Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

Photoinduced Electron Transfer RAFT Polymerization of *N,N*-dimethylacrylamide via Plasmonic Excitation of Gold Nanoparticles in water

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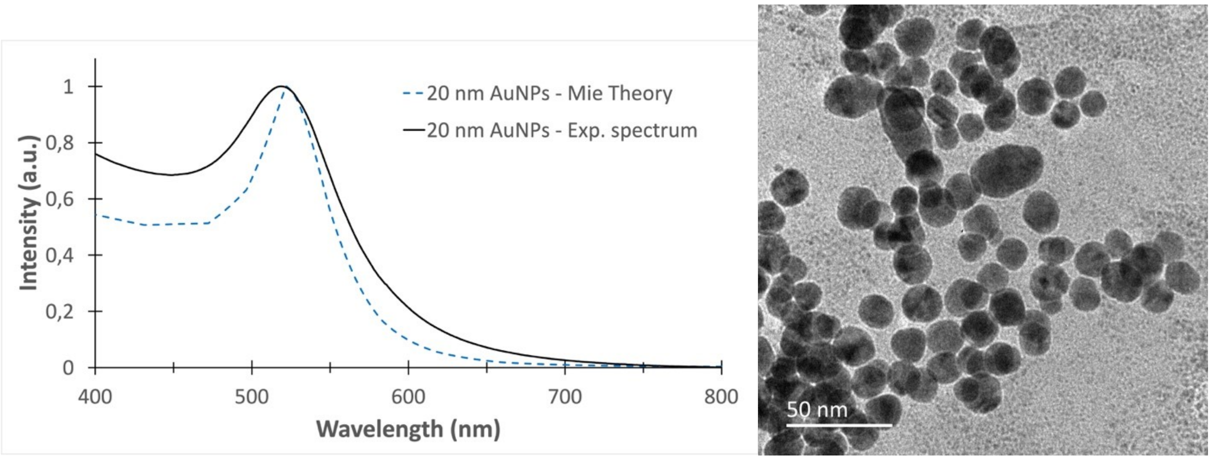


Figure S1. *Right: Experimental and extinction spectra in water of the 20 nm AuNPs. Black plain spectrum: experimental spectrum. Blue dashed spectrum: theoretical spectrum calculated by Mie theory for 20 nm nanoparticles in water. All the spectra were normalised to 1 for a better comparison. Left: TEM image of the 20 nm AuNPs.*

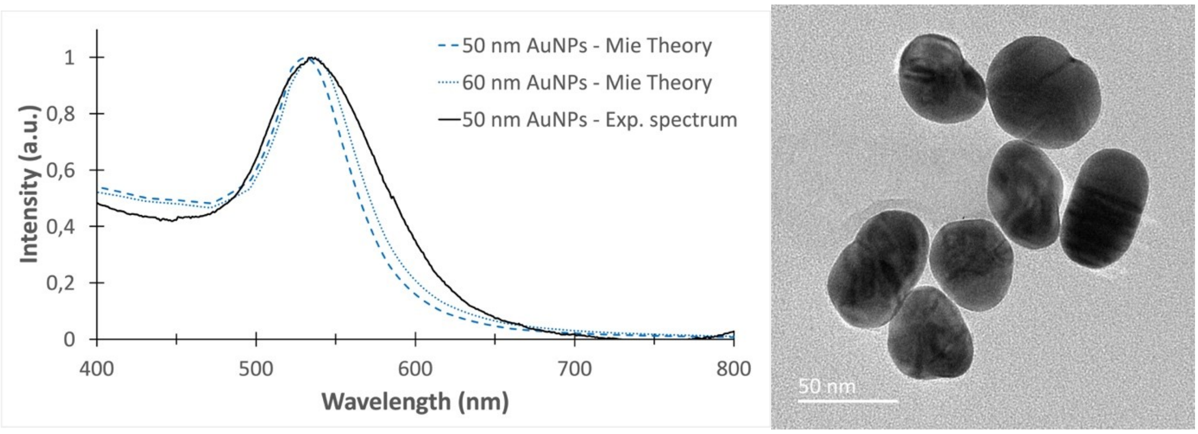


Figure S2. *Right: Experimental and extinction spectra in water of the 50 nm AuNPs. Black plain spectrum: experimental spectrum. Blue dashed spectrum: theoretical spectrum calculated by Mie theory for 50 nm nanoparticles in water. Blue dotted spectrum: theoretical spectrum calculated by Mie theory for 60 nm nanoparticles in water. All the spectra were normalised to 1 for a better comparison. Left: TEM image of the 50 nm AuNPs.*

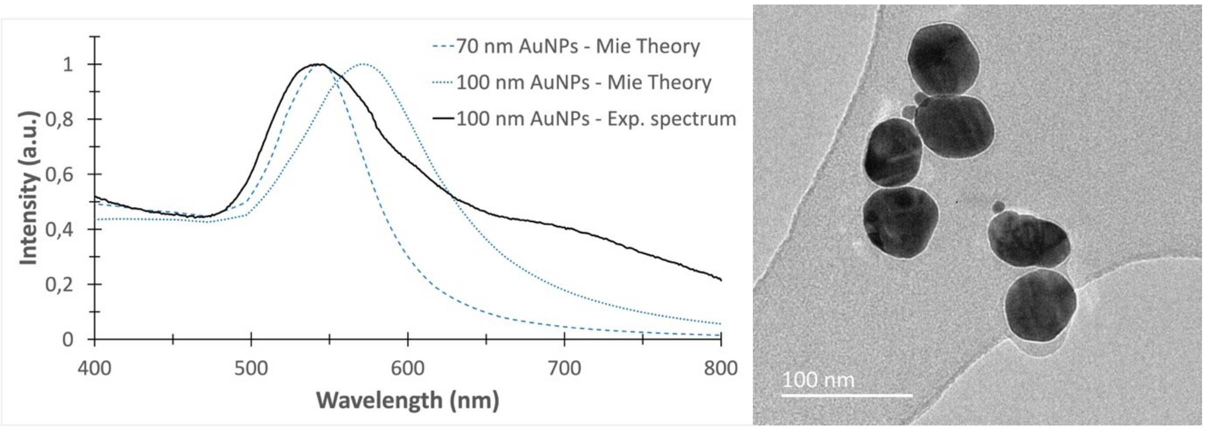


Figure S3. *Right: Experimental and extinction spectra in water of the 100 nm AuNPs. Black plain spectrum: experimental spectrum. Blue dashed spectrum: theoretical spectrum calculated by Mie theory for 70 nm nanoparticles in water. Blue dotted spectrum: theoretical spectrum calculated by Mie theory for 100 nm nanoparticles in water. All the spectra were normalised to 1 for a better comparison. Left: TEM image of the 100 nm AuNPs.*

AuNP diameter	LSPR (nm)	Width (nm)
20 nm	523	70
50 nm	539	80
100 nm	544	80

Table S1. *Positions and widths of the plasmon resonance for the AuNPs of 20, 50 and 100 nm in water.*

Figure S4*. Image of the polymerization setup under green (λmax = 514 nm) light illumination.*

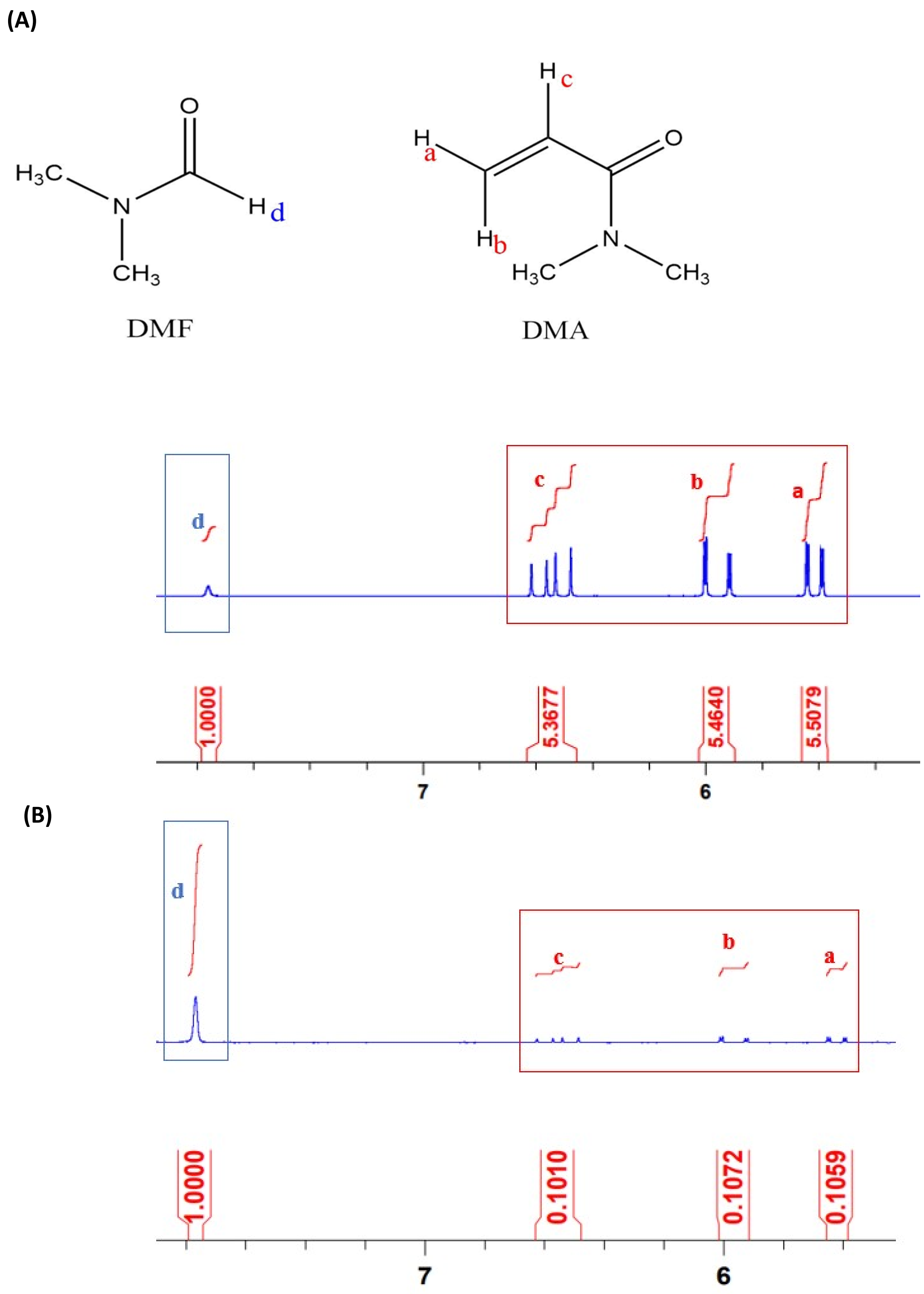
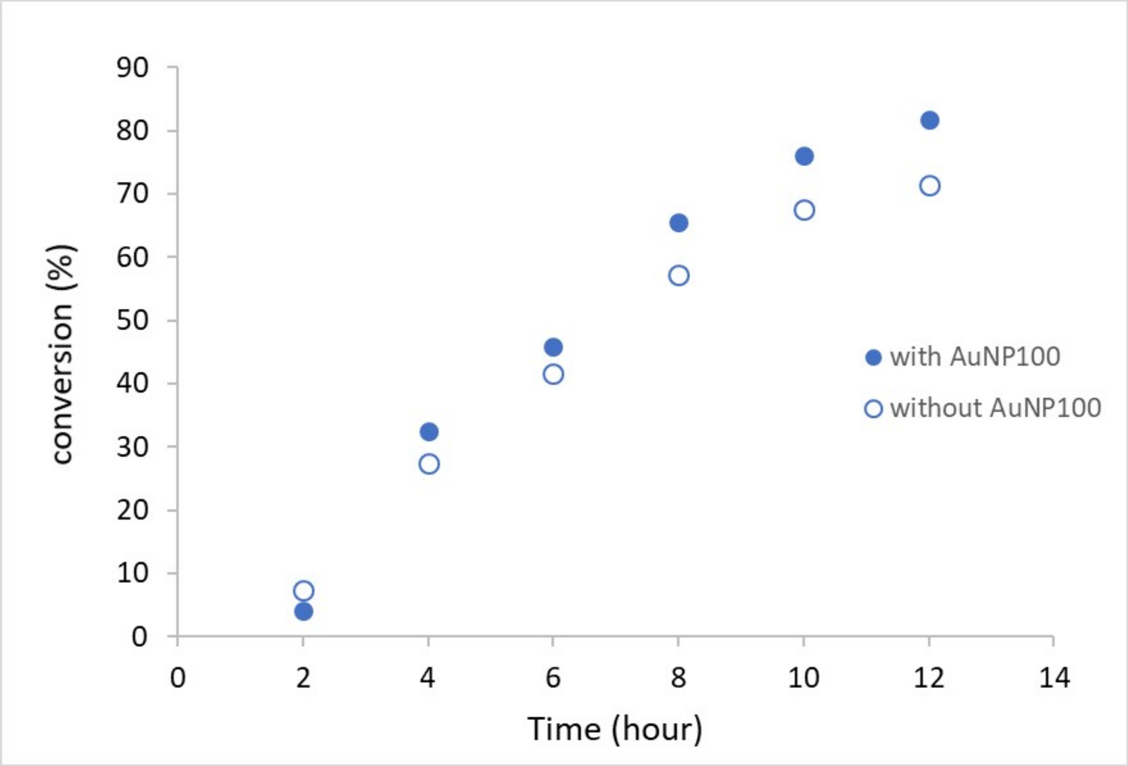


***Figure S5**. Overlaid ^{1}H NMR spectra (200 MHz, D_2O) of the reactium media at the initial time (**A**) and after 24 hours (**B**) for the PET-RAFT polymerization of DMA using CTCPA at room temperature under blue light illumination. $[DMA]_0/[CTCPA]_0/[AuNP100]_0 = 50/1/2.8x10^{-11}$, and at $[DMA]_0 = 3.85$ mol.L^{-1}.*

(A)



(B)

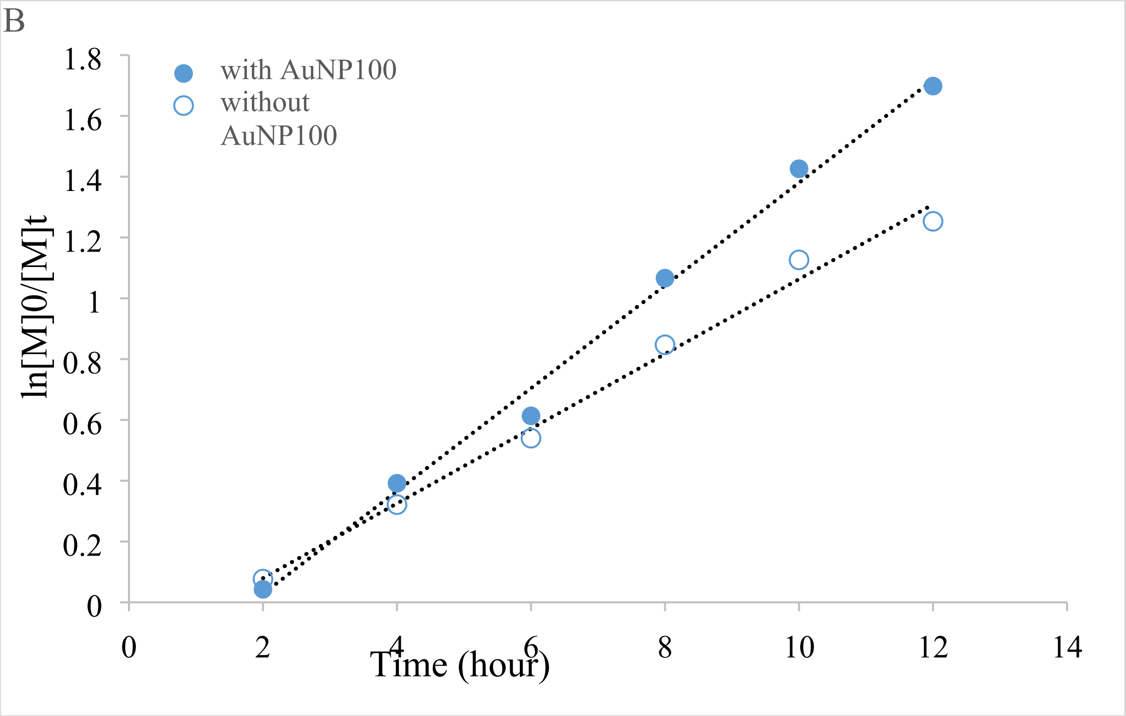
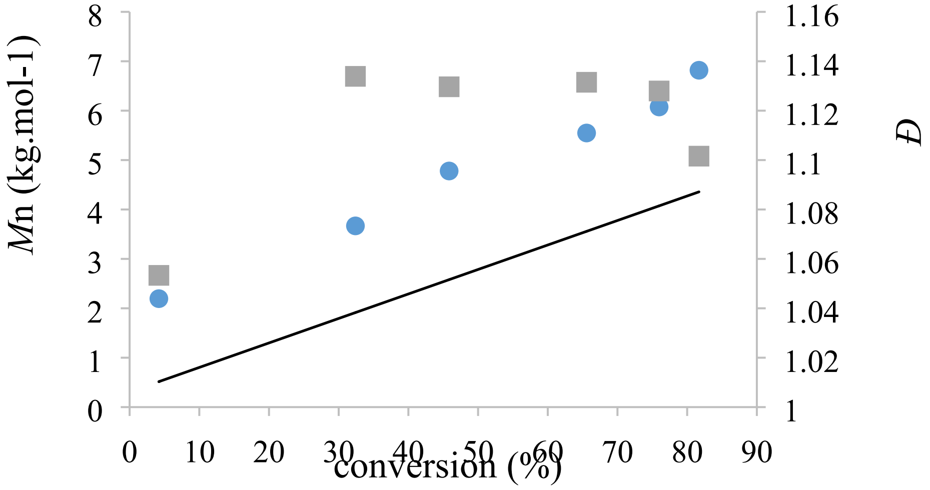


Figure S6. *(**A**) Evolution of DMA conversion and (**B**) evolution of ln($[M]_0/[M]_t$) versus time during the blue-light activated RAFT polymerization of DMA mediated through CTA in water at room temperature, with (●) and without (○) gold nanoparticles (100 nm, AuNP100).* $[DMA]_0/[CTCPA]_0/[AuNP100]_0 = 50/1/2.8x10^{-11}$*, and at* $[DMA]_0 = 3.85$ *mol.L*$^{-1}$.

(A)



(B)

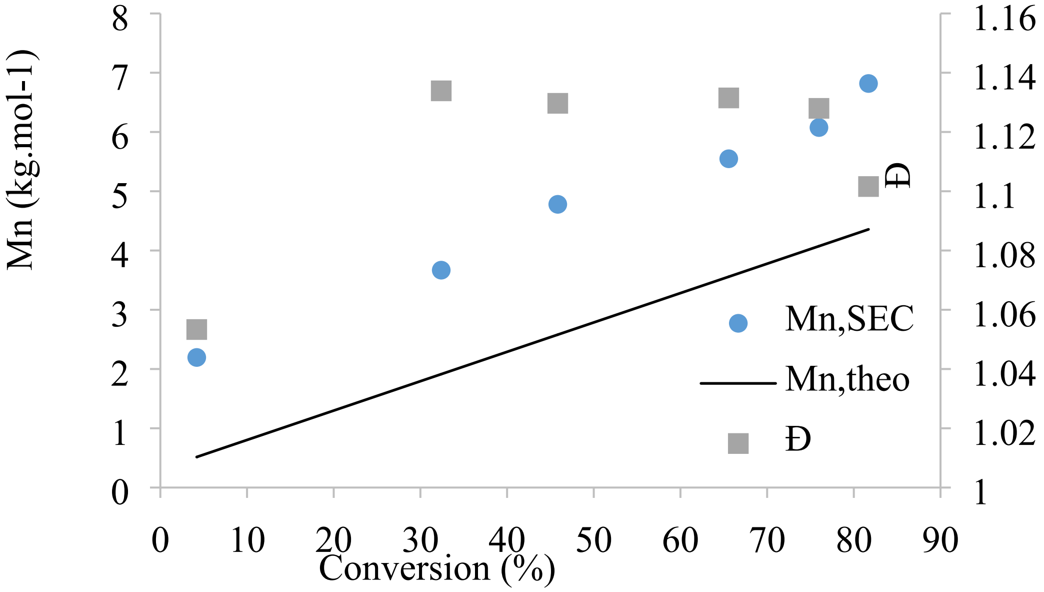
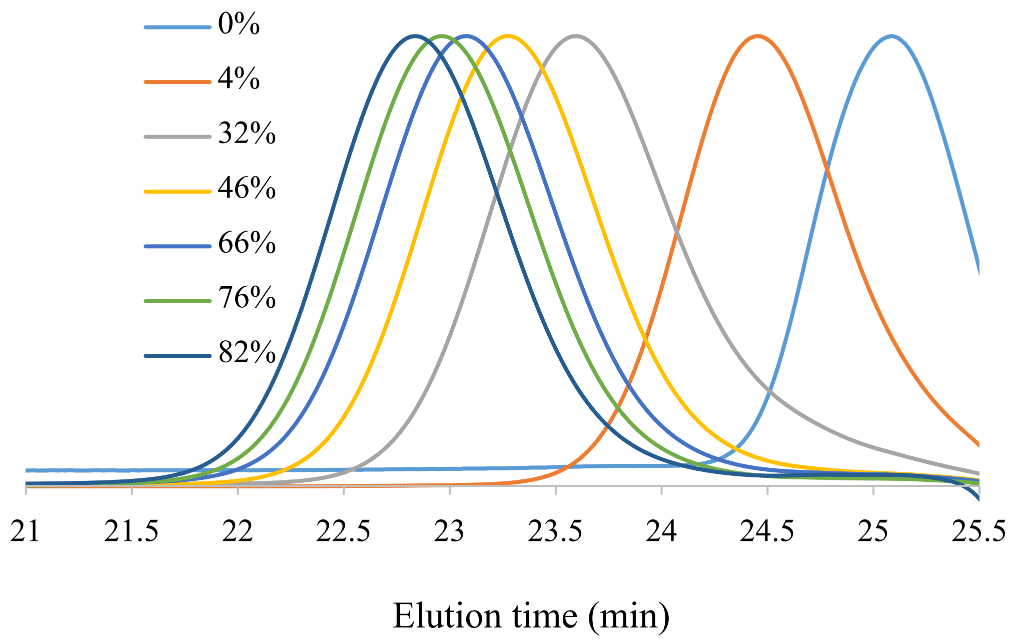


Figure S7. *Evolutions of $M_{n,SEC}$ (● or ○) and $M_{n,theo}$ (line) and Đ (■) versus DMA conversion during the blue-light activated RAFT polymerization of DMA mediated through CTCPA in water at room temperature, with (●) and without (○) gold nanoparticles (100 nm, AuNP100). $[DMA]_0/[CTCPA]_0/[AuNP100]_0 = 50/1/2.8\times10^{-11}$, and at $[DMA]_0 = 3.85$ mol.L^{-1}.*

(A)



(B)

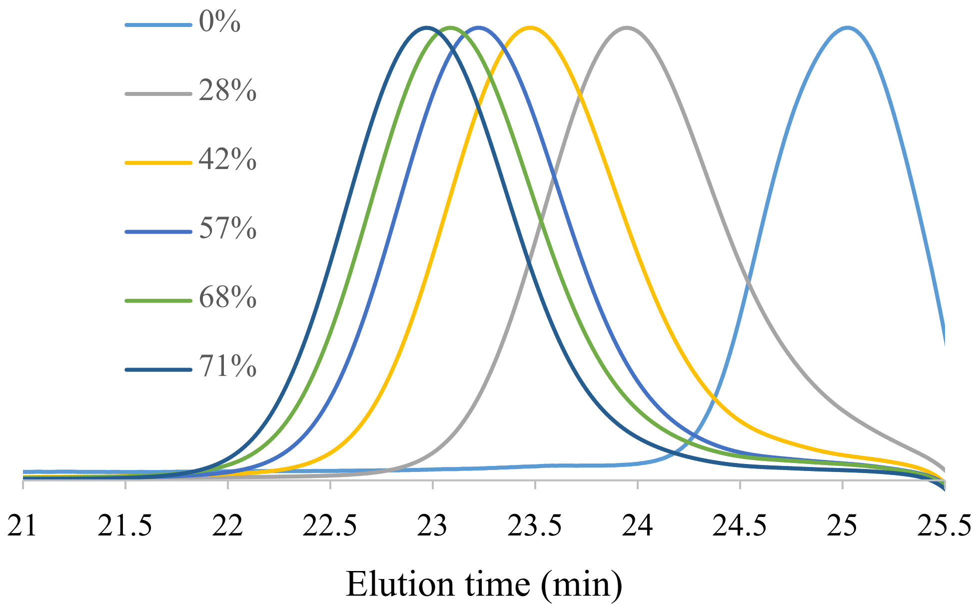


Figure S8. *Overlaid SEC traces of PDMA using RI detection obtained by blue-light activated RAFT polymerization of DMA mediated through CTCPA at different times in water ($[DMA]_0$ = 3.85 mol.L^{-1}) at room temperature with **(A)** and without **(B)** gold nanoparticles (100 nm, AuNP100). $[DMA]_0/[CTCPA]_0/[AuNP100]_0$ = 50/1/2.8x10^{-11}.*

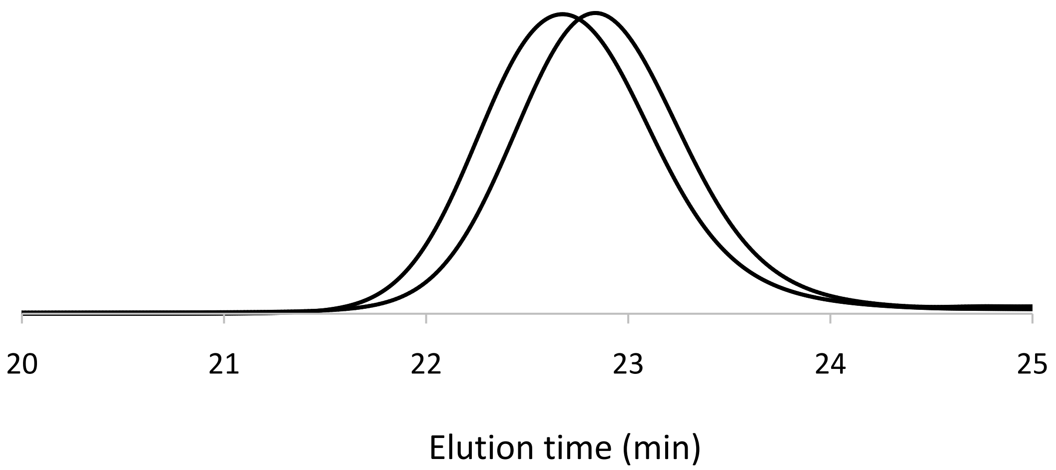


Figure S9. *Overlaid SEC traces obtained by refractive index detection (dRI, solid line) and UV detection at 309 nm (dotted line) of purified PDMA obtained by blue-light activated RAFT polymerization of DMA mediated through CTCPA ($[DMA]_0/[CTCPA]_0$ = 50/1) in water ($[DMA]_0$ = 3.85 mol.L^{-1}) at room temperature in the presence of AuNP100 (3.65 pM) (**Entry 4-DMA-CTCPA-AuNP100, Table 1**).*

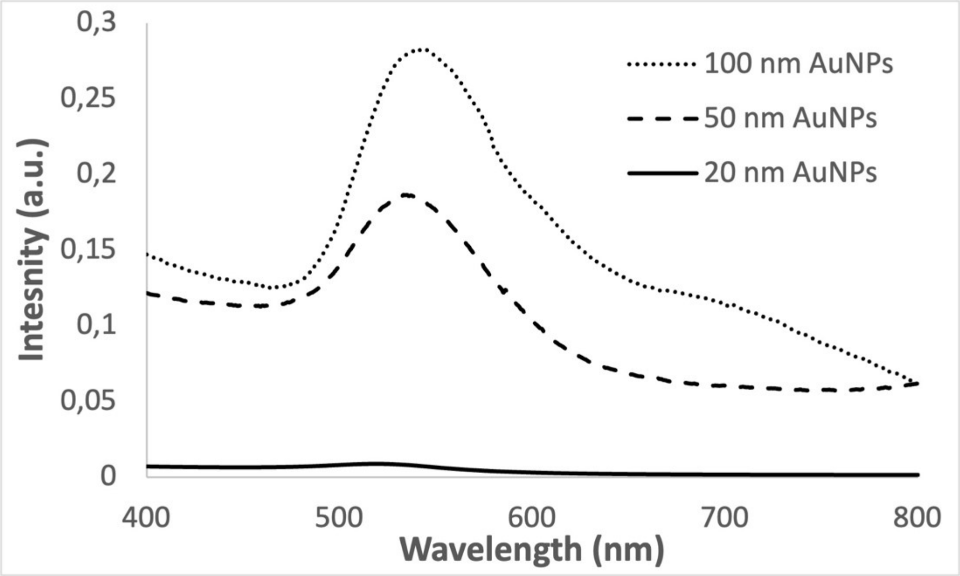
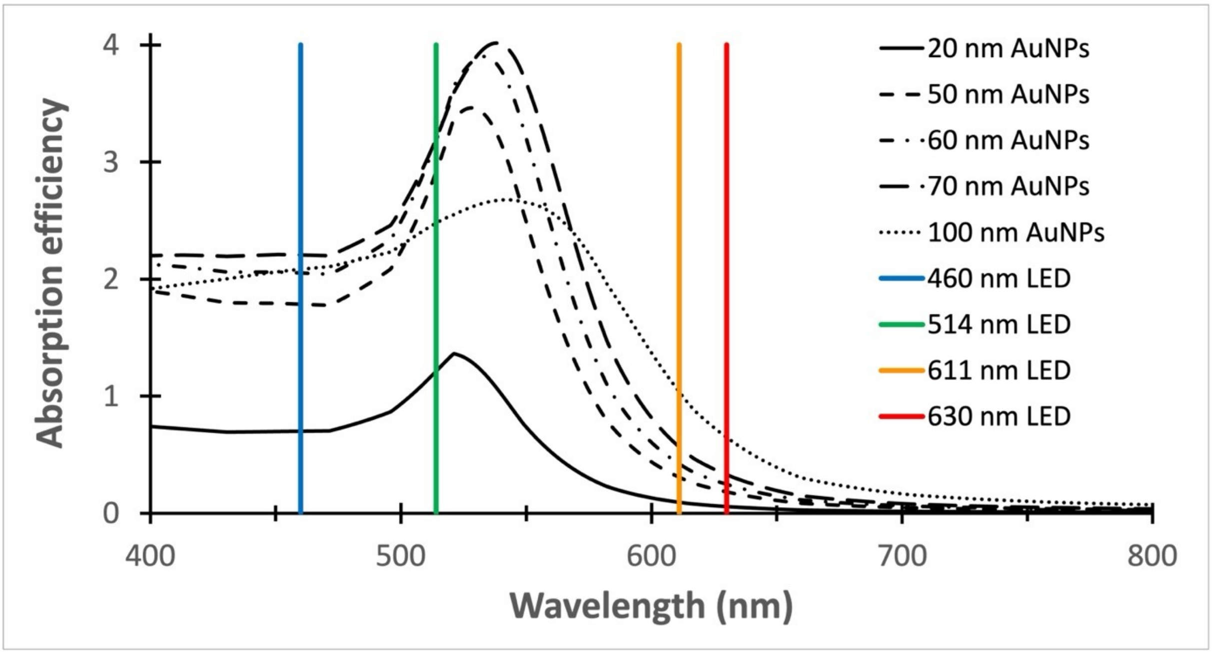


Figure S10*. Experimental extinction spectra of the LSPR for the 20 nm nanoparticles (plain line), 50 nm nanoparticles (dashed line) and 100 nm nanoparticles (dotted line). All the extinction spectra were normalised to the same concentration (3.65pM) to be comparable.*

(A)



(B)

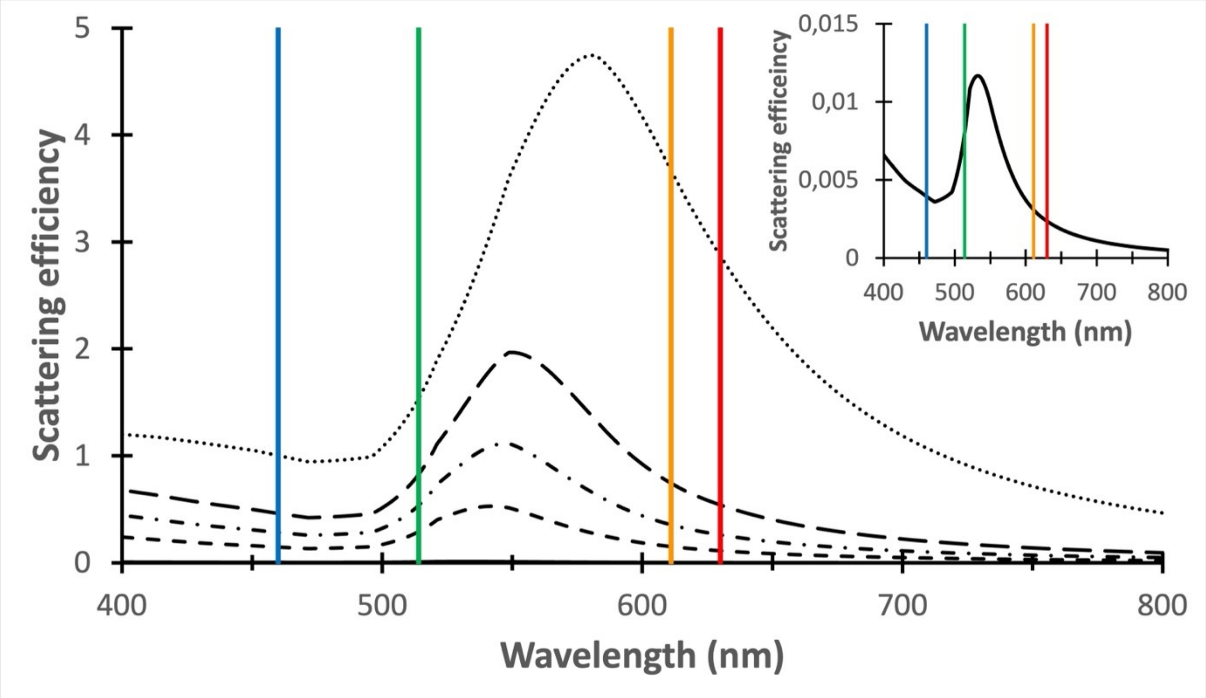


Figure S11. *(**A**) Theoretical absorption efficiency,* Q_{Abs}*, and (**B**) theoretical scattering effciency,* Q_{Scat}*, calculated in water using the Mie theory for the 20 nm nanoparticles (plain line), 50 nm nanoparticles (short dashed line), 60 nm nanoparticles (dotted-dashed line), 70 nm nanoparticles (large dashed line)* *and 100 nm nanoparticles (dotted line). The vertical lines correspond to the position of the four LEDs (Blue line: 460 nm, Green line: 514 nm, Orange line: 611 nm and Red line: 630 nm).*

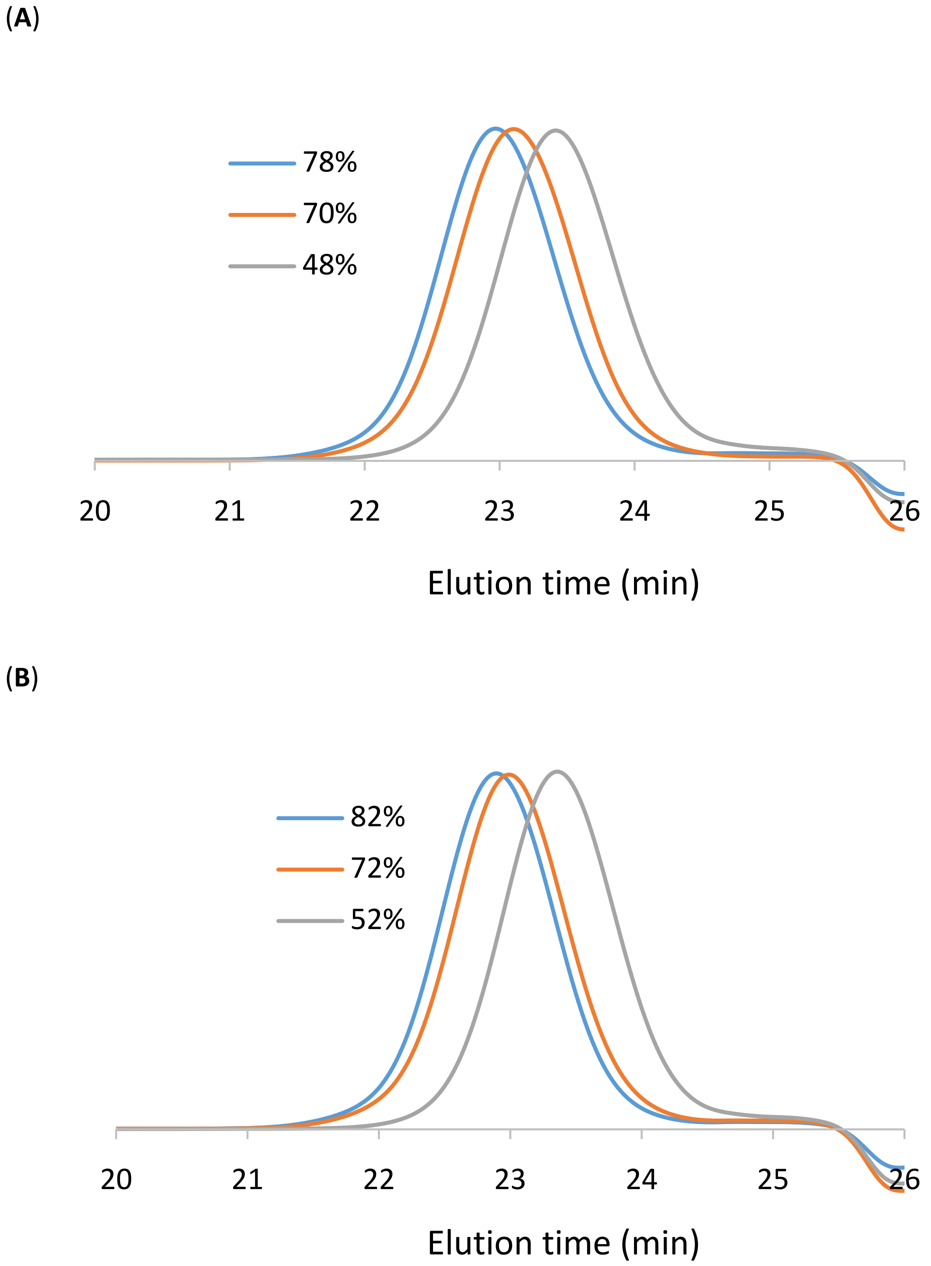


Figure S12. *Overlaid SEC traces of PDMA using RI detection obtained by green-light activated RAFT polymerization of DMA mediated through CTCPA at different times in water ([DMA]$_0$ = 3.85 mol.L^{-1}) at room temperature with [AuNPs]$_0$ = 36.5 pM with AuNP20 (**A**) (**Entry 1-DMA-CTCPA-AuNP20, Table 1**) and with AuNP50 (**B**) (**Entry 1-DMA-CTCPA-AuNP50, Table 1**). [DMA]$_0$/[CTA]$_0$ = 50/1, and at [DMA]$_0$ = 3.85 mol.L^{-1}.*

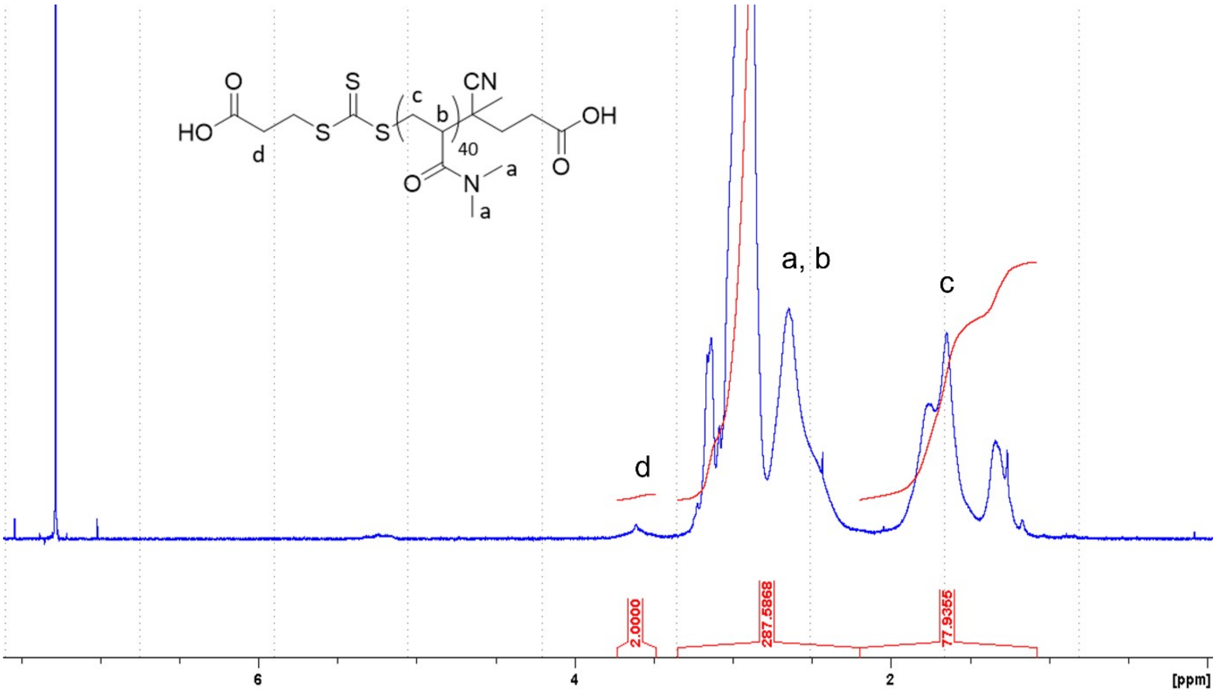


Figure S13. *^{1}H NMR spectra of PDMA obtained by green-light activated RAFT polymerization of DMA mediated through CTCPA ($[DMA]_0 = 3.85$ mol.L^{-1}) at room temperature with $[AuNPs]_0 = 36.5$ pM with AuNP50 (**Entry 1-DMA-CTCPA-AuNP50, Table 1**). $[DMA]_0/[CTA]_0 = 50/1$, and at $[DMA]_0 = 3.85$ mol.L^{-1}, DMA conversion = 82 %).*