

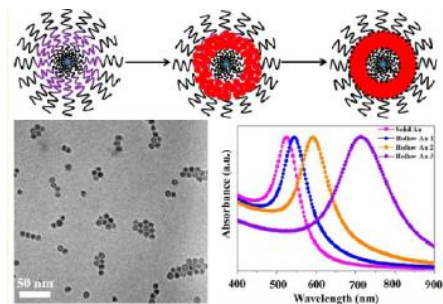


Light-enabled reversible self-assembly and tunable optical properties of stable hairy nanoparticles

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Article

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Hairy Uniform Permanently Ligated Hollow Nanoparticles with Precise Dimension Control and Tunable Optical Properties

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Supporting Information

Nanoparticle Synthesis

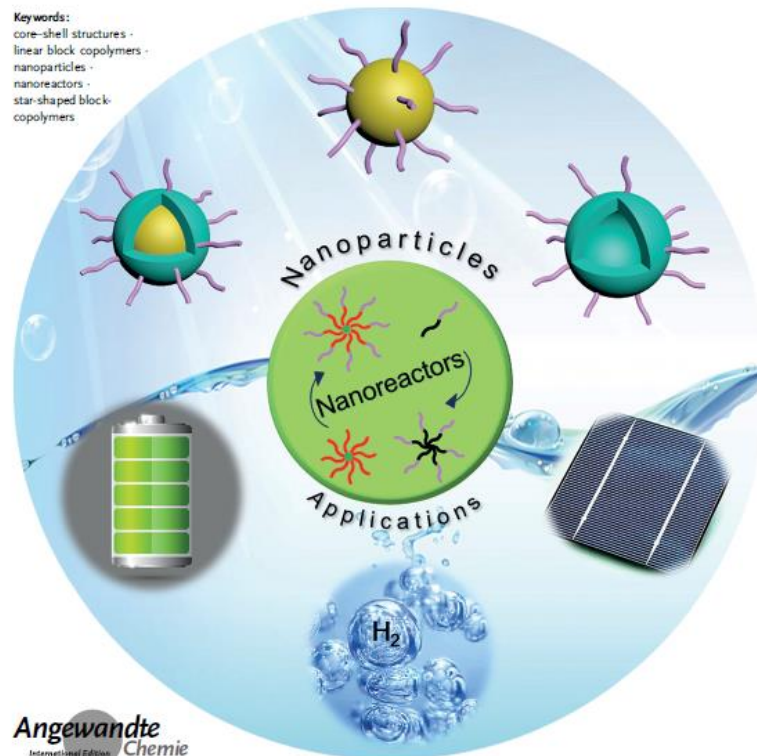
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From Precision Synthesis of Block Copolymers to Properties and Applications of Nanoparticles

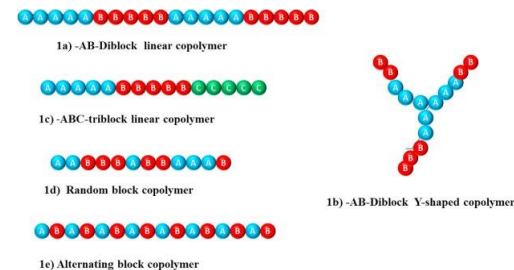
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Keywords:

core-shell structures ·
linear block copolymers ·
nanoparticles ·
nanoreactors ·
star-shaped block-
copolymers



Introduction



External triggers to regulate self-assembly of NPs

- creation of variety of functional structures and materials from nanoscopic building blocks.
- Triggers : Temperature, pH and solvent polarity
- **Why Light ?** Can be delivered remotely and instantaneously to the targeted locations noninvasively. Intensities and wavelengths can be tuned to enable the precise control over the assembly-disassembly.

Repeated self-assembly and disassembly of NPs by employing light

- Crucial prerequisite is to either graft chromophore-containing ligands onto the NP surface (**Photoresponsive NPs**)
- Possible functional end groups : $-SH$, $-OH$, and $-NH_2$ for metal NPs
- **Why NOT Thiols ?** Photoresponsive Au NP capped with SH-terminated ligands is destroyed by oxidation or thermal desorption are irradiated with UV light, resulting in the loss of photoresponsive capability and the NP aggregation

Significance of this Paper

- A versatile and robust strategy for creating monodisperse plasmonic nanoparticles (NPs) intimately and permanently capped with photoresponsive polymers .
- These hairy Au NPs can be reversibly and reliably self-assembled and disassembled upon irradiation with 365- and 254-nm UV lights, respectively.
- Synthesized amphiphilic star-like **poly(acrylic acid)-block-poly(7-methylacryloyloxy-4-methylcoumarin) PAA-b-PMAMC** diblock copolymers as nanoreactors to create in situ photoresponsive Au NPs.

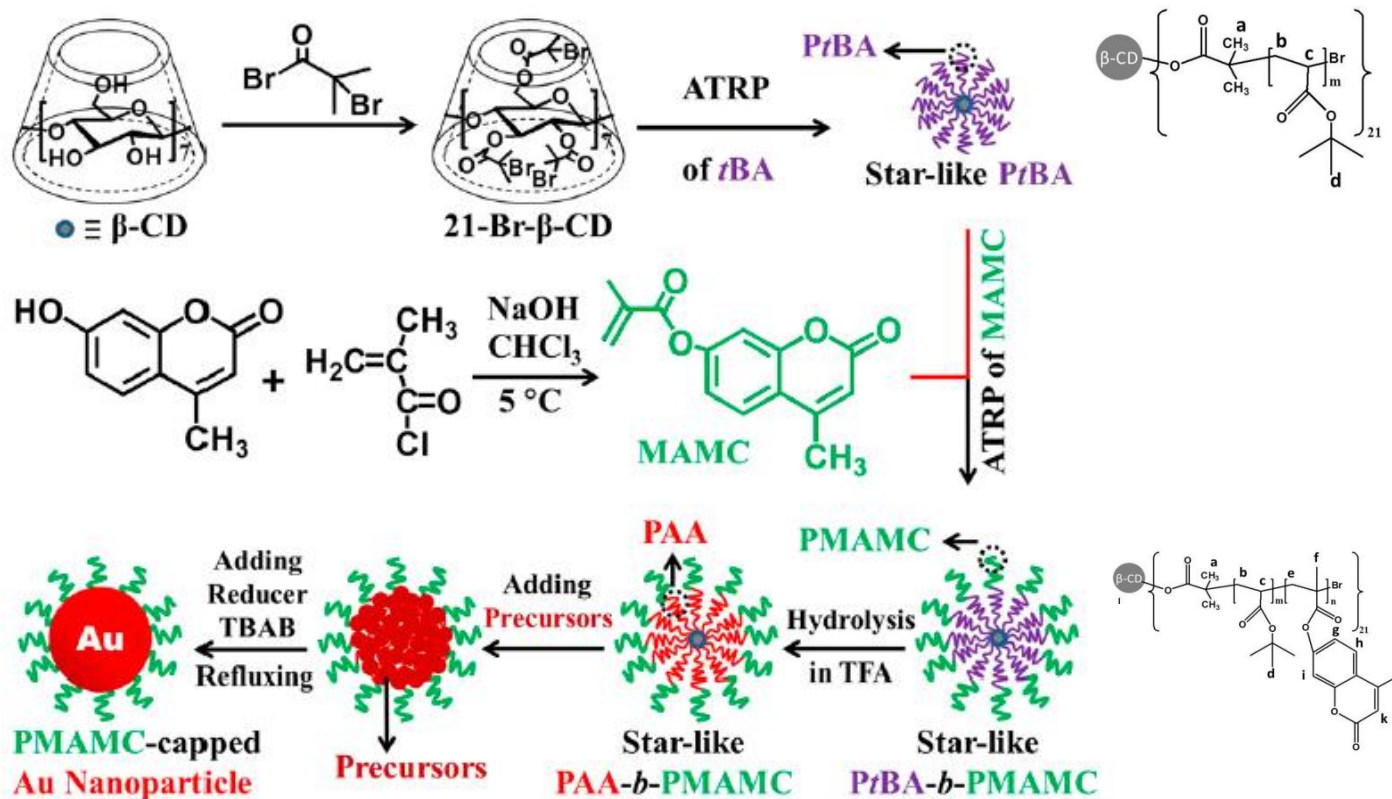


Fig. 1. Synthetic strategy. PMAMC-capped Au nanoparticles with tunable size were prepared in situ by capitalizing on amphiphilic star-like PAA-b-PMAMC diblock copolymers as nanoreactors.

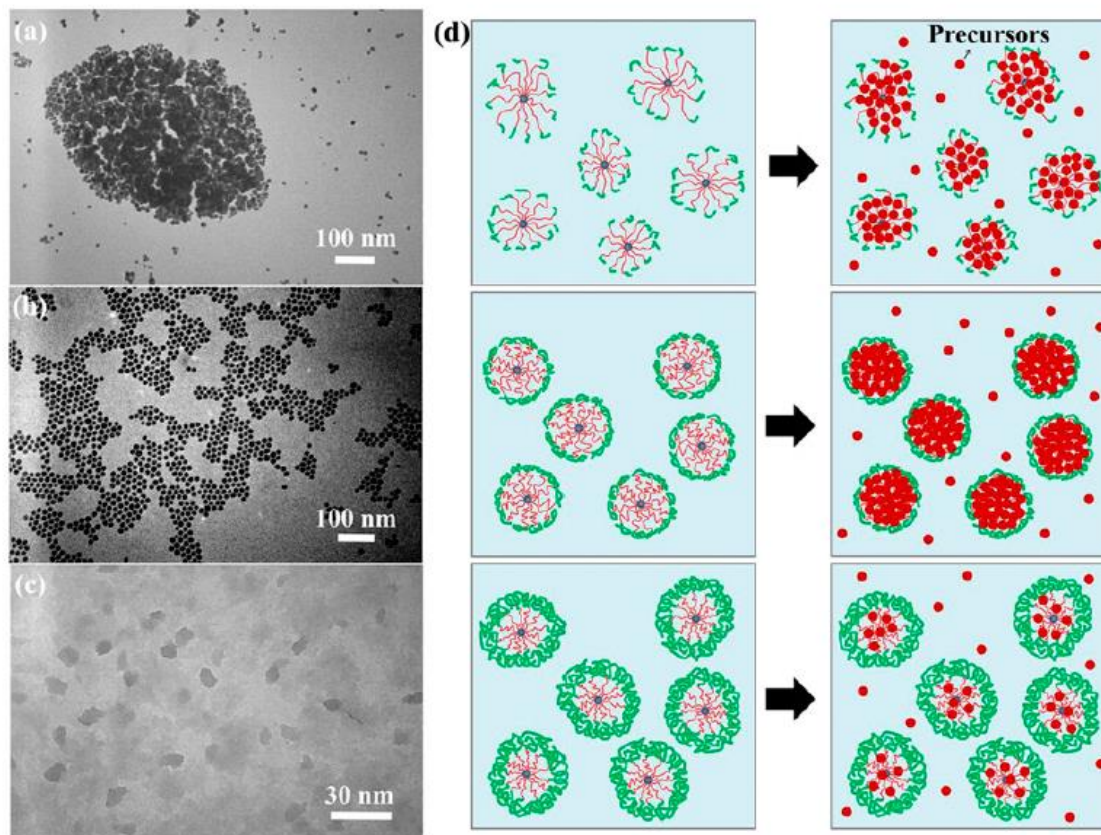


Fig. 2. Effect of MW of outer PMAMC chains on the in situ formation of Au NPs. TEM images of Au NPs formed in situ using (A) sample B, (B) sample A, and (C) sample C in SI Appendix, Table S2 as nanoreactors, respectively, in the mixed solvents of DMF and BA at the volume ratio of DMF/BA of 7/3. (D) Proposed mechanism for synthesis of uniform Au NPs (using sample A as nanoreactor where PMAMC has an intermediate MW, M_n ; central panels) and nonuniform AuNPs (using sample B in Upper and sample C in Lower as nanoreactors, where M_n of PMAMC are relatively too small and too large, respectively) in the 7/3 DMF/ BA mixed solvents.

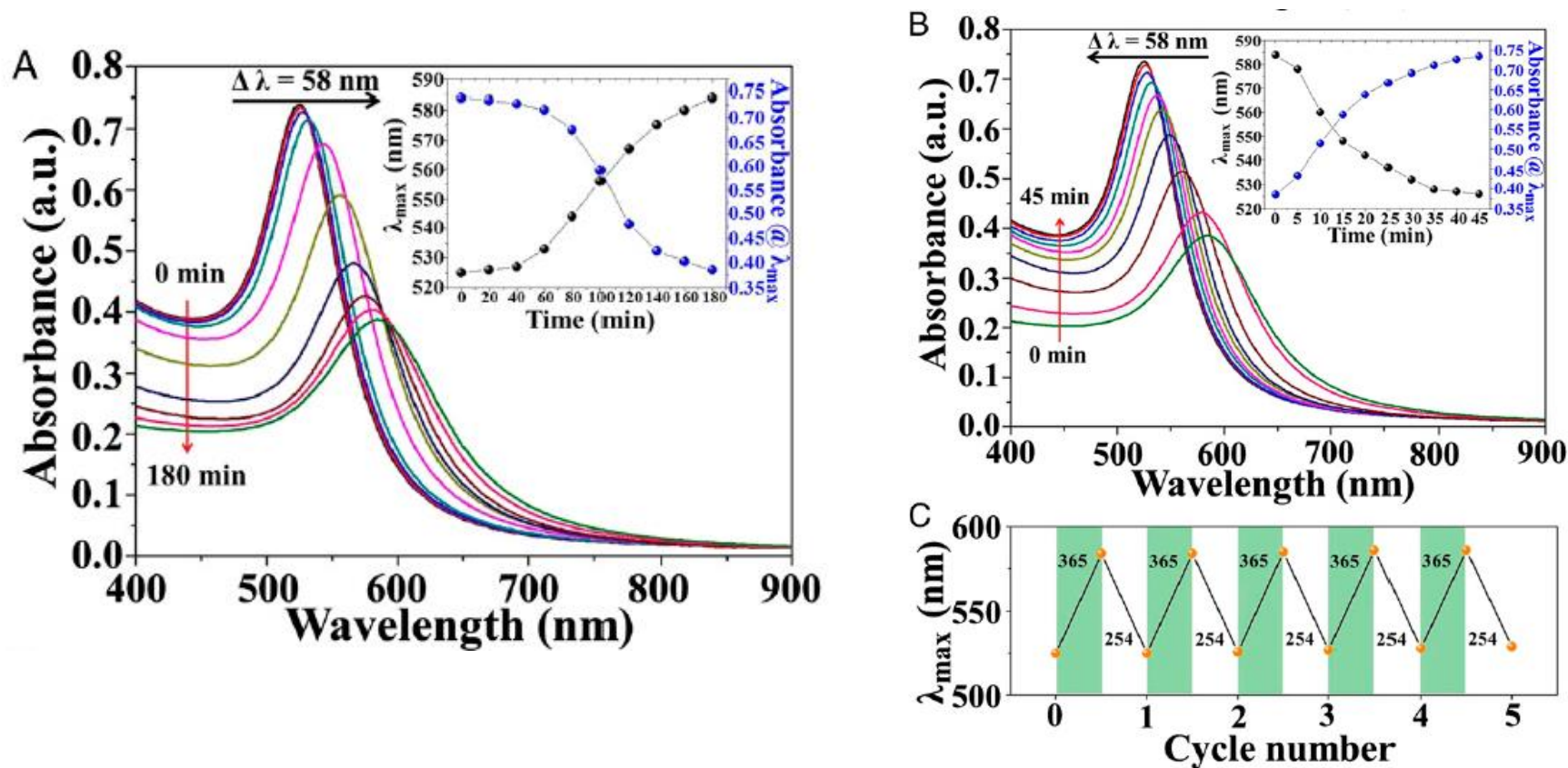
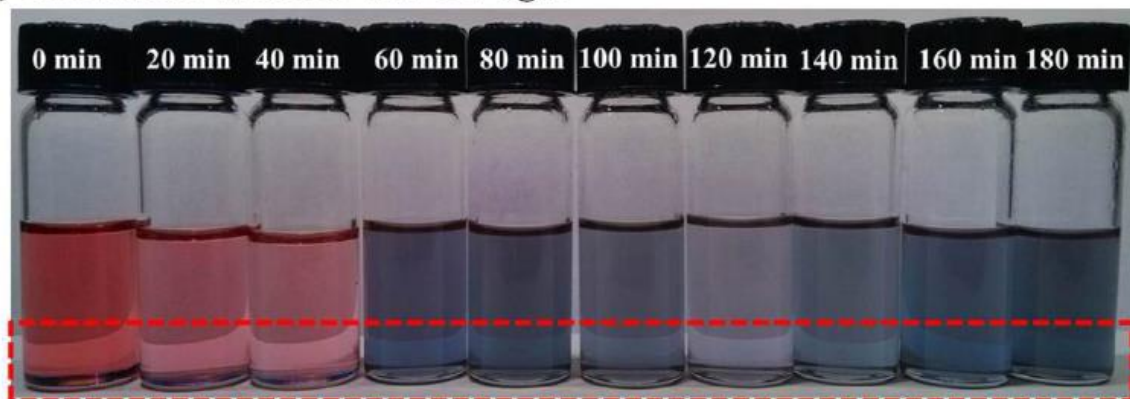


Fig. 3. Reversible optical properties of photoresponsive NPs. (A) UV-vis spectra of PMAMC-capped Au NPs CH_2Cl_2 solution ($c = 8.3 \mu\text{M}$) when irradiated with 365-nm UV light. (B) UV-vis spectra of PMAMC-capped Au NPs CH_2Cl_2 solution upon irradiation with subsequent 254-nm UV light after being exposed to 365-nm UV light for 180 min in A. (A and B, Insets) The maximum peak position λ_{max} and the absorbance of the SPR peaks at λ_{max} as a function of UV irradiation time. (C) Reversible photocontrol of the SPR peak position of PMAMC-capped Au NPs during the self-assembly (green bars) and disassembly (white bars) cycles upon the irradiation with 365- and 254-nm UV light, respectively.

(a) Irradiation with 365-nm UV light



(b) Subsequent irradiation with 254-nm UV light

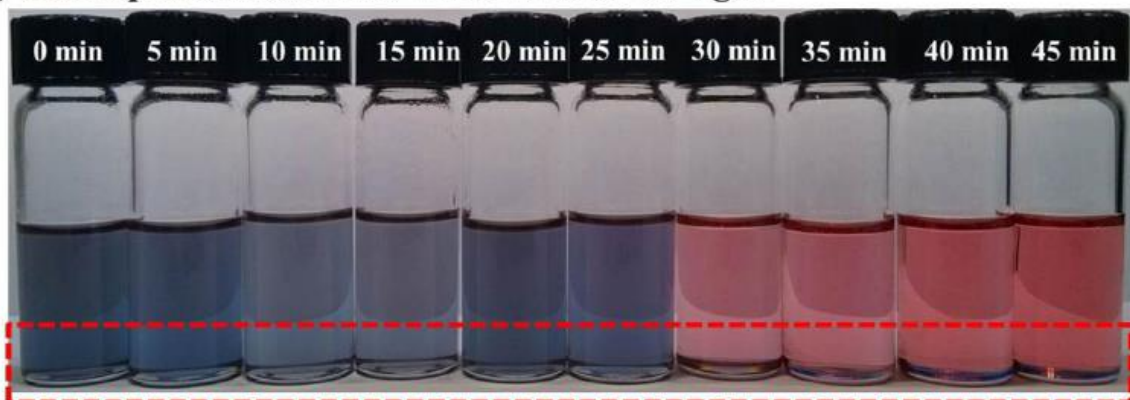
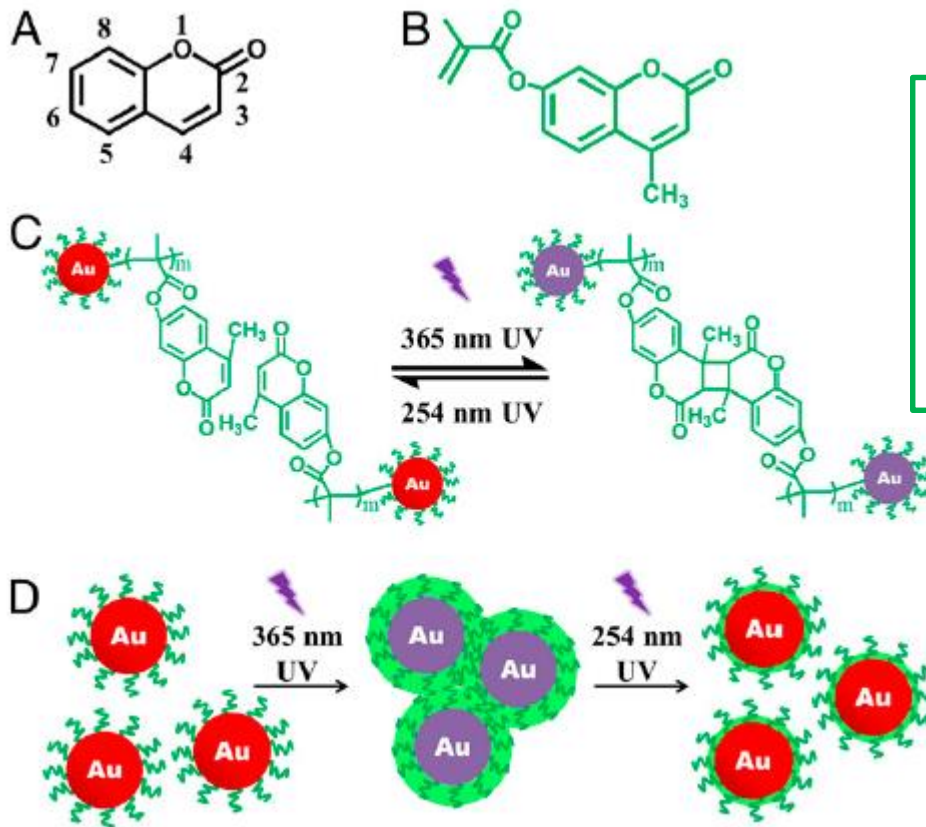


Figure S19. Digital images of PMAMC-capped Au NPs CH_2Cl_2 solution upon (a) 365-nm UV light and (b) 254-nm UV light irradiation as a function of UV exposure time. The corresponding UV spectra are shown in **Figure 3a** and **Figure 3b**, respectively. No precipitates were observed on the bottom of each vial as highlighted in the red dashed boxes.



This is 2+2 Photodimerization

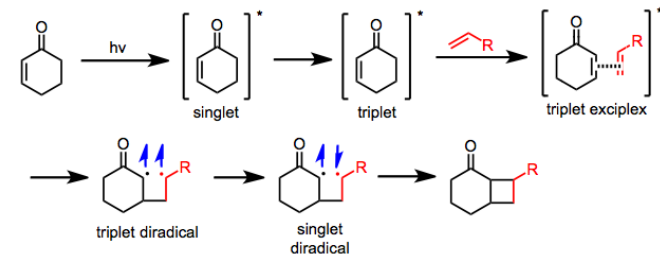


Fig. 4. Light-enabled reversible self-assembly of Au NPs intimately and permanently capped with photoresponsive polymer chains. Chemical structures of (A) coumarin and (B) MAMC (i.e., Fig. 1, Center Right). (C) Schematic illustration of photodimerization (photo-cross-linking) and photo cleavage behaviors of PMAMC chains situated on the surface of Au NPs when subjected to 365- and 254-nm UV light irradiation, respectively. (D) Stepwise representation of light-enabled self-assembly and disassembly of PMAMC capped Au NPs upon 365- and 254-nm UV light irradiation, respectively. The thicker green ring in D represents the complete photo-cross-linking of PMAMC chains, whereas the thinner green ring depicts the incomplete photocleavage

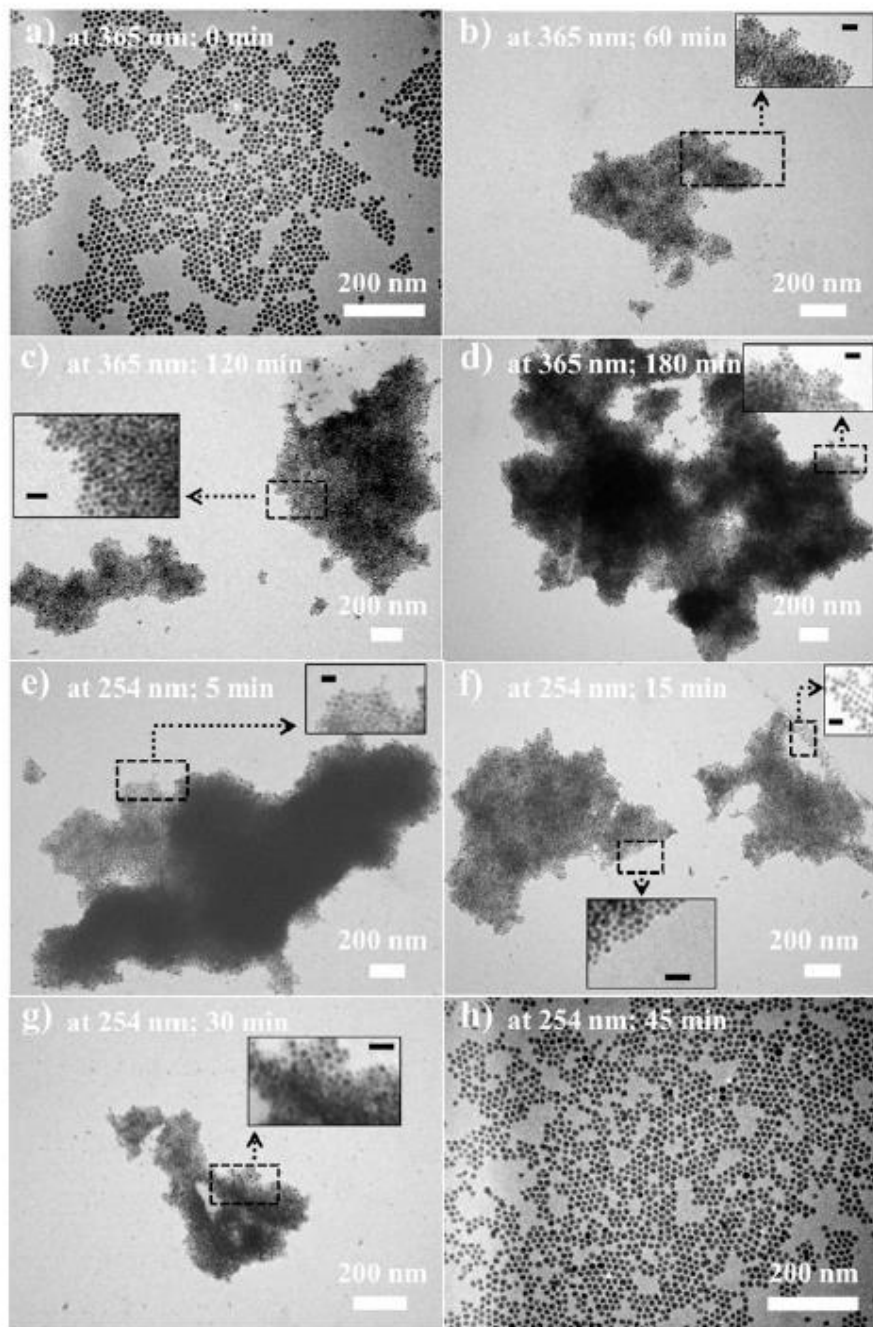


Fig. 5. Evolution of light-enabled reversible self-assembly of PMAMC-capped Au NPs with retained morphology. TEM images of PMAMC-capped Au NPs after the PMAMC-capped Au NPs CH_2Cl_2 solution ($c = 8.3 \mu\text{M}$) was exposed to (A–D) 365-nm UV light and (E and F) 254-nm UV light for a given time. The corresponding time-dependent UV–vis spectra are shown in Fig. 3 A and B, respectively. It is worth noting that images (E and F) were obtained by subsequent 254-nm UV light irradiation on the MAMC-capped Au NPs CH_2Cl_2 solution after it was previously irradiated by 365-nm UV light for 24 h. The 365-nm UV exposure times are (A) $t = 0$ min, (B) $t = 60$ min, (C) $t = 120$ min, and (D) $t = 180$ min. The 254-nm UV exposure times (E) $t' = 5$ min, (F) $t' = 15$ min, (G) $t' = 30$ min, and (H) $t' = 45$ min. (Scale bars: Insets, 50 nm.)

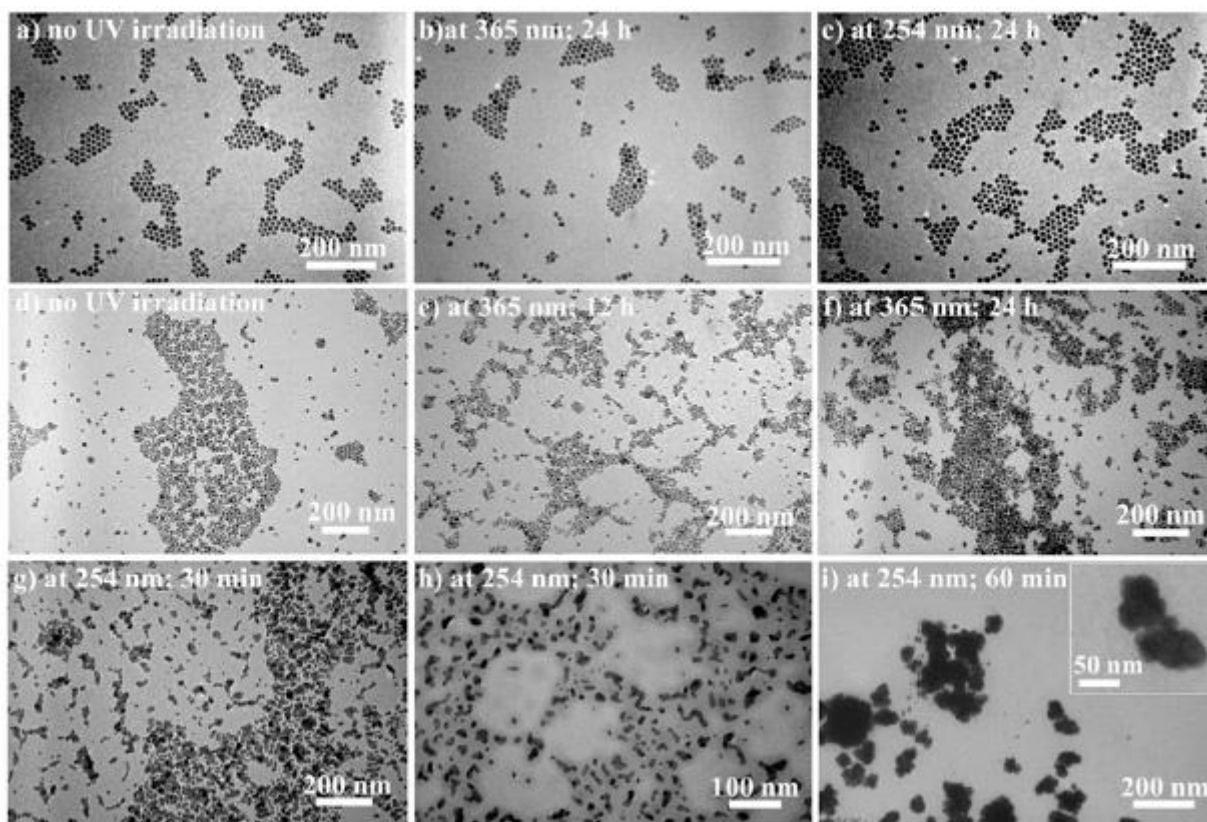


Fig. 6. Morphological evolutions of Au NPs either permanently capped with non-photoresponsive polymers or dynamically capped with small molecules. TEM images of (A) as-prepared PS-capped Au NPs before UV light irradiation, and (B and C) PS-capped Au NPs after 365- and 254-nm UV light irradiation, respectively, for 24 h. It is notable that image (C) was obtained by irradiating the PS-capped Au NPs CH_2Cl_2 solution with 254-nm UV light for an additional 24 h after it was previously exposed to 365-nm UV light for 24 h. TEM images of (D) as-prepared DDT-capped Au NPs before UV light irradiation, and (E and F; and G–I) DDT-capped Au NPs after 365-nm (for 24 h) and 254-nm (for 60 min) UV light irradiation, respectively. Notably, images (G–I) were obtained by irradiating the DDT-capped Au NPs CH_2Cl_2 solution with 254-nm UV light for an additional 60 min after it was previously exposed to 365-nm UV light for 24 h. A close-up in Inset shows the agglomeration of Au nanocrystals with no observable, individually isolated NPs.

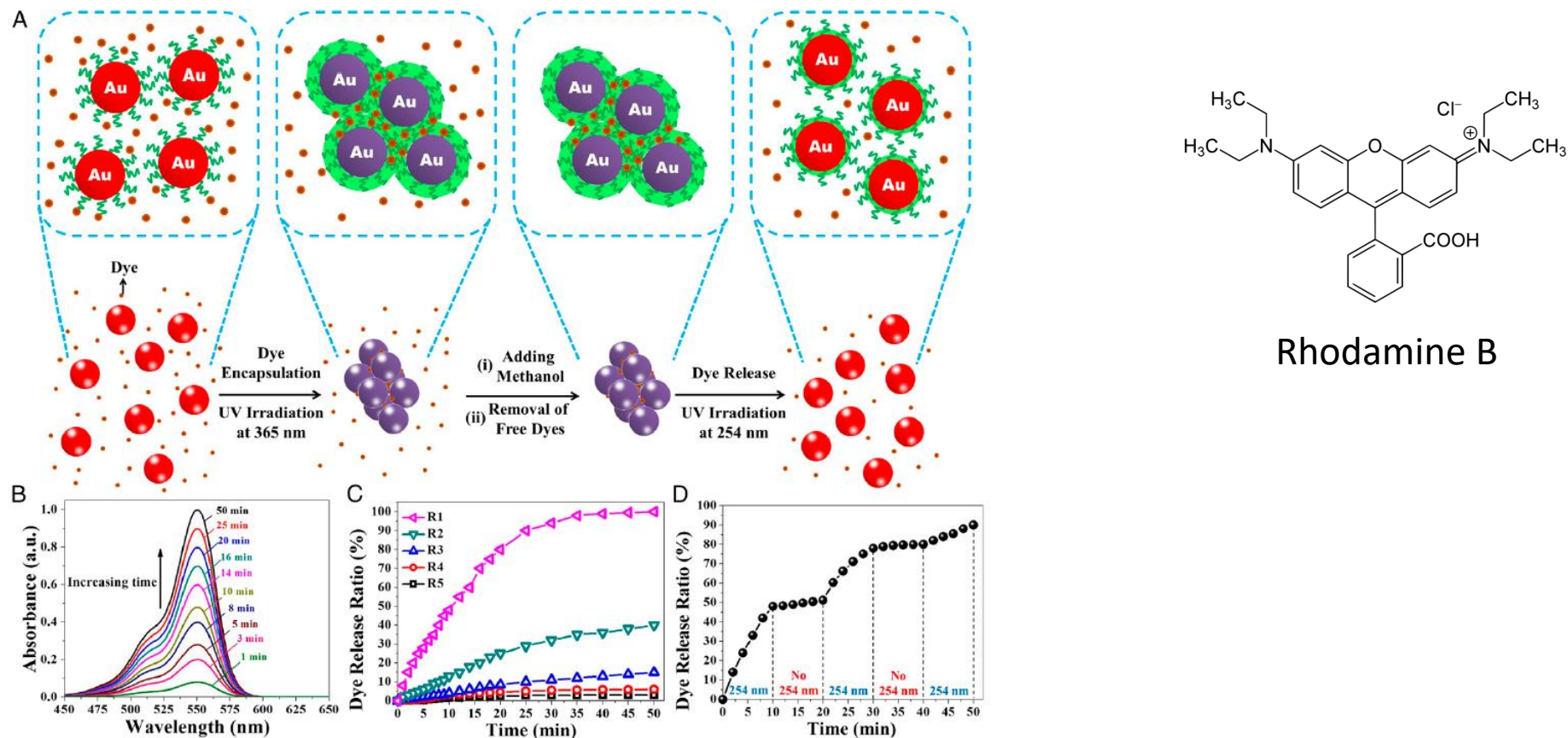


Fig. 7. Encapsulation and release of a model dye using light-enabled reversible self-assembly of PMAMC-capped Au NPs. (A) Stepwise representation of encapsulation and release of RhB molecules by capitalizing on the light-enabled reversible self-assembly of PMAMC-capped Au NPs ($c = 8.3 \mu\text{M}$) in release process R1. (B) UV-vis spectra of released RhB molecules in release process R1 as a function of 254-nm UV light irradiation time. (C) Release kinetics of RhB molecules in release processes R1–R5 at various times of 254-nm UV light irradiation. (D) Controlled release of RhB molecules in release process R6 with multiple 254-nm UV light on/off cycles. The release ratio as a function of time was determined from the absorbance intensity at 550 nm of supernatant with the saturated intensity in R1 taken as 100%.

SUMMARY

- Developed a strategy to synthesize star-like block copolymer nanoreactor allowing *in-situ* crafting of monodisperse stable hairy plasmonic NPs intimately and permanently functionalized with photoresponsive polymers.
- Amphiphilic star-like PAA-b-PMAMC diblock copolymers leads to the formation of **photoresponsive PMAMC-capped Au NPs**.
- Photoresponsive PMAMC hairs situated on the Au NP surface can be readily tuned by **controlling the ATRP time** of the respective PAA and PMAMC blocks.
- Due to stable and permanent connection between PMAMC chains and Au NP rendered by the original covalent bonding between PAA and PMAMC chains, PMAMC-capped Au NPs can be reversibly and reliably self-assembled and disassembled on demand using UV light of different wavelengths.
- These photoresponsive NPs may stand out as effective and smart nanocarriers.