Electronic Supplementary Information (ESI)

Photo-Switching of Blunt-End Stacking between DNA Strands Immobilized on Gold Nanoparticles

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Contents

S-1. Experimental details

Materials

Chemically synthesized DNAs (OPC-purified grade) were purchased from Tsukuba Oligo Service (Ibaraki, Japan). The DNA concentration was determined by measuring the absorbance at 260 nm. The molar absorbance coefficient of the Azo-TN unit incorporated in the oligonucleotide strand was regarded as 4,100 $M^{-1}\cdot cm^{-1}$ according to a previous report.[S1] Colloidal dispersions of gold nanoparticles (AuNPs) with a diameter of 15 nm were obtained from BBI Solutions (Cardiff, UK). Other chemicals were commercially available and used without further purification. Ultra-pure water (>18.1 MΩ·cm) purified with a MilliQ pure water purification system (Millipore, Billerica, MA) was used for all the experiments.

Preparation of single-stranded DNA-immobilized gold nanoparticles (ssDNA-AuNPs)

5'-Mercaptohexyl terminated single-stranded DNA (ssDNA-SH) was immobilized on the surface of AuNPs as described previously.[S2] Briefly, ssDNA-SH (5 nmol) was mixed with 1.0 mL of 15 nm AuNP dispersion (1.4×10^{12} particles·mL^{-1}) and incubated overnight at 50°C. The dispersion medium was then exchanged for sodium phosphate buffer (10 mM, pH 7.4) containing 100 mM NaCl by adding the corresponding stock solutions into the dispersion medium to reduce the electrostatic repulsion and facilitate the immobilization of ssDNA-SH strands on the AuNP surface. The mixture was further incubated at 50°C for 48 h. To remove the excess ssDNA-SH, the mixture was centrifuged at 15,000*g* for 30 min, and the supernatant was replaced with 1.0 mL of sodium phosphate buffer (10 mM, pH 7.4). The precipitate was re-dispersed by vortex mixing for several seconds. This process was repeated at least three times. Finally, the precipitate was dispersed into sodium phosphate buffer (10 mM, pH 7.4) to make a stock solution (ssDNA-AuNPs). The amount of ssDNA-SH strands immobilized on the AuNP surface was estimated as approx. 170 strands/particle by a DTT displacement assay.[S3]

Preparation of Azo-dsDNA-AuNPs

The ssDNA-AuNPs dispersion was mixed with Azo-TN-incorporated complementary ssDNA (comp-Azo) to form double-stranded DNAs on the surface of AuNPs. The concentrations of NaCl, sodium phosphate buffer (pH 7.4), and Tween 20 were adjusted to the desired degrees by adding the corresponding stock solutions into the dispersion medium. The final concentrations of ssDNA-AuNPs and comp-Azo were 2.1 nM and 0.5 μM, respectively. After the 30-min incubation at 25°C in the dark, the resulting Azo-dsDNA-AuNPs were used for the following experiments.

Characterizations

UV-vis extinction spectra and photographs of the sample solution were obtained with a Cary 50 UV-

vis spectrophotometer (Varian, Palo Alto, CA) and a FINEPIX Z digital camera (FUJIFILM, Tokyo), respectively. The size distribution of Azo-dsDNA-AuNPs was assessed by dynamic light scattering (DLS) measurements with a Zeta-sizer Nano ZS (Malvern Panalytical, Malvern, UK) equipped with a 4-mW He-Ne laser (633 nm).

Light irradiation experiments

Light irradiation was conducted using a 300 W Xenon Lamp (MAX-302, Asahi Spectra Co., Tokyo). UV light (centre wavelength: 350 nm, fwhm of 10 nm) and visible light (centre wavelength: 450 nm, fwhm of 10 nm) were collected through appropriate bandpass filters. A 365-nm LED lamp (centre wavelength: 370 nm, fwhm of 11 nm; Asahi Spectra) and a 450-nm LED lamp (centre wavelength: 450 nm, fwhm of 24 nm; Asahi Spectra), each equipped with an optical lens, were also used for the short-time irradiation of UV and visible light. The irradiation light intensity was measured by a digital UV intensity meter (UIT201; USHIO, Tokyo). The sample solution was placed in a 10-mm optical length semi-micro PMMA cuvette. The sample temperature was kept at 25°C using a Peltier-type temperature controller unit (Varian).

References

S1. H. Asanuma, X Liang, H. Nishioka, D. Matsunaga, M. Liu, M. Komiyama, *Nat. Protoc.,* 2007, **2**, 203.

S2. (a) N. Kanayama, T. Takarada, M. Maeda, *Chem. Commun.,* 2011, **47**, 2077; (b) N. Kanayama, T. Takarada, M. Fujita, M. Maeda, *Chem. – Eur. J.,* 2013, **19**, 10794.

S3. S. J. Hurst, A. K. R. Lytton-Jean, C. A. Mirkin, *Anal. Chem.,* 2006, **78**, 8313.

S-2. Base sequences of the oligonucleotides

Table S1. Base sequences of the oligonucleotides (Z denotes Azo-TN).

code	sequence (5' to 3')
ssDNA-SH	HS-$(CH_2)_6$- TACGCCACCAGCTCTA
T-ssDNA-SH	HS-$(CH_2)_6$- TACGCCACCAGCTCTT
comp-Azo	TZAGAGCTGGTGGCGTA

S-3. Dispersion behaviour of ssDNA-AuNPs

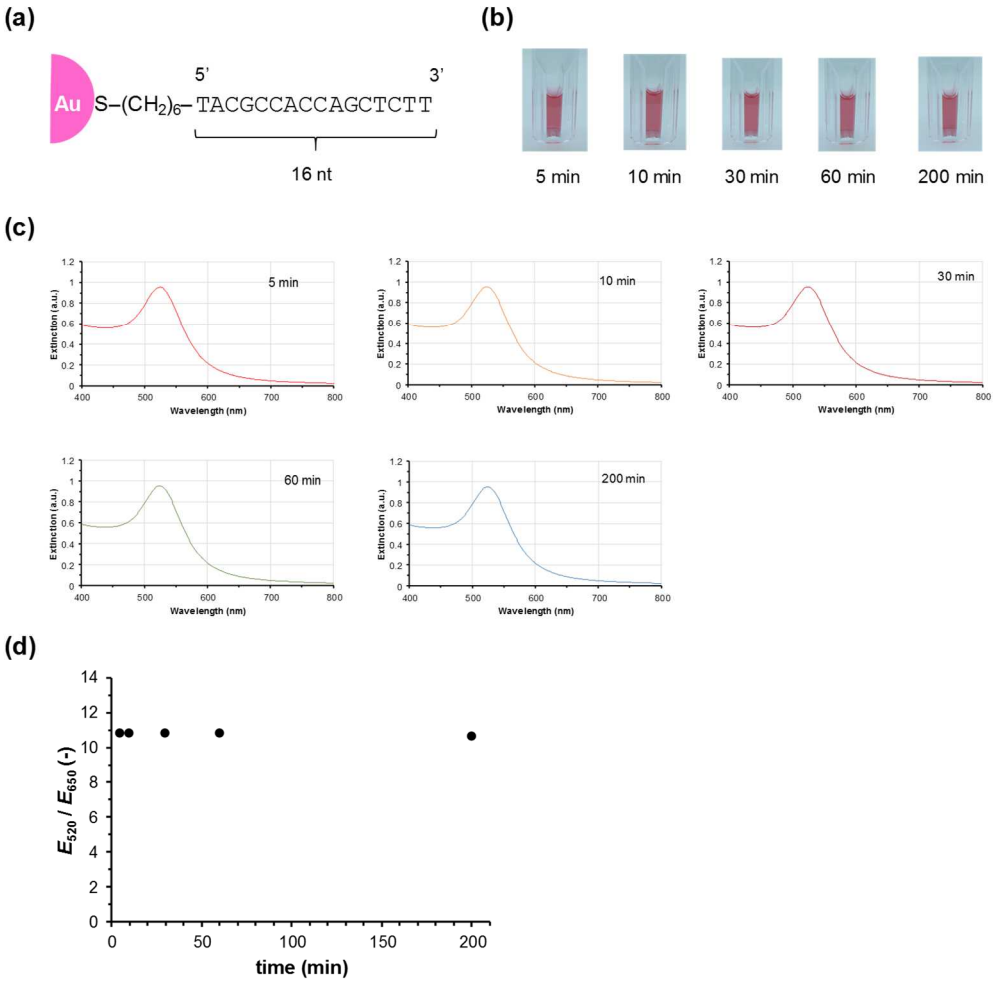


Fig. S1 (a) The base sequence of ssDNA-AuNP. (b) Photographs, (c) UV-vis extinction spectra, and (d) time course of the extinction ratio at 520 nm and 650 nm (E_{520}/E_{650}) of the ssDNA-AuNP dispersion in 2.5 mM sodium phosphate buffer (pH 7.4) containing 1.0 M NaCl and 0.01 wt% Tween 20. All measurements were conducted at room temperature. The dispersion of ssDNA-AuNPs showed no significant change in either colour or the UV-vis extinction spectrum, even in the presence of 1.0 M NaCl.

S-4. Dispersion behaviour of T-Azo-dsDNA-AuNPs with a terminal mismatch

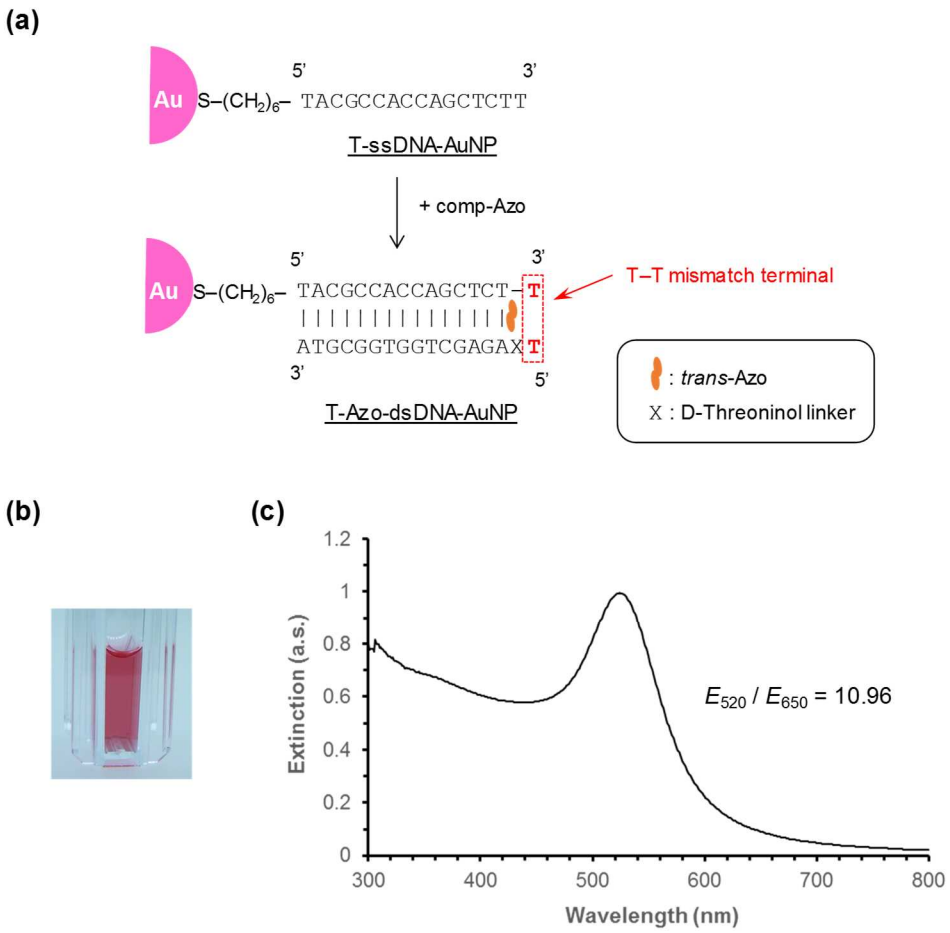


Fig. S2 (a) The base sequences of T-ssDNA-AuNP and T-Azo-dsDNA-AuNP. Note that T-Azo-dsDNA-AuNP has T–T mismatch terminals on the surface. (b) Photograph and (c) UV-vis extinction spectrum of T-Azo-dsDNA-AuNP solution in 2.5 mM sodium phosphate buffer (pH 7.4) containing 1.0 M NaCl and 0.01 wt% Tween 20 after 30-min incubation at 25°C. Unlike the Azo-dsDNA-AuNPs, the dispersion of T-Azo-dsDNA-AuNPs showed no significant change in colour or the UV-vis extinction spectrum even in the presence of 1.0 M NaCl. The higher E_{520}/E_{650} value reflects the well-dispersed state of T-Azo-dsDNA-AuNPs.

S-5. Dispersion stability of Azo-dsDNA-AuNPs in the presence of 100 mM NaCl

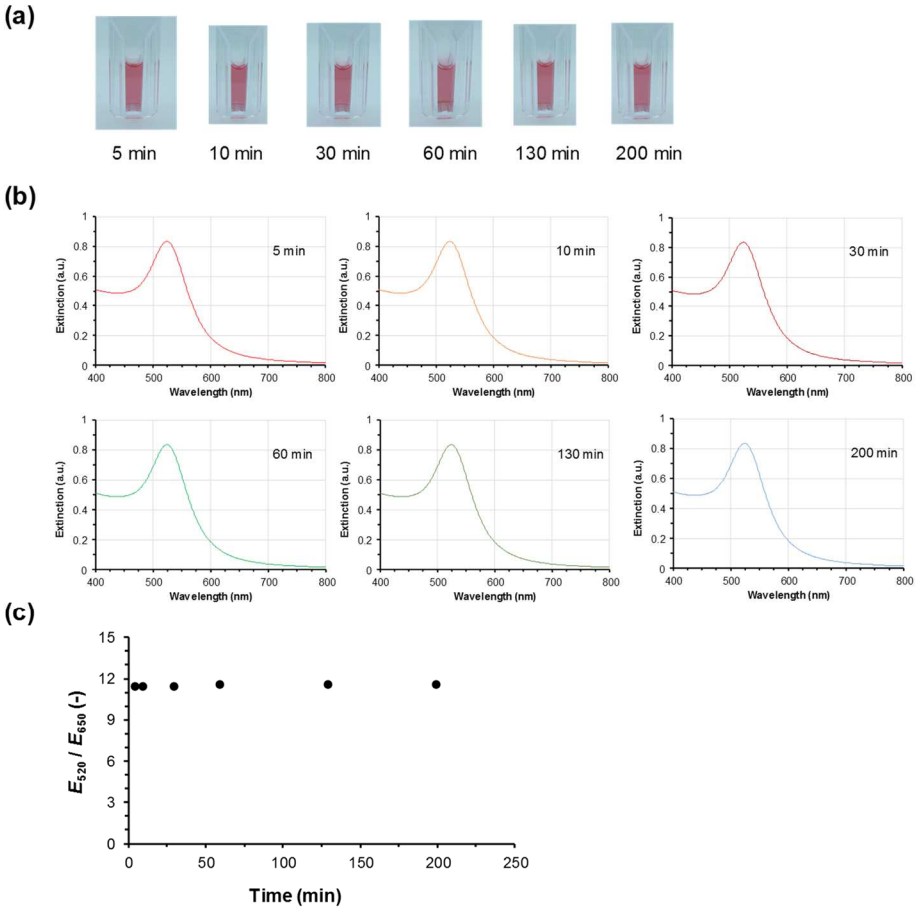


Fig. S3 (a) Photographs, (b) UV-vis extinction spectra, and (c) time course of the E_{520}/E_{650} value of Azo-dsDNA-AuNPs solution in 2.5 mM sodium phosphate buffer (pH 7.4) containing 100 mM NaCl and 0.01 wt% Tween 20. The solution temperature was kept at 25°C during the experiment. The dispersion of Azo-dsDNA-AuNPs showed no significant change in colour or the UV-vis extinction spectrum (the E_{520}/E_{650} value) in the presence of 100 mM NaCl.

S-6. Changes in the size distribution of Azo-dsDNA-AuNPs by UV light irradiation

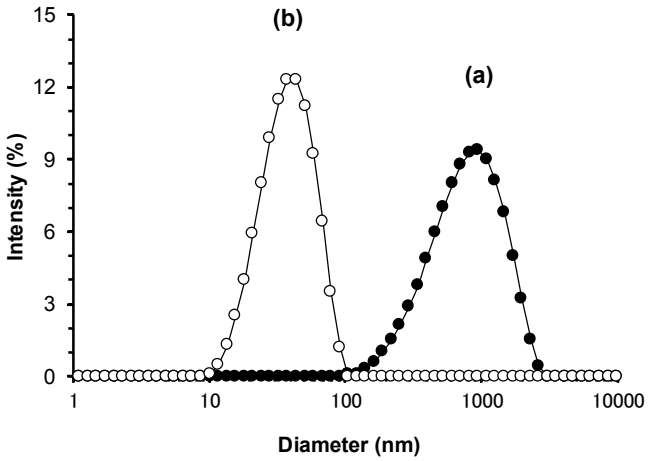


Fig. S4 Changes in the size distribution of Azo-dsDNA-AuNPs (a) before and (b) after 10-min UV light irradiation. Conditions: 2.5 mM sodium phosphate buffer (pH 7.4) containing 1.0 M NaCl and 0.01 wt% Tween 20; UV light: centre wavelength = 350 nm, 20 $mW \cdot cm^{-2}$; temperature: 25°C. Aggregates of Azo-dsDNA-AuNPs disappeared after the UV light irradiation for 10 min.

S-7. Changes in the size distribution of Azo-dsDNA-AuNPs by visible light irradiation

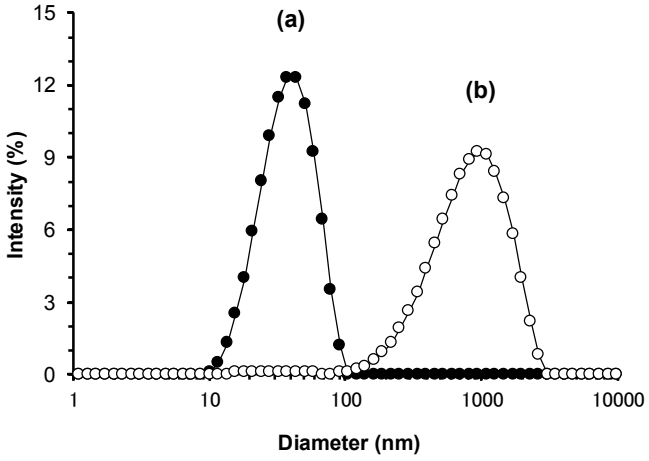


Fig. S5 Changes in the size distribution of Azo-dsDNA-AuNPs (a) before and (b) after visible light irradiation for 10 min. Conditions: 2.5 mM sodium phosphate buffer (pH 7.4) containing 1.0 M NaCl and 0.01 wt% Tween 20; visible light: centre wavelength = 450 nm, 10 $mW \cdot cm^{-2}$; temperature: 25°C. Azo-dsDNA-AuNPs formed aggregates after the visible light irradiation for 10 min.

S-8. Changes in the UV-vis absorption spectra of Azo-dsDNA solution in response to UV and visible light irradiation

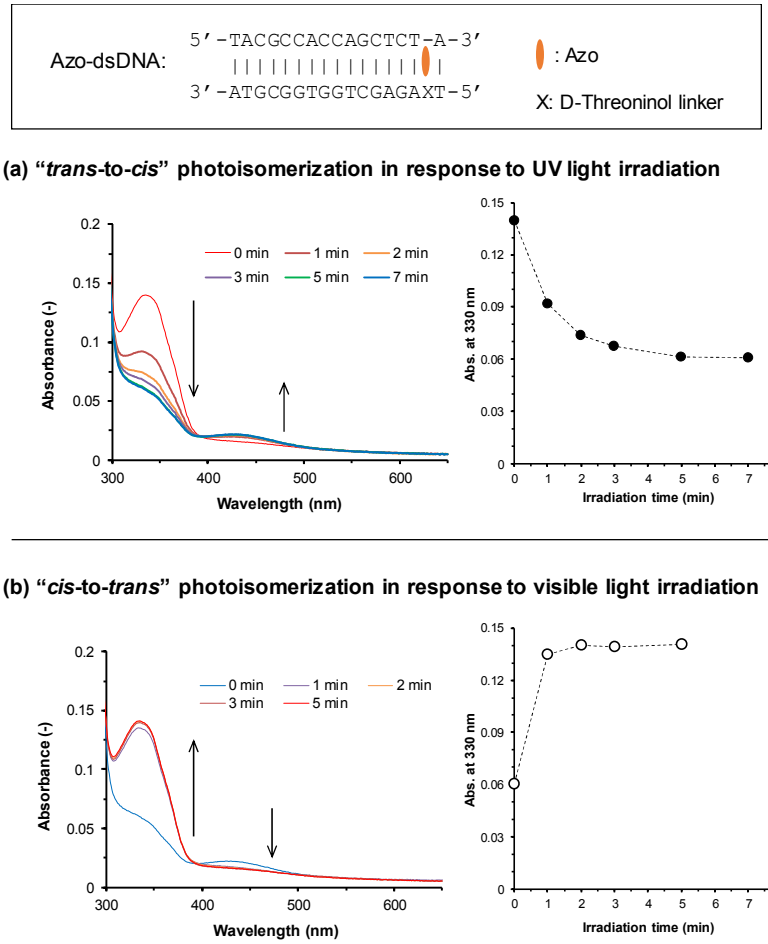
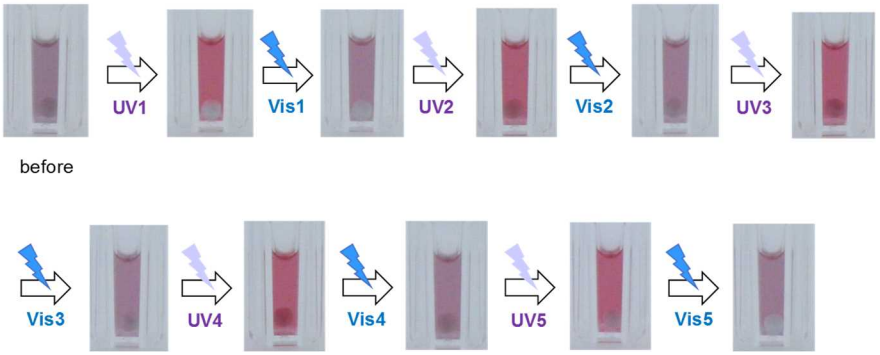


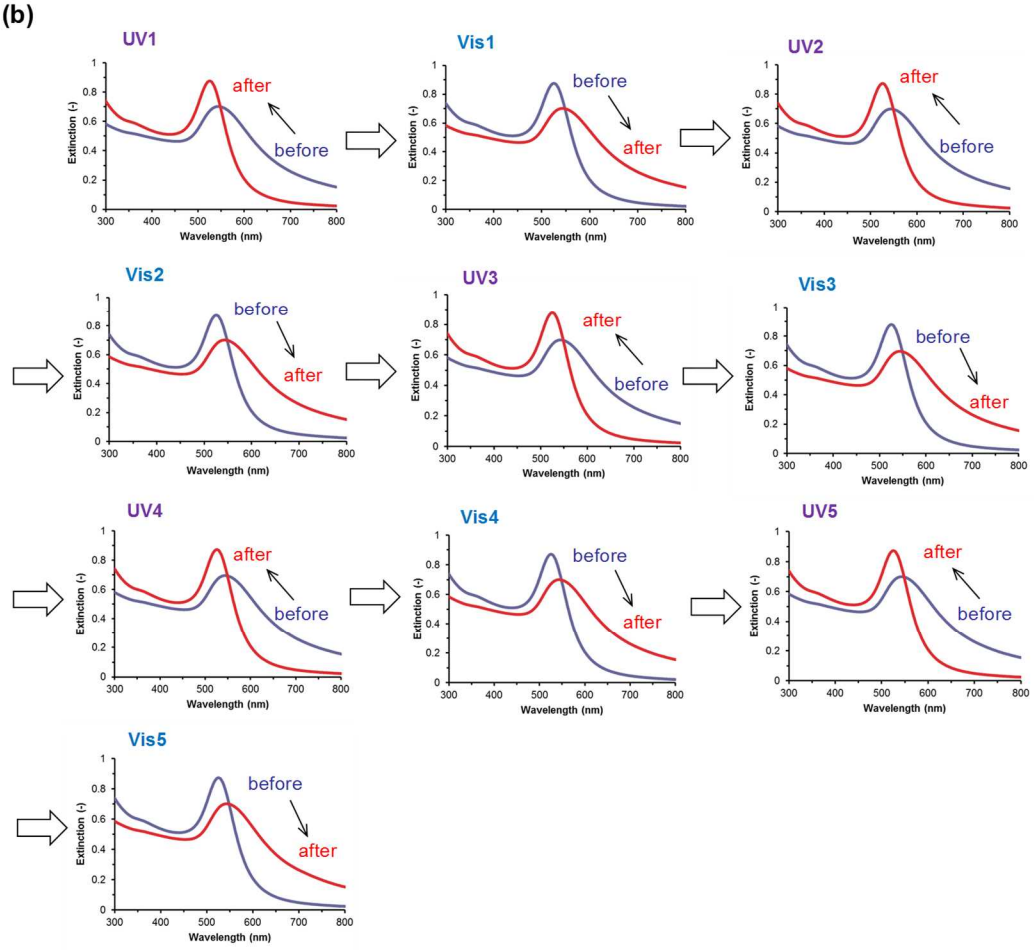
Fig. S6 Changes in the UV-vis absorption spectra and the corresponding changes in the absorbance at 330 nm of the Azo-dsDNA solution induced by (a) the *trans*-to-*cis* isomerization of Azo moiety in response to the UV light irradiation and (b) the *cis*-to-*trans* isomerization of Azo moiety in response to the visible light irradiation. Conditions: [Azo-dsDNA] = 5.0 μM in 2.5 mM sodium phosphate buffer (pH 7.4) containing 1.0 M NaCl; UV light: centre wavelength = 350 nm, 20 mW·cm^{-1}; visible light: centre wavelength = 450 nm, 10 mW·cm^{-1}; temperature: 25ºC.

S-9. Reversible transition between the aggregation and dispersion of Azo-dsDNA-AuNPs by alternating UV and visible light irradiation for 10 min each

(a)



(b)



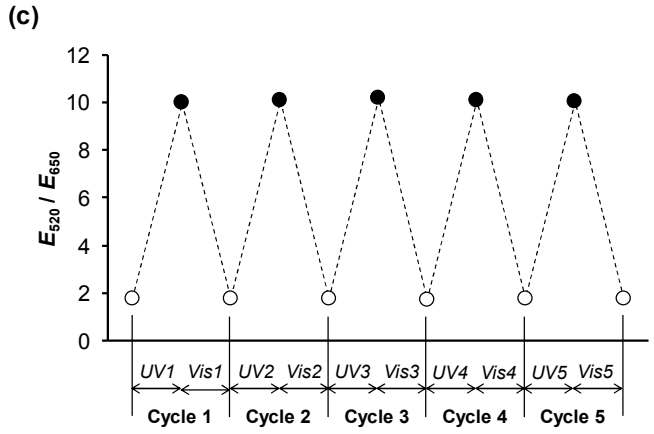
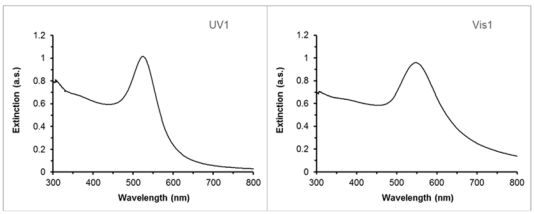


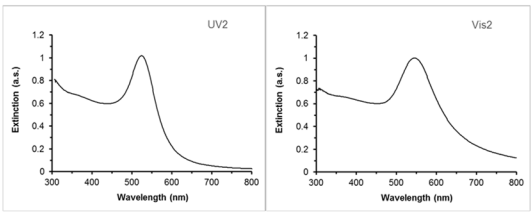
Fig. S7 Changes in (a) the solution colour, (b) the UV-vis extinction spectra and (c) the E_{520}/E_{650} value of Azo-dsDNA-AuNP solution by alternating UV and visible light irradiation for 10 min each. Conditions: 2.5 mM sodium phosphate buffer (pH 7.4) containing 1.0 M NaCl and 0.01 wt% Tween 20; UV light: centre wavelength = 350 nm, 20 mW·cm^{-2}; visible light: centre wavelength = 450 nm, 10 mW·cm^{-2}; temperature: 25°C. Note that negligible variation in the change of the E_{520}/E_{650} value was observed after five cycles of irradiation, revealing the high reversibility of the photo-responsive transition between aggregation and dispersion under these conditions.

S-10. Changes in the UV-vis extinction spectra of Azo-dsDNA-AuNP solution by alternating UV and visible light irradiation for 2 min each

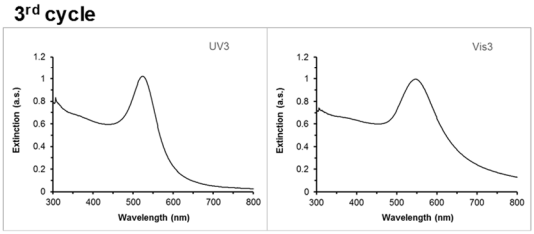
1st cycle



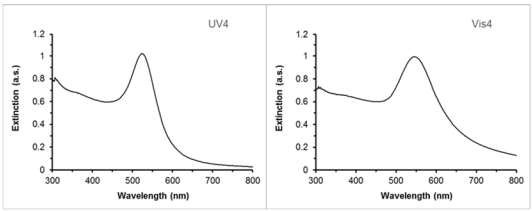
2nd cycle



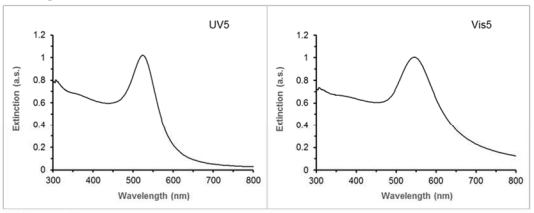
3rd cycle



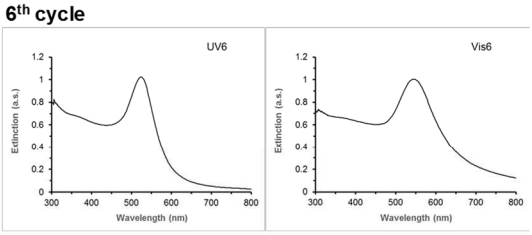
4th cycle



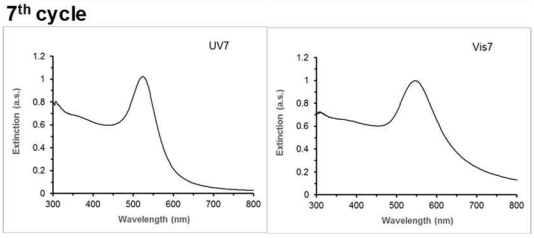
5th cycle



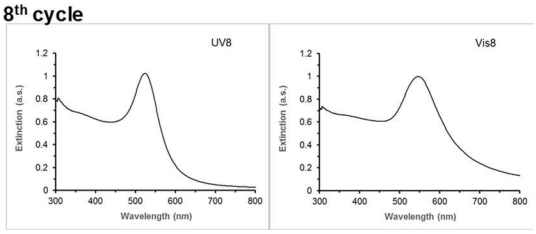
6th cycle



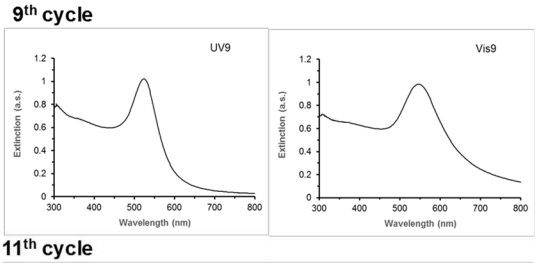
7th cycle



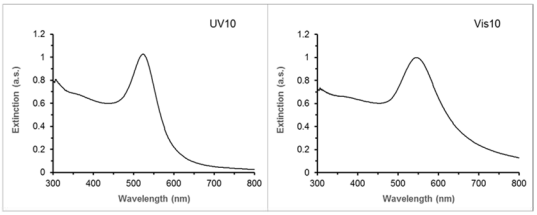
8th cycle



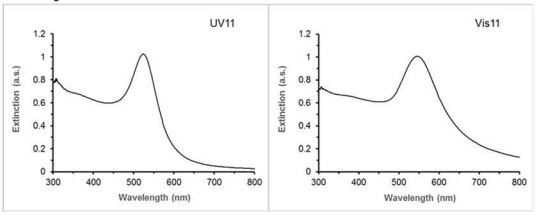
9th cycle



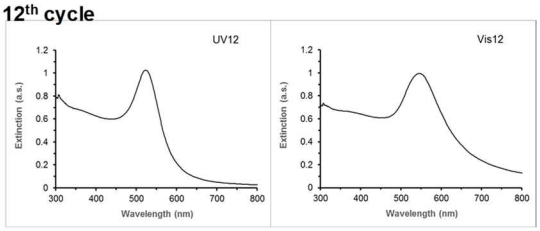
10th cycle



11th cycle



12th cycle



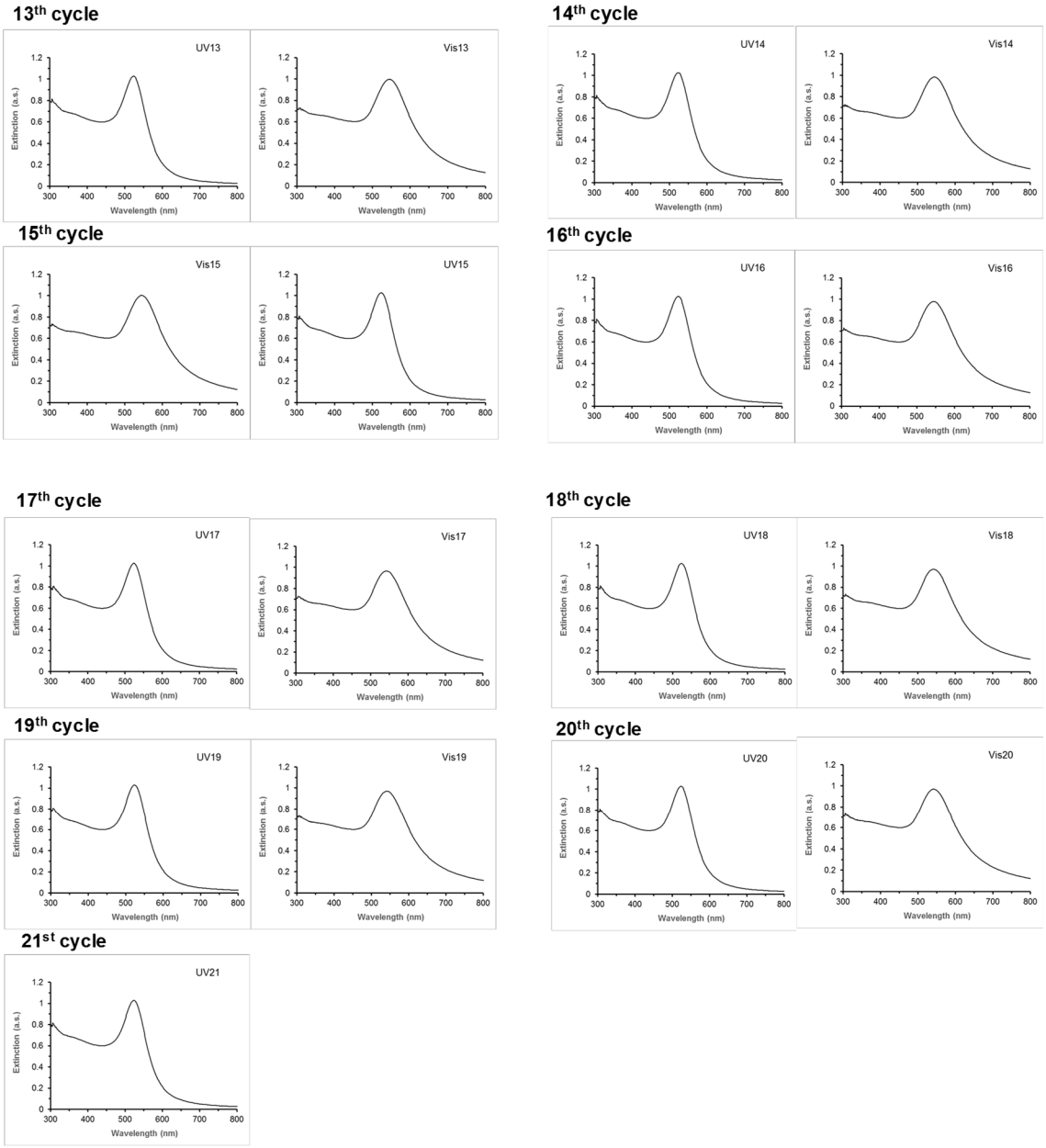


Fig. S8 Changes in the UV-vis extinction spectra of Azo-dsDNA-AuNP solution in response to alternating UV and visible light irradiation for 2 min each. Conditions: 2.5 mM sodium phosphate buffer (pH 7.4) containing 1.0 M NaCl and 0.01 wt% Tween 20; UV light: centre wavelength: 370 nm, 300 mW·cm^{-2}; visible light: centre wavelength: 450 nm, 100 mW·cm^{-2}; temperature: 25^{o}C.