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Fast Photoinduced Large Deformation of Colloidal Spheres from a Novel 4-arm Azobenzene Compound

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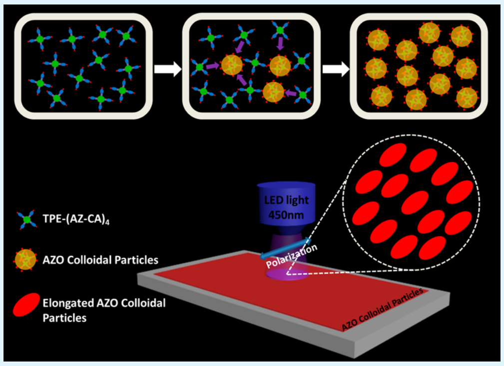
Ⓢ *Supporting Information*

ABSTRACT: A novel 4-arm shaped amphiphilic azobenzene compound was synthesized. The tetraphenylethylene (TPE) core precursor was prepared and further modified by azo coupling reaction at the four peripheral groups. Colloidal spheres could be directly prepared by self-assembly of the prepared amphiphilic azobenzene compound in selective solvents (THF/H_2O), which were characterized by using transmission electron microscopy. The colloid diameters could be controlled by adjusting the initial compound concentration and water-adding rate in the preparation processes. By irradiation with visible linearly polarized LED light (450 nm), fast photoinduced deformation of the colloidal spheres along the polarization direction was observed. A very large deformation degree ($l/d > 4$) could be easily obtained.



KEYWORDS: *self-assembly, colloidal spheres, azobenzene, deformation, linearly polarized light*

INTRODUCTION

In recent years, photochromic azobenzene and its derivatives, which can undergo reversible isomerization upon irradiation with light at an appropriate wavelength, have been widely used as functional building blocks to construct materials with various photoresponsive properties.[1−11] For example, azobenzene can act as a photon harvesting antenna to transfer energy, move the polymeric chains to form surface-relief gratings, induce the phase transition, change the hydrophilic and hydrophobic property, induce the film contraction and bending, and change the geometry of other molecules.[12−21] Among them, photoinduced deformations in different forms have attracted considerable research interest for their unique nature and potential applications in optical data storage, sensors, actuators, and artificial muscles.[19−26]

Colloidal particles with at least one dimension in nanometer to micrometer range have been widely applied in many industrial products.[27] A very feasible way to prepare colloidal particle is through the self-assembly of amphiphilic polymers in selected solvents, which can be potentially used in drug delivery systems, nanoreactors, photonic bandgap (PBG) crystals, and other applications.[28−40] In recent years, the effort to produce nonspherical colloids from spherical colloids has aroused significant interest, which can be potentially used in photonic band gap (PBG) crystals and others. For example, nonspherical colloids have been obtained by mechanically stretching spherical colloids embedded in polymeric matrixes.[41] Ellipsoidal polymer nanoparticles have been prepared from main-chain liquid crystalline polymers using a mini-emulsion technique.[42] When the colloidal spheres are from the self-assembly of amphiphilic polymers bearing push−pull azo chromophores, upon irradiation with an Ar^+ laser beam, the colloidal spheres can be significantly elongated along the polarization direction of the laser beam.[21,43] This light-driven process makes it very easy to prepare nonspherical colloids. The factors influenced the azo polymeric colloidal deformation have been investigated in our previous studies, which include amounts of azo chromophores in colloids, types of the azo chromophores, different chain architecture of the polymer and others.[44−46] Anyway, the precise nature of the photoinduced mass-transport processes is still unclear. In the previous reports, the Ar^+ laser beam (488 nm) was used as the light resource. The laser beam has good optical coherence property. If normal incoherent light can also induce this deformation, it will be better for fabrication of such nonspherical colloids. The fabrication of large area nonspherical colloids arrays will also be much easier. Furthermore, the photo deformable azo colloids were often made by self-assembly of amphiphilic azo copolymers. For the copolymers, whatever they are block copolymers or random copolymers, the exact molecular weights are not easy to control. As we know, the molecular weights will affect the self-assembly and deformation process very much. It will be better to use the molecules with exact molecular weights to form the uniform colloids.

In this study, we synthesized a novel 4-arm azobenzene compound with a hydrophobic tetraphenylethylene (TPE) core and four hydrophilic peripheral carboxyl groups. The azo

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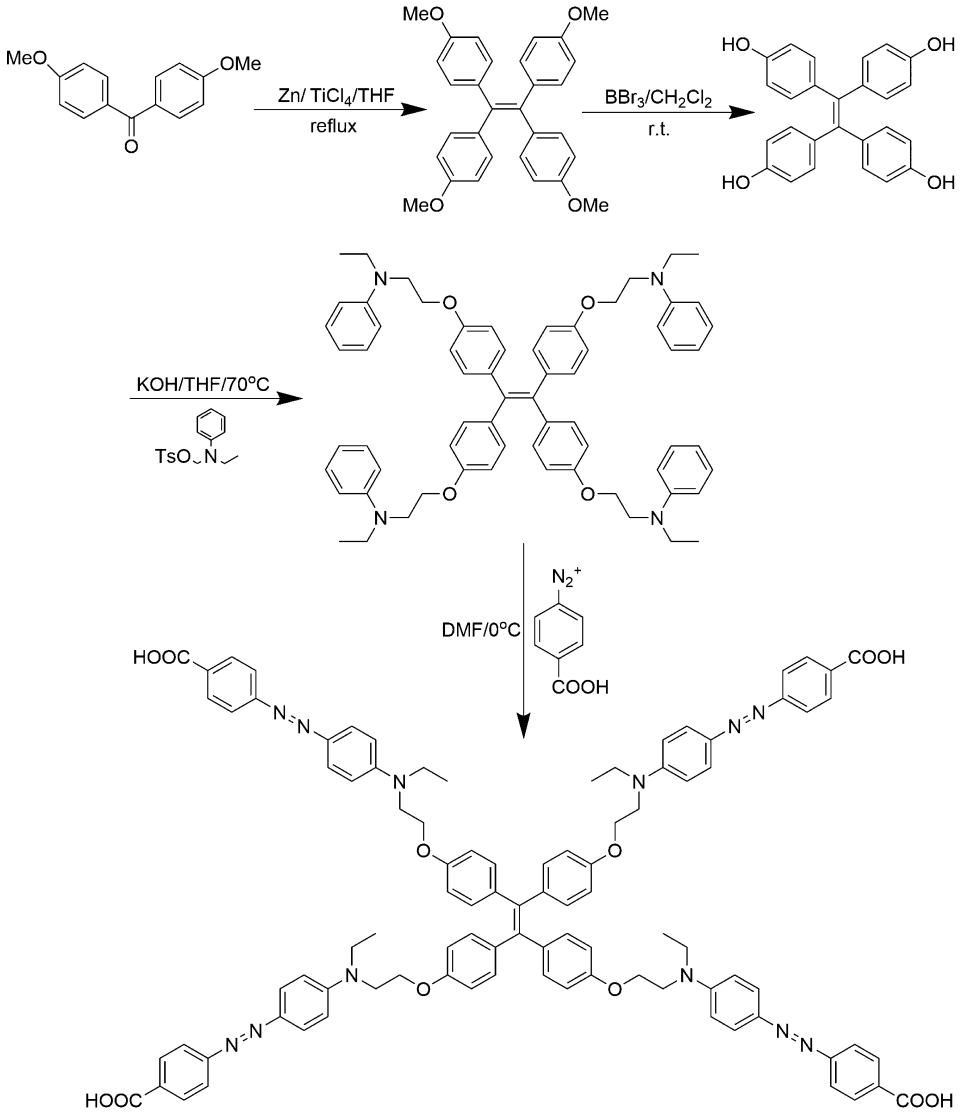
Scheme 1. Synthetic Route of 4-arm Azobenzene Compound TPE-$(AZ\text{-}CA)_4$



chromophore loading density of this compound is more than 60% (wt %). Colloidal microspheres could be directly prepared by gradually adding deionized water to the 4-arm azobenzene compound THF solution. Until now, self-assembly of such amphiphilic azobenzene optically functional materials in selected solvents have been seldom studied. Compared to polymer, this kind of molecule has well-defined structure and offers better reproducible properties. The average diameters of colloidal spheres could be controlled by adjusting the initial compound concentration and water-adding rate in the preparation processes. Moreover, the prepared azo colloidal particles showed obviously deformation behavior just by irradiation with a visible linearly polarized LED light (450 nm) instead of laser beam. The photoinduced deformation rate of the colloidal spheres along the polarization direction was very fast even with a relatively low light intensity and the deformation degree was very large.

■ EXPERIMENTAL SECTION

Materials and Characterization. 4,4′-Dimethoxybenzophenone (97%), *p*-toluenesulfonyl chloride (99%,TsCl), and boron tribromide (1.0 M in Dichloromethane) were purchased from J&K Chemical and 4-Aminobenzoic acid (99%) was received from Alfa Aesar. Tetrahydrofuran (AR, 99%) was dried over 4 Å molecular sieves. Other chemicals and solvents were purchased from the commercial sources and if it was not mentioned specifically, the reactants and solvents were used as received without further purification. Ultrapure water (resistivity >18.0 MΩ.cm) was supplied by a Milli-Q water purification system and used for all experiments. ^1H NMR spectra and ^{13}C NMR spectra were recorded on a JEOL JNM-ECA 600 NMR spectrometer using the solvent peak as internal reference. The UV−vis spectra of samples were measured using an Agilent 8453 UV−vis spectrophotometer. The colloid morphologies were examined by TEM (H-7650B, HITACHI) with an accelerating voltage of 80−120 kV. For TEM sample preparation, we added drops of diluted colloid dispersions onto a copper grid coated with carbon film and then dried under vacuum at 30 °C for 24 h. The samples were observed with an electron microscope before and after light irradiation. No staining treatment was required for the TEM observations.

Synthesis of 1,1,2,2-Tetrakis(4-methoxyphenyl)ethane (TPE-$(OMe)_4$). Zn dust (3.86 g, 60.0 mmol) was added to a solution of 4,4′-dimethoxybenzophenone (4.85g, 20 mmol) in 100 mL of dry THF. After refluxing for 12 h, the reaction was quenched with 10% K_2CO_3 (w%, 100 mL), and the mixture was cooled to room temperature and filtered. The solvent was evaporated under vacuum, and the crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether (v/v = 1:1) as the eluent. Finally, TPE-$(OMe)_4$ was obtained as a white solid in 92% yield (4.16 g). ^1H

NMR (600 MHz, $CDCl_3$) δ = 6.92 (d, 8H), 6.63 (d, 8H), 3.73 ppm (s, 12H). ^{13}C NMR (150 MHz, DMSO-d_6) δ = 157.9, 138.6, 136.7, 132.6, 113.8, 55.6 ppm.

Synthesis of 4,4′,4″,4‴-(Ethene-1,1,2,2-tetrayl)tetraphenol (TPE-(OH)$_4$). BBr_3 (30 mL, 1.0 M in CH_2Cl_2) was added dropwise slowly into TPE-(OMe)$_4$ (0.9 g, 2 mmol) dissolved in dichloromethane (40 mL) under N_2 atmosphere at 0 °C. After reacting for 8 h at room temperature and then being quenched by methanol, the mixture was poured into cold water with vigorous stirring until no more precipitate was formed. After filtration and drying, a purple solid was obtained in 95% yield (0.79 g). ^{1}H NMR (600 MHz, DMSO-d_6) δ = 9.18 (s, 4H), 6.67 (d, 8H), 6.44 ppm (d, 8H). ^{13}C NMR (150 MHz, DMSO-d_6) δ = 155.8, 138.2, 135.6, 132.4, 115.0 ppm.

***N*-(4-Methyl ethylbenzenesulfonate)-*N*-ethylaniline (NBNE).** First, 5 M aqueous NaOH (3 mL) was added dropwise into a mixture of *N*-ethoxyl-*N*-ethylaniline (1.65 g, 10 mmol) and toluenesulfonyl chloride (2.00 g, 11 mmol) in tetrahydrofuran (THF, 25 mL) with violent stirring in an ice water bath. After reacting for 5 h at room temperature, the mixture was poured into ice water (30 mL) and then extracted from water with dichloromethane (50 mL). The organic layer was washed with saturated aqueous NaCl before being dried over $MgSO_4$. Purification by column chromatography (silica gel, petroleum ether/dichloromethane = 5/1) yielded the final product as a white solid in 60% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 1.09 (t, 3H), 2.41 (s, 3H), 3.29 (q, 2H), 3.56 (t, 2H), 4.13 (t, 2H), 6.54 (d, 2H), 6.66 (t, 1H), 7.16 (q, 2H,), 7.27 (d, 2H), 7.73 (d, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 146.9, 145.0, 132.8, 130.0, 129.5, 128.0, 116.5, 111.9, 67.0, 49.0, 45.6, 21.8, 12.2.

Synthesis of TPE-(NEHA)$_4$. The mixture of TPE-(OH)$_4$ (0.35g, 0.88 mmol), *N*-(4-methyl ethylbenzenesulfonate)-*N*-ethylaniline (1.28 g, 4 mmol) and KOH (0.45 g, 8 mmol) in THF (60 mL) was heated at reflux for 3 h. The mixture was poured into an excess of water and extracted from the water using dichloromethane (100 mL). The combined organic layers were dried over $MgSO_4$. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate = 5/1) yielded TPE-(NEHA)$_4$ as a bright yellow-green viscous liquid in 80% yield (0.87g). ^{1}H NMR(600 MHz, DMSO-d_6) δ = 7.09 (t, 8H), 6.76 (d, 8H), 6.64 (t, 16H), 6.53 (t, 4H), 3.96 (t, 8H), 3.57 (t, 8H), 3.35 (m, 8H), 1.03 ppm (t,12H). ^{13}C NMR (150 MHz, DMSO-d_6) δ = 157.2, 147.8, 138.7, 136.9, 132.6, 129.7, 116.1, 114.1, 111.9, 65.9, 49.4, 45.2, 12.4 ppm.

Synthesis of TPE-(AZ-CA)$_4$. 4-Aminobenzoic acid (0.082 g, 0.60 mmol) was dissolved in sodium hydroxide solution (0.8 M, 0.75 mL), and then hydrochloric acid (37%, 0.17 mL) was dropped into the above solution. The diazonium salt of 4-aminobenzoic acid was obtained by adding an aqueous solution of sodium nitrite (0.05 g, 0.72 mmol in 0.2 mL of water) into the above mixture solution. The mixture was stirred in an ice bath for 5 min to obtain a clear solution. TPE-(NEHA)$_4$ (0.1 g, 0.1 mmol) was dissolved in 3 mL DMF, and the solution was cooled to 0 °C. The diazonium salt solution was added dropwise into the DMF solution. After reacting for 12 h, the solution was poured into plenty of water, and the precipitate was collected and dried. The raw product was dissolved in THF (5 mL) and precipitated with petroleum ether (200 mL). The final product was vacuum-dried at 60 °C for 24 h and yielded in 90% (0.16g). ^{1}H NMR(600 MHz, DMSO-d_6) δ = 13.0 (s, 4H), 8.02 (d, 8H), 7.78 (d, 8H), 7.73 (d, 8H), 6.80 (d, 8H), 6.76 (d, 8H), 6.63 (d, 8H), 4.03 (s, 8H), 3.71 (s, 8H), 3.46 (d, 8H), 1.08 ppm (t, 12H). ^{13}C NMR (150 MHz, DMSO-d_6) δ = 167.4, 157.0, 155.6, 151.5, 143.0, 138.5, 137.1, 132.5, 131.3, 130.9, 126.0, 122.2, 114.3, 111.8, 65.6, 49.3, 45.7, 12.4 ppm.

Colloidal Spheres Preparation. Suitable amounts of TPE-(AZ-CA)$_4$ were dissolved in THF to yield homogeneous solutions with different initial concentrations. The solutions were prepared by being stirred at room temperature for 24 h and then filtrated with a 450 nm membrane. For obtaining the stable colloidal suspensions, an appropriate volume of deionized water (5.0 mL) was added dropwise into the THF solutions (1.0 mL) with stirring at a proper rate (1.44—36.0 mL/h). After that, an excess of water (9-fold with respect to the solution volume) was added into the suspensions to "quench" the structures formed. The suspensions were dialyzed against water for 3 days to remove THF before further measurements.

Photoinduced Shape Deformation. The samples used for the light irradiation experiments were obtained by casting the water suspensions of the colloidal spheres on copper transmission electron microscopy (TEM) grids. The colloidal spheres were carefully dried under vacuum at 30 °C for 24 h before light irradiation. A visible linearly polarized LED light (450 nm) as the light source and the intensity was about 56 mW/cm^2. The linearly polarized LED light beam was incident perpendicularly to the TEM grid surfaces containing the colloids. The light irradiation was performed for a required time period at room temperature under the ambient conditions.

RESULTS AND DISCUSSION

The synthetic route of TPE-(AZ-CA)$_4$ was given in Scheme 1. TPE-(OMe)$_4$ was prepared using the McMurry reaction from 4,4′-dihydroxybenzophenone adopting a reported synthetic route and the spectra were in good agreement with the reported values.[47,48] Then, demethylation with BBr_3 can give TPE-(OH)$_4$ smoothly and the efficient transformation from compound TPE-(OMe)$_4$ into TPE-(OH)$_4$ was confirmed by the absence of resonance peaks of methoxy protons in the ^{1}H NMR spectrum and methoxy carbon in ^{13}C NMR spectrum after the reaction (Supporting Information, Figures S1—S4). Further treatment TPE-(OH)$_4$ with NBNE in the present of KOH afforded the functional group suitable for azo coupling reaction. The final product TPE-(AZ-CA)$_4$ was prepared by the azo coupling reaction between diazonium salt of 4-aminobenzoic acid and TPE-(NEHA)$_4$ in DMF. For TPE-(NEHA)$_4$, the chemical shifts of unreacted aniline moieties appear at 6.53 ppm, attributed to the protons at *p*-positions of the amino groups. When a slightly excessive amount of diazonium salts was used, the electrophilic substitution reaction could exclusively occur at the *p*-position of the aniline moiety with high yield. This can be proved by the changes in the ^{1}H NMR spectra observed for aniline moieties of TPE-(NEHA)$_4$ after azo coupling reaction (Figure 1). The resonance (6.53 ppm) corresponding to the protons at *p*-position of amino group totally disappears. The chemical shifts of protons *ortho* and *meta* to the amino groups shift to lower magnetic field, due to the presence of electron withdrawing groups introduced by the azo coupling reaction and the increase of the conjugation length. Similarly, the corresponding changes in ^{13}C NMR are shown in Figures S5 and S6 (Supporting Information). Furthermore, the formation of the azo group was also

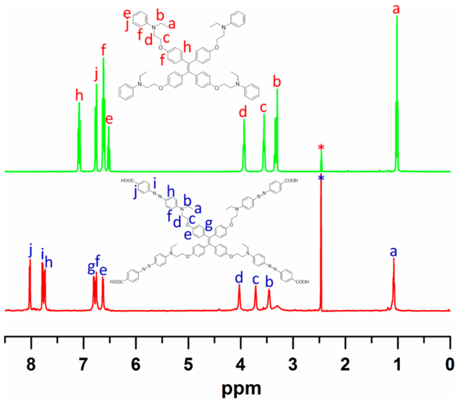


Figure 1. ^{1}H NMR spectra of TPE-(NEHA)$_4$ and TPE-(AZ-CA)$_4$ -in DMSO-d_6. Asterisks (*) indicate the solvent peak.

confirmed by the UV−vis absorption spectra (Figure 2). The desired product showed obvious absorption in the visible region (λ_{max}= 435 nm), which was the typical absorption behavior of the pseudostilbene type of azo chromophores. All the results, including ^{1}H NMR spectra, ^{13}C NMR spectra, and UV−vis spectra, indicated that the 4-arm azobenzene compound with well-defined structures was successfully prepared.

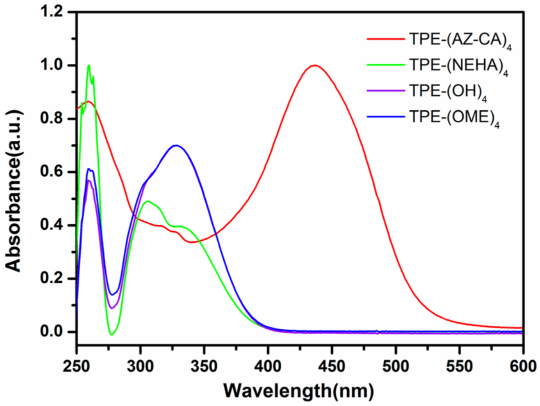


Figure 2. UV−vis spectra of TPE-(OMe)$_4$, TPE-(OH)$_4$, TPE-(NEHA)$_4$, and TPE-(AZ-CA)$_4$ in THF solution.

The colloidal spheres were prepared by hydrophobic aggregation, which was similar to the preparation of self-assembly aggregates from amphiphilic copolymers reported before.[21] Homogeneous solution of TPE-(AZ-CA)$_4$ was prepared by dissolving the azo compound in anhydrous THF, which was a good solvent for the azo compound. Deionized water was then gradually added into the above solution. As water was added to the TPE-(AZ-CA)$_4$ solution, the solubility of azo compound in the mixed solvents gradually declined, which caused the aggregation of the molecular chains to form colloidal spheres. To further understand the self-assembly process, the critical water concentration (CWC) was determined by adding water into the homogeneous solutions of TPE-(AZ-CA)$_4$ in THF, and the colloid formation processes were monitored by variation of light scattering intensity.[49] When the water content was low, the scattered light intensity was very low and nearly unchanged as the increase of the water content, which indicated that the compound was well dissolved in the mixed solvents. As the water content increased, the solubility of compound in the mixed solvents gradually declined. When the water content reached a critical value, the scattered light intensity dramatically increased. As the illustration shows (Figure 3, top), the inflection point appeared on the curve of scattered light intensity versus the water content (vol %), and at this moment, the molecules were first aggregated to form colloidal spheres. This critical value was defined as the critical water content (CWC), above which the molecule aggregation became appreciable. Figure 3 (bottom) shows the plot of the CWC versus the initial solution concentration. It can be seen that the CWC decreased as the initial solution concentration increased. To obtain well-developed aggregates, more water was continually added to the solutions to ensure that the aggregation process could be completed. After that, a large amount of water was added to the suspensions to quench the self-assembled structures. Finally, the suspensions were dialyzed against water for 3 days to remove THF from the system.

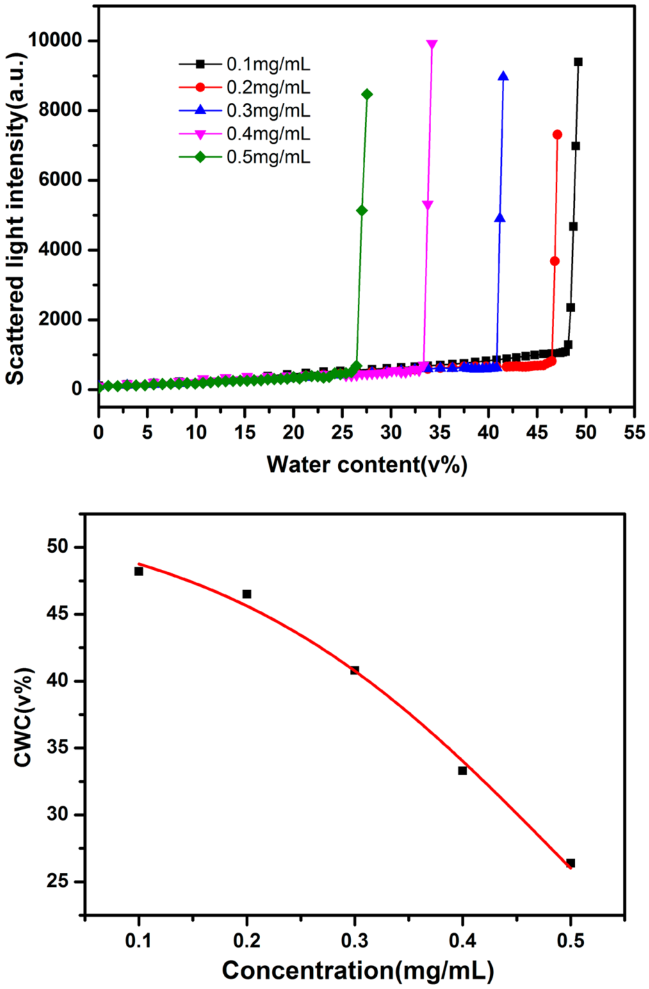


Figure 3. (Top) Plot of scattered light intensity of TPE-(AZ-CA)$_4$ H_2O/THF solution versus the water content (v%); the initial concentrations in THF were 0.1, 0.2,0.3,0.4 and 0.5 mg/mL, respectively. (Bottom) Plot of CWC vs initial solution concentration.

The average diameters of the colloidal spheres could be controlled by adjusting the initial concentration of the compound in THF and the water-adding rate. TPE-(AZ-CA)$_4$ colloidal spheres with different average particle size (in a range of 190−520 nm) were prepared by changing the water-dropping rates from 36.0 to 3.60 mL/h under the same initial concentration (0.3 mg/mL), and the corresponding typical TEM is shown in Figure 4. Experimental results indicated that the adding speed of ultrapure water had much influence on the particle size. As shown in Figure 5 (top), whether the initial concentration was high or low, the average diameters of colloidal spheres increased with the decrease in the water-dropping rate. The corresponding effect of initial concentration on particle size was also studied. There was a positive correlation between the particle size and the initial concentration in a certain scope, which can be seen in Figure 5 (bottom).

Photoinduced deformation of colloidal spheres was studied using a linearly polarized LED light (450 nm). In past reports, all the colloids made from amphiphilic polymers with push−pull azo chromophores were photoinduced deformation by visible laser beam at an appropriate wavelength. In the first

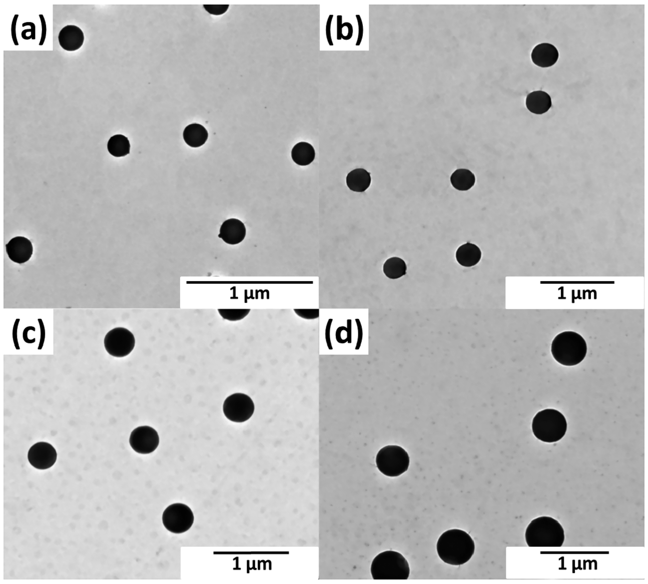


Figure 4. Typical TEM images of the TPE-(AZ-CA)$_4$ colloidal spheres with average grain size: (a) 190 nm, 36.0 mL/h; (b) 330 nm, 14.4 mL/h; (c) 400 nm, 7.2 mL/h; and (d) 520 nm, 3.6 mL/h.

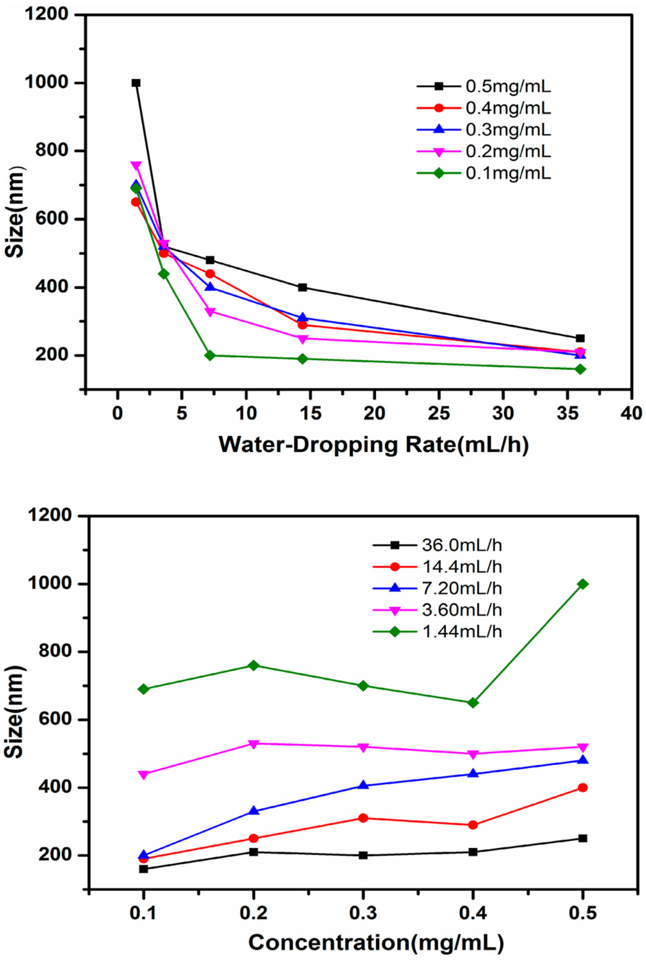


Figure 5. Diameter of the colloidal sphere as a function of (top) water-dropping rate and (bottom) initial concentration.

study, two interfering *p*-polarized Ar$^+$ laser beams were used. This interference nature of the experiment implied that the deformation might be caused by the same optical effect that results in the SRG formation. The later work showed that a linearly polarized Ar$^+$ laser single-beam with uniform intensity can also cause the shape deformation for the same type of the colloidal spheres. Laser radiation forces have been widely explored to optically move, trap, and manipulate colloidal particles. Anyway, we were somewhat surprised to observe that a linearly polarized LED light can also cause the obvious shape deformation for the azobenene colloidal spheres. Compared with optical coherent Ar$^+$ laser beam, the incoherent LED light resource can be obtained more easily and cheaply. The fabrication of large area nonspherical colloids arrays may become easier. For better understanding the photoinduced deformation properties, the "isolated" solid colloids were selectively obtained by dropping the colloids dispersions on copper TEM grids. After being carefully dried under vacuum for 24 h, the colloids on the substrates were irradiated with a linearly polarized LED light (56 mW/cm^2) for different time periods under the air-ambient condition. Shape changes of the colloids were monitored by TEM observations.

By irradiating colloids for different lengths of time (in the range of 0−30 min), we generated colloids with different deformation extents (Figure 6). The deformation behavior was characterized by average axial ratios (l/d). The average axial ratio was estimated statistically from TEM images of at least 50 colloidal particles. Figure 7 showed the relationship between the average axial ratio and irradiation time for the TPE-(AZ-CA)$_4$ colloids. The l/d ratio increased to 2.56 in less than 5 min and it reached to 4.21 finally. Compared with that reported before,[43−46] the deformation degree (l/d) of azo polymer colloids were less than 2.5 even after 30 min laser beam irradiation with an intensity about 100 mW/cm^2. The synthesized material deformation rate was also much higher than that of azo polymer colloids. This may be due to lower molecular weight and high azo chromophore loading density compared with that of azo polymer. Similar results have been observed in dendritic azo compounds, which showed much faster photoinduced SRGs inscription rate than that of azo polymers.[50] It seemed easier for the light-driven massive motion of azo compounds with small molecular weight. The results presented in this work showed that the chemical structure of the photoresponsive media could play a significant role to influence the photoinduced deformation.

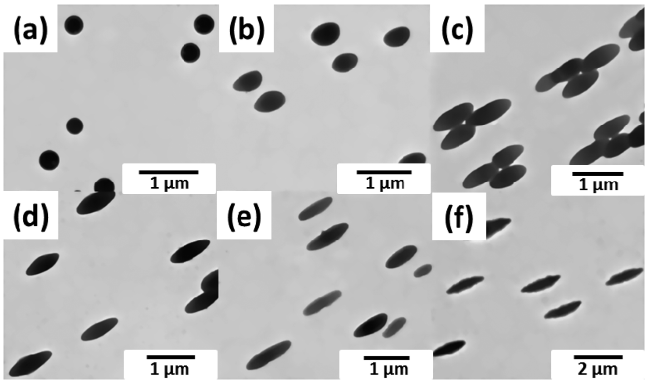


Figure 6. Typical TEM images of the 330 nm TPE-(AZ-CA)$_4$ colloidal spheres after being irradiated for different lengths of time with a linearly polarized LED light (450 nm, 56 mW/cm^2): (a) 0, (b) 2, (c) 5, (d) 10, (e) 15, and (f) 30 min.

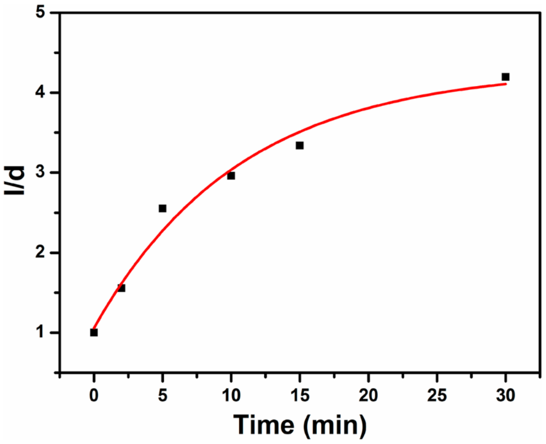


Figure 7. Relationship between the average axial ratio (l/d) of the TPE-(AZ-CA)$_4$ colloids spheres (330 nm) and irradiation time.

In addition, the photoinduced deformation behavior was also dependent on the sizes of the colloidal spheres. Figure 8 showed the typical TEM images of the TPE-(AZ-CA)$_4$ colloidal spheres with different particle size after being irradiated same time (5 min). The relationship between l/d ratio and particle size is shown in Figure S7 (Supporting Information). It can be seen that the photoinduced deformation degree of the colloids was obviously increased with the size increasing. For the larger colloids with diameter about 520 nm, the l/d ratio can reach about 4.5 in less 5 min of light irradiation. The light-driven process should be related with the light intensity variation, which could be caused by the lens-like property of the colloidal particles. This kind of microlens effect should have a correlation with the colloid size. Further investigation through both theoretical and experimental approaches are required to help us to understand the fundamental nature of such dependence.

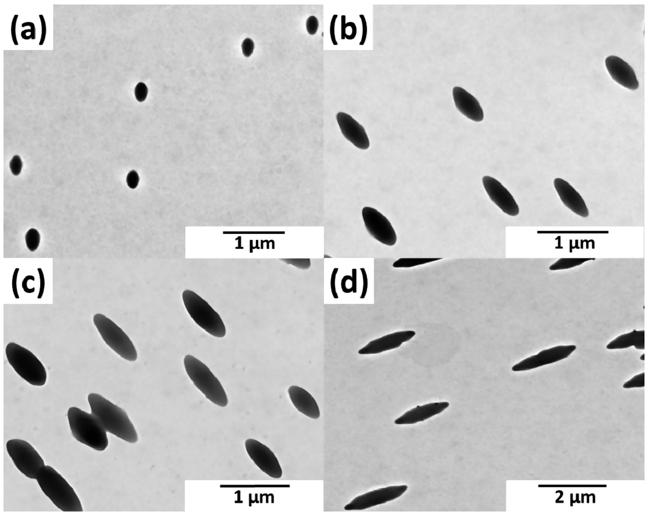


Figure 8. Typical TEM images of the TPE-(AZ-CA)$_4$ colloidal spheres after being irradiated for 5 min with a linearly polarized LED light (450 nm, 56 mW/cm^2), the initial average grain size: (a) 200 nm, (b) 330 nm, (c) 400 nm, and (d) 520 nm.

CONCLUSION

A novel 4-arm shaped amphiphilic azobenzene compound was successfully synthesized by azo coupling reaction. The materials were easily self-assembled into colloids particles in THF/H_2O dispersion medium with controllable size. The azo colloids showed very good photoresponsive properties. When irradiated with visible linearly polarized LED light (450 nm, 56 mW/cm^2), the colloids were obviously elongated in the polarization direction of the LED light. Compared with azo polymer, the synthesized material deformation rate and degree were both much higher. The l/d ratio can reach more than 4 in 5 min of light irradiation. The photoinduced deformation behavior was also dependent on the sizes of the colloidal spheres.

ASSOCIATED CONTENT

Supporting Information

^{1}H NMR and ^{13}C NMR spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b05651.

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Notes

The authors declare no competing financial interest.

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