Supporting Information

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Experimental methods : Synthesis of Nanoparticle Chains

Materials. All reagents were purchased from the following suppliers and used without further purification: sodium tetrachloroaurate (III) dihydrate and trisodium citrate and 2-mercaptoethanol (MEA) from Sigma-Aldrich; 46-mercapto-22,43-dioxo-3,6,9,12,15,18-hexaoxa-21,44-diazahexatetraconta-31,33-diyn-1-oic acid (DA-PEG) was purchased from Prochimia Surfaces; bis(p-sulfonatophenyl)- phenyl phosphine dehydrate dipotassium salt (BSPP) was purchased from Strem-Chemicals, Inc. Milli-Q water was used in all experiments.

Photocrosslinked DA-PEG-coated AuNPs chains. AuNPs were synthesized according to the well-established citrate reduction method, [1] and capped with bis(p-sulfonato-phenyl)phenylphosphine (BSPP) [2]. The average size of the Au nanoparticles was 15±1.5 nm. A freshly prepared DA-PEG solution in methanol (5 mg/mL, 100 µL) was added to an aqueous solution of AuNPs (10 mL, 2.5 nM) while stirring in the dark. The reaction mixture was kept for 2 hours at 4^{o}C in the dark to partially coat the nanocrystals with DA-PEG. Excess DA-PEG was removed by centrifugation of the AuNPs at 16 400 rpm for 15 min. Particles were suspended in milli-Q water and UV-irradiated for 15 min (254 nm light wavelength, 35 W lamp power, 10 cm from the UV lamp) in order to photocross-link the surface-adsorbed DA-PEG monomers.

Silica-coated AuNPs chains and networks. Isometric AuNPs were freshly prepared by the citrate reduction method [3] and diluted with milli-Q water to the concentration of 1.7×10^{14} particles/L or 0.2816 nM particles. The average size of the AuNPs was 12.7±1.2 nm. Formation of the AuNPs chain structures was performed by adding 2-mercaptoethanol, MEA, $HS(CH_2)_2OH$) to the AuNPs dispersion at a AuNPs: MEA molar ratio of 1 : 5000 [4]. The mixed solution of AuNPs and MEA was left at room temperature for 3 days to complete chain formation.[4] The colour of the solution gradually changed from pale pink to pale blue with the formation of the chain structure. After 3 days, AuNPs chains in 5 mL of the solution were collected by centrifugation at 10k rpm for 10 minutes and resuspended into 2 ml of milli-Q water. 0.5 µL of mercaptopropyl-triethoxysilane (MPTES) was added to the suspension and 0.5 µl of tetraethyl orthosilicate (TEOS) was then added after 1 hour. The solution

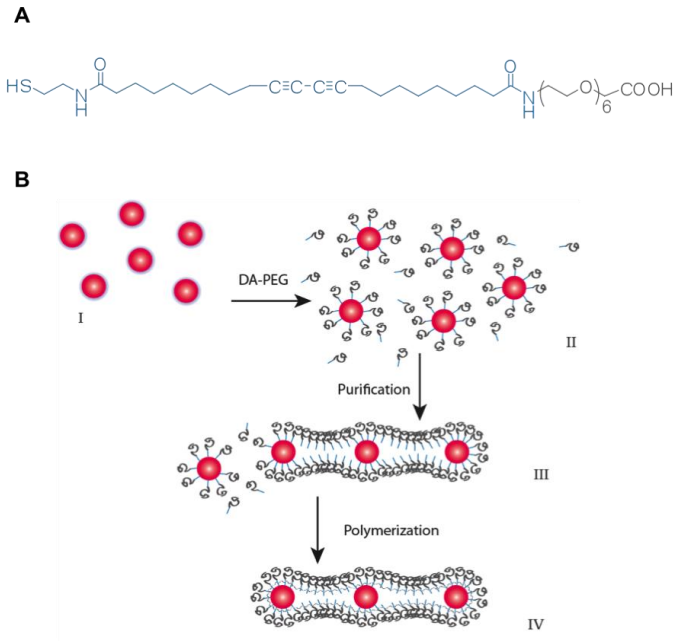
was adjusted to around pH 8 and then left at room temperature for 4 days before characterization.

Characterization methods. The photocrosslinked DA-PEG-coated AuNPs chains were analysed by TEM, UV-vis and zeta potential analysis. TEM images were obtained with a FEI Tecnai 12 transmission electron microscope operating at a bias voltage of 80 kV. All samples were deposited on carbon film 400 mesh copper (50) grids purchased from Agar Scientific Ltd. UV-visible spectra of colloidal AuNPs were collected using a Cary 300 Bio UV-vis spectrophotometer over the range from 350 to 800 nm. Zeta potential measurements were performed with a Malvern Zetasizer Nano ZS, using the DTS1060 Disposable capillary cell.

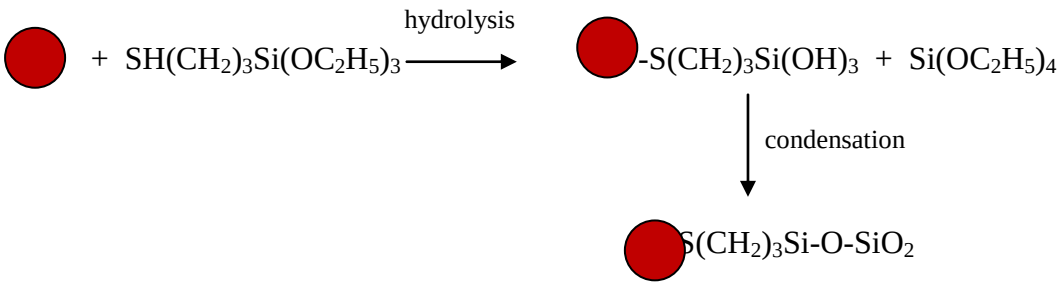
The silica-coated nanoparticle chain structures were analysed by TEM, EDX analysis, UV-vis, and FTIR. Samples were characterized by transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analyses by using a JEOL 1200 EX microscope operating at 120 keV. Samples for TEM were prepared by depositing a 3μL drop of the solution onto a carbon coated 3mm copper grid and dried in air. UV spectra were obtained by using PerkinElmer Lamda 25 spectrometer. Samples for FTIR were collected by centrifugation and dried at 40°C overnight. FTIR spectra were obtained by using PerkinElmer Spectrum One and KBr discs.

Schematic illustration of reaction schemes

Scheme S1



Scheme S1. The chemical structure of the capping ligand DA-PEG (**A**). The hydrophilic part is highlighted in grey and the hydrophobic part in blue. A schematic illustration of the AuNPs chainlike assemblies formation process (**B**): **I** AuNPs (red spheres) coated with BSPP (purple shadow); **II** Partial coverage of AuNPs by DA-PEG; **III** Formation of the AuNPs chainlike structures during the purification process; **IV** Photocross-linked DA-PEG ligands on the AuNPs assemblies.



Scheme S2 Schematic reaction of silica on the surface of AuNPs chain structures.

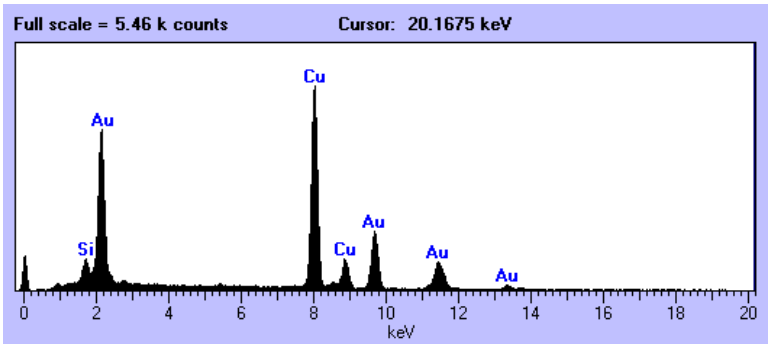


Figure S1. EDXA spectra of silica-coated AuNPs chains.

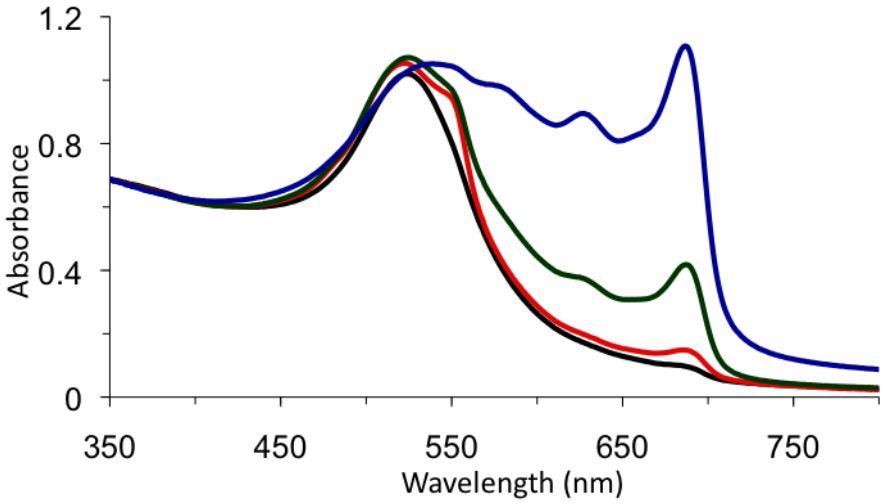


Figure S2. UV-visible spectra of mixture of photopolymerized DA-PEG and BSPP-coated AuNPs. The molar ratio between BSPP-coated AuNPs and DA-PEG is: 1:7000 for the black line; 1:14000 for the red line; 1:27000 for the green line and 1:40000 for the blue line.

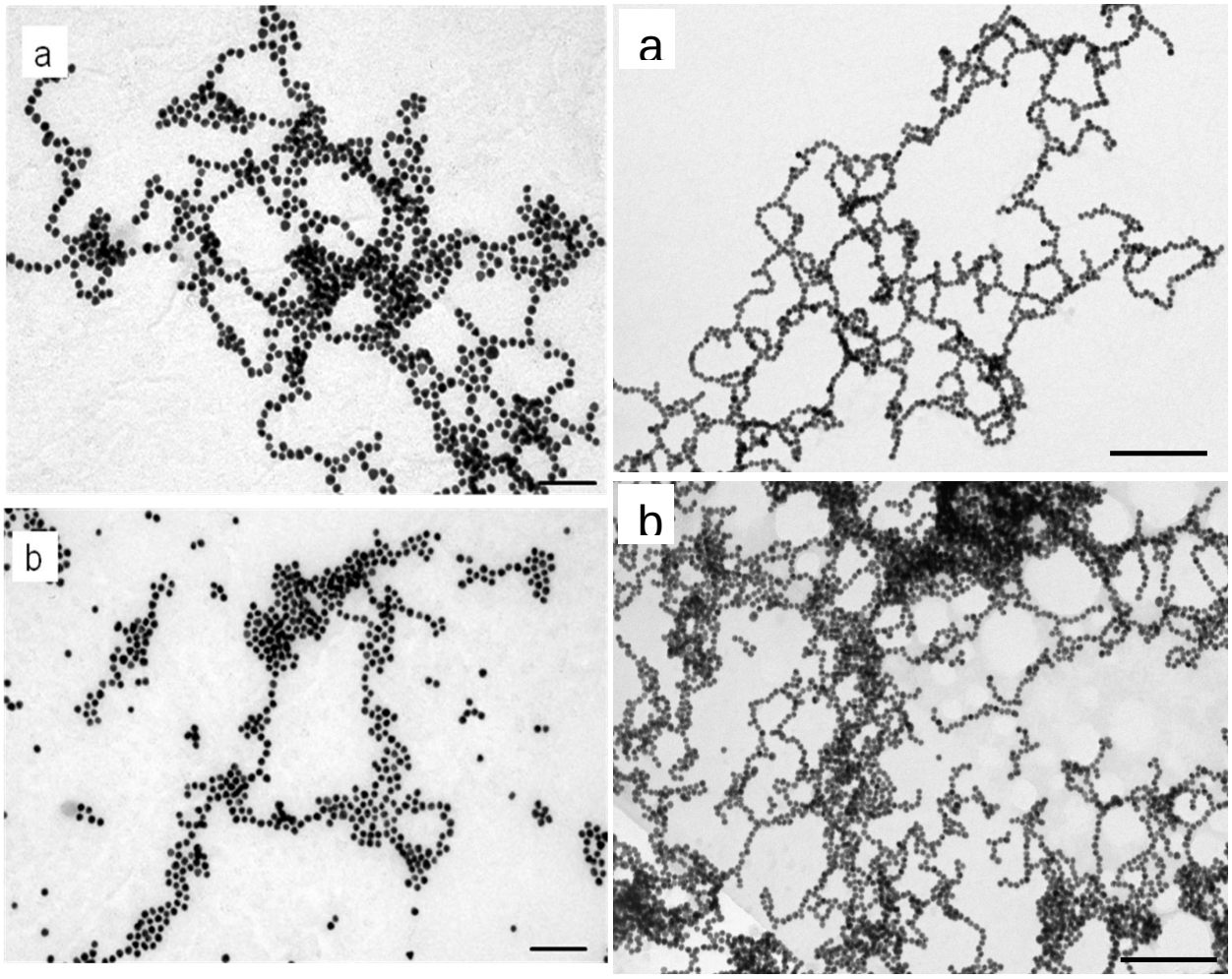


Fig. S3 Left column: TEM images of (a) photo-crosslinked and b) non-photo-crosslinked DA-PEG-coated AuNPs chains after addition of ethanol at a volume ratio of 1:1 Scale bar = 100 nm. **Right column**; TEM images of a) silica-coated and b) uncoated AuNPs chains. after addition of ethanol at the volume ratio of 1:1. Scale bars = 200 nm.

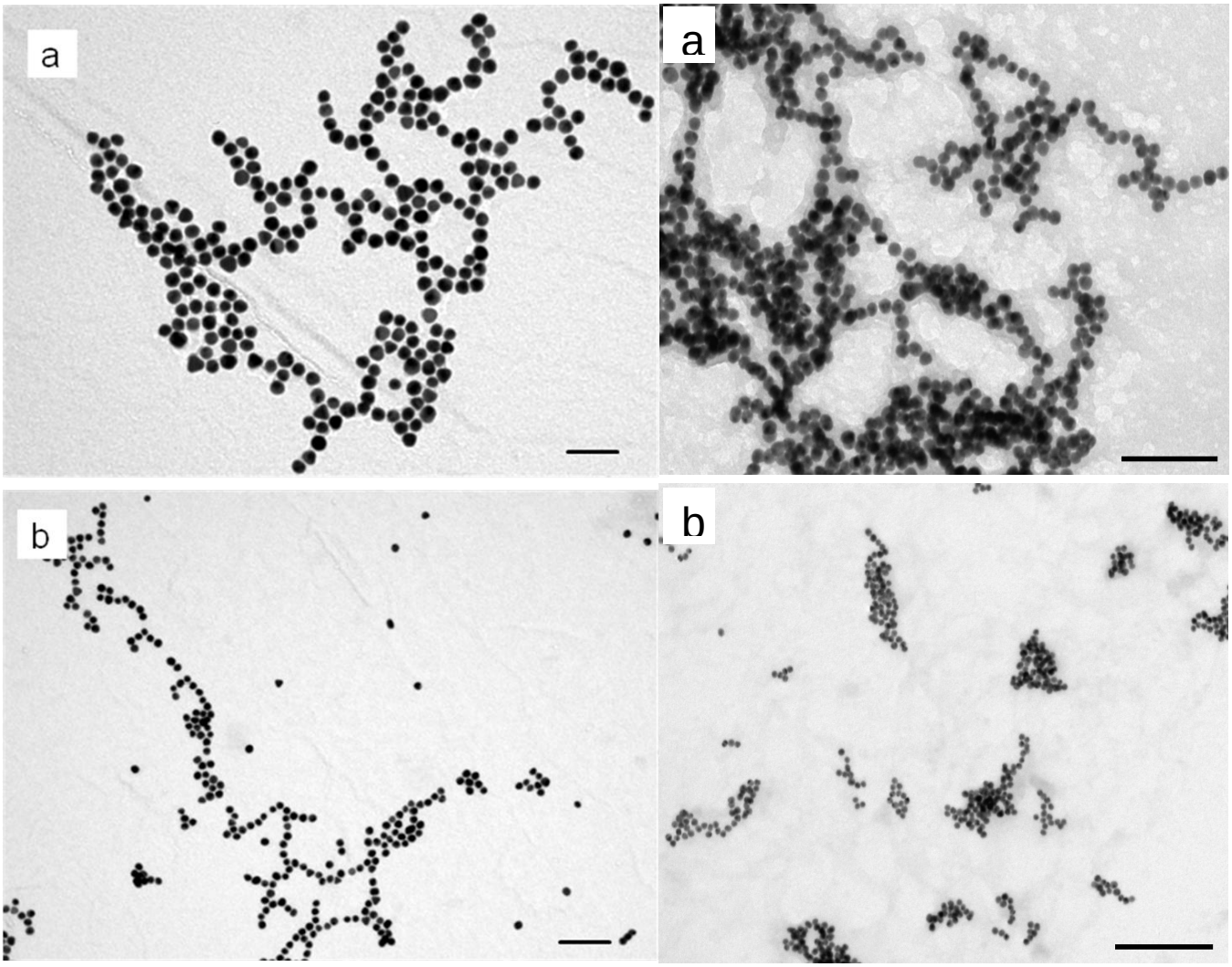


Figure S4 Left column: TEM images of photocrosslinked DA-PEG-coated AuNPs chains after sonication for a) 10 minutes and b) 20 minutes. Scale bars a = 50 nm, b = 100 nm. **Right column:** TEM images of silica coated AuNPs chains after sonication for a) 10 minutes and b) 20 minutes. Scale bars a = 100 nm, b = 200 nm.

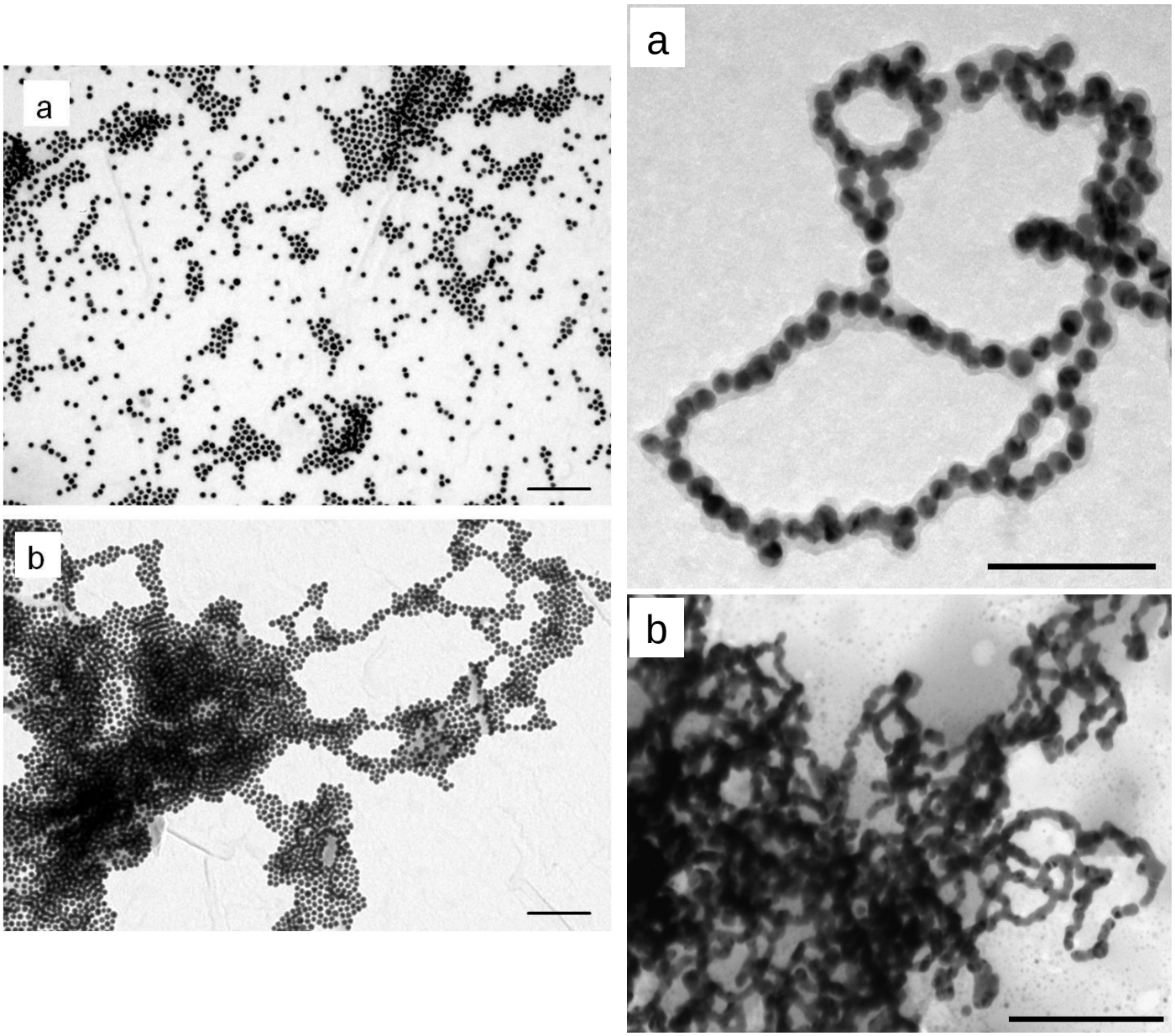


Figure S5. **Left column:** TEM images of a) polymerized DA-PEG AuNPs chains and b) non-polymerized DA-PEG AuNPs chains after heating at 70 °C for 1 hour. Scale bars a) = 100 nm and b) = 200 nm. **Right column:** TEM images of a) silica-coated AuNPs chains and b) uncoated AuNPs chains after heating at 70 °C for 10 hours. Scale bars a) = 100 nm and b) = 200 nm.

References

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