

Supporting Information for:

Azobenzene-based solar thermal energy storage enhanced by gold nanoparticles for rapid, optically-triggered heat release at room temperature

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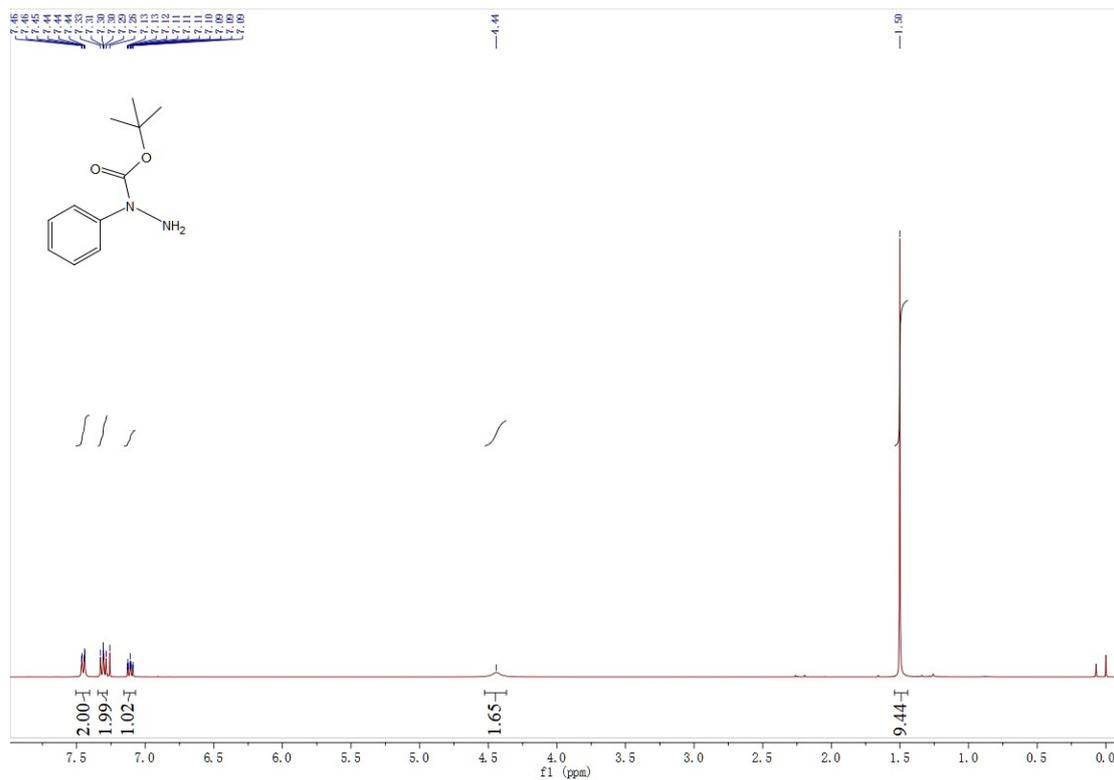


Figure S1 ¹H NMR spectrum of *tert*-butyl 1-phenylhydrazine carboxylate

¹H NMR (400 MHz, CDCl₃) δ : 7.46 (d, 2H), 7.31 (m, 2H), 7.11 (m, 1H), 6.43 (bs, 3H), 4.44 (s, 1H), 1.5 (s, 9H).

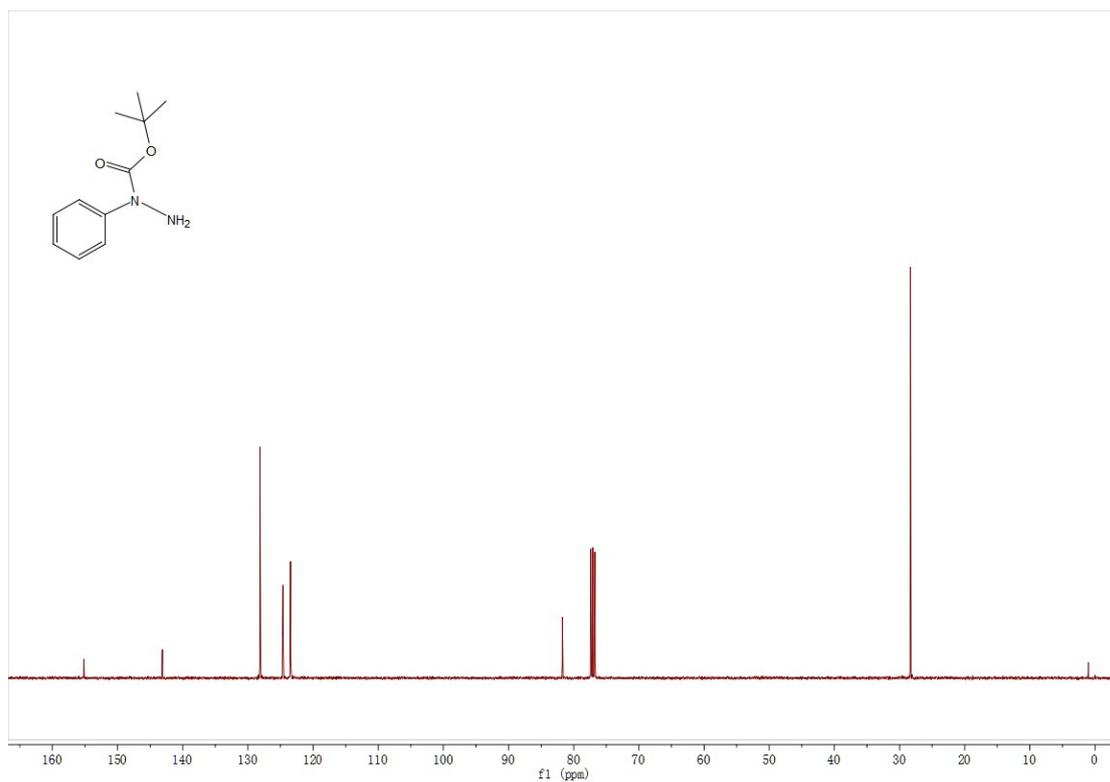


Figure S2 ¹³C NMR spectrum of *tert*-butyl 1-phenylhydrazine carboxylate

¹³C NMR (400 MHz, CDCl₃) δ : 155.6, 143.1, 128.1, 124.2, 123.8, 77.7, 76.9, 28.3.

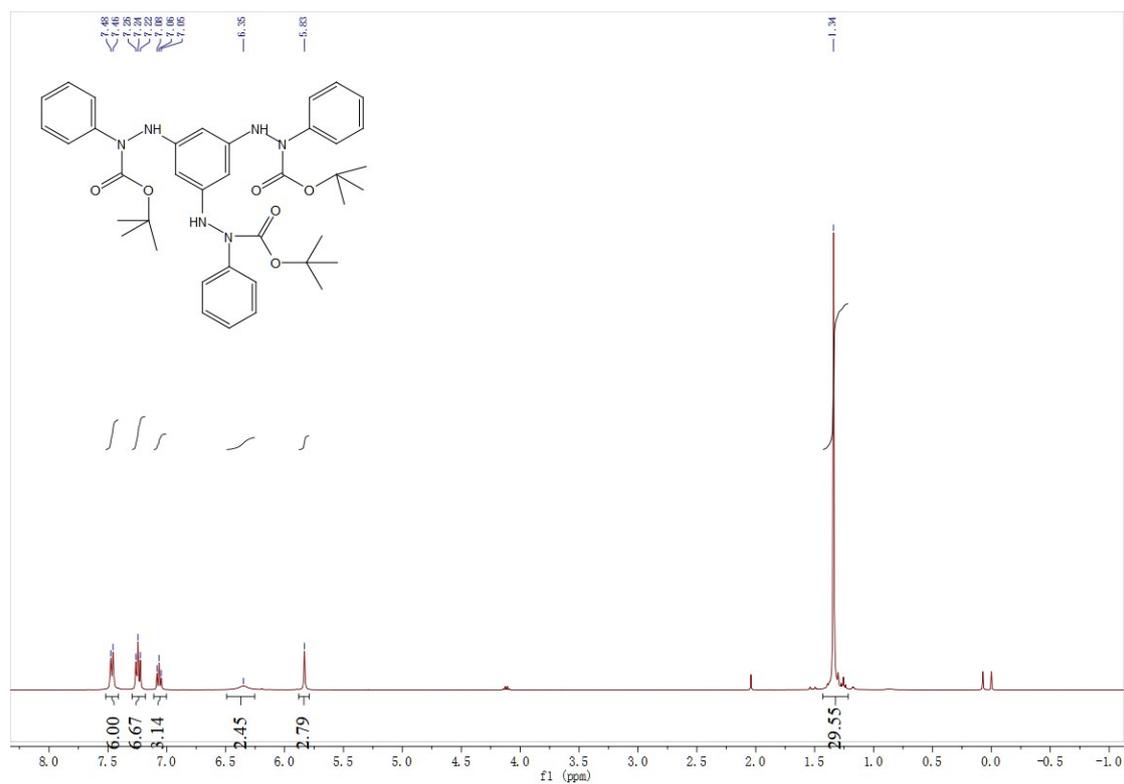


Figure S3 ¹H NMR spectrum of *N'*-[3,5-Bis(*N*-*tert*-butoxycarbonyl-*N'*-phenylhydrazino)-phenyl]-*N*-phenylhydrazinecarboxylic acid *tert*-butyl ester

¹H NMR (400 MHz, CDCl₃) δ : 7.43 (d, *J* = 8.4 Hz, 6H), 7.21 (dd, *J* = 8.4, 7.2 Hz, 6H), 7.03 (t, *J* = 7.2 Hz, 3H), 6.43 (bs, 3H), 5.81 (s, 3H), 1.32 (s, 27H).

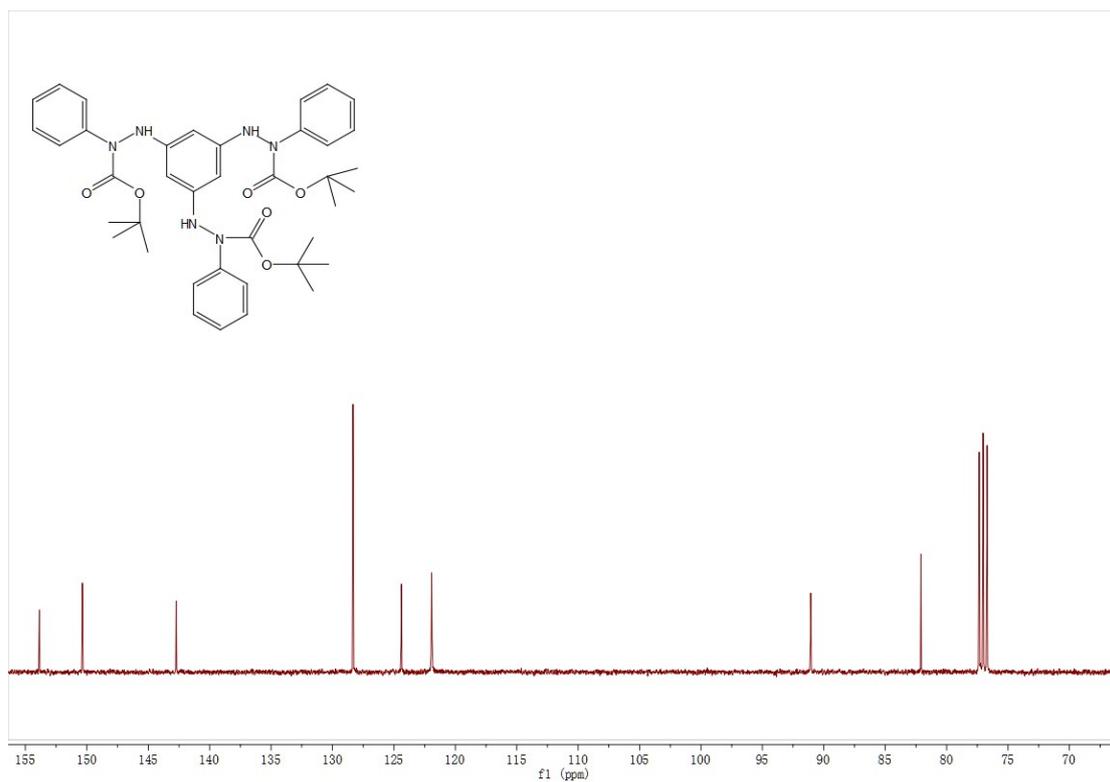


Figure S4 ¹³C NMR spectrum of *N'*-[3,5-Bis(*N*-*tert*-butoxycarbonyl-*N'*-phenylhydrazino)-phenyl]-*N*-phenylhydrazinecarboxylic acid *tert*-butyl ester

¹³C NMR (400 MHz, CDCl₃) δ : 153.6, 150.1, 142.5, 128.1, 124.2, 121.8, 90.7, 82.0, 28.1.



Figure S5 ¹H NMR spectrum of *tris*-azobenzene

¹H NMR (400 MHz, CDCl₃) δ : 8.58 (s, 3H), 8.02-7.80 (m, 6H), 7.58-7.50 (m, 9H).

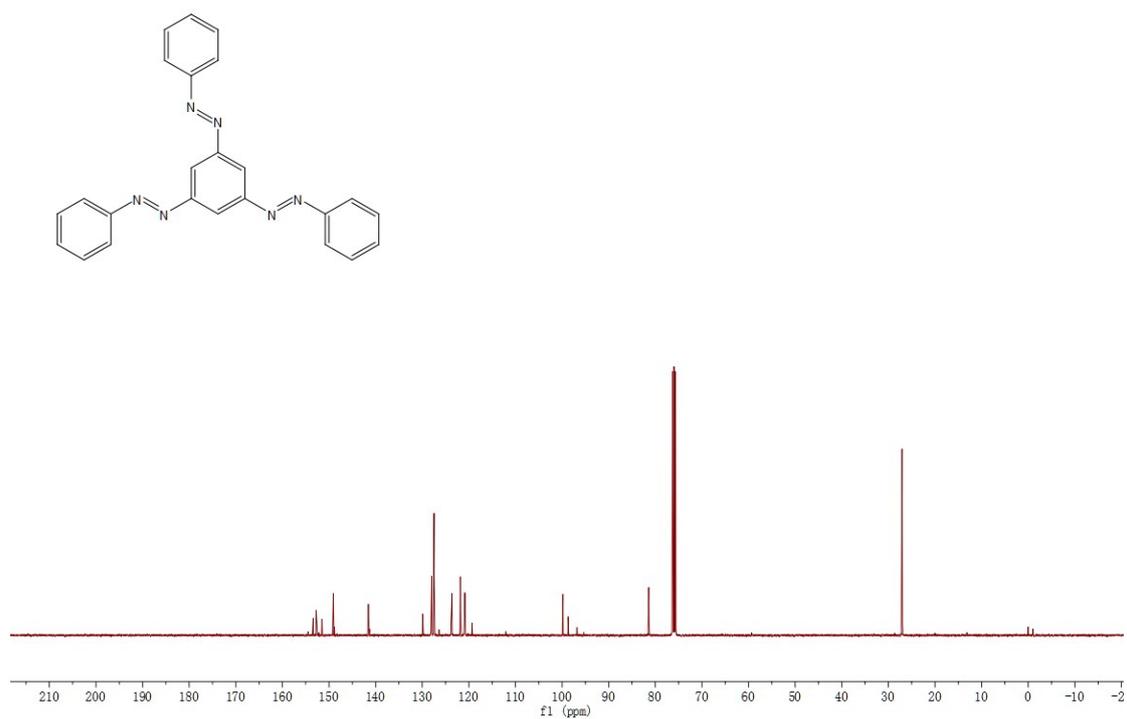


Figure S6 ¹³C NMR spectrum of *tris*-azobenzene

¹³C NMR (400 MHz, CDCl₃) δ : 153.8, 152.1, 131.6, 129.1, 124.2, 118.9.



Figure S7 Photos of AuNPs, tri-Azo and tri-Azo@AuNPs in DMF solution and corresponding PVA/AuNPs, PVA/Azo and PVA/Azo@AuNPs film.

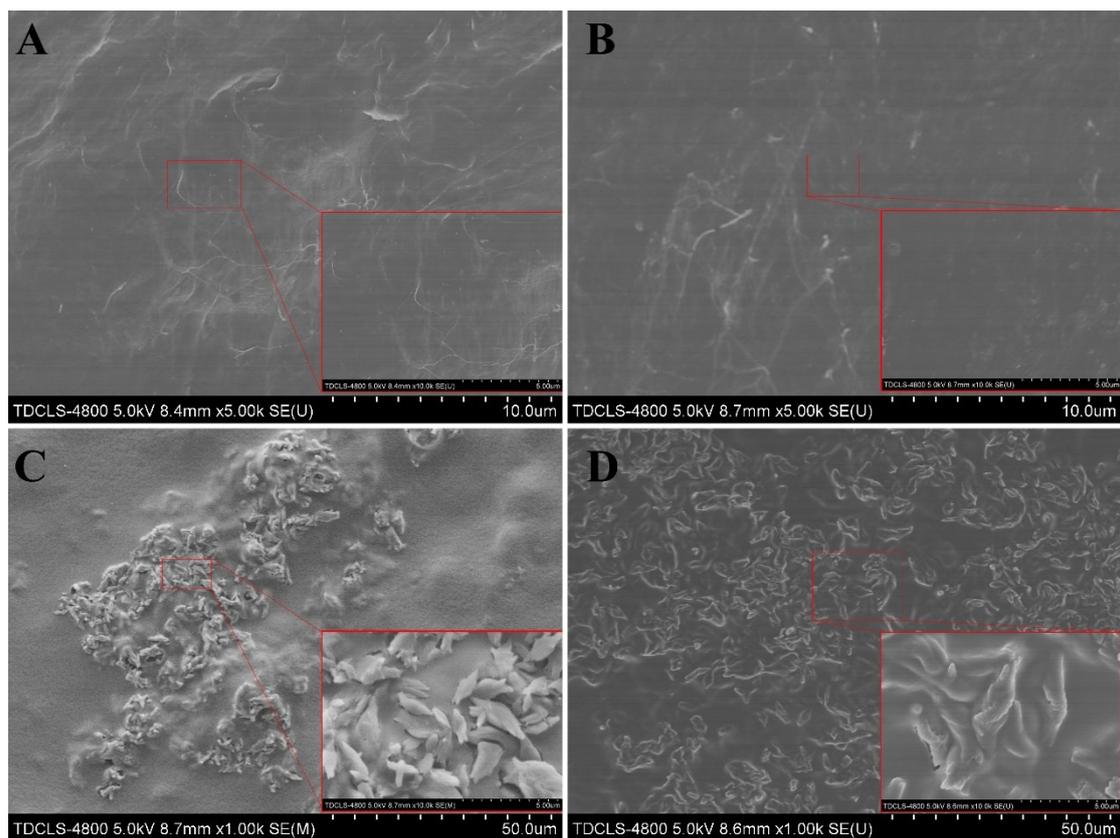


Figure S8 SEM images of PVA (A), PVA/AuNPs (B), PVA/Azo (C), and PVA/Azo@AuNPs (D) films (A and B, magnification: 5000 \times , inset: 10,000 \times ; C and D, magnification: 1000 \times , inset: 10,000 \times).

Microscopically, PVA and PVA/AuNPs films were flat and compact. While, irregular small flakes distributed on the surface of PVA/Azo and PVA/Azo@AuNPs films. Such protuberant small flakes structure was ascribed to Azo molecule. As can be seen from the inset of Figure S8 C and D, under the same magnification (10,000 \times), the small-flake like Azo molecule in the PVA/Azo@AuNPs film looks like more swollen than those in the PVA/Azo film. This may be because the Azo molecules in the PVA/Azo@AuNPs film were gathered around each AuNP.

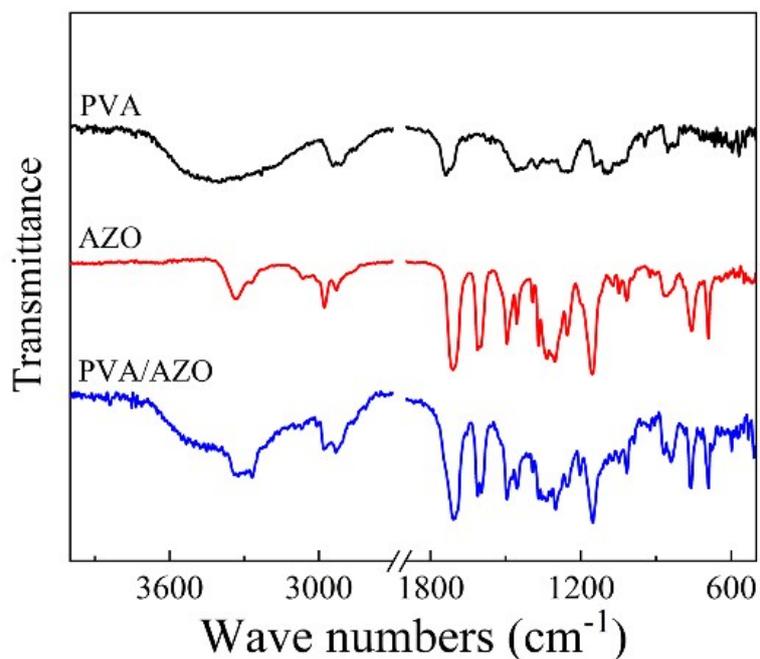


Figure S9 The FT-IR spectra of PVA, tri-Azo and PVA/Azo.

The FT-IR spectra of PVA, *tri*-Azo, and PVA/Azo samples were measured to elucidate their structures. The obtained results were similar to those reported in previous literature.[1-5] In particular, in the functional group region, the peak at approximately 1392–1300 cm^{-1} was typically attributed to the -N=N- stretching vibrations.[4-7] This peak was present in *tri*-Azo and PVA/Azo samples, indicating that the *tri*-Azo is stable and is not destroyed during the preparation process. The broad peak at 3410 cm^{-1} in the PVA spectrum was attributed to the -OH stretching vibration, which can also be observed in the PVA/Azo spectrum; however, as expected, it is not observed in Azo spectrum. Moreover, the strong peaks at approximately 3300–3000 cm^{-1} are attributed to the =C-H stretching vibrations of the benzene ring in the Azo spectrum. Furthermore, the peaks located at 1612 and 1494 cm^{-1} are attributed to the C=C stretching vibrations of the benzene ring in the Azo spectrum. Additional details of band assignments for PVA, *tri*-Azo and PVA/Azo are listed in Table S3.

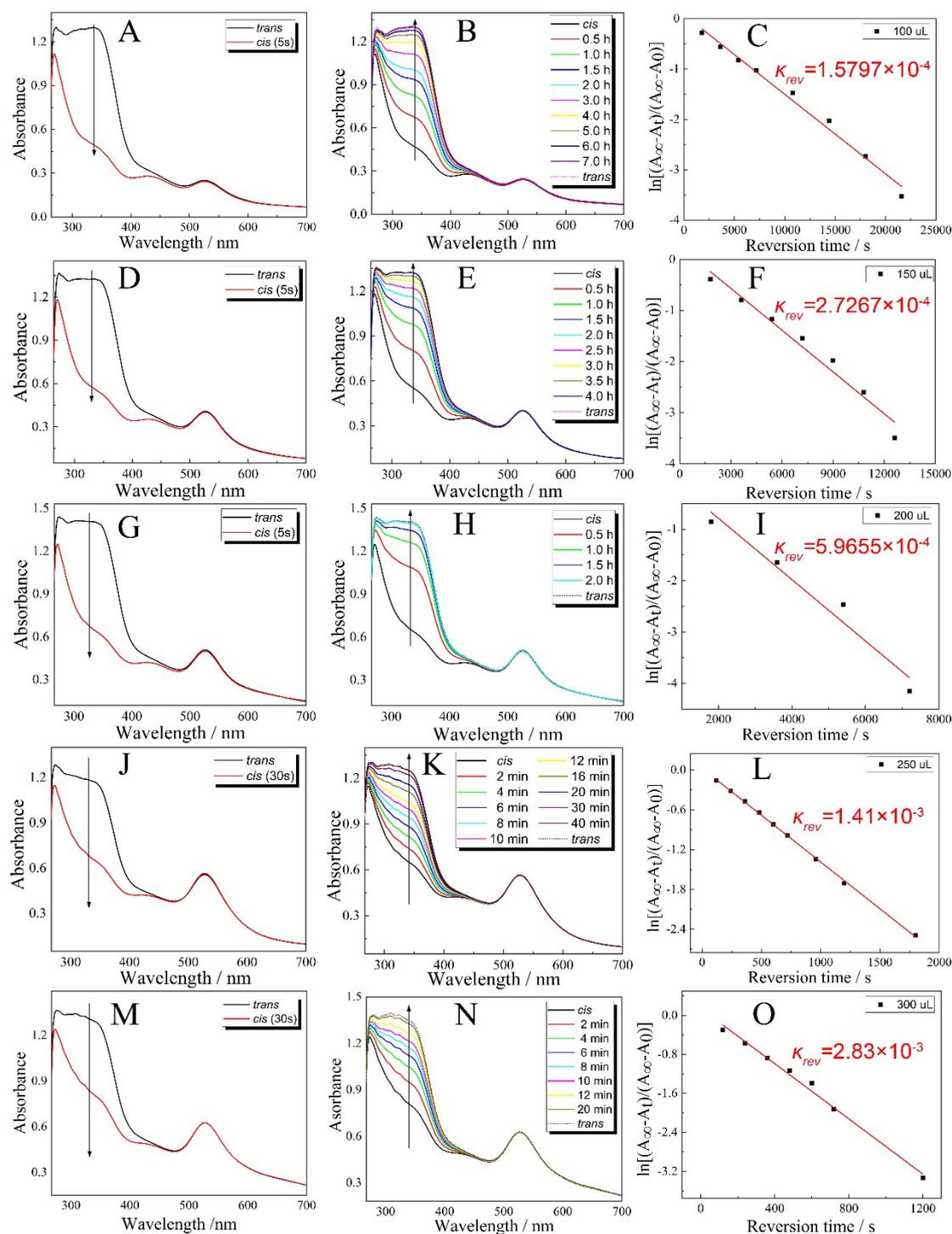


Figure S10 Accelerated effect of AuNPs on *cis*-to-*trans* isomerization of *tri*-Azo. The time-evolved UV-visible absorption spectra of *tri*-Azo at room temperature with different AuNPs aqueous volumes of 100, 150, 200, 250 and 300 uL, respectively. First column: 365 nm UV light (120 mW cm^{-2}) irradiation. Second column: in darkness. Third column: the corresponding first-order rate constants for *cis*-to-*trans* (κ_{rev}) transitions of the *tri*-Azo. The arrows are indicated test order.

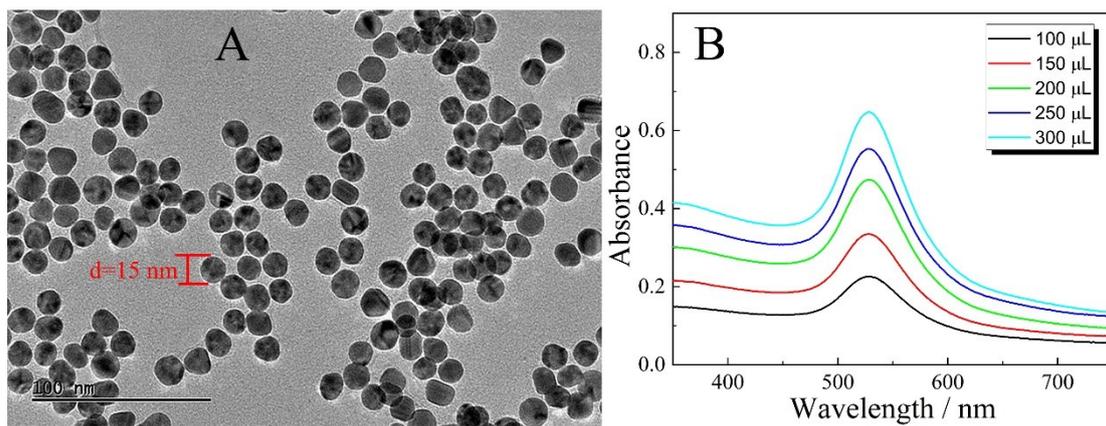


Figure S11 (A) TEM image of AuNPs; (B) UV-vis spectra of different volumes of AuNPs.

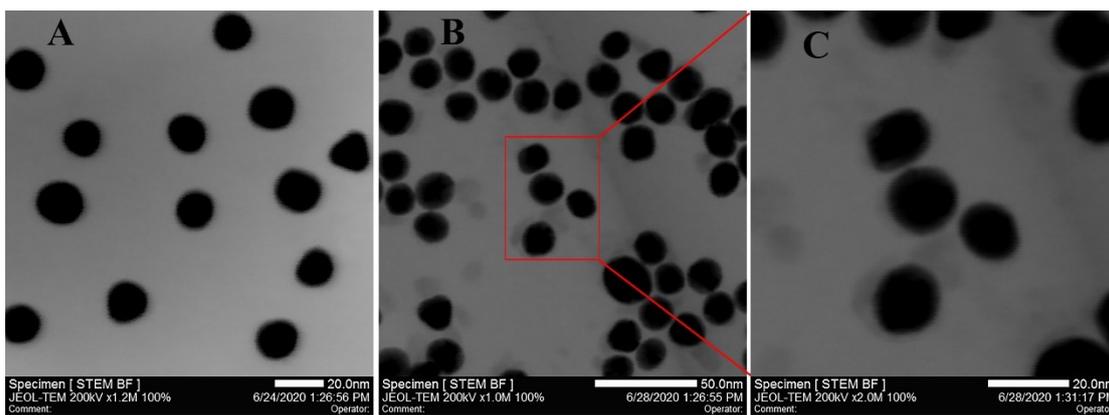


Figure S12 STEM images of PVA/ AuNPs (A) and PVA/Azo@AuNPs (B and C) film (magnification: A is 1.2M \times , B is 1.0M \times , C is 2.0M \times)

AuNPs in PVA/AuNPs films were round particles with sharp edges, while AuNPs in PVA/Azo/AuNPs films were round particles with shadow on its edges. The shadow represented Azo molecules, which were gathered around AuNPs.

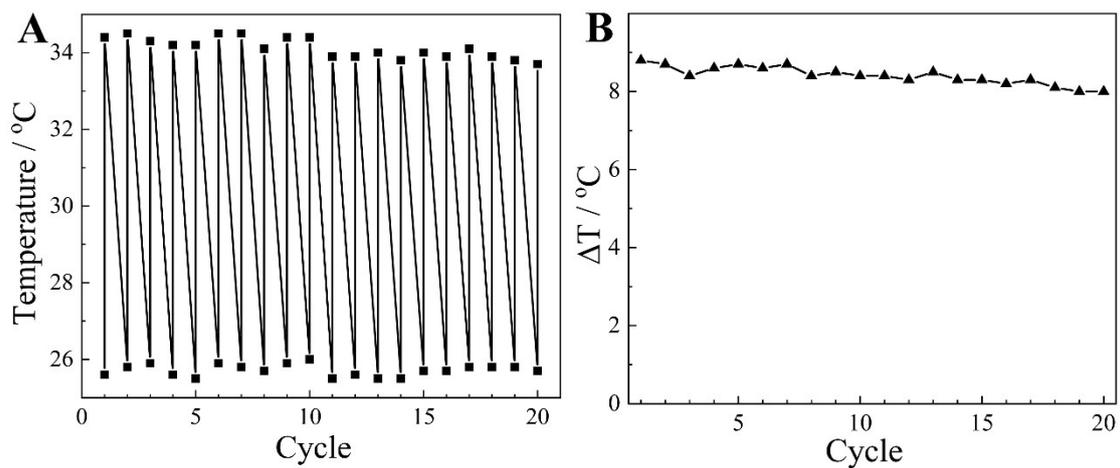


Figure S13 Cycle stability of PVA/Azo@AuNPs STF sample. (A) is the temperature changes before and after discharge procedure of the PVA/Azo@AuNP STF sample. (B) is the temperature increases during the heat release of the sample.

Table S1 The heating temperature required for the heat release and the maximum temperature difference after heat release procedure.

Reported Azo-STFs	stimulus of heat release	Max ΔT ($^{\circ}\text{C}$)	Ref.
Polymer-templated AZO	About 100 $^{\circ}\text{C}$	10	[8]
AzoPMA	Heat over 100 $^{\circ}\text{C}$	No data	[9]
rGO-bisAzo	Heating to 180 $^{\circ}\text{C}$	15	[10]
AZO-CNTs	Heating to 150 $^{\circ}\text{C}$	10	[11]
<i>tri</i> -Azo/rGO	80 $^{\circ}\text{C}$	7.1	[2]
Azoheteroarene	60 $^{\circ}\text{C}$	4.1	[1]
Polynorbornene-templated AZO	blue light at 25 $^{\circ}\text{C}$	1.5	[3]
Fabric-templated AZO	Heat over 60 $^{\circ}\text{C}$	2	[12]
	Blue light	3-4	

Table S2 The volumes of AuNPs solution, PVA solution and Azo solution used for preparing different films.

The films	solutions		
	PVA aqueous	AuNPs aqueous	Azo in DMF
PVA	2 mL	0	0
PVA/AuNPs	2 mL	100 μ L	0
PVA/Azo	2 mL	0	500 μ L
PVA/Azo@AuNPs	2 mL	100 μ L	500 μ L

Table S3 Assignment of FT-IR spectra for PVA, *tri*-Azo and PVA/Azo.

Band (cm ⁻¹)			Assignment
Azo	PVA	PVA/Azo	
	3410	3402	-OH (v)
3330		3267	C-H (v)
2979	2945	2978	CH ₂ (v _{as})
1710, 1612, 1494	1737	1706, 1612, 1494	-OH (δ) and C=C (v)
1392, 1334, 1303		1342, 1299	-N=N- (v)
1155	1107	1151	C-N (v) or C-O (v)
758, 690		759, 690	=C-H (γ)

v represents stretching vibration (v_a symmetrical; v_{as} asymmetrical), γ represents out-of-plane deformation vibration and δ represents in-plane deformation vibration.

Table S4 Concentration of AuNPs.

volume of AuNPs aqueous (uL)	Concentration of AuNPs (mol L ⁻¹)
100	5.83×10^{-10}
150	8.49×10^{-10}
200	1.19×10^{-9}
250	1.41×10^{-9}
300	1.64×10^{-9}

Equation S1

$$\ln\left(\frac{A_{\infty} - A_t}{A_{\infty} - A_0}\right) = -\kappa_{rev}t$$

A_0 is the absorption intensity of Azo and *tri*-Azo@AuNPs at metastable state (*cis*-rich) irradiated by UV light, A_t is the absorption intensity of Azo and *tri*-Azo@AuNPs reversing for " t " time and A_{∞} is the absorption intensity of Azo and *tri*-Azo@AuNPs after complete *cis-trans* reversion.

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