Supplementary Information

Plasmonic enhancement of gold nanoparticles on photocycloreversion reaction of diarylethene derivatives depending on particle size, distance from the particle surface, and irradiation wavelength

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Table S1. Polymerization conditions and characterization of poly(DE) homopolymers.[a]

Monomer	[Monomer] / mol dm^{-3}	[PEDB] / mol dm^{-3}	Conv / %	M_n[b]	M_w/M_n[b]	n[c]
1a	2.9	0.045	63	14700	1.09	41
2a	2.9	0.045	81	16600	1.06	53
3a	2.9	0.045	82	18000	1.07	54
4a	2.9	0.045	82	17800	1.09	54

[a][ATMP] = 1.0×10^{-3} mol dm^{-3}, in toluene for 60 h at 100 °C. [b]Determined by GPC. [c]Determined as the theoretical value (n = [Monomer]/[PEDB] × conv.).

Table S2. Polymerization conditions and characterization of the macro-RAFT agent and poly(**2a**)-*block*-poly(St).[a]

| Monomer	[Monomer] / mol dm^{-3}	RAFT agent	[RAFT] / mol dm^{-3}	M_n[b]	M_w/M_n[b]	n[c]	m[d]
2a	2.9	PEDB	0.075	10900	1.07	25	-
St	3.0	poly(**2a**)	0.12	11800	1.07	25	9
St	3.0	poly(**2a**)	0.030	17100	1.10	25	56

[a][ATMP] = 1.0×10^{-3} mol dm^{-3}, in toluene for 60 h at 100 °C. [b]Determined by GPC. [c]Determined as the theoretical value (n = [Monomer]/[PEDB] × conv.). [d]Determined by ^{1}H NMR spectroscopy.

Table S3. Molar absorption coefficient of the closed-ring form (ε) and photocycloreversion quantum yield ($\Phi_{c \to o}$) of Au-free poly(DE) in toluene, and enhancement factor (E) determined by one-component fitting for Au-poly(DE) in THF/water upon irradiation at various wavelengths.

| Sample	Wavelength /nm	Au-free poly(DE)		Au-poly(DE)	
				One-component fitting	
		ε /mol^{-1}dm^{3}cm^{-1}	$\Phi_{c \to o}$	E	$R^{2\,a}$
Au-poly(**1a**)	700	8900	0.00025	1.81	0.995
Au-poly(**1a**)	675	15300	0.00026	1.47	0.999
Au-poly(**1a**)	650	19900	0.00028	1.25	0.999
Au-poly(**1a**)	625	22300	0.00032	1.16	0.995
Au-poly(**1a**)	600	22300	0.00033	1.57	0.997
Au-poly(**2a**)	650	9500	0.0042	1.10	0.999
Au-poly(**2a**)	600	16100	0.0048	1.35	0.995
Au-poly(**2a**)	575	16000	0.0052	1.26	0.990
Au-poly(**2a**)	550	13000	0.0060	1.15	0.999
Au-poly(**3a**)	550	13300	0.014	0.98	0.985
Au-poly(**3a**)	525	13900	0.015	0.96	0.993
Au-poly(**3a**)	500	12000	0.016	1.04	0.973
Au-poly(**4a**)	500	8300	0.086	0.82	0.987
Au-poly(**4a**)	470	10300	0.091	0.92	0.970
Au-poly(**4a**)	450	9300	0.10	0.85	0.997

[a]R^2 represents the correlation coefficient in the fitting.
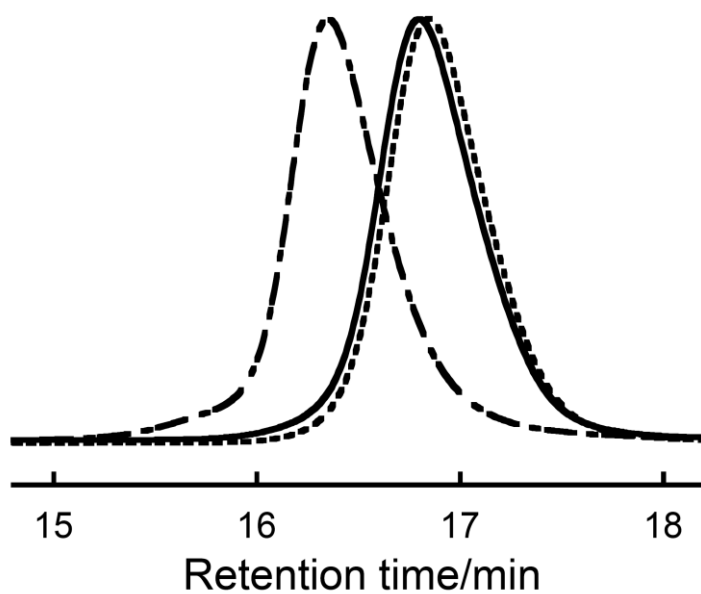
Figure S1. GPC elution curves of poly(**2a**) as the macro-RAFT agent (-----), poly(**2a**)$_{25}$-*block*-poly(St)$_9$ (——), and poly(**2a**)$_{25}$-*block*-poly(St)$_{56}$ (-——-).
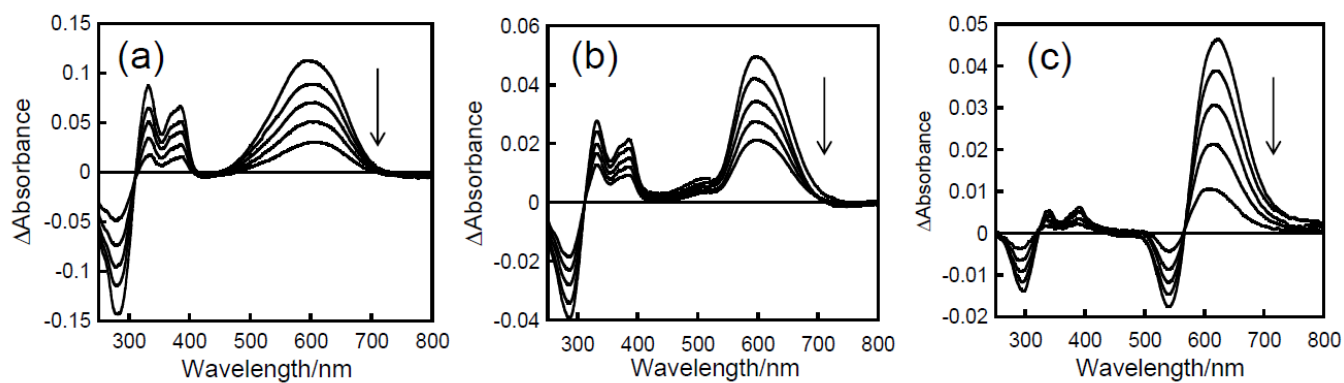
Figure S2. Difference spectral changes of (a) Au-poly(**2a**) ($d = 4$ nm) in methanol, (b) Au-poly(**2a**) ($d = 14$ nm) in THF/water (30/70 vol/vol), and (c) Au-poly(**2a**) ($d = 41$ nm) in THF/water (30/70 vol/vol) upon irradiation at 600 nm.
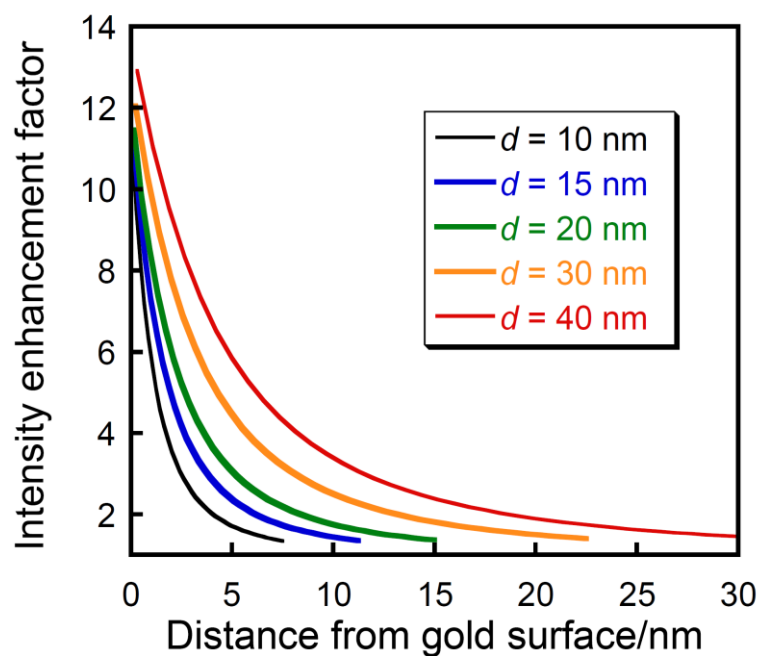
Figure S3. Intensity enhancement factor around various sized gold nanoparticle upon irradiation at 600 nm calculated based on Mie theory. Refractive index of the medium is set to be 1.400. The horizontal axis represents the distance from the nanoparticle surface. The vertical axis represents maximum intensity enhancement factor.