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Electronic Supplementary Information

Reversible Janus Particle Assembly via Responsive Host-Guest Interactions

Ying Zhou, [ab] Dongsheng Wang, [a] Shilin Huang, [a] Günter Auernhammer, [a] Yujian He, [b]

Hans-Jürgen Butt [a] and Si Wu*[a]

[a]Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

[b]College of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, 19A YuQuan Road, Beijing 100049, China

*Email: wusi@mpip-mainz.mpg.de

Experimental section

Materials

12-aminododecanoic acid was purchased from Alfa Aesar. Mono-6-thiol-β-cyclodextrin (thiolated β-CD) was purchased from Zhiyuan Bio-Technology Co., Ltd. Di-tert-butyl dicarbonate (BOC), triethylamine, 4-(dimethylamino)pyridine (DMAP), poly(acrylic acid) (PAA) (M_n= ~450,000), α-cyclodextrin (α-CD) and 4-aminoazobenzene were purchased from Sigma Aldrich. Trifluoroacetic acid, N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) and (benzotriazol-1-yloxy) tripyrrolidinophosphonium hexafluorophosphate (PyBOP) were purchased from Carl Roth. Fluorescent sulphate polystyrene colloidal particles (1 μm, F-8851) were purchased from Invitrogen Inc. All the solvents (HPLC grade) were purchased from Sigma Aldrich and were used without further purification. Milli-Q water (18.2 MΩ•cm), which was provided by a Sartorius Arium 611 VF purification system, was used throughout the research.

Instruments

NMR spectra were measured on a Bruker-spectrospin spectrometer (250 MHz). Optical microscopy (HAL 100) was used to observe reversible assembly of Janus particles. A home-built laser scanning confocal microscope (LSCM)[1] was used to observe the aggregates of Janus particles. UV/Vis absorption spectra were measured on a Lambda 900 spectrometer (Perkin Elmer). SEM images were obtained on a Zeiss 1530 Gemini system. For glancing angle deposition, the particle monolayer was coated with chromium and gold using Edwards FL 400 at a pressure of 10^{-6} mbar. The angle of incidence of Au vapor flow, θ, measured from the substrate

(90º being vertical to sample), is adjusted by tilting the sample holder in the vacuum chamber. For photo-controlled assembly, LEDs with the wavelength of 365 nm and 530 nm were used (Mightex Systems).

Synthesis

The azobenzene-containing polymer pAzo was synthesized according to the route in Figure S1.

Synthesis of Compound 1. 12-aminododecanoic acid (1.000 g, 4.65 mmol), di-tert-butyldicarbonate (1.010 g, 4.65 mmol) and triethylamine (TEA) (0.775 mL, 5.58 mmol) were dissolved into 15 mL of methanol. The reaction was kept 60 ºC overnight. After removing the solvent by a rotary evaporator, the obtained solid was dissolved in ethyl acetate, and washed with HCl solution (0.25 M) twice. The white solid was then dried in a vacuum oven to obtain the product (Compound 1). Yield: 93%. ^{1}HNMR: δ=11.98 (s, 1H; -COOH), δ=6.76 (t, J=5.6 Hz, 1H; -CO-NH-), δ=2.89 (q, J=6.5 Hz, 2H; -CH2-), δ=2.19 (t, J=7.3 Hz, 2H; -CH2-), δ=1.49 (t, J=7.1 Hz, 4H; -CH2-), δ=1.38 (s, 9H; -CH3), δ=1.24 (s, 14H; -CH2-). ^{13}CNMR: δ=174.4 (-COOH), δ=155.5 (-CO-NH-), δ=77.2 (Me3-C-), δ=33.6, 29.4, 29.0, 28.9, 28.7, 28.5, 28.2, 26.2 (-CH2-), δ=24.5 (-CH3). MS: calculated 315.24, found 315.2.

Synthesis of Compound 2. Compound 1 (0.157 g, 0.50 mmol), EDC (0.096 g, 0.50 mmol) and DMAP (0.020 g, 0.16 mmol) were dissolved into 10 mL of dichloromethane (DCM) at room temperature. The solution was stirred for 20 min. Then, 4-aminoazobenzene (0.094 g, 0.50 mmol) was added into the solution. The reaction was kept at room temperature for 24 h. After removing the precipitation by filtration, the product in the filtrate was purified by chromatography on silica gel with acetone/ethyl acetate. Then, the product and CF_3COOH (3 mL) were dissolved in DCM

(10 mL). The solution was stirred for 1 h at room temperature. The resulted solution was washed by saturated Na_2CO_3 solution. The solvent was removed by a rotary evaporator. The dark red solid was further washed by water for several times to obtain the Compound 2. Yield: 60%. ^{1}HNMR (Figure S2): δ=10.28 (s, 1H; -CO-NH-), δ=7.84 (6H; Ar-H), δ=7.56 (3H; Ar-H), δ=2.75 (t, J=7.5 Hz, 2H; -CH_2-), δ=2.35 (t, J=7.5 Hz, 2H; -CH_2-CO-), δ=1.60 (t, J=7.5 Hz, 2H; -CH_2-), δ=1.51 (2H; -CH_2-), δ=1.25 (14H; -CH_2-). ^{13}CNMR (Figure S3): δ=171.81 (-CO-NH-Ar), δ=151.99, 147.30, 142.46, 130.95, 129.37, 123.63, 122.26, 119.12 (Ar-C), δ=36.47 (-CH_2-), δ= 28.86, 28.78, 28.63, 28.48, 27.08, 25.74, 24.97 (-CH_2-). MS: calculated 394.55, found 395.0

Synthesis of pAzo. PAA (0.144 g, 2.00 mmol of the repeat unit), PyBOP (0.062 g, 0.12 mmol), DMAP (0.015 g, 0.12 mmol) and Compound 2 (0.05 g, 0.1 mmol) were dissolved in DMF (20 mL). The mixture was stirred at room temperature for 24 h. The product was purified by dialysis against Milli-Q water using a dialysis membrane (cut-off molecular weight: 7000) for 3 days. The grafting density determined by ^{1}HNMR is 3% (Figure S4). ^{1}HNMR: δ=7.81, 7.58 (azobenzene groups), δ=1.0-2.0 (PAA chain).

Preparation and assembly of Janus particles

Preparing monolayer of colloidal particles. A closely-packed monolayer of 1 μm red fluorescent sulfated latex particles (F-8851, Invitrogen Inc.) was prepared by depositing the particles on a silicon wafer.[2] In brief, 200 μL water/ethanol dispersion (volume ratio 1:1) containing 1 wt% latex particles in Milli-Q water is dropped onto the water surface in a Petri dish. Then, 10 μL of sodium dodecyl sulphate (2 wt% in water) solution is added to water to reduce the surface tension and induce the particles into form a close-packed monolayer. A silicon

wafer (1.5 cm × 1.5 cm, pretreated by Piranha solution) was used to pick up a floating monolayer of particles. The particle array was dried before use.

Preparing Janus Particle 1, 2 and 3. Different Janus particles were fabricated by the glancing angle deposition (GLAD) technique according to literature.[3] In brief, the particle monolayer was coated with 1.2 nm of chromium and 25 nm of gold, using evaporation with Edwards FL 400. We chose 5º, 30º and 90º to prepare different Janus particles with different gold patch areas. After the gold vapor deposition, the gold-coated Janus particles were immersed into thiolated β-CD solution (1×10^{-3} mol/L) for 4 hours to let thiolated β-CD self-assemble onto the gold surface of the particles. After that, particles on silicon wafer were rinsed by water for several times and then redispersed in water via ultrasonication. The concentration of Janus particle is ~10^9 particles/mL.

Reversible Janus particle assembly induced by pAzo and α-CD. A suspension of Janus particles (10 μL, ~10^9 particles/mL) in Milli-Q water was dropped on a sample holder on an optical microscope. Discrete particles were dispersed in water due to the electrostatic repulsion. Aqueous solution of pAzo was prepared and the pH of the solution was adjusted to 9 by Na_2CO_3. Then, pAzo (10 μL, 0.5 mg/mL) was added into the Janus particle dispersion. The Janus particle assembly was observed by the optical microscope in situ (Movie S1-S3). To induce disassembly of the superstructures of Janus particles, α-CD solution (10 μL, 10^{-2} mol/L) was added into the dispersion of aggregates of Janus particles. The disassembly process was observed by the optical microscope in situ (Movie S4-S6).

Photo-controlled reversible Janus particle assembly. Small clusters of Janus particle 2 were prepared by adding pAzo (200 μL, 0.5 mg/mL) into dispersion of discrete Janus Particle 2 (200

μL, ~10^9 particles/mL). To disassemble the clusters of Janus particles, the dispersion was irradiated by UV light (365 nm, 25 mW/cm^2, 15 min). To reassembly the Janus particles, the dispersion was irradiated visible light (530 nm, 30 mW/cm^2, 15 min). The short wavelength light (λ < 560 nm) of the optical microscope was filtered during the imaging process. We tried one cycle for photo-controlled assembly.

Calculation of the grafting ratio of thiolated β-CD on Au patches of Janus particles

Calculation method 1 (Using the measured data from thiolated β-CD on flat Au films[4])

The surface concentration of thiolated β-CD on flat Au films is 0.7 × 10^{-10} mol/cm^2.[4] We assume the surface concentration of thiolated β-CD on Au patches of Janus particles is the same.

The areas of Au patches on every Particle 1, Particle 2 and Particle 3 are 1.57 × 10^6 nm^2, 7.85 × 10^5 nm^2, and 2.2 × 10^5 nm^2, respectively.

So, every Particle 1, Particle 2 and Particle 3 contain about 6.6 × 10^5, 3.3 × 10^5, 0.92 × 10^5 β-CD, respectively.

Calculation method 2 (Using the measured data from thiolated β-CD on Au nanoparticles[5])

Every Au nanoparticle (diameter ~8 nm) can graft 50 β-CD.[5] We assume the grafting density of β-CD on Au patches of Janus particles is the same as that on Au nanoparticles.

On Au nanoparticles (diameter 8 nm), every β-CD occupies about 4 nm^2.

The areas of Au patches on every Particle 1, Particle 2 and Particle 3 are 1.57 × 10^6 nm^2, 7.85 × 10^5 nm^2, and 2.2 × 10^5 nm^2, respectively.

So, every Particle 1, Particle 2 and Particle 3 contain about 4×10^5, 2×10^5, 0.55×10^5 β-CD, respectively.

The calculated results from the above two methods are identical. So, we believe the calculated results are reliable.

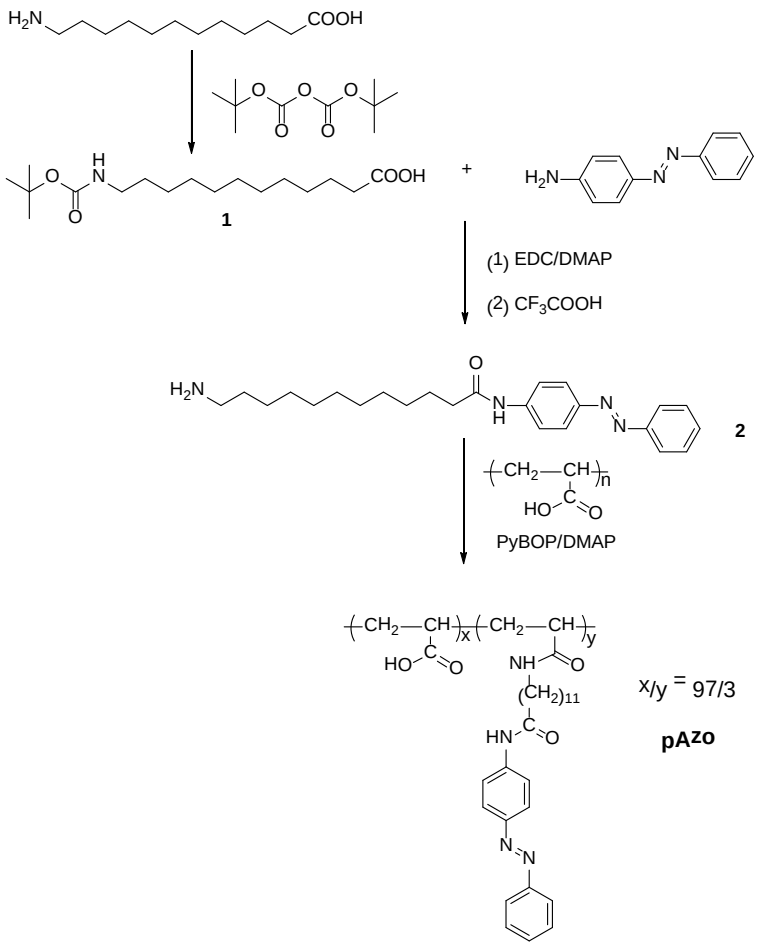

Figure S1. Route for synthesis of pAzo.

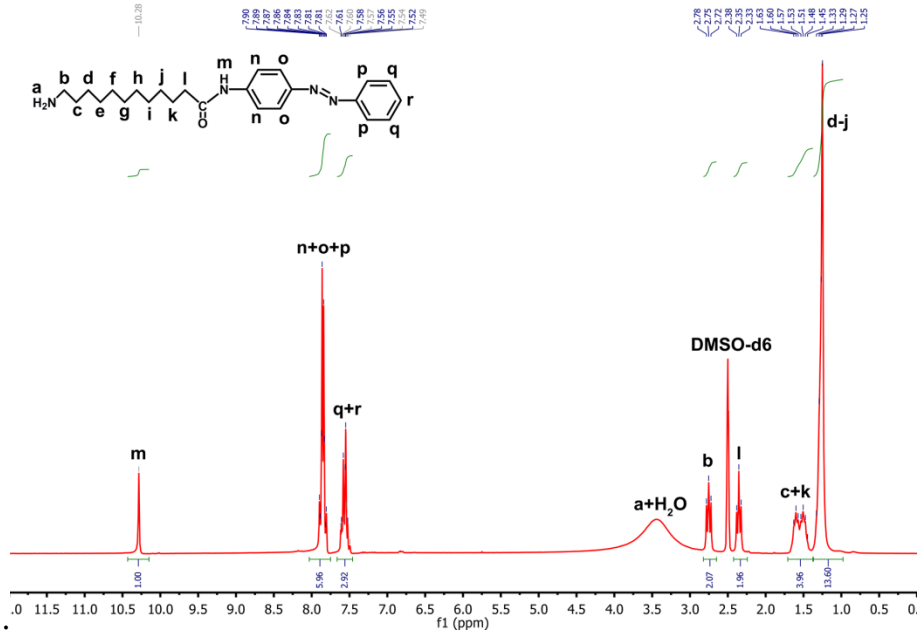

Figure S2. [1]HNMR spectrum of the Azo compound 1 in DMSO-d6.

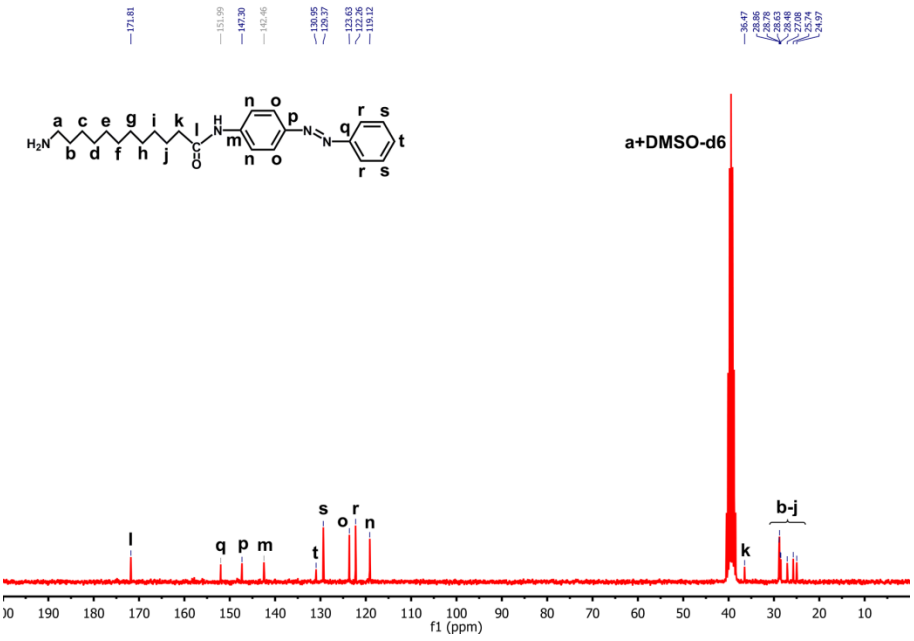

Figure S3. [13]CNMR spectrum of the Azo compound 1 in DMSO-d6.

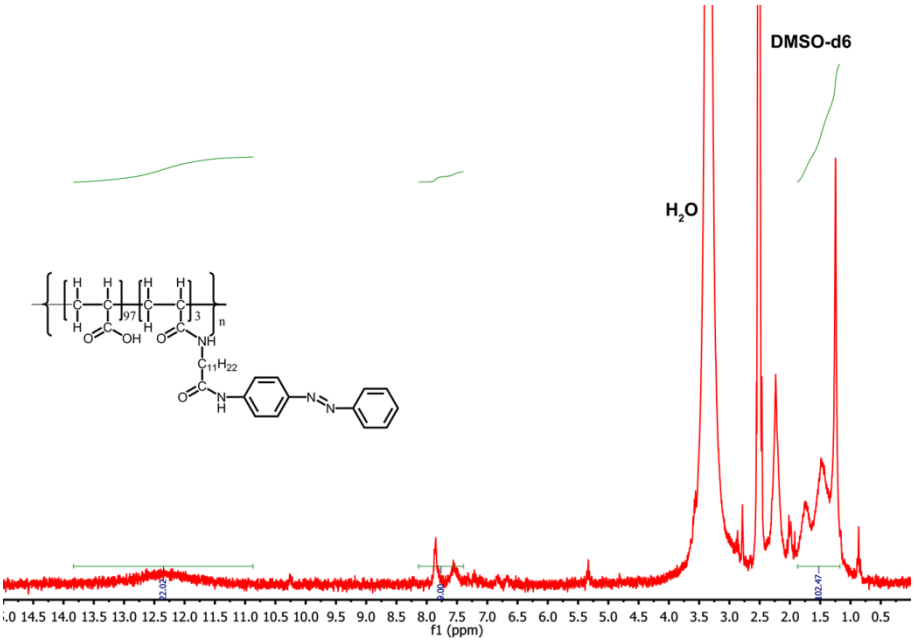

Figure S4. [1]HNMR spectrum of pAzo in DMSO-d6.

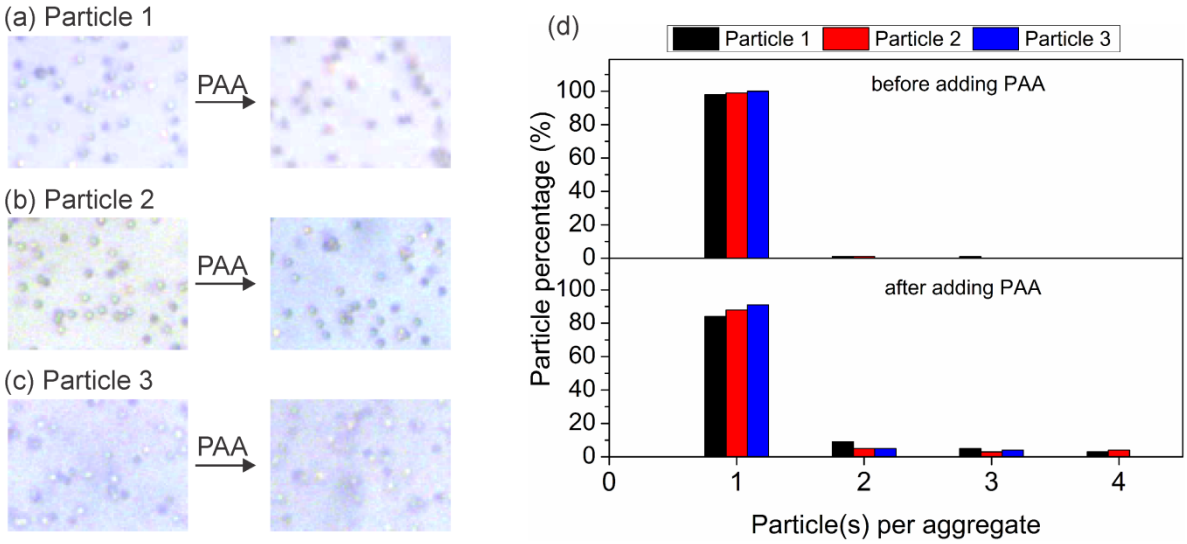

Figure S5. Optical microscopy images before and after adding aqueous solution of PAA (0.5 mg/mL, 10 μL) into the Janus particle dispersions (~10^9 particles/mL, 10 μL): (a) Particle 1, (b) Particle 2, and (c) Particle 3. (d) Number distribution of Janus particle aggregates consisting of different numbers of particles before and after adding PAA. The diameter of the particles is 1 μm. The statistical results are obtained from ~400 particles. The concentrations of substances and the experimental time of this control experiment are the same with the experiment of pAzo-induced assembly in Figure 2 in the main text. This control experiment indicates that the host-guest interaction between β-CD and azobenzene is the driving force for Janus particle assembly.

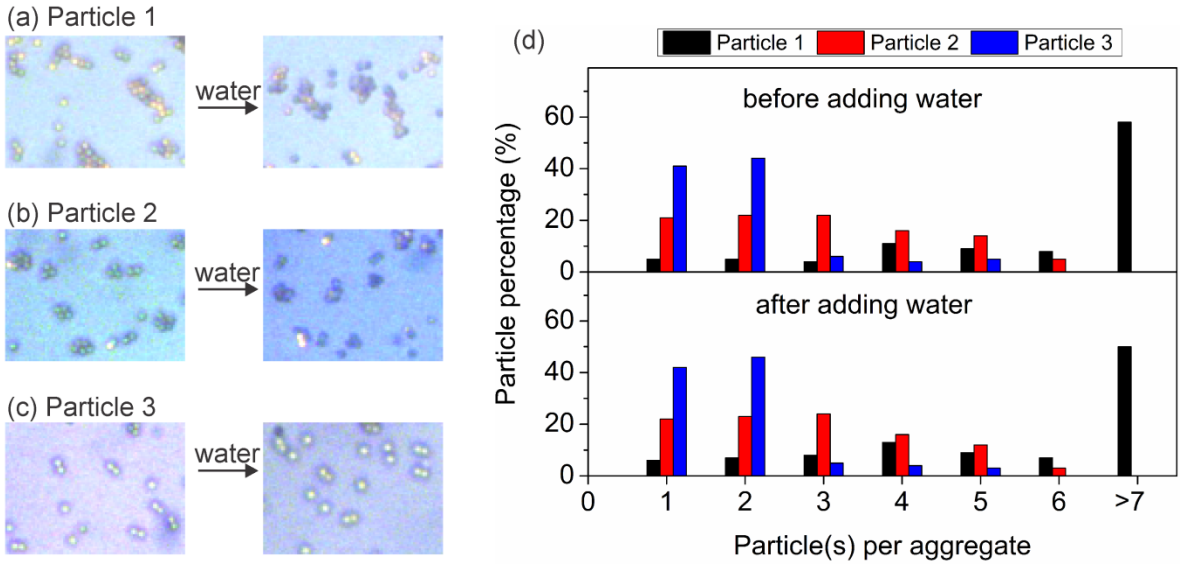

Figure S6. Optical microscopy images before and after adding water (10 μL) into the dispersions of aggregates of Janus particles and pAzo (~10^9 particles/mL, 10 μL): (a) Particle 1, (b) Particle 2, and (c) Particle 3. (d) Number distribution of Janus particle aggregates consisting of different numbers of particles before and after adding water. The diameter of the particles is 1 μm. The statistical results are obtained from ~400 particles. The concentrations of substances and the experimental time of this control experiment are the same with the experiment of α-CD-induced disassembly in Figure 2 in the main text. This control experiment confirms that α-CD but not water triggers the disassembly.

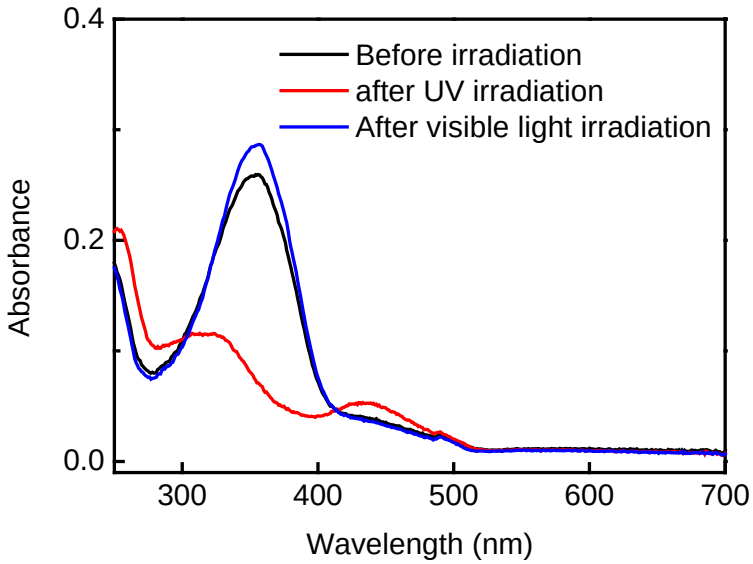

Figure S7. UV–vis absorption spectra of aqueous solution of pAzo before irradiation, after UV irradiation (365 nm, 25 mW/cm^2, 5 min), and after visible light irradiation (530 nm, 30 mW/cm^2, 5 min). The strong band at ~360 nm is the π-π* absorption band of the trans isomer. The weak band at ~450 nm is the n-π* absorption band of the cis isomer.

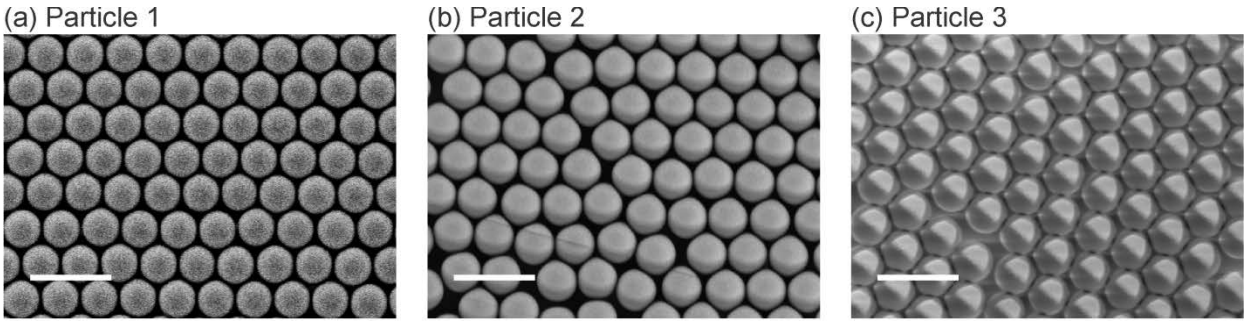

Figure S8. SEM images of arrays of Janus particles on a substrate. The scale bar is 2 μm. Most particles form hexagonally packed arrays with little defects. The areas of gold patches on the particles were observed by SEM either using the array or using isolated particles. The statistical results from ~200 particles show that the gold patches for Particle 1, 2, and 3 were 50±5%, 25±2%, and 7±1%, respectively. This result is in accordance with the results in literature.[3] The shape of the gold patches depends the monolayer orientation in the domains.[3] Gold patches with sharp corners is caused by shadowing by neighboring particles.[3]

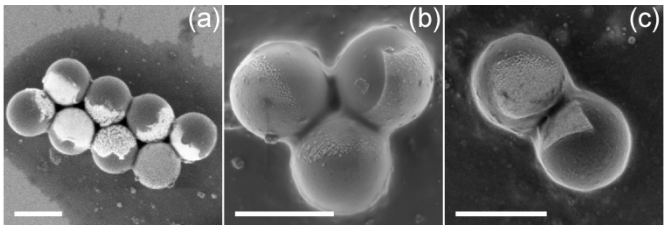

Figure S9. SEM images of aggregates of Janus particles: (a) aggregates of Particle 1, (b) aggregates of Particle 2, (c) aggregates of Particle 3. The scale bar is 1 μm.

SEM images were obtained on dried samples. The drying process may deform the morphology of assembled structures.

Movies

Movie 1: Assembly of Janus Particle 1 by adding pAzo.

Movie 2: Assembly of Janus Particle 2 by adding pAzo.

Movie 3: Assembly of Janus Particle 3 by adding pAzo.

Movie 4: Disassembly of aggregates of Janus Particle 1 and pAzo by adding α-CD.

Movie 5: Disassembly of aggregates of Janus Particle 2 and pAzo by adding α-CD.

Movie 6: Disassembly of aggregates of Janus Particle 3 and pAzo by adding α-CD.

The speed of all movies is 3 times of the real speed.

References

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