switching of DASAs to a relatively hydrophilic derivative. This demonstrates that the hydrophilic cargo (fluorescein sodium salt) was encapsulated within the w/o Pickering emulsions until visible light was irradiated to trigger the Pickering emulsions inversion. Therefore, this simple but powerful application of the functionalized Pickering emulsions showed promising potential in visible light controlled cargos release and related areas.



Figure 6. (a) Photographs of fluorescein sodium salt encapsulation by SM-C₉D stabilized Pickering emulsions: w/o (left), o/w (right), where visible light was utilized as stimuli before homogenization; (b) Fluorescence microscopic images of the corresponding Pickering emulsions shown in (a). Scale bar: 200 μ m.

CONCLUSIONS

In summary, by tuning the surface chemistry using photochromic DASAs-modified SM particles, we have successfully prepared interfacially active functional particles for the formulation of Pickering emulsions. These functional SM particles show structure isomerization characteristics upon visible light irradiation. Particularly, DASAs grafing on SM-C₇D and SM-C₉D can switch from a conjugated, colored form to a ring-closed, colorless structure upon irradiation with visible light. Such transformation makes the hydrophilicity/hydrophobicity of the surface of colloidal emulsifiers switchable, thus driving the emulsions inversion from w/o to o/w. Owing to the appropriate amphiphilic structure, the high yields and the simple synthetic procedures of the DASAs photoswitches, these functionalized SM particles are important complementary to previous classes of photoswitches for Pickering emulsions.

The potential application of these photoswitches was demonstrated through encapsulation of fluorescein sodium salt in w/o droplets and release in the visible light mediated emulsions inversion. We anticipate that this remote controlled inversion strategy would provide unique opportunities for application in areas such as biocatalysis in biphasic systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

XPS spectra, TG curves, Water contact angles, UV-Vis absorption spectra and appearance of emulsions with different functional silica microspheres.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Table of Contents Graphic



Pickering emulsions stabilized by functional silica microspheres exhibit behaviors of visible light responsive inversion, cargos encapsulation and release.